Worker Environment Research. IV. The Effect of Dust Derived from Several Soil Types on the Dissipation of Parathion and Paraoxon Dislodgable Residues on Citrus Foliage

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There have been several episodes of poisonings of agricultural workers in fields and groves that had previously been treated with certain organophosphorus insecticides (QUINBY and LEMMON 1958, MILBY et al. 1964, BAILEY 1972, SPEAR et al. 1975). In response to this problem, both the state of California and the Federal Government have established regulations to control the interval between pesticide application and reentry of agricultural field workers (CALIF. DEPT. of AGR. 1971, U.S. DEPT. of LABOR 1974).

Semi-logarithmic plots of the data for pesticide dissipation from plant surfaces frequently do not exhibit simple first-order kinetics. GUNTHER and BLINN (1955) recognized that such plots are generally composed of a series of three discontinuous lines with rate constants k_1, k_2, and k_3, respectively, where $k_1 > k_2 > k_3$. These lines were designated as sloughed residue, degradation residue, and persistence residue curves, respectively. Both the rate constants and the existing residue level at which the rate changes occur determine the quantity of toxicant present at the designated reentry date. A reentry interval is thus valid if the above two parameters are reasonably constant for a given pesticide on a given crop. That it has not always been valid is evident from incidences of field worker poisonings where the observed interval exceeded legal requirements.

The small number of reported episodes indicates that reentry standards have been quite effective and suggests that some highly variable factors are responsible for the exceptions. GUNTHER and BLINN (1955) and others (WESTLAKE et al. 1973, GUNTHER et al. 1973, SPEAR et al. 1975, SPENCER et al. 1975) have proposed that orchard dust and/or solid components of wettable powder formulations on foliage may be important factors influencing the quality and quantity of toxic dislodgable residues and are important "relay" sources of toxicants to workers.

Foliar dust may be important as its sorptive properties may stabilize pesticides or facilitate their conversion to more toxic compounds. GUNTHER and BLINN (1955) reported that as much as 80% of the applied pesticide is quickly lost to the orchard soil through initial runoff of the applied spray and subsequent

Bulletin of Environmental Contamination & Toxicology,
Vol. 15, No. 5

sloughoff of the initial spray deposit. The contaminated soil through the action of wind or mechanical agitation serves as a ready source for further foliar contamination. If the foliar dust can be established as the causative agent for worker illnesses, it can be effectively removed by spray washing of the trees (GUNTHER 1973). The runoff water will also aid in the degradation of parathion in orchard soil (IWATA et al. 1974).

This study was undertaken to determine the influence of several soils (dust) resident on orange leaves on the dissipation rate of parathion, the rate of conversion of parathion to paraoxon, and the dissipation rate of the paraoxon formed.

Experimental

The chemical and physical properties of the soils used are in Table I. Each soil was sieved to pass through a 100-mesh screen. The first 5 soils were selected on the basis of rate and quantity of parathion adsorbed from a 20 ppm aqueous solution. The solubility of parathion in water is 20-25 ppm (GUNTHER et al. 1968). The Visalia silt loam was collected from a citrus grove which was the site of a 1974 worker-poisoning episode. Pike's Peak clay was included as it is used in some insecticidal formulations and has appeared to stabilize parathion and paraoxon (CARMAN et al. 1975).

TABLE I. Physical and chemical properties of the soils used.

Soil type	pH	Organic matter, %	Mechanical analysis, % μ 50-250	2-50	<2	Saturation %
Laveen loamy sand San Bernardino Co.	8.7	0.1	94	1	5	21
Santa Lucia silt loam Santa Barbara Co.	5.6	19.5	34	42	24	94
Windy loam Amador Co.	6.0	10.8	51	40	9	54
Madera sandy loam Riverside Co.	6.7	1.4	60	28	12	27
Visalia silt loam Tulare Co.	5.2	2.5	24	57	19	35
Pike's Peak clay	4.7	0.1	0.4	27	73	128

A 20 ppm aqueous solution of parathion was prepared by adding an appropriate quantity of parathion in hexane to a selected volume of deionized water, evaporating the hexane at ambient temperature, and shaking the solution for 2 h at 25°.

From the well stirred slurries, 0.20-ml aliquots were removed with an Eppendorf syringe and applied to the top surfaces of living Valencia orange leaves and to Teflon sheets. The slurry drop was spread with a microspatula to cover uniformly as much of the leaf surface as possible. The Teflon sheet served as an inert surface from which the dislodgable residue could be quantitatively removed so that the amount of parathion actually applied to each leaf could be determined.

