was formed by microbial metabolism of PBB in the dogs' gut and that it was then excreted in the feces. PBB levels in the feces were about 7 ppm. The hydroxy metabolite levels in the feces were about an order of magnitude less. DBF metabolites were not found in the feces.

This work has demonstrated that the high temperatures in the gas chromatograph may cause 6-hydroxy-2,4,5,2',4',5'-HBB to decompose to DBFs, which are then detected by MS. GC–MS is extensively used as the sole screening method for metabolites and contaminants occurring in foods and in the environment (Alford, 1977). Results obtained by this technique which indicate the presence of brominated DBFs should be confirmed by other analytical techniques in order to show that the brominated DBFs have not been formed from hydroxy-PBBs during analysis.

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LITERATURE CITED

Alford, A., *Biomed. Mass Spectrom.* **4**, 1 (1977).
Bowes, G. W., Mulvihill, M. J., DeCamp, M. R., Kende, A. S., *J. Agric. Food Chem.* **23**, 1222 (1975).
Chen, J.-Y. T., *J. Assoc. Off. Anal. Chem.* **48**, 380 (1965).
Curley, A., Burse, V. W., Jennings, R. W., Villanueva, E. C., Kimbrough, R. D., *Bull. Environ. Contam. Toxicol.* **14**, 153 (1975).
Gardner, A. M., Righter, H. F., Roach, J. A. G., *J. Assoc. Off. Anal. Chem.* **59**, 273 (1976).
Hoeting, A. L., *Assoc. Food Drug Off. U.S.Q. Bull.* **40**, 35 (1976).
Hutzinger, O., Safe, S., Zitko, V., "The Chemistry of PCB's", CRC Press, Cleveland, Ohio, 1974, pp 1, 135 ff, 226.
Jacobs, L. W., Chou, S., Tiedje, J. M., *J. Agric. Food Chem.* **24**, 1198 (1976).
Jansson, B., Sundström, G., *Biomed. Mass Spectrom.* **1**, 386 (1974).
Jensen, S., Sundström, G., *Nature (London)* **251**, 219 (1974).
Kimbrough, R. D., *Arch. Environ. Health* **25**, 125 (1972).
McKinney, J. D., Chae, K., Gupta, B. N., Moore, J. A., Goldstein, J. A., *Toxicol. Appl. Pharmacol.* **36**, 65 (1976).
Phillipson, D. W., "Gas Chromatographic Retention Times of Chlorinated Dibenzofurans", Food and Drug Administration, Washington, D.C., private communication, 1977.
Roach, J. A. G., Pomerantz, I. H., *Bull. Environ. Contam. Toxicol.* **12**, 338 (1974).
Sundström, G., Wachtmeister, C. A., *Chemosphere* **4**, 7 (1975).
Sundström, G., Hutzinger, O., Safe, S., *Chemosphere* **5**, 11 (1976a).
Sundström, G., Hutzinger, O., Safe, S., *Chemosphere* **5**, 267 (1976b).

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Worker Environment Research: Methidathion Applied to Orange Trees

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Methidathion (Supracide) was applied to orange trees, and residue levels of methidathion and its oxygen analogue on substrates pertinent to field worker safety were determined. Primary emphasis was placed on dislodgable foliar residues, but dislodgable fruit residues, grove dust residues, and pesticide concentration in air were also determined. Prebloom, postbloom, and early and late summer treatments were made to encompass the normal seasonal application periods; climatic data were collected. Three different geographical areas in California were used. Applications included two dilute spray rates and one low-volume rate. Posttreatment residue levels depended on initial pesticide deposition. High atmospheric oxidant levels did not correlate with enhanced oxon formation due to the many variables operative in the tests conducted.

Methidathion (Supracide, GS-13005) is currently recommended for use on citrus trees in California for the chemical control of the California red scale, *Aonidiella aurantii* (Mask.) (Ciba-Geigy Corp., 1977; University of California, 1976). It has an assigned tolerance for residues of 2 ppm in or on grapefruits, lemons, and oranges (*Federal Register*, 1975). To insure below-tolerance fruit, no more than two applications per growing season can be made and at least 45 days must elapse between applications; it cannot be applied within 14 days of harvest (Ciba-Geigy Corp., 1977). Methidathion is highly toxic to honey bees and severe losses may be expected if used when bees are present at treatment time or within a day thereafter (University of California, 1975). Thus, it is used as a pre- or postbloom and/or summer spray. In California, the probable application period for this scalicide is from late February to late March and from mid-May to late October. Methidathion is used extensively in California; of the organophosphorus pesticides, its usage in 1976 ranked third after dimethoate and parathion (California Department of Food and Agriculture, 1976). The Department of Food and Agriculture temporarily set 30 days as the reentry interval or time that must elapse between pesticide application and legal entry into the treated field by workers to engage in any activity requiring substantial contact with treated foliage such as pruning or harvesting (California Administrative Code, 1976). The 30-day interval was considered temporary until a more definitive reentry study could be conducted under California conditions and guidelines.

The California Department of Food and Agriculture conducted limited studies on foliar residues following application of methidathion to orange trees (Maddy, 1975). Reported here are more extensive residue data for methidathion and its oxygen analogue (GS-13007) in the orchard environment to assist in setting a worker reentry

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interval based upon field tests.

EXPERIMENTAL SECTION

Location. Extensive studies were conducted at two citrus growing regions. The Southern California site was the Citrus Research Center, Riverside, in Riverside County. The Central California site, located about 160 miles northwest of Riverside, was the Superior Farms, Delano, in Kern County. A supplementary study was conducted at a third site located about 70 miles north of Delano on the Pandol Ranch, Centerville, in Fresno County.

Plots. At each location and for each treatment, three replicate field plots were used. All plots consisted of at least three adjacent rows of mature orange trees.

In Riverside the planting distance was 18 × 21 ft. The grove consisted of adjacent rows of six trees each. Of the 42 plots treated, 36 consisted of four adjacent rows (24 trees) and six consisted of three adjacent rows (18 trees).

In Delano the planting distance was 22 × 22 ft in a quincunx pattern. Of the 36 plots treated, 32 consisted of three rows of 11 trees each (33 trees) and four consisted of six rows of five trees each (30 trees).

In Centerville the planting distance was 24 × 24 ft. Plots consisted of three rows with a minimum of 10 trees each (30 trees).

Formulation. The only marketed formulation is a 2E which is a 2-lb active ingredient (AI)/gal of emulsifiable concentrate. All applications were made using Supracide 2E originating from a single batch of guaranteed analysis.

Treatment. All treatments were made with the same equipment and by the same personnel. Dilute applications were made at spray concentrations of 1.0 and 2.0 pt of Supracide 2E/100 gal of water using an oscillating boom spray rig. For dilute applications, the total spray volume used per acre is governed by the density of the foliage and tree height. The Riverside, Delano, and Centerville groves were consequently treated at 1500, 2250, and 1450 gal/acre, respectively, which for the 1-pt rate correspond to the application of 3.75, 5.63, and 3.63 lb of AI/acre, respectively.

All low-volume applications used 100 gal of spray/acre and were made with a Kinkelder machine equipped with a tower to give coverage of both upper and lower portions of the tree canopy. The Riverside, Delano, and Centerville groves used 15.0, 22.5, and 14.5 pt/acre, respectively.

Oil sprays with methidathion, only included in the Riverside series, consisted of 1.4 gal of narrow range (NR) 415 oil with 0.5 pt of Supracide 2E/100 gal and 0.7 gal of NR 415 oil with 1.0 pt of Supracide 2E/100 gal, both applied at the rate of 1500 gal of spray/acre.

Spray applications were made with a single-side boom delivery to opposing sides of each row in a plot. The inner row trees thus received on both sides of the tree, one direct application and a less direct application from one row removed. Samples for residue analysis were collected only from the inner row trees of the experimental plots.

Timing. Four different treatments corresponding to prebloom, postbloom, early summer, and late summer applications were made. Riverside plots were treated on Mar 12, May 16, July 11, Aug 15, and Sept 12, 1977. Delano plots were treated on Mar 28, May 20, July 8, and Aug 19, 1977. The Centerville plot was treated only on July 7, 1977. With one exception, different plots were used each time and applications were not retreatments of the same plots. Because of an unseasonal tropical storm which forced abandonment of the plots treated with the late summer applications in Riverside (Aug 15), substitution plots treated Sept 12 were applied to plot areas previously treated in the March 12 and May 16 series.

