

THE ROLE OF FOLIAR PARTICULATE MATTER IN  
THE DEGRADATION OF THE DISLODGEABLE FOLIAR  
RESIDUES OF THE ORGANOPHOSPHOROUS PESTICIDES

TECHNICAL REPORT

Contract 4277

from

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## INTRODUCTION

The work undertaken under this contract had as its general objective the elucidation of the role of foliar dust in the process by which agricultural fieldworkers are exposed to organophosphate pesticide residues while harvesting, thinning or pruning tree crops. An important aspect of the work has been to contrast the decay patterns of a liquid flowable versus a wettable powder formulation of ethyl parathion with a view towards further clarifying the role of the inert particulates in the wettable powder formulation.

The field studies subsequently discussed were carried out in citrus groves in Tulare County during June and July, 1976. The temperatures during this period were unusually cool, the average daily high during late June was near 85°F, roughly 10°F below normal. Nightly lows were also below average and foliar dew occurred frequently. Trace amounts of rainfall were recorded on July 9 and 15. In general, the effect of these conditions appears to have been to suppress the production of paraoxon to levels substantially lower than those we have normally seen for red scale applications of ethyl parathion. Nonetheless, both the dislodgeable and the available residues of paraoxon were greater in the wettable powder plot than in that treated with the liquid flowable formulation. Further, at least a portion of this difference appears attributable to the added dust load on the foliage contributed by the inert ingredients of the wettable powder formulation. Therefore, despite the unusual weather pattern we have been able to obtain data relevant to the effect of formulation on the chemical decay process and on the relative degree of worker hazard.

## METHODS AND PROCEDURES

### Field Studies

Ethyl parathion was applied to Valencia orange trees in two test plots. The plots were each 2-acre portions separated from each other by 220 feet, in one 20-acre grove. This grove was double planted: within each row trees were planted in pairs 5 feet apart with 15 feet between each pair of trees. There were 20 feet between rows. The grove was located in Tulare County (T.17S.R.26E. Sec. 4) in an area of mixed soil, Hanford Sandy Loam and Ramona Loam. Applications of 7.5 lb AIA parathion were made to each plot on 19 June 1975. The formulation in plot #3 was 25% wettable powder (WP); that in plot #6 was 8 lb/gal liquid flowable (LF).

One pre-application foliar residue sample was collected on 14 June. Subsequently, samples for residue and dust analysis were collected on days 0 (after the foliage had dried), 1, 3, 7, 14, 28, and 42 post-application (DPA). Matched samples were collected on each day by the methods of Popendorf, et al.<sup>1</sup> and of Gunther, et al.<sup>2</sup>; the former is commonly referred to as the "available" or "vacuum" samples, and the latter as the "dislodgeable" or "punch" samples. Modifications to the available method as published included a hexane rinse of the vacuum nozzle to remove and collect particulates adhering to the interior surface of this device; for the dislodgeable method, a 3-cm punch was used to collect 48 leaf discs in each sample, c.f. 1.8 or 2.5 cm punch.<sup>2</sup> After collection, all samples were stored on dry ice until transferred to the laboratory. Dust weights on the vacuum samples were determined from pre- and post-sample weighings of the 90-mm Millipore filter and

its container. Dust weights on punch samples collected in these plots could not be obtained due to the methods of residue extraction and particle collection employed within the laboratory; however, samples from other groves similarly treated were taken for comparison. In these cases, dust weights from the washed leaf discs were determined by collecting the particulates retained in the water-with-surfactant washings (after extraction of the pesticides with chloroform) on pre-weighed Whatman GF/C filters.<sup>1</sup>

Because the available and dislodgeable samples are taken from different leaves, no direct comparisons of these methods is normally possible. To verify not only that the dislodgeable dust determined from the punches contained the available particles as a sub-set and that the former represented essentially all surface particles, a single sample of 48 whole leaves was therefore chosen for multiple particle analyses. They were picked and sampled first by the normal available residue method, but instead of being sized and discarded, they were divided into 4 sets of 12, each of which was then washed according to the usual dislodgeable residue method. The leaves were then dried and xeroxed. The leaves, filter and wash water were submitted for independent microscopic testing and xeroxed sheets were used to determine the surface area.

#### Methods Development

As a first step in studying the role of foliar particulate matter it was necessary to develop methods to transfer the particulate material from the foliage to surfaces suitable for microscopic examination. Because of the basic differences between the two residue

collection procedures,<sup>1,2</sup> the procedures developed for microscopic examination differ as described below.

The leaf punch samples were prepared by the revised dislodgeable residue method of Gunther, et al.<sup>2</sup> In the separatory funnel, the density of the chloroform floated the dust at the interface and permitted the pesticide to be removed in the chloroform, leaving the dust with the aqueous portion. The chloroform solution of pesticide was analyzed as described by Spear, et al.<sup>3</sup> The aqueous-dust mixture of approximately 350 ml was then transferred to the microscopy laboratory. Two aliquot dilutions (1:20 and 1:40) were prepared in 100 ml glass-distilled water and filtered onto 47-mm diameter 0.4  $\mu$  pore size Nuclepore filters. The more properly loaded filter was selected for particle analysis.

The available residue filter samples were extracted with 150 ml of benzene by agitation for one hour. They were then centrifuged and most of the benzene was decanted from the filter and dust. An additional 100 ml of benzene was added and the above steps were repeated leaving approximately 10 ml of benzene, Millipore filter fragments and dust to be submitted in their centrifuge bottle to our microscopists for analysis. The benzene solution of pesticide was also analyzed as described above.<sup>3</sup>

The weight of the particulates on the vacuum filter was known. 200 ml of 1:1 mixture of MEK and MeOH were added to the 250 ml centrifuge bottle. The fragments of 90-mm Millipore filter dissolved in approximately 5 minutes. A stirring rod was used to gently break up clumps. The particulates were resuspended by gentle swirling. An aliquot calculated to contain close to 0.5 mg of particulates, was

pipetted, using a graduated pipet, into about 50 ml of the mixed solvent in the funnel of a 47-mm diameter glass Millipore filter assembly equipped with a 47-mm diameter Nuclepore filter of 0.4  $\mu$  pore size. House vacuum was used for filtration. With approximately 1/2 cm of fluid remaining in the filter, the walls of the funnel were washed down with mixed solvent from a wash bottle, without disturbing the surface of the filter. The filter was air dried while awaiting further analysis.

#### Preparation of Samples for Microscopic Examination

To prepare a sample for microscopic examination, a section of about 1/8 of the filter was mounted on a glass slide with a mounting medium that clears the filter so that particles can be counted and sized using a light microscope. The mounting medium was 1:1:2:2 tetrachloroethane in which Nuclepore filter material (polycarbonate) is dissolved to make the medium viscous so that the particulates cannot move easily.

The details of the technique for mounting the filter section for microscopy follow:

1. Two or three drops of mounting medium are placed on a glass microscopic slide.
2. The filter section is placed on the mounting medium, particle side up.
3. A cover slip is placed on the filter and the mounting medium is allowed to flow to the edge of the cover slip.
4. The cover slip is sealed to the slide with clear collodion nail polish applied with a brush. This retards evaporation of the solvent.