The young trees, about 6 ft high, were contained in 5-gal pots. After leaf application the trees were kept in a greenhouse at 25±5°C and 50±20% relative humidity. Treated leaves were periodically removed from the trees up to 30 days after application. The leaves were washed 3 times with a No. 3 camel's hair brush in a stream of deionized water delivered from a polyethylene wash bottle. The combined wash, made up to 50 ml with deionized water, was extracted 3X for 20 sec, each time with 25 ml of hexane. Sodium sulfate was added to the combined hexane extracts. The hexane solution was filtered and then concentrated to about 5 ml in a Kuderna-Danish apparatus. Parathion and paraoxon in the extracts were quantitated by glc using a 1/8-in. x 5-ft glass column containing 10% DC200 coated on 80/100 mesh Gas Chrom Q, an alkali flame ionization detector, and an electronic integrator. The column, conditioned by the procedure of IVES and GIUFFRIDA (1970), was operated at 216°C.

RESULTS AND DISCUSSION

The soils used present a fair range of properties (See Table I). For example, the pH ranges from 4.7 to 8.7, organic matter from 0.1 to 19.5%, and percent saturation from 21 to 128. An alkaline pH would be expected to promote hydrolysis of the residues, especially paraoxon (FEST and SCHMIDT 1973). The composition of the organic matter is not known, but if lipoid, both parathion and paraoxon binding would be enhanced in soils having high organic matter. Adsorption is also enhanced by a high surface area. The external surface area is related to the particle sizes measured by mechanical analysis and is highest for Pike's Peak clay. Saturation percentage is an expression of water-holding capacity of the soils and thus adsorptivity and total surface area, both external and internal. High saturation percentage values correspond to high total surface areas.

The semi-logarithmic plots of the dislodgable residue data for both parathion and paraoxon with respect to time are presented in Figures 1 and 2. As expected, with all 6 soils the zero-day dislodgable parathion residue level was lower on the leaves than on the inert Teflon sheet, an effect caused by partitioning of parathion from the water component of the soil slurry to leaf waxes (GUNTHER and BLINN 1955).

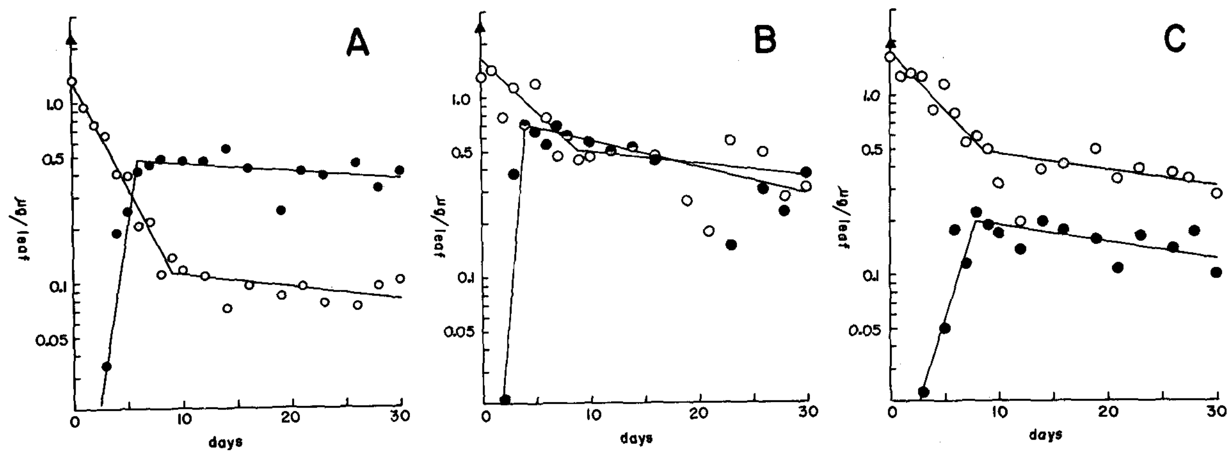

Figure 1. Dislodgable residues of parathion (○) and paraoxon (●) recovered from Valencia orange leaves treated with an aqueous slurry of parathion (▲) and soil dust derived from (A) Laveen loamy sand, (B) Santa Lucia silt loam, and (C) Windy loam.