Sampling. *Foliage.* Using a leaf punch sampler, 2.54-cm diameter disks were excised from each of 40 mature leaves free of surface moisture and collected directly in an 8-oz (240-mL) jar. The portion of the tree about 1.2 to 1.8 m above ground was sampled. The procedure used was to punch leaf disks at 45° intervals around each of eight trees, but with only five disks per tree starting from different sampling positions to afford five disks from each of eight sampling positions (Gunther et al., 1973; Iwata et al., 1977).

Duplicate samples were collected from each of three replicate treatment plots. Samples in transit to the laboratory were kept in a cold ice chest. Samples were processed within 24 h of collection.

Fruit. Mature fruit was collected by taking a fruit-bearing stem and then clipping the fruit to allow it to fall directly into a 3-gal (11.4-L) sample jar. Each sample consisted of 20 fruit collected by taking one fruit from each of four quadrants around each of five trees. Duplicate samples were collected from each of three replicate treatment plots. Samples were processed within 24 h of collection.

Soil. Dust samples were collected by the method of Spencer et al. (1977) by vacuuming the surface soil through a 100-mesh screen using a portable vacuum cleaner. The inner dimensions of the screen mounted on a wooden frame were 23 × 55 cm. Samples were collected near the edge of the tree canopy from opposite sides of each of six trees. Since furrow irrigation often left wet soil on the furrow side of the trees, samples were collected from areas between the trees in-row. This procedure was followed even in drip-irrigated groves to have all samples collected from corresponding areas of the grove floor. One sample was collected from each replicate treatment plot. Samples collected in cloth vacuum bags were transferred to glass jars and stored in the freezer prior to extraction and analysis.

Air. Two Greenburg-Smith impingers, each containing 200 mL of ethylene glycol, were connected in tandem. The air intake was placed 60 cm above ground next to the trunk of a tree which had been treated with a low-volume spray. Two sets of impingers were used and each was simultaneously operated for 2 h while drawing 5 L/min.

Processing. *Dislodgable Foliar Residues.* The procedure recommended by Iwata et al. (1977) was followed. The following tests were conducted prior to use of the method. Simulated leaf washes (300 mL of water, 12 drops of wetting agent solution, and 10 mL of saturated NaCl solution) were each fortified with 40 μg each of methidathion and its oxon. Different sets of duplicate samples were partitioned 2, 3, or 4 times using 50 mL of CH_2Cl_2 and 1 min shaking each time. Average recoveries as a result of two, three, and four partitionings were 96, 91, and 98%, respectively, for methidathion and 104, 94, and 99%, respectively, for the oxon. Using two partitionings, recoveries were determined for different levels of fortification. Using simulated leaf washes, average recoveries from three replicate samples fortified at 4000, 400, and 40 μg of methidathion were 92 ± 5, 92 ± 3, and 92 ± 3%, respectively. Average recoveries from three samples fortified with 400, 40, and 4 μg of oxon were 98 ± 3, 108 ± 3, and 99 ± 2%, respectively.

To determine how much of the dislodgable residues is carried into the leaf, untreated leaf disks were shaken once with 100 mL of water, 4 drops of a wetting agent solution, and 40 μg each of methidathion and its oxon. Average recoveries of 83 ± 6% methidathion and 84 ± 6% oxon demonstrate that about 15% of each compound was lost from the aqueous phase into the leaf disks. This result was simply accepted as an unavoidable part of the overall procedure and no attempt was made to correct for the loss.

Penetrated Foliar Residues. The sample of 40 leaf disks was macerated with 100 mL of acetone for 2 min in a semi-micro Waring Blendor can. The extract was vacuum filtered and 100 mL of hexane was used to rinse the can and funnel. The combined extract was placed in a sample storage bottle and Na_2SO_4 added. The sample was stored at about 4 °C pending analysis.

The following tests were conducted prior to use of the method described above. Leaf disks in the Blendor can were fortified with methidathion and its oxon prior to the addition of acetone to obtain a procedural recovery. Recoveries for samples fortified with 10, 1.0, and 0.1 ppm methidathion were 87 ± 5, 83 ± 3, and 82 ± 4%, respectively, and for samples fortified with 1.0 and 0.1 ppm oxon were 79 ± 6 and 70 ± 3%, respectively.

Further tests were conducted with laboratory treated leaves. Freshly picked whole leaves were treated by individually immersing each leaf for a few seconds in a solution of 1 mL of Supracide 2-lb/gal of EC and 50 mg of analytical standard oxon in 800 mL of water; the Supracide concentration was equivalent to a 1 pt of 2EC/100 gal spray tank mix. Leaves were allowed to air-dry for about 2 h before leaf punches were taken.

To estimate the extraction efficiency of the acetone blending procedure, the pulp remaining after filtering the acetone macerate was Soxhlet extracted using 1:9 methanol–chloroform (Bowman et al., 1968). The Soxhlet extraction was conducted for 2 h and then again for another 2 h with fresh solvent. The acetone blending procedure gave 5.92 ± 0.59 ppm methidathion and 0.26 ± 0.04 ppm oxon. The first 2-h Soxhlet extraction gave 0.85 ± 0.11 ppm methidathion and 0.06 ± 0.01 ppm oxon. The second 2-h Soxhlet extraction gave an additional 0.13 ± 0.06 ppm methidathion and <0.01 ppm oxon. Thus, the blending procedure removed 86% of the methidathion and 81% of the oxon. No correction was made for extraction efficiency in the data reported in this study.

Leaf disks taken from laboratory treated leaves were stored at 8 °C to determine the effect of storage on dislodgable and penetrated residue levels. After 0, 4, 11, and 18 days of storage, dislodgable methidathion residues were 0.63 ± 0.04, 0.51 ± 0.04, 0.50 ± 0.03, and 0.40 ± 0.03 $\mu g/cm^2$, respectively, and after 0, 4, and 11 days of storage, dislodgable oxon residues were 0.10 ± 0.01, 0.06 ± 0.01, and 0.06 ± 0.01 $\mu g/cm^2$, respectively. After 0, 4, and 11 days of storage, penetrated methidathion residues were 5.92 ± 0.59, 3.25 ± 0.46, and 3.78 ± 0.19 ppm, respectively, and penetrated oxon residues were 0.26 ± 0.04, 0.05 ± 0.01, and 0.07 ± 0.02 ppm, respectively. These results indicated that samples should be processed within a day or two of collection. Thus, all samples were processed within 24 h of collection. The storage study was conducted with freshly treated leaves which were considered the most difficult to store without adverse changes in residue levels. With leaves on which residues have weathered for several days, storage at 8 °C may be acceptable. It is possible that frozen storage would be acceptable even for freshly treated leaves. Both these latter options were not tested for methidathion.

Fruit. Dislodgable Residues. To a 3-gal jar containing 20 oranges was added 350 mL of water and 12 drops of a 1:50 dilution of Sur-Ten wetting agent solution. The jar was capped, placed on its side, and rotated at 55 rpm for 5 min. The liquid was decanted into a temporary holding bottle retaining the fruit in the jar. The procedure was repeated using 100 mL of water and a 3-min time interval. The second liquid was combined with the first.

The combined liquid was poured into a 500-mL separatory funnel, paying particular attention to transferring all the associated fruit dust. The wash liquid was then extracted twice using 50 mL of CH_2Cl_2 and 1 min shaking each time. Each extract was placed into a sample storage bottle and Na_2SO_4 was added to take up the water unavoidably transferred. The sample was stored at about 4 °C pending analysis.

The oblate diameter of each fruit was measured, and assuming a sphere, an approximation of the total surface area represented by the fruit sample was obtained (however, see Turrell, 1946).

Dislodgable Foliar Dust. The procedure of Westlake et al. (1973) was used. The aqueous leaf wash was carefully decanted and vacuum filtered through a disc of Whatman No. 1 filter paper which had previously been equilibrated with the moisture in the air and weighed. The aqueous filtrate was used to wash the leaf disks two more times. The filter paper was dried for 3 days at 110 °C, allowed to equilibrate with the moisture in the air for 1.5 days, and then reweighed. The amount of dust collected was determined by the difference in the filter paper weights. For further discussion, see Popendorf and Leffingwell (1977).