The technique for counting and sizing the particles follows:

1. A Leitz Orthomat phase contrast microscope was used. The microscope is equipped with a 40X phase contrast, apochromatic objective lens, a Heine phase condenser, and a 10X eyepiece.
2. A Porton grating is mounted in the eyepiece to define a field and to size the particles. The width (100L) of the Porton grating is calibrated in microns, using a stage micrometer. This width squared defines the area of 1 field and "L" is used to determine the diameters of the circles on the grating used for sizing the particles by the formula  $d = L \sqrt{2n}$ . All particles in 100 to 200 fields are counted until at least 100 particles are sized.

## RESULTS AND DISCUSSION

### Weather

The weather variables measured at the Fresno airport, 25 miles to the NW of the test plots, are plotted in Figure 1. Temperatures for most of the interval were unusually cool, the average daily high during late June being near 85°F, roughly 10 degrees below normal. Nightly lows were also subnormal with frequent foliar dew. Trace rainfall was recorded July 9 and 15.

### Residues

Figures 2 and 3 show the dislodgeable residues from the two plots over the study period. Plot 3 (Figure 2) and plot 6 (Figure 3) are the wettable powder and liquid flowable plots, respectively. Figures 4 and

5 are the corresponding available residue results. These data appear in Tables 1 and 4.

In addition to these two plots for which both residue and microscopic particulate data were obtained, residue decay data were collected from four other plots which received identical applications. These plots, 2 receiving WP applications and 2 receiving LF applications, were on different soil types elsewhere in the county. Insofar as these data bear on the formulation differences under study herein, the residue results from all six plots will be discussed at this point.

In order to compare the decay processes in the LF versus the WP plots, it is useful to fit the data to a differential equation model as we have done in the past.<sup>4</sup> The model is given by the following equations:

$$\frac{dx_1}{dt} = -a_1 x_1$$

$$\frac{dy_1}{dt} = -b_1 y_1$$

$$\frac{dx_2}{dt} = -a_3 x_2 + b_3 y_1 - a_2 x_2$$

where

$$x_1 = \text{short-term parathion component in ng/cm}^2$$

$$y_1 = \text{long-term parathion component in ng/cm}^2$$

$$x_2 = \text{paraoxon residue in ng/cm}^2$$

Hence, the total parathion residue is

$$w = x_1 + y_1, \text{ ng/cm}^2$$

Table 5 contains the parameter estimates for the dislodgeable residues for the plots. There are several striking differences in the rate data of Table 5 between the wettable powder plots, 1-3, and the liquid flow-

able plots, 4-6. In particular, the short-term oxon production rate  $a_3$  is substantially less in plots 4-6 than in plots 1-3. This difference is also seen for the long-term parathion decay rate  $b_1$  although this difference has somewhat less significance for worker hazard.

As a result of this difference in short-term oxon production, the peak paraoxon residue is always greater in the WP plot as compared to the LF plot, independent of any relative differences in initial deposits between the various plots. However, because these oxon levels are all generally less than normal, presumably because of the abnormal weather, little practical difference can be seen in oxon levels by day 28 between the LF and WP plots.

The available residues from plots 3 and 6 also show an even higher oxon peak in the WP versus the LF application than comparable dislodgeable residues. This difference persists over the entire period but again, the residues are quite low by day 28 and no practical difference was demonstrated.

#### Particulates

In general, the particle size data from both the dislodgeable and available residue samples showed considerable variability. The basic set of data from the light microscope (LM) analyses is shown in Table 6. The size index numbers correspond to those in the Porton reticle and, at the magnifications used, the particle diameter in microns is given by  $d = .65 \sqrt{2^n}$  where  $n$  is the reticle index number. The number of particles observed in each size range and category was first divided by the sampled leaf area then multiplied by a "scaling factor" determined from the aliquot-sample volume ratio and the observed-area to

total-filter-area ratio, resulting in the quantities listed in Table 6, particles per  $\text{mm}^2$  of leaf surface. The variability in these data is sufficiently large that it was not possible either to detect any differences in the particle size distribution between LF and WP plots nor to discriminate if there existed trends of this distribution over time.

The variability of this data can be explained at least in part by the nature of the particulate material and the technique used for analysis. Foliar particulates have a tendency to agglomerate and form "clumps" on the leaf surfaces. These clumps can be observed directly on the leaf surface, under the microscope or by eye, as patterns of ridges or mounds formed during the movement and evaporation of surface droplets. This non-homogeneous particle distribution results in varying proportions of clumps (irregular aggregates of small particles) and large clusters ( $>30 \mu$  diameter) which remain throughout the sample preparation and are reported on Table 6b. At the other end of the spectrum, particles smaller than  $1.0 \mu$  were not counted using the LM because of the limits of resolution for this type of equipment. Because the median particle size occurs very near this limit and the observed sample distributions often lacked homogeneity, the statistical parameters for the particle size distribution were quite sensitive to small fluctuations in the counts of size 2, 3 and 4 particles, thus resulting in the large variability of estimated mean sizes determined from Table 6a.

Further analyses of some of these samples by the electron microscope (EM) clarified this issue. Four filtered samples were transferred to 200 mesh nickel specimen grids for observation using a

Siemens Elmiskop I<sup>®</sup> transmission EM. These grids were scanned at magnifications as large as 20,000X, but particles smaller than 0.1  $\mu$  were not observed. Electromicrographs at 2,000X were prepared from these samples (several examples are appended). The results of a particle size analysis of these micrographs is shown in Table 7. These data indicate that the particles tend to conform to a log-normal distribution, geometric mean 1.73  $\mu$  and geometric deviation of 2.37. Nearly 30% of these particles would not have been resolvable by the light microscope. Assuming that a similarly large fraction of particles was also unobservable from our other LM samples, we attempted to interpret the existing truncated distribution resulting from the LM by means of a best-fit analysis against a theoretical log-normal distribution. This method assumes that the observed data includes the median and at least some portion of the truncated side of the distribution; however, because the geometric mean for these samples was in the range of the smallest two frequencies observed, slight fluctuations in the counts of the two or three smallest particles resulted in comparatively large changes in the estimated statistical parameters. Only the LM results of samples 3F14, 6F42 and 3P1 agreed with the EM data. Because of the limitations of the LM in this size range, we feel the EM results are most reliable and that the use of the LM to size foliar particles in this manner is severely limited.

It was, however, possible to gain some insight into foliar particle transfer by considering the time trends for total particles (<30  $\mu$  diameter) per unit area and the various characteristic particles

(clumps, diatoms and fibers) per unit area. Table 8 shows the result of linear regression analyses of these measures versus time. Only in the case of total particles from the dislodgeable samples of plot 3 did a significant regression occur and that indicated an increase in number of total particles over time. Additional data on foliar dust weight versus time was obtained in these plots only for available residues. Table 9 shows the dust weights in  $\mu\text{g}/\text{cm}^2$  for the available residues from plots 3 and 6. Although the available dust weight in both plots again increases slightly with time, in neither case was the regression of dust versus time found to be significant at the 5% level. As a result, it would appear that residue decay is primarily a chemical process and that physical particulate transport is of little significance.