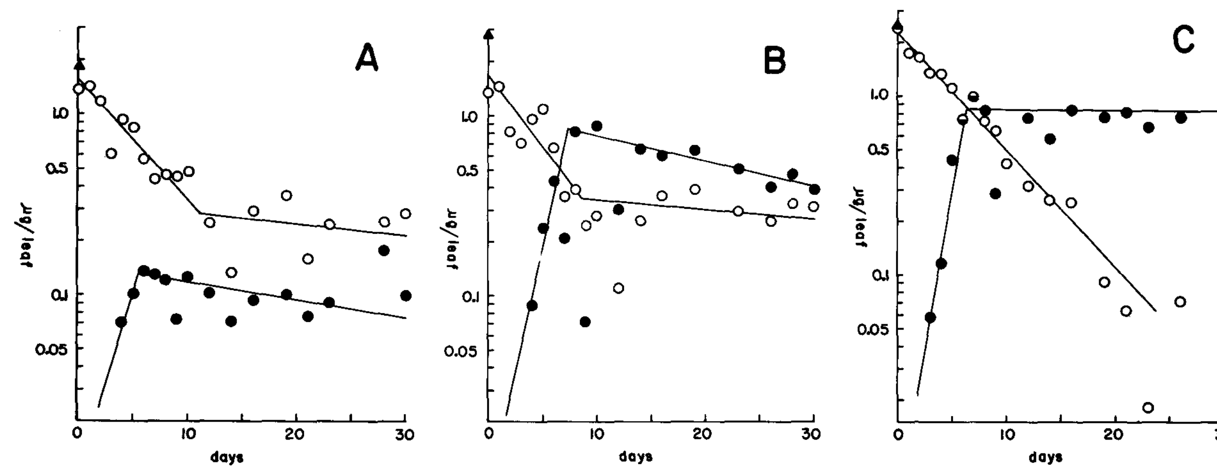

Figure 2. Dislodgable residues of parathion (○) and paraoxon (●) recovered from Valencia orange leaves treated with an aqueous slurry of parathion (▲) and soil dust derived from (A) Madera sandy loam, (B) Visalia silt loam, and (C) Pike's Peak clay.

The parathion residue decline during the first day is not pronounced. The absence of the sloughed residue curve is probably due to the fact that the cleaned leaves were selected to be horizontal and protected from agitation and that leaves with obvious disruptions of the coated soil were excluded. For all 6 soils, the graphs are linear initially with Laveen loamy sand exhibiting the highest dissipation rate. This soil has a high pH, low organic content, and low surface area. For the other soils, the initial rate of dissipation varies slightly but is about half of that for Laveen soil. This includes Madera sandy loam which has low surface area and organic content comparable to Laveen but a pH 2 units lower. Thus, pH appears to be more important in determining initial dissipation rate than either organic matter (in general) or surface area.

Except for Pike's Peak clay, the initial parathion dissipation rates change to a lower rate at about 10 days. Because of the high variability of the data, it is not possible to say if there is a change of rate with Pike's Peak clay. The parathion residue level at which the rate changes is dependent upon the soil and is lowest for Laveen loamy sand at about 0.1 μg/leaf. For Visalia silt loam and Madera sandy loam, the break occurs at about 0.3 μg/leaf. For Santa Lucia silt loam and Windy loam, the break occurs at about 0.5 μg/leaf. The parathion dissipation rates after the break are low and do not vary greatly between soils. The total result of these effects is that after 30 days 4% of the original parathion remains on the Laveen soil, 15% on Santa Lucia, 20% on Windy, 8% on Madera, 14% on Visalia, and 2% on Pike's Peak clay.

Dislodgable residues of paraoxon were not present in detectable quantities until at least the second day and then rose to a maximum at about the 8th day. After that time the paraoxon levels diminished at a rather low rate for all 6 soils. This rate may be the same for all 6 soils and is of the same order of magnitude as the dissipation rate for parathion. At the 30th day the paraoxon levels were about 0.36 μg/leaf for Laveen, 0.25 for Santa Lucia, 0.10 for Windy, 0.08 for Madera, 0.4 for Visalia, and a high of 0.8 for Pike's Peak clay. When corrected for the slight change of molecular weight, the values correspond to 17, 11, 5, 3, 15, and 34%, respectively, of the applied parathion.

Combining the parathion and paraoxon residue values at 30 days shows that 21% of the toxicant remains with Laveen, 26% with Santa Lucia, 25% with Windy, 11% with Madera, 29% with Visalia, and 36% with Pike's Peak clay. These values undoubtedly represent significant levels of toxicants. The recommended reentry interval for parathion on citrus is 21 days.

SUMMARY

Parathion sorbed to dust can persist as dislodgable residues on citrus leaves. Semi-logarithmic plots of parathion dislodg-

able residue data were initially linear for the 6 soils studied and then a distinct change to lower rates occurred with 5 of the soils. As initial rates and the residue level at the rate change are dependent on the soil, foliar dust is implicated as a causative factor in the non-uniformity of residue dissipation rates.

Soils can influence the conversion of parathion to paraoxon. Paraoxon levels differed greatly with the type of soil and were highest with Pike's Peak clay. Thus, its use in a parathion formulation could produce relatively high levels of paraoxon dislodgable residues. It is significant that, second to Pike's Peak clay, the highest total dislodgable residue level was found with Visalia silt loam which was collected from a grove where a worker poisoning episode had occurred in 1974.

ACKNOWLEDGMENTS

The assistance of L. Lund and R. A. Elliot for the soil analyses is gratefully acknowledged. This work was supported in part by the Environmental Protection Agency under contract No. 68-01-2479 and by Regional Research Project W-45.

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