Soil Thin-Layers. Grove soil samples from untreated Riverside, Delano, and Centerville plots were each sieved through a 100-mesh screen. A 100-g sample of dust was added to 20 mL of water mixed with 0.25 mL of Supracide 2EC. Additional water was added to obtain a soil slurry which was then spread on glass plates to give a 1-mm thick soil thin-layer. After air-drying for several hours, the plates were placed outside (Sept 16, 1977) and exposed to direct sunlight throughout the day. Samples were collected by scraping off 80 cm^2 areas of soil.

Extraction of Soil Dust. A 10-g aliquot of the soil dust sample was placed in a 4-oz (118-mL) bottle. Then 10 mL of 10% aqueous acetone, followed by 10 mL of hexane were added. The bottle, closed with an aluminum-lined screw-cap, was shaken at 200 strokes/min for 20 min. The extract was filtered by draining through a funnel containing about 25 g of sodium sulfate. Two 25-mL portions of acetone were used to rinse the bottle, soil, and sodium sulfate. The combined extract and rinse were stored at 4 °C pending analysis.

The following test was conducted prior to use of the method. About 0.25 mL of Supracide 2E was mixed with 80 mL of water and then 200 g of Centerville soil dust was added. The slurry was spread on aluminum foil and allowed to air-dry. Aliquots of the dry soil dust were used to determine extraction efficiency.

A 10-g aliquot mixed with 3 g of coarse sand was placed into a glass Soxhlet thimble containing a 1-cm layer of coarse sand (Spencer et al., 1977). The dust was extracted for 4 h using an azeotropic acetone–hexane (59:41) mixture. The average of three replicate samples was 263 ± 11 ppm methidathion for the Soxhlet extraction and 240 ± 15 ppm for the described procedure. The procedure used was therefore deemed adequate for the field samples.

Air Samples. To 200 mL of ethylene glycol in a 2000-mL separatory funnel was added 100 mL of $CHCl_3$ and 800 mL of water. The mixture was shaken for 1 min and the $CHCl_3$ layer was drawn off into a 500-mL Erlenmeyer flask. The extraction was repeated three more times using 50 mL of $CHCl_3$ and 1 min shaking each time. The combined extract was dried with Na_2SO_4 and the solvent removed. Procedural recovery from ethylene glycol samples fortified with 100, 10, 5, and 1 μg was 90 ± 7, 91

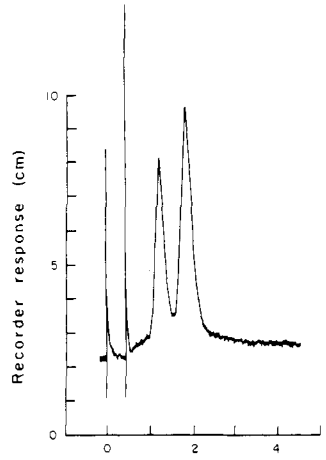

Figure 1. Flame photometric detector response to 5.0 ng of methidathion oxygen analogue and 3.0 ng of methidathion. Retention times were 1.2 min for the oxygen analogue and 1.9 min for methidathion.

± 11, 84 ± 4, and 110 ± 20%, respectively, for methidathion and 97 ± 6, 120 ± 20, 94 ± 10, and 140 ± 20%, respectively, for the oxon.

As a preliminary test, 100 μg each of methidathion and its oxon were placed in a U-tube and the latter was connected directly to the intake of a Greenburg-Smith impinger charged with ethylene glycol. A second impinger was connected in tandem with the first. Then 5 L/min of air was drawn through the U-tube and impingers for 100 min. The volume of air sampled was 500 L or 0.5 m^3.

The amount of material recovered from the first impinger was 3.9 ± 0.9 μg of methidathion and 1.5 ± 0.1 μg of oxon. No material was recovered from the second impinger (however, see Van Dyk and Visweswariah, 1975). The amount recovered from the U-tube was 96 ± 3 μg of methidathion and 90 ± 11 μg of oxon.

Given the vapor pressure of methidathion as 2.33×10^{-6} mm of Hg at 20 °C (Ciba-Geigy, Supracide Technical Bulletin) and using the equation $W/V = PM/RT$, the vapor concentration is 38 μg/m^3. Thus, the amount of methidathion trapped by the impingers should be less than 19 μg, as found.

Analysis. All samples were analyzed by gas chromatography using a Varian 1700 gas chromatograph (GC) equipped with an alkali flame detector, a Hewlett-Packard 5710A GC equipped with a nitrogen/phosphorus alkali flame detector, or a Tracor MT-220 GC equipped with a flame photometric detector. Glass columns were packed with 5% Apiezon N on 60/80 mesh Gas-Chrom Q.

Figure 1 shows the resolution obtained for methidathion and its oxon. Data were obtained using the Tracor MT-220 equipped with a 30 cm × 4 mm i.d. column with inlet, column, and detector temperatures of 228, 205, and 220 °C, respectively, and a nitrogen carrier gas flow rate of 80 mL/min.

RESULTS AND DISCUSSION

Since agricultural field workers, primarily fruit pickers, are exposed to residues of methidathion applied to orange trees, residue data pertinent to worker exposure were obtained. The field tests conducted were designed to fairly and accurately represent methidathion usage for control of pests in California citriculture. Prebloom, postbloom, and early and late summer treatments were made to encompass the normal seasonal application periods. Applications were made in Riverside (Riverside County), Delano (Kern County), and Centerville (Fresno County)

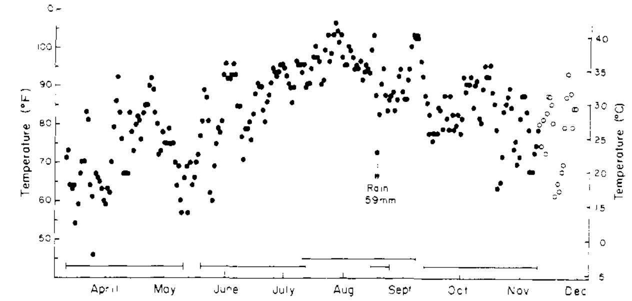

Figure 2. Daily maximum air temperature at the University of California. The sampling period after each application is denoted by ⊢⊣; closed circles are temperature values during the actual sampling period. Data are supplied through the courtesy of the U.S. Department of Commerce, National Weather Services Office, Riverside, Calif.

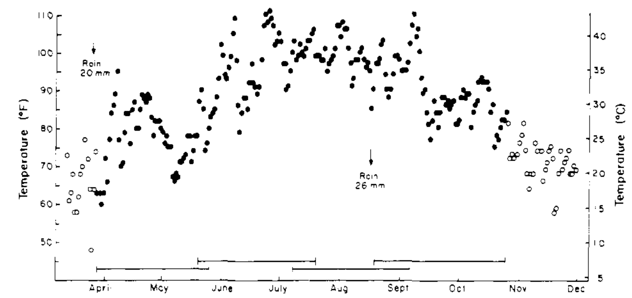

Figure 3. Daily maximum air temperature at the Kern County Air Terminal, Bakersfield, Calif. (approximately 30 miles southeast of Delano). The sampling period after each application is denoted by ⊢⊣; closed circles are temperature values during the actual sampling period. Data are supplied through the courtesy of the U.S. Department of Commerce, National Weather Services Office, Bakersfield, Calif.

to represent the different geographical areas in the state where methidathion usage would be greatest. Applications were made with an oscillating boom sprayer at both the normally used and University of California recommended (University of California, 1976) rate of 1 pt of the 2EC formulation/100 gal of water and at the maximum concentration permitted by the label of 2 pt/100 gal (Ciba-Geigy Corp., 1977). Low-volume applications using a total of 100 gal of spray/acre were also made in view of the current trend towards this type of spray application (Carman et al., 1972; Carman, 1975). The spray treatments were made in what turned out to be a very dry year as the result of below-average rainfall. As the dry, dusty California conditions have been generally accepted as contributing to worker poisoning episodes via transfer of toxicant-bearing dust from foliage or soil to workers, residue data were collected under ideal field conditions in this respect. The maximum daily air temperature and rainfall data obtained from official collection stations near the test sites are shown in Figures 2, 3, and 4 because of the emphasis on collection of climatic data (Task Group, 1974). Qualitatively, the same basic weather pattern exists for all three regions. The main difference is that California's Central Valley has more days above 38 °C (100 °F) than southern California. Residue levels of both the parent pesticide and its more toxic alteration product, the oxygen analogue or "oxon" were determined.