Significant comparisons can be made between the LF and WP applications in terms of both weight and numbers of the various foliar particulates as shown in Table 10. Only for the available residues are the number of fibers/ $\text{mm}^2$  significantly different (at the 5% level) between the two plots. For both types of residue samples the number of diatoms and the number of total particles were significantly different at levels below 2.5%. Again for these measures, the available residues showed a larger difference than the dislodgeables. The ratio of excess diatoms to excess particles for the dislodgeable samples is equal to the ratio observed in the initial WP formulation (CNTL samples); however, proportionately fewer excess diatoms were collected by the vacuum nozzle of the available sampling method. It thus appears that this latter method samples a somewhat selective subgroup of the total

or dislodgeable foliar particulates. The significance of this difference awaits further inquiry.

A direct comparison between the two basic analytic techniques to remove particles from the leaf surface was made by multiple particle analyses. The results of sequential vacuuming then washing of the same leaves are shown on Table 11. These results indicate that the vacuum removed approximately 25% of both diatoms and small particulates but proportionately few fibers. The water wash removed more than 99% of all categories of foliar particulate material. It appears from this and earlier results that fibers are highly variable in their frequency of occurrence and in their ability to cling to the leaf surface. They do not appear to represent a potential "internal standard" for the quantity of wettable powder either disposed or remaining.

Returning to Table 9 for a moment, it can be seen that the dust weights from the available residues are also significantly higher in the WP plot with the average difference being about  $4.3 \mu\text{g}/\text{cm}^2$  or about 1/3 more than the average available dust weights obtained for the LF plots. Comparable dislodgeable data from days 0, 3 and 7 in the two similarly treated pairs of plots (plots 1-2 and 4-5 mentioned earlier) indicated an average difference of  $12 \mu\text{g}/\text{cm}^2$  or about an additional 10% of the LF dust load. This  $12 \mu\text{g}$  is almost exactly the dust expected for a deposit of  $2,500 \text{ ng}/\text{cm}^2$  parathion with a 25% WP. This suggests that a large fraction of the deposited wettable powder is available, i.e.  $4.3/12$  or 35%; this is approximately the same percentage as the ratio of available to dislodgeable chemical residues from Tables 1-4. The newly deposited dusts and in particular the

smaller particles are probably less firmly attached than the existing deposit of natural foliar dust. Notably, despite the fact that no pesticide-saturated dust particles were added to the LF plot, the available fraction of the chemical residues are nearly as large as for the WP plots.

It thus appears that the wettable powder formulation contributed significantly to both the overall and certain characteristic populations of particulates on the leaf surface; however, some portion of these particles was also contributed by the general disturbance and activity in the grove during applications. Furthermore, it appears that once deposited, these particles did not appear to sluff off significantly over the 42 days of observation.

#### SUMMARY

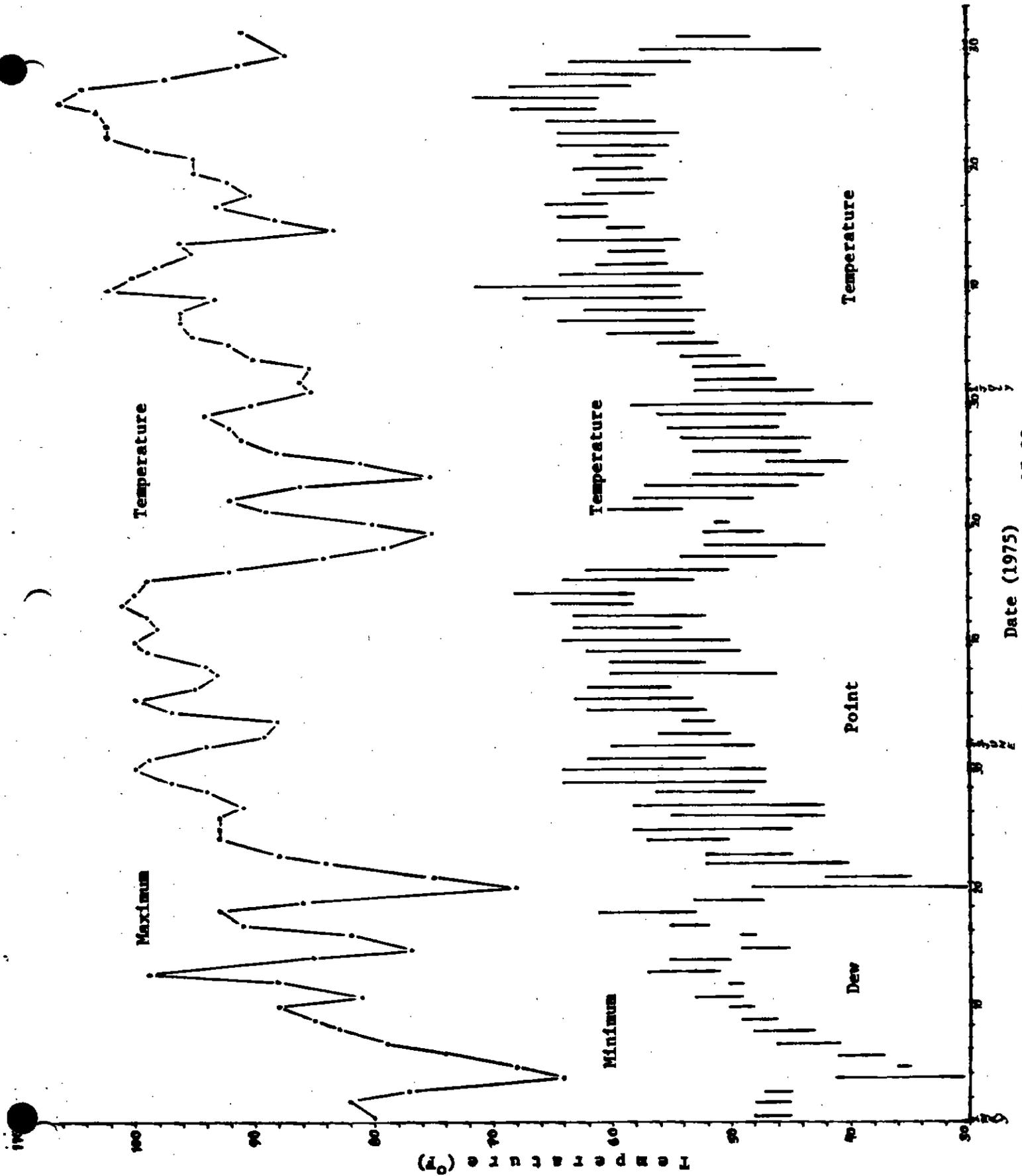
Matched applications of WP and LF parathion were applied to Valencia orange trees. Significant differences were observed between these test plots in terms of both paraoxon production and surface foliar particulates; moreover, these differences were generally more apparent when determined from the available residues as compared to the dislodgeable residues. Although the initial deposit of parathion appears to have been 25% larger in this WP plot than the LF plot, the dislodgeable paraoxon in the WP plot was typically 2 times larger than the LF plot, while for available residues this ratio was often more than 3.5. Although the wettable powder appears to contribute significantly to the small particle (<30  $\mu$  diameter) and diatom populations, a natural population of fibers was observed in pre-application samples

and fibers in the WP plot were not conclusively more frequent than in the LF plot. The diameter of foliar particulates other than "clumps" (<30  $\mu$  diameter) were log-normally distributed with a median diameter in the range of 1.7  $\mu$ . The use of the light microscope was found adequate to count the characteristic particles and most of the foliar particulates, however, it did not allow accurate estimates of the size distribution statistics. The use of the electron microscope was therefore employed to verify the above median particulate diameter and that 99.9% of the particulates are larger than 0.2  $\mu$ .

