their stability to the hepatic carboxylesterases (Soderlund and Casida, 1977). However, it apparently has little effect on metabolism and elimination in vivo.

The difference between the cis and trans isomers of cypermethrin in the amounts retained in the fat is of interest. In terms of lipophilic character, there is little difference between the two isomers, and experiments in mice (Hutson et al., 1981) show that the amount reaching fat is similar with both isomers. The difference lies in the rate of release from this tissue. It is possible that hydrolysis of the ester bond occurs in the fatty tissue, perhaps catalyzed by a lipase. This hydrolysis would be expected to proceed much more rapidly with the trans isomer than with the cis isomer.

The rapid elimination of cypermethrin from rats is due primarily to the efficient cleavage of the ester bond giving rise to polar metabolites which are further oxidized and conjugated before excretion. The structural elucidation of these metabolites and their mechanisms of formation will be described in a subsequent paper.

ACKNOWLEDGMENT

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Phenthoate Applied to California Citrus Trees: Residue Levels on Foliage and Soil, in Air, and on and in Fruit

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Phenthoate [Cidial, ethyl α-[(dimethoxyphosphinothioyl)thio]benzeneacetate] was field applied to California orange, lemon, and grapefruit trees. Applications included two dilute spray rates and one low-volume rate. Residue levels of phenthoate and its oxygen analogue (oxon) were determined for assisting in setting worker reentry safety intervals and legal fruit tolerances. The half-lives for the dissipation of phenthoate from orange, lemon, and grapefruit rind were 15 ± 1, 20 ± 8, and 20 ± 5 days, respectively. The maximum rind residue of phenthoate oxon was 0.09 ppm in orange rind. No determinable phenthoate residues (>0.03 ppm) were found in the edible portion of the citrus fruits. Dislodgeable phenthoate residues dissipated rapidly from foliage. The half-lives were 3.6 ± 0.3 and 3.1 ± 0.3 days for phenthoate dissipation from orange and lemon foliage, respectively. The maximum oxon level found was 0.07 $\mu g/cm^2$ of leaf surface. Phenthoate appeared to persist longer on orange fruit surfaces ($t_{1/2} = 10$ days) than on the corresponding foliar surfaces ($t_{1/2} = 3.9$ days). Phenthoate dissipation from soil dust on the grove floor after a 7.5 lb of AI (1500 gal)$^{-1}$ acre^{-1} application had a $t_{1/2}$ value of 29 days. The highest level of phenthoate and its oxon found were 180 and 30 ppm, respectively. Air samples collected from under a tree after a 7.5 lb of AI (100 gal)$^{-1}$ acre^{-1} application contained 10 μg of phenthoate/m^3 at 3-days postapplication and lesser amounts thereafter.

Phenthoate [ethyl α-[(dimethoxyphosphinothioyl)thio]benzeneacetate; Cidial, Elsan, Papthion, Tanone] is a broad-spectrum scalicide/thripsicide/acaricide that has been used for ~18 years for pest control on citrus in the Mediterranean countries. It is a potentially useful insecticide for the chemical control of the California red scale (*Aonidiella aurantii* Mask) and the woolly whitefly (*Aleurothrixus floccosus*) in California. The woolly whitefly has moved into portions of southern California but has not yet developed into a major pest.

Fruit residue data for phenthoate after application to mature lemon, grapefruit, and orange trees and dislodgeable foliar residue data after application to orange trees were reported by Iwata et al. (1977a). However, the U.S. Environmental Protection Agency (EPA) has requested that additional information be provided prior to the granting of a registration for use of phenthoate on citrus. Since the emphasis on residue data relevant to assessing worker exposure to cholinesterase-inhibiting insecticide residues was not as great in 1973–1974 when the tests were conducted as it currently is, Iwata et al. (1977a) did not provide data on dislodgeable residue levels of phenthoate

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oxon, dislodgeable residues on fruit, and residues on the mobile soil dust of the citrus grove. Additional fruit residue data have also been requested for product registration, especially as to levels of other "regulable residues" such as the oxygen analogue of the parent insecticide. Therefore, reported here are additional fruit, soil, and foliar residue data for phenthoate applied to mature, orange, grapefruit, and lemon trees for use in setting fruit tolerances and worker reentry intervals for California. Required data for Florida citrus will be provided by other investigators.