Figures 5, 6, and 7 give the semilogarithmic plots of the foliar dislodgable residue data; all data points represent the mean of six samples. The lines connecting the data points were drawn to reasonably and usefully represent the residue dissipation to indicate the trend in the data. This is especially true for residues of methidathion oxon where the residue level is the result of a complex process

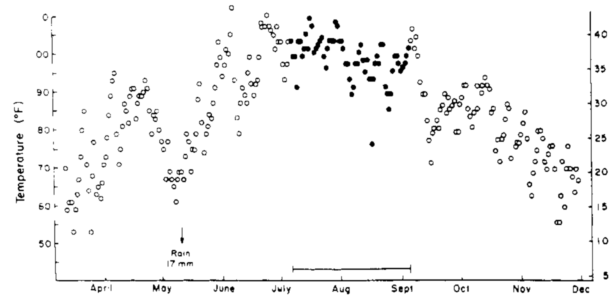

Figure 4. Daily maximum air temperature at the Kearney Horticultural Field Station, Parlier, Calif. The sampling period after the application is denoted by ⊢⊣; closed circles are temperature values during the experimental period. Data are supplied through the courtesy of the University of California Agricultural Research and Extension Center, Parlier, Calif.

of compound formation and dissipation. All residue values are based on 40 leaf disks (2.54 cm in diameter) having a total surface area of 405 cm^2/40 disks.

The residue data shown in Figures 5–7 do not represent anything unexpected. The data points are similar to those found for a number of other organophosphorus compounds. A number of obvious and previously observed conclusions (Gunther et al., 1977) can be made from inspection of Figures 5–7. In all cases, residue levels are always higher after a low-volume application than after a dilute application of the same amount of active ingredient per acre. Thus, worker exposure hazards are greater after low-volume applications and a longer reentry interval would be required. Residue levels are always higher after an oscillating boom spray application using a spray concentration of 2 pt/100 gal than for 1 pt/100 gal. As observed with other compounds, the methidathion residue dissipation curves and oxon residue formation/dissipation curves tend to be parallel to each other in spite of the different application methods and spray concentrations used. Residue levels at a given time after spraying are therefore governed by the initial deposition of pesticide on the foliage. All methidathion dissipation curves are characterized by an initial rapid residue decrease ("degradation" curve) followed by a slower residue decrease ("persistence" curve). Often an even slower rate of decrease is evident, particularly after low-volume applications. All analyses were generally discontinued after residue values dropped below 0.01 $\mu g/cm^2$ of leaf surface which is equivalent to about 50 mg of compound over the entire tree assuming that an average 20-year-old orange tree has a leaf surface area of 5×10^6 cm^2 (Gunther et al., 1973).

Figure 8 shows the methidathion and oxon data after application as an inclusion in an oil spray. Small amounts of spray oil can cause high mortality of immature stages of California red scale. The oil did not retard dislodgable

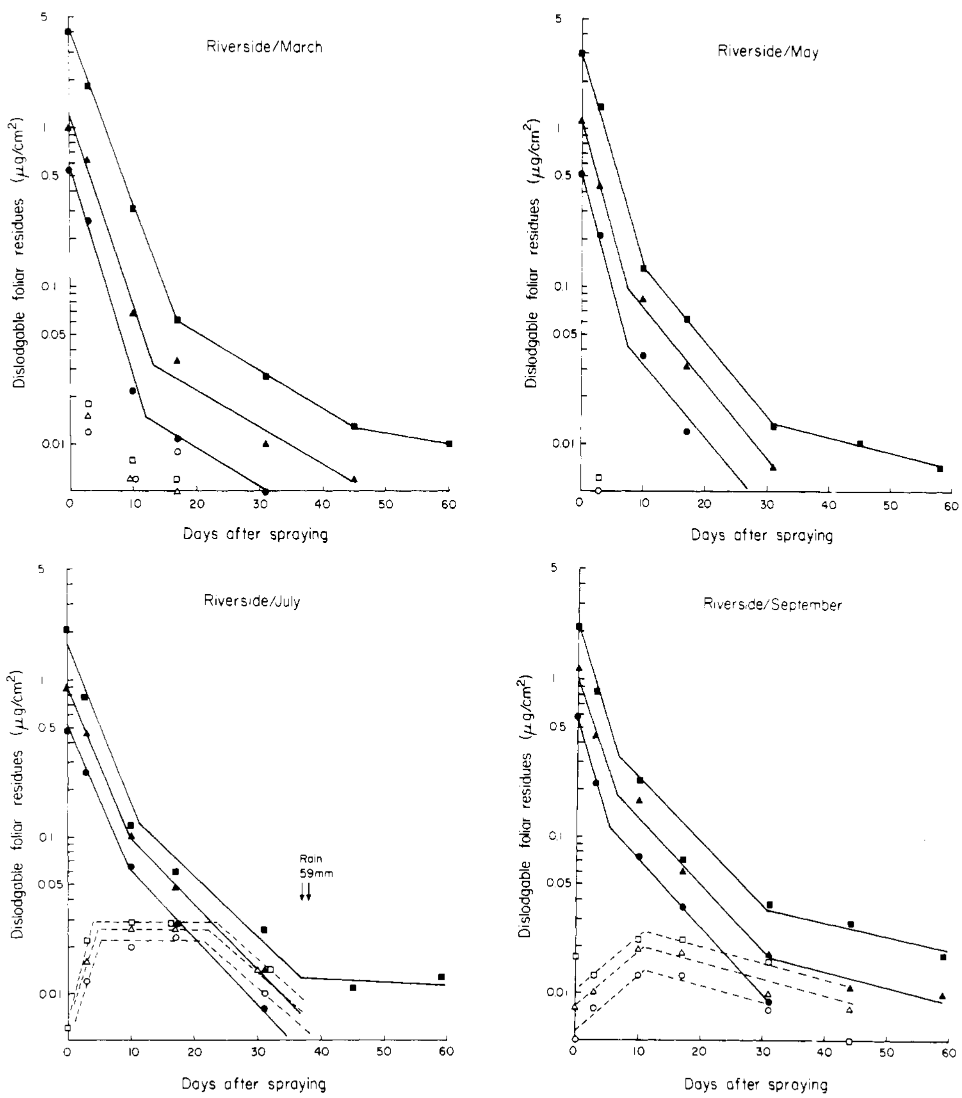

Figure 5. Dissipation curves for dislodgable foliar residues of methidathion and methidathion oxon (open symbols) after a Supracide application to orange trees at 3.75 (●) and 7.50 (▲) lb of AI (1500 gal)$^{-1}$ acre^{-1} and at 3.75 lb of AI 100 gal^{-1} acre^{-1} (■).