Measurements of neither particulate size, characteristic particle frequency, nor dust weight were found to change significantly with time. Therefore, this data cannot support the claim that the more rapid degradation of parathion ( $a_1$  and  $b_1$  of Table 5) is the result of physical losses of foliar particulates. It remains possible that certain large clumps of material are lost after application but this loss is not reflected in any measured particle population parameter. Although the wettable powder formulation seem to affect the rate of parathion decay and paraoxon production, the observed importance of weather and of particle/pesticide availability suggest that this affect may be more strongly associated with the particle microclimate.

REFERENCES

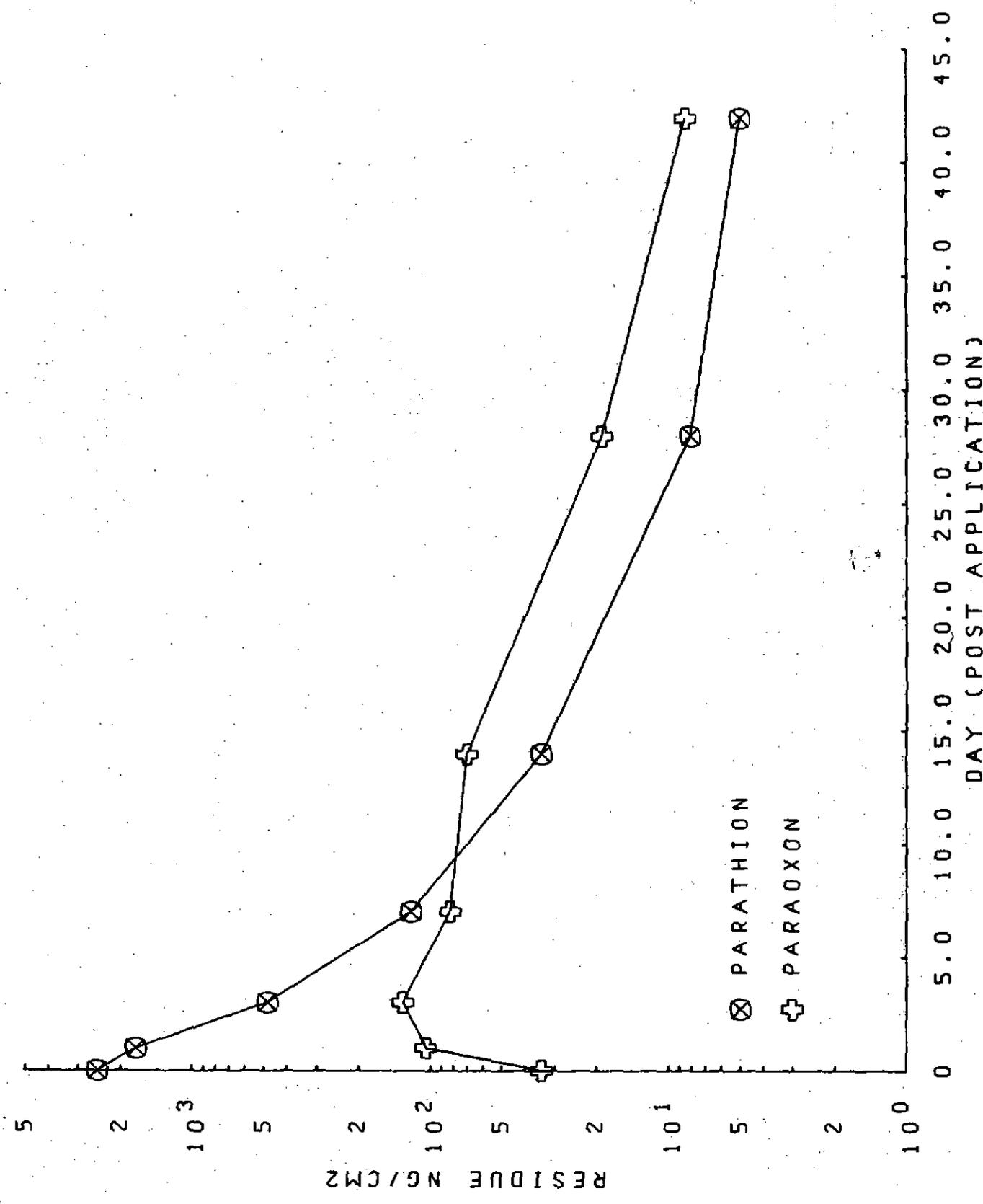
1. Popendorf WJ, Spear RC, Selvin S: Collecting Foliar Pesticide Related to Potential Airborne Exposure of Workers. Environ. Sci. and Tech. 9:583, 1975.
2. Gunther FA, Barkley JH, Westlake WE: Worker Environment Research II. Sampling and Processing Techniques for Determining Dislodgeable Pesticide Residues on Leaf Surfaces. Bull. Environ. Contam. Toxicol. 12:641-644, 1974.
3. Spear RC, Popendorf WJ, Leffingwell JT, Milby TH, Davies, JE Spencer WF: Exposure and Response of Fieldworkers to Weathered Residues of Parathion. Arch. Environ. Health, in press.
4. Popendorf WJ: An Industrial Hygiene Investigation into the Occupational Hazards of Parathion Residues to Citrus Harvesters, University of California, Berkeley, June 1976.