EXPERIMENTAL SECTION

Treatment and Sampling. Trees were located on the University of California Citrus Research Center, Riverside, CA. Treatments were made by using Cidial 4EC formulation supplied by Montedison S.p.A. (Italy) and containing 4 lb of active ingredient (AI)/gal (0.48 kg of AI/L). Low-volume applications using 100 gal of spray/acre (9.4 hL/ha) were made by using a Kinkelder machine equipped with an air tower. Dilute applications were made by using an oscillating boom spray rig.

The recommended fruit sampling procedure of Gunther (1969) was followed whenever possible. However, as fruits treated with an unregistered insecticide are legally unmarketable, all applications were conducted by using trees on the Citrus Research Center to avoid the necessity of purchasing and destroying unsampled fruit. Consequently, the constraints of the limited availability of trees for the purposes at hand made it necessary to deviate from the optimum conditions. Each sampling pattern used is described below.

Oranges. For the 1978 study, one plot, each consisting of five adjacent rows of nine trees each, was used for each application rate. Treatments were made on July 28, 1978, at rates of 6.0 and 3.0 lb of AI (1200 gal)$^{-1}$ acre^{-1} [6.7 and 3.4 kg AI (112 hL)$^{-1}$ ha^{-1}] and at 6.0 lb of AI (100 gal)$^{-1}$ acre^{-1} [6.7 kg of AI (9.4 hL)$^{-1}$ ha^{-1}]. Fruit samples were collected from the center three rows of the five-row treatment plot. For each treatment, two field samples were collected from each of the three rows at each sampling date. Each sample consisted of 28 fruit, 1 from each quadrant of each of 7 trees; trees at the end of the row should not be used for sample collection (Gunther, 1969).

For the 1979 study, three replicate plots, each consisting of four rows of six trees each, were used for each application rate. Treatments were made on April 20, 1979, at rates of 7.5 and 3.8 lb of AI (1500 gal)$^{-1}$ acre^{-1} [8.4 and 4.2 kg of AI (140 hL)$^{-1}$ ha^{-1}] and at 7.5 lb of AI (100 gal)$^{-1}$ acre^{-1} [8.4 kg (9.4 hL)$^{-1}$ ha^{-1}]. Fruit samples were collected from the center two rows of the four-row treatment plot. For each of three replicate plots for each treatment rate, two field samples were collected at each sampling date. Each sample consisted of 20 fruit, 5 from each quadrant distributed over 10 trees (row-end trees included). The leaf disk samples were collected from the center eight trees of the four-row treatment plot. For each of the three replicate plots for each treatment rate, two samples were collected at each sampling date. Each sample consisted of 40 leaf disks (2.5-cm diameter) as described by Gunther et al. (1973). Soil dust samples were collected by the method of Spencer et al. (1977) by vacuuming the surface soil through a 100-mesh screen (23 × 55 cm) using a portable vacuum cleaner. Samples were collected near the edge of the tree canopy from one side of each of eight trees in the center of each plot. Due to furrow irrigation, samples were collected from areas between the trees in row. One sample was collected from each replicate treatment plot at each sampling interval. Samples were stored in

glass jars at 8 °C prior to extraction and analysis.

Lemons. For the 1978 study, three replicate plots, each consisting of a minimum of four adjacent rows of six trees each, were used for each treatment rate. Applications were made on Oct 6, 1978, at rates of 7.5 and 3.8 lb of AI (1500 gal)$^{-1}$ acre^{-1} [8.4 and 4.2 kg of AI (140 hL)$^{-1}$ ha^{-1}] and at 7.5 lb of AI (100 gal)$^{-1}$ acre^{-1} [8.4 kg of AI (9.4 hL)$^{-1}$ ha^{-1}]. Two fruit samples were collected from each of the three replicate plots at each sampling date. Each sample consisted of 32 fruit, 1 fruit from each quadrant of each of 8 trees. Two leaf disk samples were collected from each of the three replicate plots at each sampling date for each treatment. Each sample consisted of 40 leaf disks (2.5-cm diameter) taken from 8 trees as described by Gunther et al. (1973).