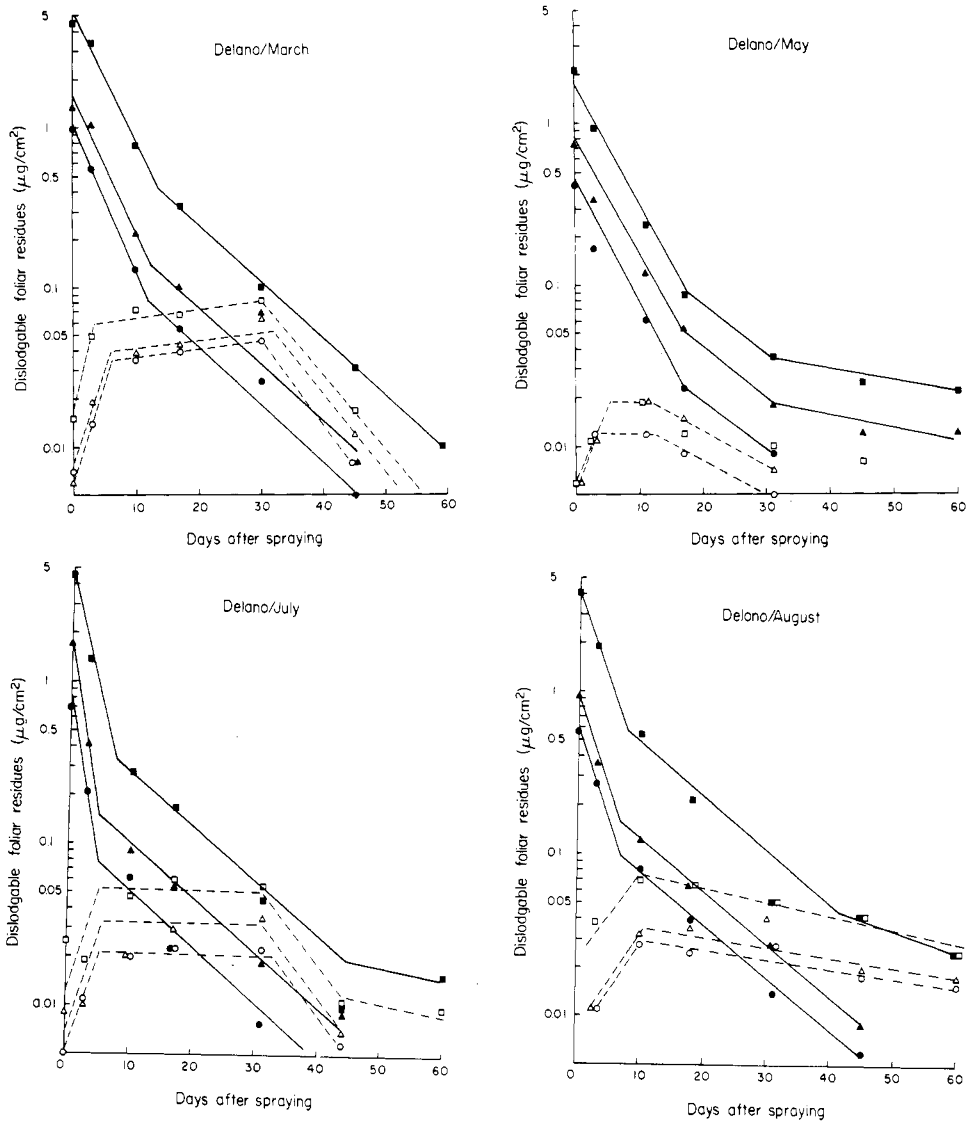

Figure 6. Dissipation curves for dislodgable foliar residues of methidathion and methidathion oxon (open symbols) after a Supracide application to orange trees at 5.63 (●) and 11.3 (▲) lb of AI (2250 gal)$^{-1}$ acre^{-1} and at 5.63 lb of AI (100 gal)$^{-1}$ acre^{-1} (■).

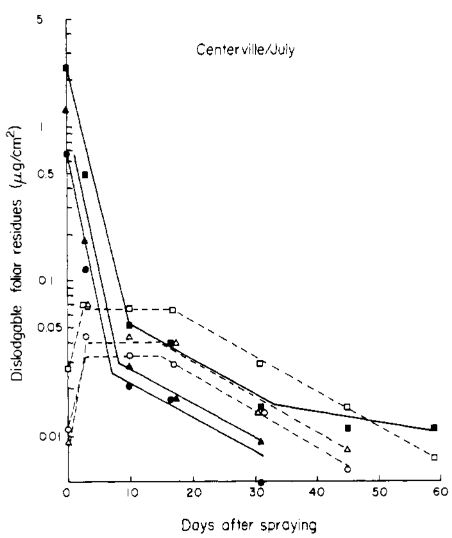

Figure 7. Dissipation curves for dislodgable foliar residues of methidathion and methidathion oxon (open symbols) after a Supracide application to orange trees at 3.63 (●) and 7.25 (▲) lb of AI (1450 gal)$^{-1}$ acre^{-1} and 3.63 lb of AI (100 gal)$^{-1}$ acre^{-1} (■).

foliar residue dissipation. Here, residues appear to dissipate even faster than those from non-oil spray appli-

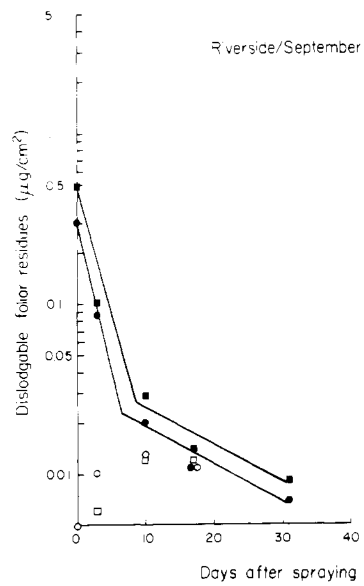

Figure 8. Dissipation curves for dislodgable foliar residues of methidathion and methidathion oxon (open symbols) after a Supracide oil spray application to orange trees at 1.88 lb of AI plus 21.0 gal of NR 415 oil (1500 gal)$^{-1}$ acre^{-1} (●) and 3.75 lb of AI plus 10.5 gal of NR 415 oil (1500 gal)$^{-1}$ acre^{-1} (■).

Table I. Dislodgable Foliar Residues ($\mu g/cm^2$) of Methidathion and Methidathion Oxon Residues[a]

lb of AI/acre	gal/acre	day	methidathion	oxon
3.75	1500	0	0.56	
		3	0.012	
		10	0.004	
7.50	1500	0	1.10	0.002
		3	0.022	
		10	0.006	
3.75	100	0	0.79	0.008
		3	0.018	<0.002
		10	0.008	
1.88 (21.0 gal NR 415 oil)	1500	0	0.14	
		3	0.006	
		10		
3.75 (10.5 gal NR 415 oil)	1500	0	0.28	
		3	0.014	
		10	0.008	

[a] Applied Aug 15, 1977, to Valencia orange trees on the Citrus Research Center, Riverside, Calif.

cations. Nigg et al. (1977) reported that inclusion of spray oil did not prolong the dislodgable citrus foliar residues of ethion, another organophosphorus insecticide.

Table I gives the residue data for the Riverside late summer application. One day after application 2.32 in. (59 mm) of rain fell over a 2-day period. Dislodgable foliar residues of methidathion were reduced by 95% for both oil and non-oil treatments. Oxon residues were too low to have much significance but the 0.008 $\mu g/cm^2$ present at zero day after a low-volume treatment decreased to below 0.002 $\mu g/cm^2$ after the rain. After 10 days all methidathion residues were below 0.01 $\mu g/cm^2$. Gunther et al. (1977) reported significant decreases in foliar dislodgable residues of parathion and paraoxon after a 2.5 in. (64 mm) rainfall. From evidence to date, it appears that rainfall below 2 in. (51 mm) over a 48-h period has only limited affect on the foliar dislodgable residue levels on citrus trees.

The zero-day residue for the low-volume application was only 0.79 $\mu g/cm^2$ which was much lower than it should have been. Although applications were made under acceptable weather conditions in the morning, a very strong wind began to blow soon after application. Since the zero-day residues for the two dilute applications were as expected, it can only be speculated that deposition of pesticide on to the foliage by low volume was somehow affected by the weather conditions that day.

No definite relationship exists between the methidathion residue data given in Table II and the climatic temperature data given in Figures 2 and 3. For example, the July application in Riverside experienced the highest overall air temperature, yet the number of days required for methidathion residues to drop to 0.1 $\mu g/cm^2$ was no less than for the March and May applications.

It is clear that methidathion oxon is formed from methidathion shortly after application (Figures 5–7). The amount formed is governed by the amount of methidathion deposited. During the first 7 to 10 days while methidathion levels are high, oxon levels build up. The data in Table II show that, in general, the longer the methidathion level stay high (above 0.1 $\mu g/cm^2$), the greater the amount of oxon formed. During the 10- to 30-day postapplication interval oxon levels remain essentially constant as oxon formation is approximately matched by oxon dissipation. Thus, worker exposure to oxon residues at 10 days is generally no greater than at 30 days. After 30 days postapplication, methidathion residues are too low to substantially replenish the oxon so that oxon levels fall off.