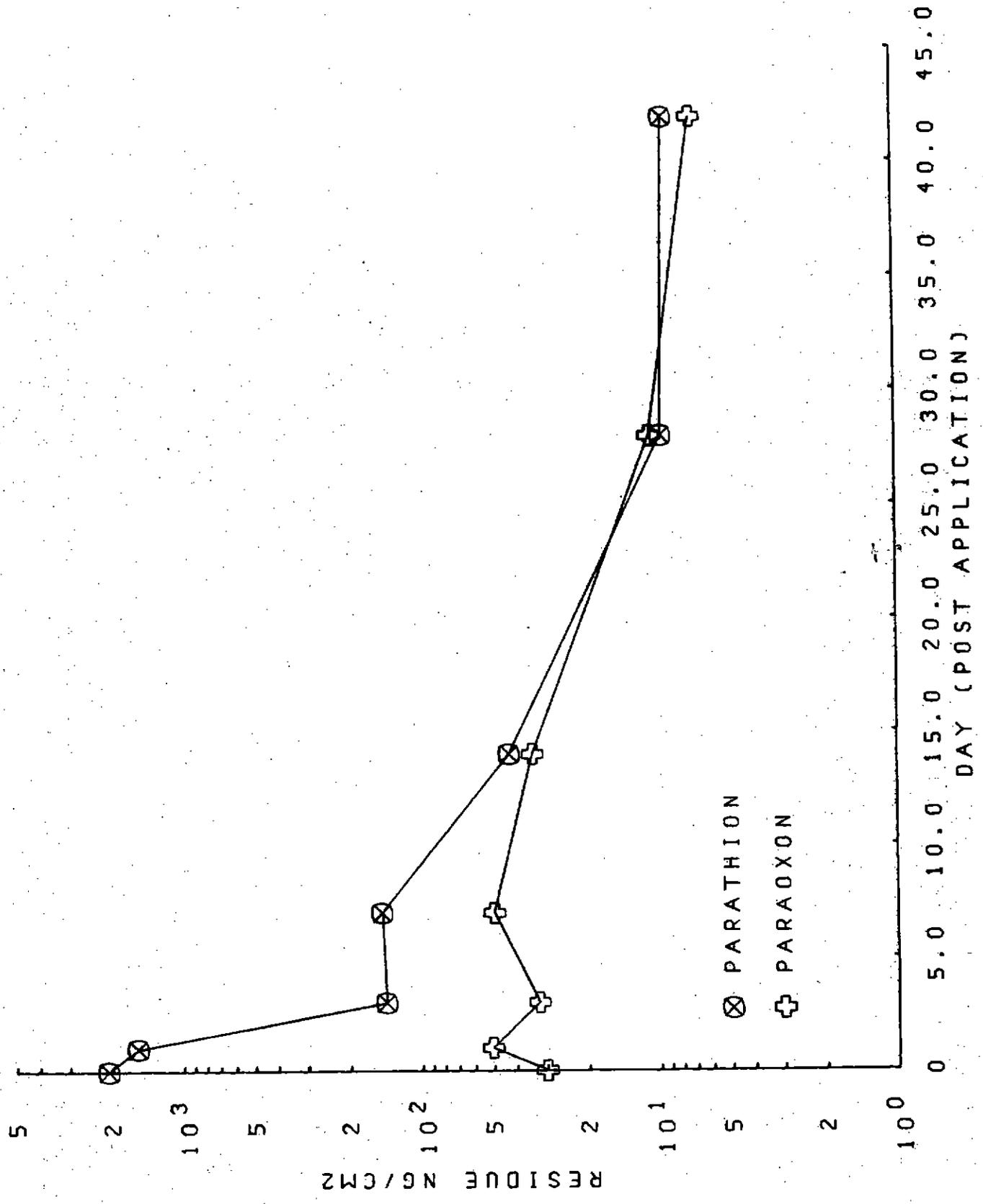
Date (1975)  
 Application Dates: June 17-20

Daily temperatures recorded at Fresno, California (25 mi NW upwind) of test plots. Minimum temperature - Dew Point spread indicated by verticle bars.

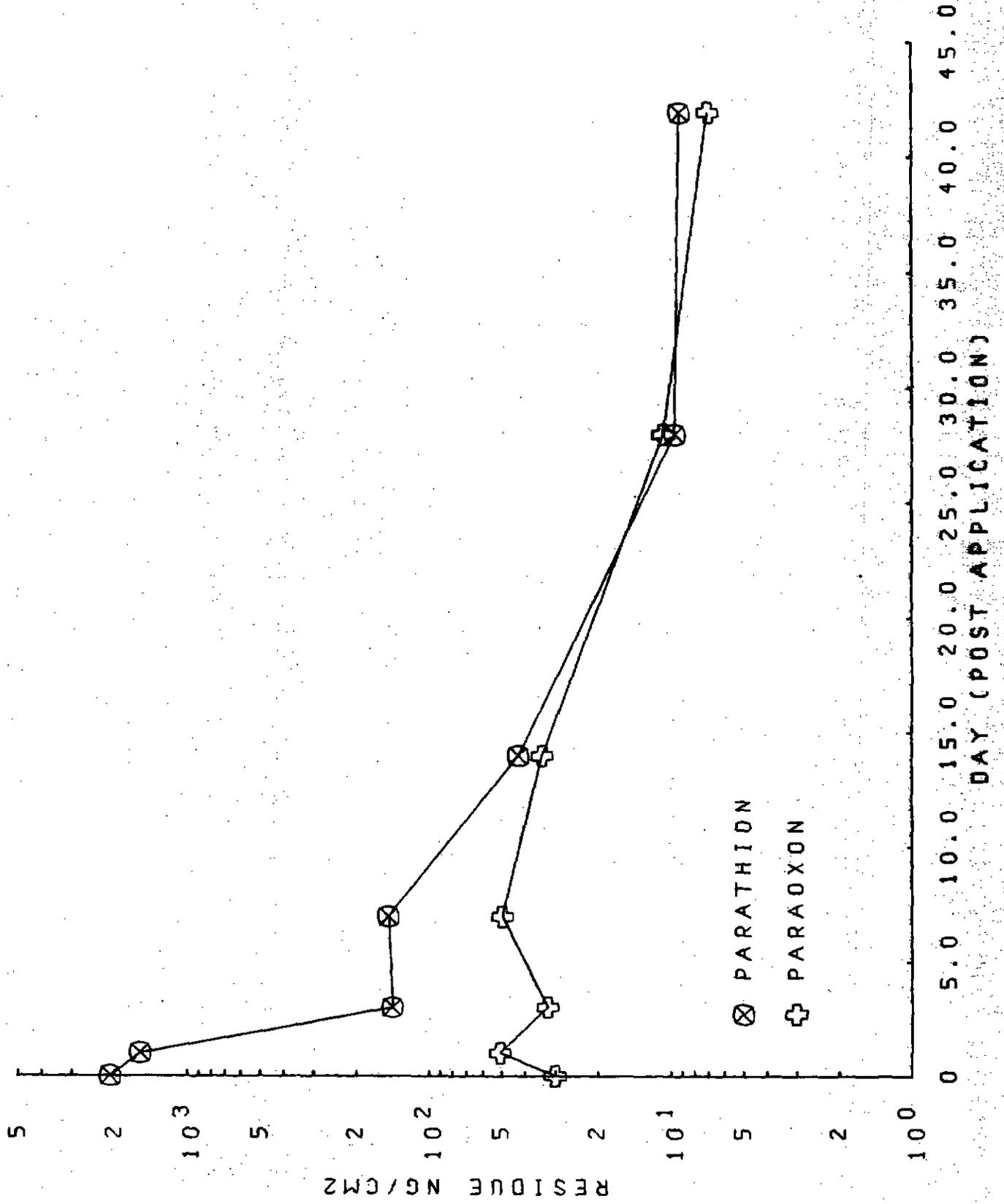
PLOT 3 (DISLUDGEABLE)



PLOT 6 (DISLUDGEABLE)