For the 1979 study, three replicate plots, each consisting of three adjacent rows of six trees each, were used for each application rate. Applications were made on Oct 26, 1979, at rates of 9.0 and 4.5 lb of AI (1800 gal)$^{-1}$ acre^{-1} [10 and 5.0 kg of AI (168 hL)$^{-1}$ ha^{-1}] and at 9.0 lb of AI (100 gal)$^{-1}$ acre^{-1} [10 kg of AI (9.4 hL)$^{-1}$ ha^{-1}]. Two fruit samples from the center four trees were collected from each of the three replicate plots for each sampling date. Each sample consisted of 32 fruit, 2 fruit from each quadrant of each of 4 trees.

Grapefruits. For the 1978 study, one plot, each consisting of three adjacent rows of fourteen trees each, was used for each application rate. Treatments were made on July 14, 1978, at rates of 6.0 and 3.0 lb of AI (1200 gal)$^{-1}$ acre^{-1} [6.7 and 3.4 kg of AI (112 hL)$^{-1}$ ha^{-1}] and at 6.0 lb of AI (100 gal)$^{-1}$ acre^{-1} [6.7 kg of AI (9.4 hL)$^{-1}$ ha^{-1}]. Fruit samples were collected from ten trees located in the center row of the three-row treatment plot. By use of six different preselected combinations of five trees each, six samples were collected at each sampling date. Each sample consisted of 20 fruit, 1 from each quadrant of each of 5 trees.

For the 1979 study, three replicate plots, each consisting of four trees, were used for each application rate. Treatments were made on June 1, 1979, by manually spraying the trees to achieve complete coverage. The spray mixtures used were 1.0 and 0.5 pt of Cidial 4EC/100 gal of water. Fruit samples were collected from each four-tree replicate by collecting one fruit from each quadrant of the tree from each of four trees to give a sixteen-fruit sample.

Processing. *Dislodgeable Foliar Residues.* The procedure of Iwata et al. (1977b) was used. Briefly, the procedure entailed shaking the sample 3 times, each time with 100 mL of water containing a surfactant, and then extracting the combined aqueous wash twice, each time with 50 mL of CH$_2$Cl$_2$ to recover residues for analysis.

Dislodgeable Fruit Residues. The procedure of Iwata et al. (1979) was used. Briefly, the procedure entailed rotating, for several minutes on its side, a 3-gal jar containing the sample twice, each time with water containing a surfactant, and then extracting the combined aqueous wash twice, each time with 50 mL of CH$_2$Cl$_2$. Samples were stored at 4 °C pending analysis.

The oblate and prolate diameter of each fruit was measured to obtain the total surface area represented by the fruit sample (Turrell, 1946).

Fruit Residues. A 100-g sample of chopped rind or pulp was macerated with 300 mL of acetone for 5 min in a Waring Blendor jar. The extract was vacuum filtered through a Buchner funnel. A 50-mL aliquot of the extract and 50 mL of benzene were placed in a 125-mL separatory funnel, and the mixture was shaken gently for 30 s. The lower aqueous phase was discarded, and the upper phase was passed through a funnel containing Na$_2$SO$_4$ into a

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flask. The funnel and Na_2SO_4 were rinsed with 25 mL of benzene. The solvent was removed on a rotary evaporator and the residue was dissolved in acetone for GLC analysis. Results were calculated on the basis that the total acetone extract volume was 380 mL (300 mL acetone of plus 80 mL of water from 100 g of sample).

Soil Dust Residues. The procedure of Iwata et al. (1979) was used. Briefly, the procedure entailed extracting 10 g of soil dust by adding 10 mL of 10% aqueous acetone, followed by 10 mL of hexane, and then shaking for 20 min. The extract was stored at 4 °C pending analysis.

Analysis. All samples were analyzed by gas chromatography using a Hewlett-Packard N/P detector. A 1.2 m × 2 mm i.d. glass column packed with 4% OV-101 on 80–100-mesh Gas-Chrom Q was used with a carrier gas flow rate of 30 mL/min nitrogen. Inlet, column, and detector temperatures were 200, 190, and 250 °C, respectively. Analytical standards of phenthoate (99%) and its oxon were supplied by Montedison USA, Inc., New York 10036.