Table II. Maximum Methidathion Oxon Levels ($\mu g/cm^2$) Found on Foliage

low-volume application location	month	days required for methidathion residues to be 0.1 $\mu g/cm^2$	max. oxon level found
Riverside	Mar	15	0.018
	May	13	0.006
	Jul	14	0.029
	Sept	19	0.022
Delano	Mar	31	0.083
	May	17	0.019
	Jul	23	0.061
	Aug	31	0.069
Centerville	Jul	8	0.070

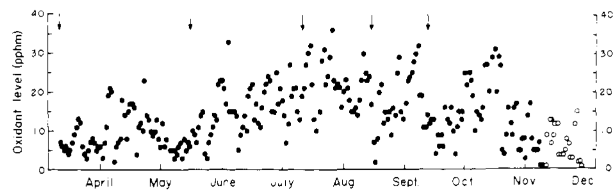

Figure 9. Daily highest hourly average oxidant level recorded at Rubidoux, Calif. (5 miles northwest of the University of California). Each spray application is denoted by an arrow (↓); closed circles are oxidant values during the actual sampling period. Data are supplied through the courtesy of the South Coast Air Quality Management District, Eastern Zone.

The reason for a more persistent methidathion residue in the Delano grove as shown in Table II is not known. If high air temperatures in areas were the governing factor in residue dissipation, residues should have decreased faster from the Delano groves than from the corresponding Riverside groves. The Delano grove consisted of very large trees where a minimum amount of open space was present between trees. Since the trees could shade each other from direct sunlight and air movement through the grove would be minimal, one might speculate that these factors played an important role in allowing residues to persist.

It has been suggested that ozone or oxidant levels in air due to air pollution are responsible for toxic oxon formation and hence need to be considered when establishing worker reentry intervals (Spear et al., 1977a). The oxidant levels in Riverside are shown in Figure 9. In California total oxidant is essentially all ozone. Although under laboratory conditions it has been clearly demonstrated that ozone can convert organophosphorus compounds to their oxygen analogues, the field data do not clearly show a correspondence due to the many other variables that are operative. Delano and Centerville are located in California's Central Valley where poisoning episodes have predominantly occurred. However, oxidant levels over the same time period shown in Figure 9 did not exceed 9 pphm (parts per hundred million) in Delano and did not exceed 17 pphm in Centerville. In contrast, levels in Riverside are normally above these levels and approach 40 pphm. Yet dislodgable foliar residues of oxon for Riverside trees are generally low and the maximum level found is about 0.03 $\mu g/cm^2$ while oxon levels for Delano and Centerville are generally much higher and approach maximum levels of about 0.09 $\mu g/cm^2$ (Table II). Spear et al. (1978) have shown that under laboratory conditions with trees with low foliar dust levels, little parathion to paraoxon conversion occurs regardless of ozone level (0 or 30 pphm) and with

Table III. Amount of Dust Recovered from Orange Leaves[a]

location	application	dust collected, µg/cm², replicate A	B	C	D	E	F	mean
Riverside	low-volume	122	175	192	162	187	215	176
	dilute	131	142	157	137	120	136	137
	none	162	163	171	155	176	162	165
Delano	low-volume	106	120	113	94	127	102	110
	dilute	85	87	98	70	66	84	82
	none	121	110	107	116	112	99	111
Centerville	low-volume	178	226	157	211	205	258	206
	dilute	133	137	133	114	140	151	135
	dilute oil	231	213	215	225	242	207	222

[a] Leaf-disk samples collected 31-days postapplication.

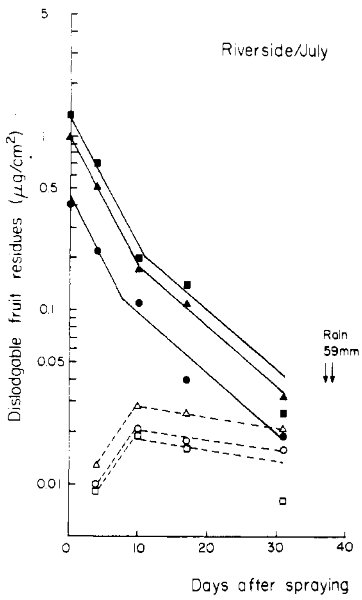

Figure 10. Dissipation curves for dislodgable fruit residues of methidathion and methidathion oxon (open symbols) after a Supracide application to orange trees at 3.75 (●) and 7.50 (▲) lb of AI (1500 gal)$^{-1}$ acre^{-1} and at 3.75 lb of AI (100 gal)$^{-1}$ acre^{-1} (■).

high foliar dust levels significant paraoxon formation occurs in the absence of ozone and formation is further enhanced in the presence of 30 pphm ozone. Dust levels on the foliage are, therefore, quite important to residue persistence and conversion to the oxon.

Figure 10 shows the levels of dislodgable residues on the orange fruit. Pesticide deposition and residue dissipation patterns were qualitatively similar to those found for foliage (Figure 5, July). Methidathion appeared to persist slightly longer on the fruit surface than on foliage; degradation and persistence half-lives were 3 and 7 days, respectively, for foliage and 4 and 9 days, respectively, for fruit. Similar to foliage, oxon levels increased during the initial 10 days and the levels were comparable to those on foliage. An anomaly was that the oxon levels on fruit after a low-volume application were less than those from dilute applications. The 59 mm (2.3 in.) of rain decreased both methidathion and oxon levels below 0.005 µg/cm².

Since foliar dust is believed to be the primary vehicle by which toxic residues are transferred from foliage to workers, an estimate of the foliar dust was made. Leaf samples from the Riverside, Delano, and Centerville groves were collected 31-days postapplication from the early summer (July) treatment plots. Data are given in Table III. The data are consistent with the fact that no runoff occurs from a low-volume treatment; dust loads for leaves collected from low-volume and control plots were 176 and 165 µg/cm², respectively, for Riverside and 110 and 111 µg/cm², respectively, for Delano. The Centerville control plots were treated with an oil spray and these plots were also adjacent to a dirt road. This combination accounts for the result that leaf dust on the control plot (222 µg/cm²) was a little higher than the low-volume treated leaves (206 µg/cm²). The ratio of dust levels found on leaves from dilute applications to that from low-volume applications were 0.78, 0.75, and 0.66, respectively, for the Riverside, Delano, and Centerville plots. Thus, about 30% of the dust was removed by the dilute application sprays; this reduction is generally evident by visual inspection of the leaves. Low-volume data show that dust levels were highest in Centerville (206), intermediate in Riverside (176), and lowest in Delano (110) groves. The Centerville grove consisted of smaller trees with considerable open space between trees. The grove floor gave rise to dust very easily. The Delano grove consisted of very large trees with a minimum of open space between trees. Very little air movement occurred through the grove. Thus, little opportunity existed for airborne dust. The Riverside grove was intermediate in tree size and the orchard dust was available but not easily airborne; this tree size is most representative of California citrus plantings.

Worker reentry intervals should be based on residue data showing the most hazardous conditions resulting from good agricultural practice and maximum application rates. Based solely on residue levels, for this study the data for the prebloom (March) application made in Delano (Figure 7) should be used. Methidathion dissipated quite slowly and consequently considerable opportunity for conversion to its oxon existed. The data show the highest levels of oxon and methidathion of all the experiments conducted. No significant change in oxon levels occurred between 10 and 30 days and methidathion levels decreased during this time. Based on foliar dust alone, the Centerville grove (Figure 9) posed the greatest risk to workers. No attempt is made to relate the residue levels found to the possible toxicological response of exposed workers; this long-sought relationship currently does not exist for any pesticide.

