Worker Environment Research V. Effect of Soil Dusts on Dissipation of Paraoxon Dislodgable Residues on Citrus Foliage

J. D. Adams, Y. Iwata, and F. A. Gunther
Department of Entomology
University of California
Riverside, Calif. 92502

ADAMS et al. (1976) reported that dust from soils or a particular clay often used in wettable powder formulations could influence dislodgable foliar residue levels of paraoxon derived from parathion. Thirty days after application, as much as 34% of the originally applied parathion was found as paraoxon in the dislodgable residues on citrus leaves. Paraoxon dislodgable residue levels were dependent upon the percentage of conversion of parathion to paraoxon and to the retention of the paraoxon formed. The first factor changed with the type of dust used, but the second did not appear to vary greatly with dust type.

The presence of paraoxon on foliar dusts may be a substantial factor in episodes of fieldworker poisoning where parathion has been used (SPEAR 1976). It is currently believed that foliar dusts are carriers of toxic residues to workers (CARMAN et al. 1952, GUNTHER and BLINN 1955, GUNTHER et al. 1973, WESTLAKE et al. 1973, SPEAR et al. 1975, SPENCER et al. 1975), and that paraoxon is the critical toxicant (MILBY et al. 1964) in the infrequent poisonings of fieldworkers upon legally entering parathion-treated groves. This suggestion is supported by the report (NABB et al. 1966) that paraoxon is absorbed more rapidly through animal skin than is parathion.

Since paraoxon has been suggested as a decisive factor in fieldworker poisoning and dissipates quite slowly from dust resident on orange leaves (ADAMS et al. 1976), this additional study was performed to provide data for the calculation and comparison of dissipation rates of paraoxon sorbed to dusts.

MATERIALS AND METHODS

The dust types listed in Table I which were used by ADAMS et al. (1976) were used here, and with a few exceptions, the same procedures were used. A 200 ppm aqueous solution of paraoxon was prepared by adding 20 ml of a 1 mg/ml hexane solution of paraoxon to 100 ml of distilled water, evaporating the hexane in a stream of air, and shaking for 1 hr. Ten ml of this solution was pipetted into a 30-ml, screwcap vial containing 5.00 g of dust, and the vial was shaken for 2 hr. The resulting amount of paraoxon available for adsorption to a dust was 20 times greater than the

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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[a/] Tulare Co.	5.2	2.5	24	57	19	35
Pike's Peak clay	4.7	0.1	0.4	27	73	128

[a/] A silt loam collected from a Visalia orchard, not necessarily a soil type.

amount of parathion used in the previous study (ADAMS *et al.* 1976). The slurries made for each dust were applied by the previously reported procedure to Teflon sheet (control) and to leaves of living Valencia orange trees maintained in a greenhouse at 25 ± 5°C and 50 ± 20% relative humidity. Residues were extracted and quantitated by the procedure of ADAMS *et al.* (1976) except that the combined aqueous wash was extracted 5X with 25 ml of hexane each time rather than 3X. Five extractions left paraoxon equivalent to less than 0.1 μg/leaf from washes containing 40 μg/leaf (*i.e.*, less than 0.25%) whereas 3 extractions left about 8% of the paraoxon. Thus, paraoxon levels reported by ADAMS *et al.* (1976) may have been about 10% low.

Residue levels and corresponding day of sampling were processed by computer for analysis of variance and linear regression analysis. Both programs converted residue values into natural logarithms before analysis because it was expected that the dissipation rates would be proportional to residue levels. That is, dissipation was expected to be due to one or more first-order processes, and therefore a logarithmic transformation of the residue values would be a linear function of time.

RESULTS AND DISCUSSION

Initial dislodgable paraoxon residues from leaves are 49, 42, 38, 31, 41, and 45 μg/leaf for Laveen loamy sand, Santa Lucia silt loam, Windy loam, Madera sandy loam, Visalia silt loam, and Pike's Peak clay, respectively. The corresponding initial residues from Teflon sheets (control) are 41, 39, 38, 41, 44, and 38 μg/sheet, respectively. Three of the data points for the leaves are higher than the corresponding dislodgable residues for Teflon, two are lower, and one is the same. There does not appear to be a systematic difference for the two surfaces on the initial paraoxon dislodgable residue levels as observed previously with parathion by ADAMS *et al*. (1976). Lower parathion levels on leaves were attributed to partitioning of parathion into the leaf waxes in which it is quite soluble (OKAMURA *et al*. 1977). As paraoxon is 100X more water soluble (less lipophilic) than parathion (WILLIAMS 1951) it may not have partitioned into the leaf waxes as readily as parathion. Alternatively, paraoxon may have been more readily adsorbed to the soil solids than parathion, resulting in a decrease of paraoxon available for partitioning from the soil - water slurry into a leaf surface.

Dislodgable residue data with respect to time are presented as semi-logarithmic graphs in Figures 1 and 2. Data from the leaves are represented as open circles and data from Teflon sheets as closed triangles. Except for Pike's Peak clay, the graphs appear to have slightly lower slopes after about the tenth day. A statistical test (BROWNLEE 1953) was used to determine how significantly the data deviate from linearity. For this test, the data were grouped in pairs and examined by analysis of variance. The degrees of freedom are $N_1 = 2$ and $N_2 = 10$, and the calculated variance ratios for deviation from regression are shown in Table II. For a significant departure from a straight line, the data variance ratio would equal or exceed 1.9 at the 80% confidence level and 4.1 at the 95% level. The variance ratio of 6.4 for Windy loam signifies that at the 95% confidence level, the residue data cannot be represented by a straight line. For Madera sandy loam, the 1.9 variance ratio signifies that the data deviate from a straight line at the 80% confidence level. Deviation from linearity is not statistically significant at the 80% level for the other four dusts.