Method Validation. Aqueous leaf washes obtained from 40 leaf disk (2.54-cm diameter) samples were fortified with 400, 40, and 4 μg (equivalent to 1.0, 0.1, and 0.01 μg/cm^2 of leaf surface) of phenthoate and its oxon and the recoveries determined. Recoveries and standard deviations (three samples) were 94 ± 4, 92 ± 7, and 100 ± 3%, respectively, for phenthoate and 94 ± 6, 99 ± 9, and 104 ± 6%, respectively, for the oxon. No "corrections" were made to the field sample data.

Chopped rind and pulp samples were each fortified in the blender jar prior to the addition of the acetone to obtain procedural recoveries. Recoveries and standard deviations (three samples) for rind samples fortified at 10, 1, and 0.1 ppm of phenthoate were respectively 99 ± 3, 107 ± 9, and 94 ± 10% for orange, 105 ± 8, 101 ± 3, and 89 ± 4% for lemon, and 91 ± 4, 98 ± 9, and 106 ± 7% for grapefruit. Recoveries and standard deviations (three samples) for pulp (edible portion) samples fortified at 1, 0.1, and 0.05 ppm of phenthoate were respectively 92 ± 11, 87 ± 7, and 65 ± 16% for orange, 102 ± 2, 89 ± 8, and 71 ± 9% for lemon, and 101 ± 6, 92 ± 7, and 98 ± 3% for grapefruit. Recoveries and standard deviations (three samples) for samples fortified at 0.1 and 0.05 ppm of phenthoate oxon were respectively 92 ± 1 and 120 ± 10% for orange rind and 110 ± 6 and 100 ± 11% for orange pulp. For orange rind analysis, values needed to be corrected for background interferences as determined from unfortified control samples. No "corrections" were made to the field sample data for fruit residues.

All further tests described below were conducted by using lemon fruit collected 68 days after treatment of trees at 7.5 lb of AI (100 gal)$^{-1}$ acre^{-1} (low volume).

Some fruits were water-washed prior to peeling and processed to determine if residues were on or in the rind. Water-washed fruit had residues of 2.1 ± 0.1 ppm of phenthoate (individual values: 2.2; 2.0; 2.0), and unwashed fruit had residues of 1.9 ± 0.2 ppm of phenthoate (2.1; 1.7; 1.9). Since there was no statistically significant difference in the two residue values, the major portion of the rind residues were in, rather than on, the rind as would be expected for 68-day field-weathered fruit.

Since the fruit rind extraction procedure used here differed from that used previously by Iwata et al. (1977a), a comparison of the two methods was made. Residues found after processing with acetonitrile according to the method of Iwata et al. (1977a) were 1.8 ± 0.4 ppm of phenthoate (2.2; 1.6; 1.5), and residues found after processing with acetone as described herein were 2.1 ± 0.1 ppm of phenthoate (2.2; 2.0; 2.0). Thus, the residue values

are comparable for the two methods.

For estimation of the extraction efficiency of the acetone blending procedure, the pulp remaining after filtering the acetone rind macerate from the washed fruit was Soxhlet-extracted using methanol–chloroform (13:87 azeotropic mixture). The Soxhlet extraction (no thimble, only glass wool) was conducted for 2 h and then again for another 2 h with fresh solvent. The tests were conducted by using three samples. The acetone blending procedure yielded 2.1 ± 0.1 ppm of phenthoate (2.2; 2.0; 2.0), the first 2-h Soxhlet extraction gave an additional 0.53 ± 0.08 ppm of phenthoate (0.62; 0.47; 0.51), and the second 2-h Soxhlet extraction gave negligible residues (<0.01 ppm). For confirmation that Soxhlet extraction was not decomposing the pesticide, 25 μg of phenthoate was added to the boiling flask and control samples of lemon rind were extracted. Recovery after 2-h of heating was 103 ± 4% (102; 99; 107). Thus, the efficiency of the acetone blending procedure used for field-weathered lemon rind was 81% [2.1/(2.1 + 0.5)].