Penetrated Foliar Residues. For the dilute application using the 1.0 pt/100 gal rate, the penetrated methidathion residues in the leaves were determined using the leaf disks after the dislodgable residues were removed. Data are given in Table IV. Oxon residues were about 1 ppm or less for the few samples analyzed. Analyses were discontinued due to rapid gas chromatographic column deterioration from the concentrated leaf extracts. Although data for the early summer applications in Delano and Centerville test plots give good semilogarithmic plots, the other data are scattered. The foliar methidathion data of Maddy (1975) are also as irregular as reported here. Since residues within the leaves cannot be transferred to

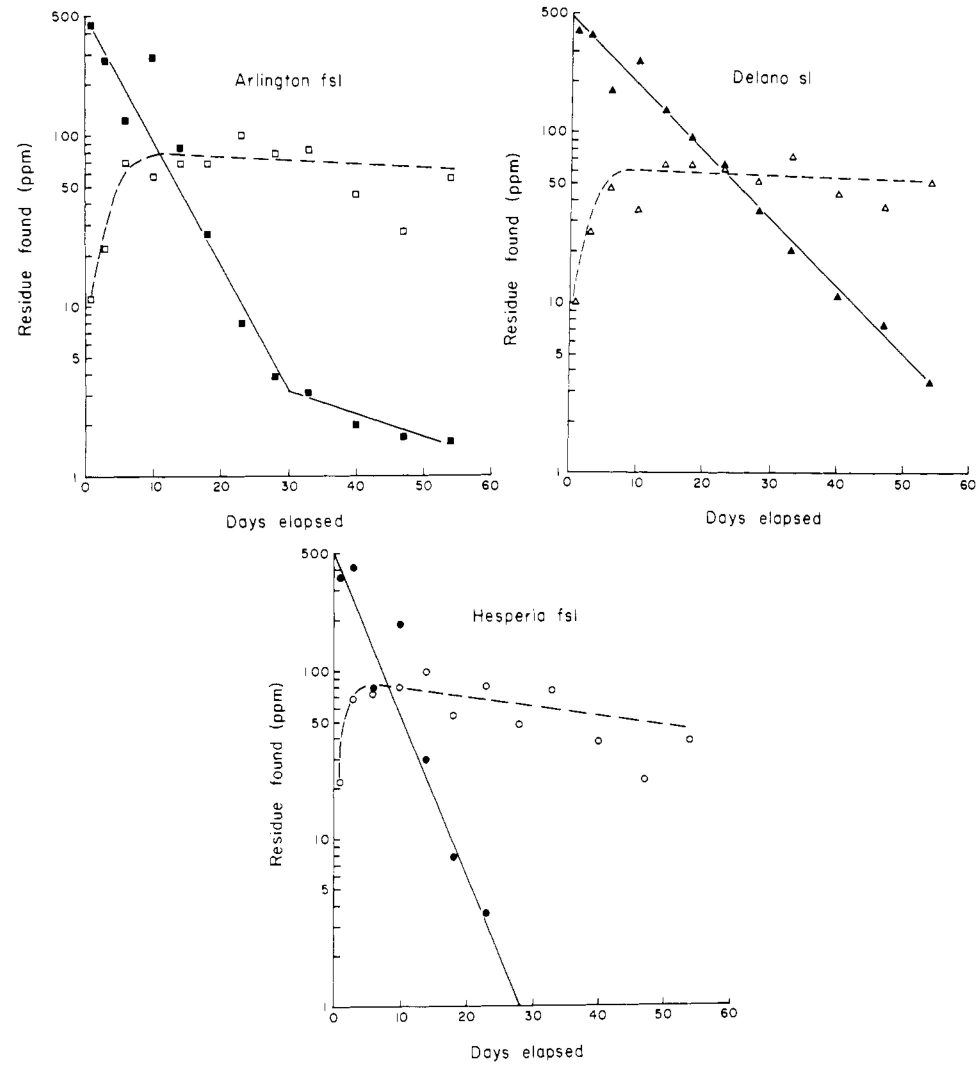

Figure 11. Methidathion (closed symbols) and methidathion oxon (open symbols) levels on thin layers of soil previously treated with methidathion.

workers and are not used for food or feed, further examination into this irregularity was not made.

Soil. A study of the behavior of pesticides sorbed to dry soil is desirable for a number of reasons. The primary reason is that dislodgable residues on foliage and fruit are thought (Gunther et al., 1977) to be predominantly associated with soil dust particles. Thus, a study of the behavior of pesticides sorbed to dry dust may give some information about its behavior on foliar dust. Also, since pesticides reach the orchard soil through spray drift and runoff, this toxicant-bearing soil could potentially become airborne through the action of wind or mechanical agitation and deposit on tree foliage or on the workers. The actual importance of this process, however, has not been verified, but from data generated using student picking crews in parathion-treated orange groves, Spear et al. (1977b) concluded that the dermal dose data obtained indicated that soil dust played a relatively unimportant role in the immediate exposure process; since about 80% of the dermal paroxon dose obtained by the volunteers appeared to be deposited above the waist, the foliar residue was considered the more appropriate indicator of worker hazard.

Comparison of methidathion behavior on the three citrus grove soil dusts under identical environmental conditions was conducted. All three orchards were located in areas typed by soil maps as a sandy loam. A slurry, prepared by mixing each dust (<100 mesh) with water containing some Supracide formulation, was spread as a 1-mm thick film on plates and allowed to air-dry for a few hours. The soil thin-layers were then placed outside and exposed to the maximum available sunlight. The data are shown in Figure 11.

Methidathion dissipation was first-order; the Riverside soil exhibited a rate change after 30 days after the level had decreased to less than 1% of the initial level. For the Riverside, Delano, and Centerville soil dusts, the initial rate constants (k) were 0.168, 0.0911, and 0.223 day^{-1}, respectively, the half-lives ($\ln 2/k$) were 4.1, 7.6, and 3.1 days, respectively, and the times required for methidathion to drop to 1% of the initial level ($\ln 100/k$) were 27, 51, and 21 days, respectively. Thus, methidathion dissipates from the Riverside soil about equally fast as from the Centerville soil and about twice as rapidly as from the Delano soil.

Conversion to the oxon was most rapid during the initial 10 days and reached levels of 60 to 80 ppm. Once formed, oxon levels appear to be relatively constant over the test period with evidence for slight decreases.

The soil thin-layer technique gives some interesting data but is overall a poor predictor of dislodgable foliar residue behavior. Methidathion dissipation from the foliar surface exhibits a rate change after about 10 days but from the soil surface it is essentially strictly first-order. Oxon levels relative to methidathion levels are far greater for soil than for the foliar surface. Oxon levels on soil remain relatively