PLOT 6 (DISLUDGEABLE)



PLOT 6 (AVAILABLE)

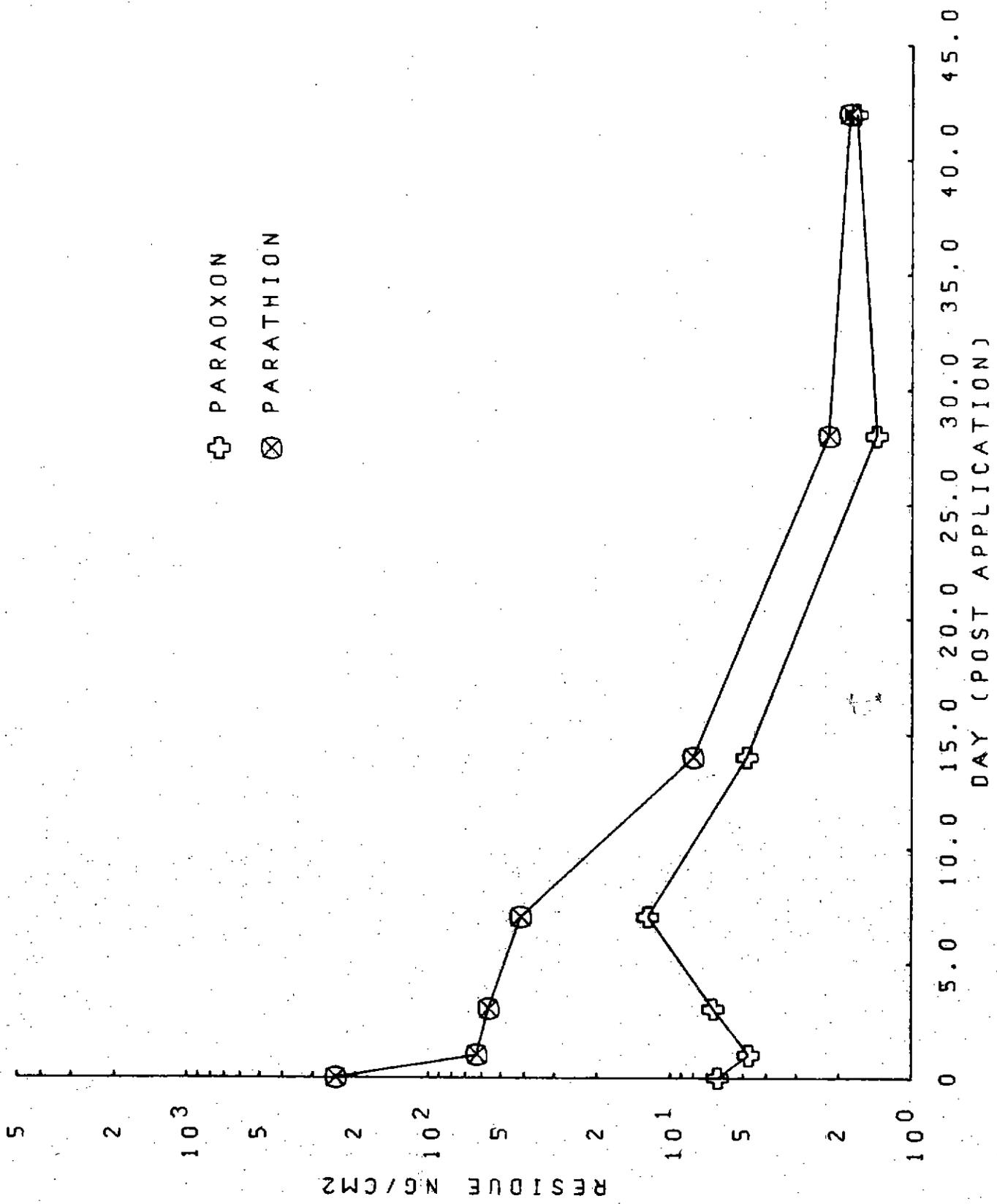


TABLE 1

PLOT: 3 (Ferrier)	APPLICATION RATE: 7.5 lb AIA	RESIDUES:
PESTICIDE: Parathion	GALLONAGE: 1500/acre	AVAILABLE <input type="checkbox"/>
FORMULATION: WP	APPLICATION DATE: 6/19/75	DISLODGEABLE <input checked="" type="checkbox"/>

<u>DAY, POST-APPLICATION</u>	<u>RESIDUE (ng/cm<sup>2</sup>):</u>	
	<u>PARATHION</u>	<u>PARAOXON</u>
0	2481	34
1	1713	104
3	480	130
7	120	82
14	34	70
28	8.1	19
42	5.0	8.5

TABLE 2

PLOT: 6 (Ferrier)                      APPLICATION RATE: 7.5 lb AIA                      RESIDUES:  
 PESTICIDE: Parathion                      GALLONAGE: 1500/acre                      AVAILABLE   
 FORMULATION: LF                      APPLICATION DATE: 6/19/75                      DISLODGEABLE

<u>DAY, POST-APPLICATION</u>	<u>RESIDUE (ng/cm<sup>2</sup>):</u>	
	<u>PARATHION</u>	<u>PARAOXON</u>
0	2074	30
1	1560	50.5
3	141	32.2
7	147	49.5
14	42.6	34
28	9.6	10.7
42	9.2	7.0

TABLE 3

PLOT: 3 (Ferrier)

APPLICATION RATE: 7.5 lb AIA

RESIDUES:

PESTICIDE: Parathion

GALLONAGE: 1500/acre

AVAILABLE 

FORMULATION: WP

APPLICATION DATE: 6/19/75

DISLODGEABLE 

<u>DAY, POST- APPLICATION</u>	<u>RESIDUE (ng/cm<sup>2</sup>):</u>	
	<u>PARATHION</u>	<u>PARAOXON</u>
0	304.8	8.8
1	398.6	34.7
3	127.9	31
7	39.5	26.2
14	11.7	18.5
28	3.2	4.3
42	1.7	2.4

TABLE 4

PLOT: 6 (Ferrier)	APPLICATION RATE: 7.5 lbs AIA	RESIDUES:
PESTICIDE: Parathion	GALLONAGE: 1500/acre	AVAILABLE <input checked="" type="checkbox"/>
FORMULATION: LF	APPLICATION DATE: 6/19/75	DISLODGEABLE <input type="checkbox"/>

<u>DAY, POST-APPLICATION</u>	<u>RESIDUE (ng/cm<sup>2</sup>):</u>	
	<u>PARATHION</u>	<u>PARAOXON</u>
0	239.7	6.3
1	62.5	4.7
3	55.9	6.6
7	41.3	12.3
14	8	4.8
28	2.2	1.4
42	1.8	1.7

Table 5 Tabulation of experimental T-V estimated punch rate coefficients (day<sup>-1</sup>) and initial conditions (ng/cm<sup>2</sup>): Model II.