Unwashed lemon fruit were stored in paper bags for 2 and 7 days at 8 °C to determine the effect of short-term storage prior to processing. Rind residues for unstored fruit were 1.9 ± 0.2 ppm of phenthoate (2.1; 1.7; 1.9), and residues after 2 and 7 days of storage were 1.5 ± 0.1 (1.4; 1.5; 1.5) and 1.1 ± 0.1 ppm (1.1; 1.0; 1.1), respectively. The data indicate that the residue level is dropping by a first-order process with a half-life of 9 days. Generally, at least 3 days was required to peel, chop, and freeze fruit samples after collection of samples in the numbers involved in the present study.

Chopped samples were frozen for later extraction. Immediate extraction with acetone would have required additional delay in processing the stored fresh fruit. Immediate processing of some lemon rind gave residues of 2.1 ± 0.1 ppm of phenthoate (2.2; 2.0; 2.0), and aliquots of the same sample stored for 2, 3, and 5 weeks under frozen condition had residues of 1.8 ± 0.1 (1.9; 1.8; 1.7), 1.8 ± 0.1 (1.7; 1.9; 1.8), and 2.0 ± 0.2 ppm (1.9; 2.0; 2.2), respectively. Over this 5-week period no changes in residue levels occurred from frozen storage.

After acetone blending, the extracts were stored until analysis. Analysis of unstored extracts gave a residue value of 2.1 ± 0.1 ppm of phenthoate (2.2; 2.0; 2.0), and aliquots of the same extract after 2, 3, and 5 weeks of storage at 8 °C gave values of 1.8 ± 0.1 (1.7; 1.9; 1.7), 1.8 ± 0.1 (1.7; 1.9; 1.9), and 2.0 ± 0.2 ppm (2.1; 2.1; 1.8), respectively. Thus, phenthoate was stable in the acetone extract over the 5-week period studied.

Air. Samples were collected by using polyurethane (PU) foam, open-cell polyether type, density 0.021 g/cm^3 (Lewis et al., 1977). Air was drawn at 5 L/min for 100 min through a glass tube (19 mm i.d.) containing a 3-in. (76-cm) plug of PU foam. The sampler was located 30 cm above the ground. The insecticide was recovered by 2-h Soxhlet extraction of the foam with acetone.

A glass U-tube containing 100 μg of phenthoate was attached to the inlet of the PU foam sampler and air was drawn at 5 L/min for 100 min to check for insecticide retention and recovery. The U-tube contained 87 ± 7 μg of phenthoate, and 13 ± 2 μg of phenthoate was recovered from the foam, indicating excellent retention of phenthoate vapors using this procedure.

Regulable Residues. Takade et al. (1976) reported on the residues of ring-labeled [14C]- and [32P]phenthoate separately applied to orange fruit under field conditions. After 14 days, 41% of the applied 14C activity and 43% of the applied 32P activity remained; loss of the rest of the applied activity was attributed to volatilization. Of the
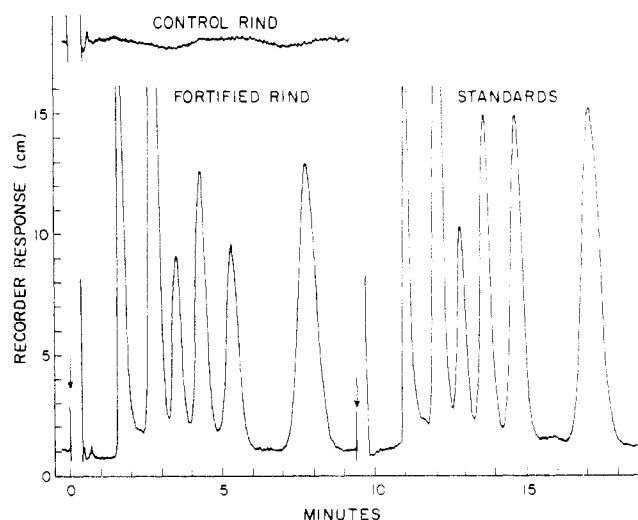
Figure 1. Gas chromatograms of extracts from control orange rind and rind fortified at 1.0 ppm each of dimethoate, malathion, parathion, phenthoate oxon, phenthoate, methidathion, and ethion (listed in order of elution; malathion and parathion are unresolved) and for 4.0 ng of each insecticide standard. Chromatograms for rind represent injection of extractives from 4.0 mg of rind. Retention times on the 5% OV-17 column were 3.5 min for the oxon and 4.3 min for phenthoate; a flame photometric detector was used.