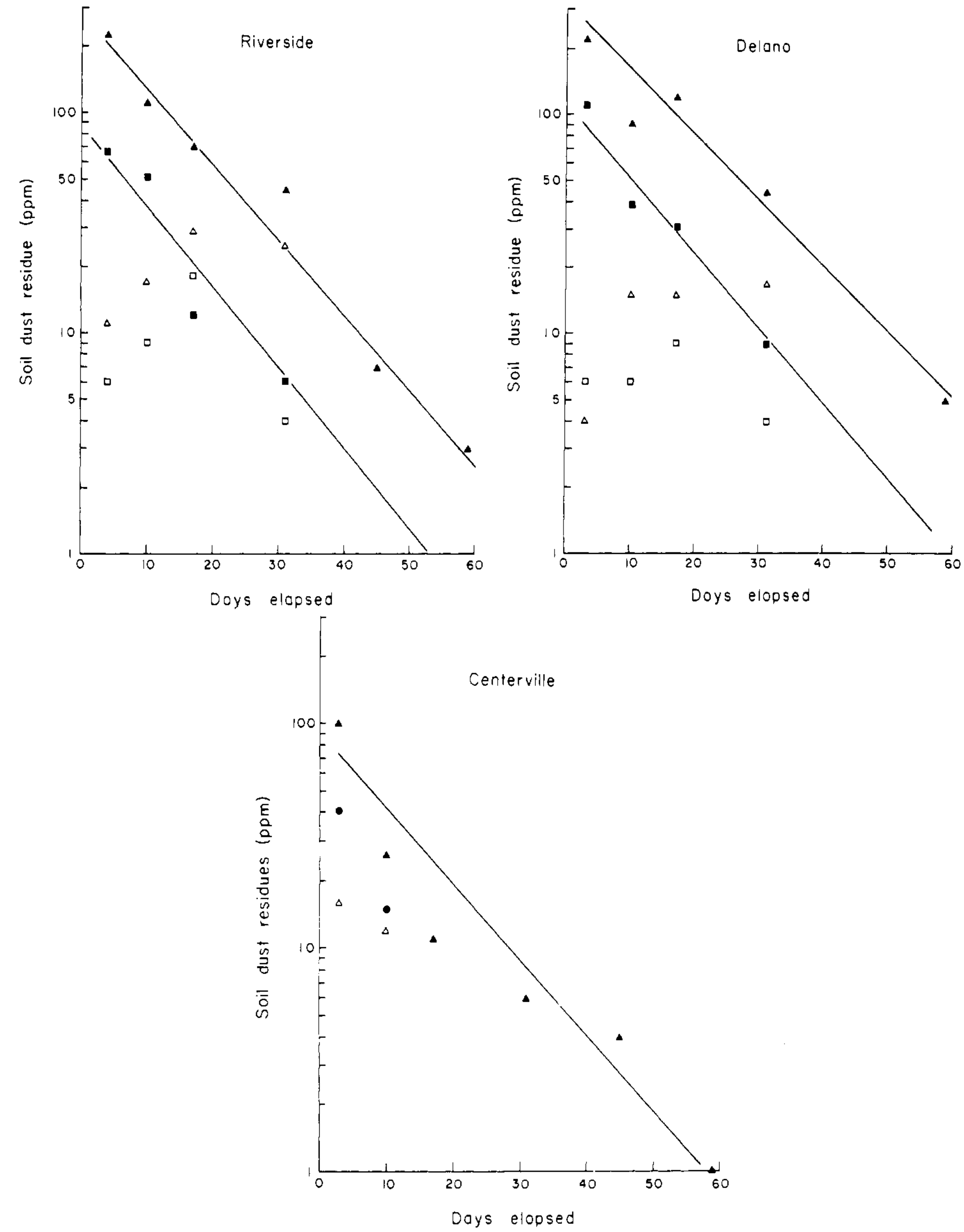

Figure 12. Methidathion (closed symbols) and methidathion oxon (open symbols) levels on mobile dust collected from early summer methidathion-treated orange groves. Plots were treated at the 1 pt/100 gal (circle) and 2 pt/100 gal (triangle) dilute rates and by low volume (square).

constant, whereas on foliar surfaces they dissipate rapidly after methidathion levels are low. The amount of oxon formed is similar for all soils but on foliar surfaces less oxon is formed in Riverside than in the other two regions. Only one correlation, possibly coincidental, is significant. Methidathion has half-lives of 3.1, 4.1, and 7.6 days on Centerville, Riverside, and Delano soils, respectively, and Table II shows that the number of days required for methidathion levels to drop to 0.1 $\mu g/cm^2$ on foliage are, respectively, about 8, 15, and 26 days. It is possible that the technique of Adams et al. (1976, 1977) would have been a better predictor of the field residue behavior. These authors applied the soil to citrus leaves rather than to glass plates.

Figure 12 shows the data for the methidathion and its oxon found in the mobile soil dust from plots in Riverside, Delano, and Centerville which were sprayed in early summer. Although quite erratic, the data still provide the basic information sought. As previously demonstrated by Gunther et al. (1977), soil dust residues are lower after a low-volume application than after a dilute application. Initial deposits can be up to 300 ppm methidathion and they appear to dissipate by first-order kinetics similar to those on the soil plates (Figure 11). Unlike the soil plates, field residues dissipated slower and equally rapid ($t_{1/2}$ = 9–10 days) for all locations. Oxon residue behavior on soil was similar to foliar residues in that once methidathion levels were low, oxon levels declined.

Air. To see if any methidathion could be found in the air of the experimental plots, two sets of two Greenburg-Smith impingers connected in tandem and each charged with ethylene glycol, were placed under a tree located in the center of a plot treated by low-volume; trees had been treated 3 days earlier (Riverside, Sept). Since the low-volume-treated trees always have the highest levels of dislodgable foliar residues, it was thought these trees would yield the most methidathion vapor. Air was sampled at 5 L/min for 2 h (0.6 m^3 total). Quantitation of the gas chromatographic peak corresponding to methidathion gave for impinger sets A and B, 6.8 and 6.1 μg, respectively, in the first impinger and 6.5 and 7.3 μg, respectively, for the second impinger. Since both the first

Table IV. Methidathion Residues (ppm) in Orange Leaves[a]

lb of AI/acre	gal/acre	day	methidathion pre-bloom	post-bloom	early summer	late summer
			Riverside			
7.50	1500	0	14.0	17.7	22	
		3	9.7	8.9	11	
		10	4.9	7.7	7.5	
		17	4.6	10.2	5.8	
		31	3.1	10.8	9.1	
		45	6.1	15.3	9.5	
		59	6.5	6.7	10	
			Delano			
11.3	2250	0	7.3	9.6	19	14
		3	7.7	8.7	20	6.7
		10	6.9	15	13	5.7
		17	5.1	17	13	5.3
		31	6.0	28	12	3.7
		45	3.6	28	14	4.5
		59	3.6	31	13	4.6
			Centerville			
7.5	1450	0			43	
		3			22	
		10			20	
		17			17	
		31			18	
		45			12	
		59			12	

[a] Each value is the mean of six samples.

and second impingers contained an average of 6.7 μg and a reagent blank gave 4.7 μg, it was concluded that no detectable (>1 μg) levels of methidathion were collected and therefore the air concentration was less than 2 μg/m^3 under the tree.

NOTE ADDED IN PROOF

To save space and avoid confusing complexity in tables and graphs, only average residue values (usually from six field replicates) are reported herein. The reader should recognize that variations within a set of field replicates can be quite large.

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LITERATURE CITED

Adams, J. D., Iwata, Y., Gunther, F. A., *Bull. Environ. Contam. Toxicol.* **15**, 547 (1976).
Adams, J. D., Iwata, Y., Gunther, F. A., *Bull. Environ. Contam. Toxicol.* **18**, 445 (1977).
Bowman, M. C., Beroza, M., Leuck, D. B., *J. Agric. Food Chem.* **16**, 796 (1968).
California Administrative Code, Title 3, Chapter 4, Subchapter 1, Group 2, Article 23, ACF-59-036, July 1976.
California Department of Food and Agriculture, Pesticide Use Report by Commodity, 1976.
Carman, G. E., "Citrus", Häfliger, E., Ed., Ciba-Geigy Technical Monograph No. 4, Switzerland, 1975, pp 28–34.
Carman, G. E., Westlake, W. E., Gunther, F. A., *Bull. Environ. Contam. Toxicol.* **8**, 38 (1972).
Ciba-Geigy Corporation, 1977 Sample Labels, 1977 p 130.
Fed. Regist. **40**, 25674 (1975).
Gunther, F. A., Westlake, W. E., Barkley, J. H., Winterlin, W., Langbehn, L., *Bull. Environ. Contam. Toxicol.* **9**, 243 (1973).
Gunther, F. A., Iwata, Y., Carman, G. E., Smith, C. A., *Residue Rev.* **67**, 1 (1977).
Iwata, Y., Knaak, J. B., Spear, R. C., Foster, R. J., *Bull. Environ. Contam. Toxicol.* **18**, 649 (1977).
Maddy, K. T., "A Study of Foliar Residues Following Application of Supracide to Orange Trees", California Department of Food and Agriculture, ACF 59-172, 1975.
Nigg, H. N., Allen, J. C., Brooks, R. F., Edwards, G. J., Thompson, N. P., King, R. W., Blagg, A. H., *Arch. Environ. Contam. Toxicol.* **6**, 257 (1977).
Popendorf, W. J., Leffingwell, J. T., *Bull. Environ. Contam. Toxicol.* **18**, 787 (1977).
Spear, R. C., Popendorf, W. J., Spencer, W. F., Milby, T. H., *J. Occup. Med.* **19**, 411 (1977a).
Spear, R. C., Popendorf, W. J., Leffingwell, J. T., Milby, T. H., Davies, J. E., Spencer, W. F., *J. Occup. Med.* **19**, 406 (1977b).
Spear, R. C., Lee, Y., Leffingwell, J. T., Jenkins, D., *J. Agric. Food Chem.* **26**, 434 (1978).
Spencer, W. F., Iwata, Y., Kilgore, W. W., Knaak, J. B., *Bull. Environ. Contam. Toxicol.* **18**, 656 (1977).
Task Group on Occupational Exposure to Pesticides, T. H. Milby (Chairman), "Occupational Exposure to Pesticides", Report to the Federal Working Group on Pest Management, Washington, D.C., 1974.
Turrell, F. M., "Tables of Surfaces and Volumes of Spheres and of Prolate and Oblate Spheroids, and Spheroidal Coefficients", University of California Press, Berkeley and Los Angeles, 1946.
University of California, Toxicity of Pesticides to Honey Bees, Leaflet 2286, Dec 1975.
University of California, 1976–1978 Treatment Guide for California Citrus Crops, Leaflet 2903, Aug 1976.
Van Dyk, L. P., Vishweswariah, K., *Residue Rev.* **55**, 91 (1975).
Westlake, W. E., Gunther, F. A., Carman, G. E., *Arch. Environ. Contam. Toxicol.* **1**, 60 (1973).

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