Paraoxon dissipation rate constants were calculated for the last 20 days of this study by regression analysis and are listed in Table II. The rate constants are listed as the upper 95% confidence limits. In each case the lower limit is zero (no dissipation). The upper limits of the dissipation rate constants are of interest for several reasons. First, they are conservatively high estimates. Second, they do not vary greatly, *i. e.*, they are all within an order of magnitude of each other and range from 0.0056 to 0.0312 day^{-1}. Third, they represent very low rates of dissipation. For all dusts, the highest rate constant

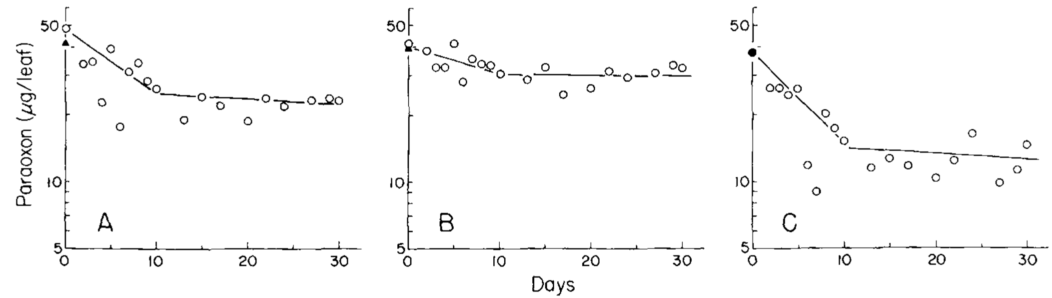

Figure 1. Dislodgable residues of paraoxon (o) recovered from orange leaves treated with an aqueous slurry of paraoxon (▲) and soil dust derived from A) Laveen loamy sand, B) Santa Lucia silt loam, and C) Windy loam.

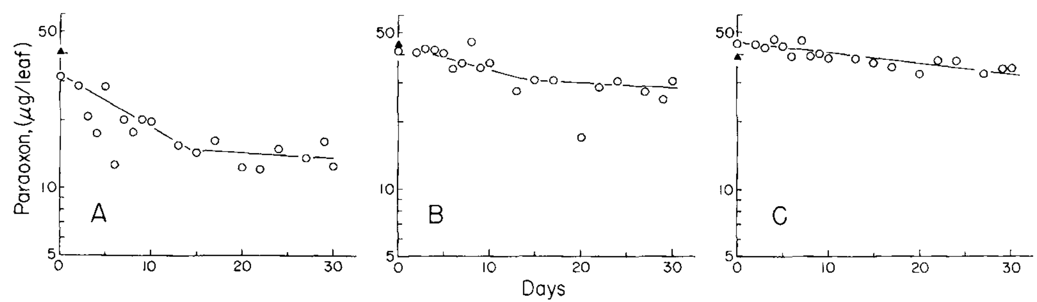

Figure 2. Dislodgable residues of paraoxon (o) recovered from orange leaves treated with an aqueous slurry of paraoxon (▲) and soil dust derived from A) Madera sandy loam, B) Visalia silt loam, and C) Pike's Peak clay.

TABLE II

Selected data and statistical parameters for paraoxon dissipation from dusts

Dust Type	Variance ratio	Dissipation rate constant (day^{-1})[a/]	Paraoxon residue levels (μg/leaf)[b/] Start	30 days	Percent paraoxon remaining
Laveen loamy sand	1.4	0.0116	46	23	49
Santa Lucia silt loam	1.3	0.0056	41	30	74
Windy loam	6.4	0.0221	38	10	27
Madera sandy loam	1.9	0.0272	32	14	43
Visalia silt loam[c/]	1.2	0.0312	44	28	65
Pike's Peak clay	0.8	0.0113	45	33	73

[a/] The dissipation rate constants are expressed as the upper 95% confidence limit.

[b/] Residue levels were estimated from the Figures 1 and 2.

[c/] Silt loam collected in a Visalia orchard, not necessarily a soil type.

is 0.0312 day^{-1} and represents a half-life of 22 days. Since the dissipation rate constant is probably lower than 0.0312 day^{-1}, the true half-life for paraoxon sorbed to any of these six dusts is probably greater than 22 days. The rate of dissipation during the first 10 days is quite important as subsequent paraoxon dissipation is slow.

Although organic matter of soil is frequently important in the adsorption and desorption of pesticides (BAILEY and WHITE 1970), there is no apparent relation here between organic content of the soils and paraoxon residue levels after 30 days. For example, ranking the soils according to percent of paraoxon remaining after 30 days from highest to lowest gives percents of soil organic matter of 0.1, 19.5, 2.5, 0.1, 1.4, and 10.8, respectively.

Ranking percent clay content according to percent of paraoxon remaining after 30 days from highest to lowest gives 73, 24, 19, 5, 12, and 9, respectively. Thus, high clay content is associated with high paraoxon retention. Ranking percentage saturation values similarly gives 128, 94, 35, 21, 27, and 54, respectively. Except for the last value, high percentage saturation values correspond to high paraoxon residues. Since both percent clay content and percentage saturation are related to the total surface area (external and internal) of a soil, the amount of surface area appears to be more important than soil organic content for the persistence of paraoxon on these soils.

Deviations from linearity (Figs. 1 and 2) in the semilogarithmic plots suggest that there is more than one mode of adsorption of paraoxon to the dusts and that at least one of these modes imparts a greater stability to paraoxon than other modes. Pesticides can be adsorbed to internal surfaces of clays (BAILEY and WHITE 1970) and this may be the mode of binding which limits the dissipation of paraoxon from soils. The fact that the dusts which exhibit the highest paraoxon residue levels have the greatest total surface area tends to support this suggestion.

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