recovered activity, 12% of the ^{14}C activity and 30% of the ^{32}P activity were through acetone washing and extraction; the rest was recovered by combustion of the residual solids. Of the acetone-extractable ^{14}C activity, 94% was due to phenthoate and 3% to the oxon. Of the acetone-extractable ^{32}P activity, 46% was due to phenthoate, 12% to the oxon, and 26% to the O,O-dimethyl thio- and dithiophosphoric acids; the remaining 16% could not be identified as to chemical structure. The oxon found represented less than 0.2% of the applied ^{14}C activity and less than 2% of the applied ^{32}P activity; O,O-dimethyl thio- and dithiophosphoric acids are not unique to phenthoate degradation. Excluding consideration of polar degradation products not extractable with acetone, the only regulable residue should be the parent compound as little oxon was formed.

The U.S. EPA requires that an analytical method to determine regulable residues of phenthoate in the presence of other insecticides with established tolerances on citrus be demonstrated. In 1977, 16 organophosphorus insecticides were used on California citrus (California Department of Food and Agriculture, 1977). One additional material (dialifor) is used in Florida (Florida Cooperative Extension Service, 1976). The gas chromatographic OV-101 column used for the residue study herein was not specific for phenthoate; methidathion, if present, and with an almost identical retention time, would interfere with quantitation. A 90 cm × 4 mm i.d. column packed with 5% OV-17 on 70–80-mesh Chromosorb G (DMCS-AW) used at a column temperature of 220 °C and a 70 mL/min nitrogen carrier gas flow rate gave the desired separations. Figure 1 shows a gas chromatogram for orange rind fortified with 1.0 ppm [0.2 ppm of whole fruit (Gunther, 1969)] each of dimethoate, malathion, parathion, phenthoate oxon, phenthoate, methidathion, and ethion and then processed. A 90% recovery of the oxon and an 83% recovery of phenthoate are indicated by comparison with peak heights obtained from standard solutions. On the basis of the data of relative retention times given for a 5% OV-17 column of Bowman and Beroza (1970), demeton, diazinon, dimethoate, dioxathion, malathion, mevinphos,

monocrotophos, naled, and phosphamidon elute from the column prior to parathion, and azinphosmethyl, carbophenothion, and phosalone elute after ethion. Injection of standards showed that trichlorfon and oxydemetonmethyl elute before parathion, dialifor elutes after ethion, and methidathion does not interfere with analysis. Thus, conditions for the analysis of phenthoate in the presence of all organophosphorus insecticides currently used on citrus were achieved. Only interferences from the parent insecticides were considered.

A GC retention time obtained in conjunction with a flame photometric detector is a good indication of insecticide identity. However, additional confirming data are required to support identification. Since GC retention times for a compound on different stationary phases are often highly correlated, independent confirmatory techniques must be used (Elgar, 1971). Bowman and Beroza (1965) devised a simple method for the identification of pesticides based on the partitioning of a pesticide between two immiscible liquid phases. The partitioning value or "p value", determined by distributing a solute between equal volumes of two immiscible phases, is defined as the fraction of the total solute partitioning into the upper phase. Each pesticide has a characteristic p value which is practically independent of the pesticide concentration and the presence of plant and animal extractives.

By use of the isooctane–80% acetone system, p values were obtained for phenthoate and parathion standards and were 0.62 and 0.72, respectively; Bowman and Beroza (1965) listed a parathion p value of 0.76. The benzene extract prepared from 1 ppm of fortified rind as described under Fruit Residues was used after solvent removal, and p values (mean of six samples) were 0.64 ± 0.02 for phenthoate and 0.73 ± 0.01 for parathion.