	short term parathion				long term parathion				paraoxon	
	decay	oxidation	yield	initial	decay	oxidation	yield	initial	decay	initial
	a <sub>1</sub>	a <sub>3</sub>	a <sub>3</sub> /a <sub>1</sub>	a <sub>4</sub>	b <sub>1</sub>	b <sub>3</sub>	b <sub>3</sub> /b <sub>1</sub>	b <sub>4</sub>	a <sub>2</sub>	a <sub>5</sub>
1	.555	.034	6.1%	2075	.035	.94x10 <sup>-3</sup>	2.6%	21	.062	41
2	.312	.039	12.5%	2368	.017	.31x10 <sup>-4</sup>	.2%	16	.086	5
3	.457	.034	7.4%	2628	.035	.15x10 <sup>-1</sup>	43%	22	.091	9
4	.438	.021	4.8%	2689	.006	.47x10 <sup>-4</sup>	.8%	17	.039	6
5	.281	.010	3.6%	2509	.007	.97x10 <sup>-3</sup>	14%	13	.054	65
6	.362	.014	3.9%	1737	.009	.52x10 <sup>-2</sup>	57%	13	.071	5

Table 6 Light microscope particle analyses data.  
 Samples are identified by plot number, sample type (F=vacuum filter, P=punch), and days post-application.

Table 6a Frequency per  $\text{mm}^2$  of particulates of diameters  $d$ ,  $0.9 < d < 30 \mu$

n= d( $\mu$ )	2	3	4	5	6	7	8	9	10	11
available										
F - PA*	17.1	20.0	11.6	7.6	1.4	2.2	1.1	0.	0.	0.
3F0	8.1	10.1	9.6	14.1	16.6	14.6	21.7	13.1	0.5	4.0
3F1	15.0	14.3	8.8	22.4	16.3	15.0	8.8	13.6	0.	1.4
3F3	4.6	9.9	22.7	22.7	22.1	18.1	9.3	4.7	0.6	0.
3F7	3.9	16.1	23.3	17.2	12.8	11.7	8.9	4.4	0.6	0.
3F14**	9.1	21.2	21.9	15.2	10.7	5.2	8.4	4.3	2.8	1.6
3F28	6.9	17.8	21.8	33.9	29.3	31.0	27.6	11.5	1.7	0.
3F42	9.3	24.9	25.5	10.4	20.9	16.2	9.3	2.9	0.6	0.
6F0	11.8	12.9	10.2	7.5	6.4	3.2	1.1	2.1	3.2	0.
6F1	2.5	4.7	3.5	6.9	10.4	6.9	7.9	1.9	1.3	0.
6F3	22.2	15.7	13.4	8.3	6.0	3.2	3.7	0.5	0.5	0.9
6F7	8.0	9.9	11.3	9.9	4.7	2.3	3.3	3.3	0.	0.
6F14	29.0	42.4	21.2	20.1	10.6	3.3	3.3	0.5	1.1	0.
6F28**	4.9	8.6	9.8	10.0	9.3	6.5	3.9	2.3	0.9	0.4
6F42	20.7	29.9	25.3	15.0	9.8	6.3	9.8	3.4	2.9	0.6
dislodgeable										
P - PA*	58.7	66.1	91.8	69.8	47.7	22.0	44.1	25.7	25.7	11.0
3P0	120.2	100.1	120.2	48.1	40.1	16.0	36.0	24.0	16.0	4.0
3P1	120.8	135.5	93.5	102.8	56.1	37.4	32.7	18.7	4.7	0.
3P3	76.1	64.1	52.1	60.1	36.0	36.0	28.0	8.0	12.0	0.
3P7	192.6	188.3	188.3	109.5	70.0	56.9	43.8	26.3	30.6	8.7
3P14**	40.2	126.4	222.2	173.3	131.8	80.9	73.5	37.3	9.5	5.3
3P43	125.2	109.5	177.4	193.0	140.8	151.3	93.9	67.8	31.3	5.2
6P0	96.0	158.9	168.9	79.5	43.0	49.6	39.7	26.5	3.3	9.9
6P1	40.1	44.1	64.1	40.1	48.1	32.0	16.0	32.0	20.0	4.0
6P3	95.5	86.8	69.4	39.1	60.8	26.0	43.4	17.4	26.0	0.
6P7	70.5	189.2	133.5	129.8	59.3	44.5	77.9	37.1	11.1	3.7
6P14	4.0	32.0	56.1	152.2	140.2	112.2	128.2	60.1	36.0	0.
6P28	62.6	54.5	90.8	50.5	48.4	40.4	32.3	24.2	10.1	6.0
6P42	7.8	31.4	66.8	78.5	62.8	74.6	55.0	43.2	23.6	3.9
CNTL***	27.3	74.1	31.1	50.7	50.7	39.0	70.2	19.5	11.7	7.8

\* pre-application sample collected four days prior to initiating degradation test.  
 \*\* average of replicated values as shown on Table 6C.  
 \*\*\* control sample of wettable powder formulation, suspended in distilled water, filtered and analysed. Values listed are thousand particles per mg of dust.

Table 6b

Characteristic particle frequency per  $\text{mm}^2$  and extrapolated size distribution parameters estimated by log-normal regression analysis.

	total ( $<30\mu$ )	clumps ( $>30\mu$ )	diatoms	fibers	mean diam.	geom dev
available						
F - PA*	61.0	2.2	0.	1.4	0.8	4.9
3F0	112.4	6.5	5.0	3.5	4.4	2.4
3F1	115.6	5.4	5.4	7.5	-	-
3F3	114.7	1.2	6.4	7.0	4.2	1.8
3F7	99.0	7.8	3.3	6.7	4.0	1.9
3F14**	103.0	2.2	7.8	2.0	-	-
3F28	181.7	14.4	11.5	5.2	4.6	1.9
3F42	119.5	3.5	3.5	5.8	3.2	2.2
6F0	58.6	3.2	1.1	1.1	-	-
6F1	46.1	9.2	0.3	3.8	4.7	2.2
6F3	74.4	2.3	0.9	4.1	-	-
6F7	52.8	7.5	0.0	1.4	.47	7.0
6F14	131.8	3.3	2.2	2.8	.42	3.6
6F28**	57.7	1.6	0.4	3.2	-	-
6F42	123.8	4.6	0.6	4.0	1.6	3.1
dislogeable						
P - PA*	462.7	36.7	0.	7.3	1.5	5.1
3P0	524.8	52.1	24.0	16.0	.21	6.7
3P1	584.2	51.4	4.7	9.3	1.9	2.7
3P3	372.6	24.0	20.0	20.0	1.1	4.3
3P7	915.1	74.4	192.6	35.0	.36	5.7
3P14**	910.4	14.8	121.6	25.4	-	-
3P42	1095.5	47.0	26.1	36.5	3.7	2.3
6P0	675.4	36.4	13.2	10.0	1.1	3.6
6P1	340.5	44.1	4.0	8.0	3.0	3.1
6P3	464.4	34.7	0.0	8.7	-	-
6P7	756.7	52.0	22.2	7.4	2.8	2.5
6P14	761.2	44.1	4.0	48.1	6.4	1.8
6P28	419.9	32.3	6.0	12.1	2.4	3.2
6P42	420.3	98.2	3.9	43.2	5.7	2.0
CNTL***	374.3	42.9	132	74.1	4.0	2.7

\* pre-application sample collected four days prior to initiating degradation test.

\*\* average of replicated values as shown on Table 6C.

\*\*\* control sample of wettable powder formulation, suspended in distilled water, filtered and analysed. Values listed are thousand particles per mg of dust.

Table 6c

Replicated particle analyses of particulates and characteristic particles.

	n= d( $\mu$ )=	2	3	4	5	6	7	8	9	10	11
3F14(1)		16.3	28.2	32.7	21.4	13.5	5.6	3.4	2.3	1.1	0.6
(2)		7.3	25.9	24.2	12.4	11.8	5.6	11.3	5.6	2.3	2.3
(3)		3.9	9.6	9.0	11.8	6.7	4.5	10.7	5.1	5.1	2.3
6F28(1)		0.9	6.6	9.9	12.7	12.7	10.8	2.3	2.8	1.4	0.
(2)		8.9	10.8	9.9	7.5	6.1	2.3	5.6	1.9	0.5	0.9
3P14(1)		75.4	142.4	213.7	167.6	121.5	41.9	33.5	4.2	4.2	4.2
(2)		29.9	89.7	141.0	196.6	128.2	128.2	81.2	64.1	8.5	8.5
(3)		29.9	149.6	307.7	179.5	162.4	81.2	106.8	51.3	12.8	8.5
(4)		25.6	123.9	226.5	149.6	115.4	72.6	72.6	29.9	12.8	0.

	total ( $<30\mu$ )	clumps ( $>30\mu$ )	diatoms	fibers
3F14(1)	125.0	6.2	7.3	3.4
(2)	108.7	3.4	6.2	1.7
(3)	68.7	3.9	10.1	1.1
6F28(1)	60.1	1.4	0.	4.2
(2)	54.4	2.8	0.9	2.3
3P14(1)	808.6	25.1	29.3	33.5
(2)	876.0	38.5	149.6	21.4
(3)	1089.7	4.3	183.8	21.4
(4)	829.0	29.9	123.9	25.6

Table 7

Electron microscope particle analyses data. Observed particles in selected fields at 2000 x; these fields were selected for particle size information (>7 particles per  $2^2$  field) and therefore cannot be used to estimate frequency per  $\text{mm}^2$ .

equivalent "n" from LM						2	3	4	5	6	7	8	9	10
d( $\mu$ )=	.23	.33	.46	.65	.92	1.3	1.8	2.6	3.7	5.2	7.4	10.	15.	21.
3F3	0	0	2	5	4	7	7	3	4	0	2	2	1	0
3P0	0	0	5	8	3	11	14	6	3	4	5	0	0	1
6P0	0	2	4	8	7	12	12	14	2	1	3	3	0	0
CNTL	2	1	1	3	4	9	10	4	5	1	1	1	0	0

	total ( $<30\mu$ )	clumps ( $230\mu$ )	diatoms	fibers	mean diam.	geom. dev.
3F3	37	0	1	1	1.78	2.6
3P0	60	0	5	2	1.73	2.5
6P0	68	1	0	0	1.59	2.3
CNTL	42	0	3	2	1.55	2.4

Table 8 Results of linear regression analyses ( $y = a + bx$ ) where  $y$  = frequency (from Table 6b) and  $x$  = time; regression coefficient  $r$ , degree of freedom and value of Student  $t$ -test, and significance level  $\alpha$  where appropriate.

available residues	Sample	a	b	r	df	t	$\alpha$
total	3F	109.6	.81	.46	5	1.15	
clumps		5.4	.06	.22	'	.50	
diatoms		5.78	.03	.15	'	.35	
fibers		5.56	-.01	-.10	'	-.23	
total	6F	60.9	1.25	.56	5	1.52	
clumps		5.25	-.05	-.27	'	-.63	
diatoms		.84	-.003	-.06	'	-.14	
fibers		2.50	.03	.40	'	-.98	
dislodgeable residues							
total	3P	576.6	13.9	.80	4	2.63	<.05
clumps		46.37	-.074	-.06	'	-.12	
diatoms		66.0	-.11	-.02	'	-.04	
fibers		18.34	.48	.72	'	2.07	
total	6P	593.1	-3.3	-.30	5	-.69	
clumps		35.19	1.0	.07	'	2.19	
diatoms		9.21	-.12	-.24	'	-.56	
fibers		10.24	.69	.61	'	1.74	

Table 9

Available dust weight results. Preapplication<sub>2</sub> samples were collected from these plots with  $9.0 \pm 1. \mu\text{g}/\text{cm}^2$ . Regression analysis of weight (y) versus time (x) follows,  $y = a + bx$ ; regression coefficient (r), degrees of freedom, and value of Students t-test are shown.

	Plot 3(WP)	Plot 6(LF)
DPA	Wt. $\mu\text{g}/\text{cm}^2$	Wt. $\mu\text{g}/\text{cm}^2$
0	14.7	12.8
1	18.9	8.9
3	14.8	10.7
7	15.5	11.2
11	17.3	13.5
28	15.3	12.3
42	17.8	14.4
	<hr/>	<hr/>
mean	16.3	12.0
s.d.	1.7	1.9

regression analysis:

a	16.0	10.9
b	.03	.08
r	.25	.68
df	5	5
t	.57	2.07

Table 10

Results of t-test for the significance of differences between the mean characteristic particle frequencies ( $\text{mm}^{-2}$ ) for WP (plot 3) and LF (plot 6) applications. Significance level based on one-tailed test.

	total particulates ( $<30\mu$ )	clumps ( $\geq 30\mu$ )	diatoms	fibers
<b>available residues</b>				
F - PA	61.0	2.2	0.	1.5
3F avg	116.	5.9	6.8	4.6
6F avg	75.	4.3	0.8	3.0
Sp	31		21	1.9
$t_{15}$	2.67	.98	5.55	1.81
$\alpha$	<.01		<.001	<.05
<b>dislodgeable residues</b>				
P - PA	462.7	36.7	0.0	7.3
3P avg	787.4	38.4	83.8	24.3
6P avg	548.3	48.8	7.6	19.6
Sp	221	23.3	58.7	13.6
$t_{14}$	2.15	-.56	2.57	.68
$\alpha$	<.025		<.025	

Table 11 Results of one whole leaf sample collected in plot 3 (WP) and subjected to multiple analyses: available sample collected and analysed, dislodgeable sample collected and analysed, and cleaned leaves directly analysed for remaining material.

	total particles ( $<30\mu$ )	clumps ( $>30\mu$ )	diatoms	fibers
available	129. <u>+28</u>	13.1 <u>+1.2</u>	5.4 <u>+3.9</u>	3.4 <u>+4.4</u>
dislodgeable	515. <u>+140</u>	161. <u>+44.</u>	19.9 <u>+15.6</u>	32.2 <u>+18.3</u>
remaining	.04	1.1	$>0.001$	.14
% removed by washing	99.99	99.3	$>99.99$	99.6
% removed by vacuum	20.	8.	21.	10.