A third independent method for confirmation of identity is chemical conversion to another compound. The technique given here is to convert the parent insecticide to its oxygen analogue to obtain a different GC retention time value (Singh and Lapointe, 1974; Singh and Cochrane, 1979). The benzene extract prepared from 1 ppm of fortified rind as described under Fruit Residues was used. After removal of the solvent, the residue was dissolved in 50 mL of hexane, and the solution was extracted 3 times with acetonitrile (25, 10, and 10 mL successively) by shaking vigorously for 30 s each time. The combined acetonitrile extracts were partitioned with 50 mL of fresh hexane and 30-s shaking. The solvent was removed from the acetonitrile extract in a rotary evaporator, and the residue was transferred with 2 mL of benzene to a 22 mm i.d. glass column containing 10 g of Florisil and topped with a glass wool plug. The column was eluted with 90 mL of hexane (discarded) and 100 mL of 5% diethyl ether in hexane. The solvent was removed from the eluate and the residue was dissolved in 1 mL of acetone. Then, 10 mL of a 1:1000 dilution of commercial household liquid bleach (5.25% sodium hypochlorite by weight) was added, and the mixture was allowed to stand for 10 min. After addition of 15 mL of water, the mixture was extracted twice with 25-mL portions of dichloromethane and 1-min shaking each time. The solvent was removed from the combined extracts, and the residue was dissolved in acetone for GC analysis. Figure 2 shows a partial conversion of phenthoate to its oxon.

RESULTS AND DISCUSSION

Complete fruit residue dissipation curves for phenthoate applied to orange, lemon, and grapefruit trees were reported by Iwata et al. (1977a). However, only limited data on dislodgeable foliar residues which are relevant to worker

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Table I. Orange Rind Residues (ppm) of Phenthoate[a]

appli-cation[b]	days after spraying	replicate[c]						mean	SD
		A	B	C	D	E	F		
A	10	0.60	0.70	0.64	0.64	0.69	0.78	0.68	0.06
	19	0.45	0.38	0.41	0.46	0.37	0.41	0.41	0.04
	39	0.28	0.22	0.22	0.20	0.19	0.27	0.23	0.04
B	10	2.4	2.8	1.9	1.8	1.8	1.9	2.1	0.4
	19	1.7	1.4	1.5	1.3	1.3	1.5	1.5	0.2
	39	0.70	0.67	0.74	0.76	0.73	0.77	0.73	0.04
C	10	3.2	4.9	4.0	5.4	5.7	3.8	4.5	1.0
	19	2.0	2.9	2.5	1.6	2.4	2.8	2.4	0.5
	39	1.3	1.8	2.0	1.3	1.7	1.4	1.6	0.3

[a] Applied July 28, 1978, to trees located on the Citrus Research Center, Riverside, CA. [b] A, 3.0 lb of AI (1200 gal)$^{-1}$ acre^{-1}; B, 6.0 lb of AI (1200 gal)$^{-1}$ acre^{-1}; C, 6.0 lb of AI (100 gal)$^{-1}$ acre^{-1} (low volume). [c] Pretreatment samples and all samples collected from an untreated control plot contained less than 0.06 ppm.

Table II. Orange Rind Residues (ppm) of Phenthoate Oxygen Analogue[a]

appli-cation[b]	days after spraying	plot[c]						mean	SD
		A		B		C			
		1	2	1	2	1	2		
A	3		0.04	0.04	0.04			0.04	
	10	0.07	0.08	0.06	0.06	0.08	0.09	0.07	0.01
	19	0.07	0.06	0.05	0.05	0.06	0.06	0.06	0.01
	39	0.06	0.06	0.05	0.07	0.06	0.06	0.06	0.01
	59	0.08	0.09	0.08	0.08	<0.02	<0.02	0.06	
B	3		0.03	0.06	0.04			0.04	0.02
	10	0.03	0.04	0.06	0.05	0.05	0.07	0.05	0.01
	19	<0.03	<0.03	0.05	0.04	0.05	0.05	0.05	0.01
	39	0.03	0.03	0.04	0.05	0.06	0.08	0.05	0.02

[a] Applied April 20, 1979, to trees located on the Citrus Research Center, Riverside, CA. [b] A, 7.50 lb of AI (1500 gal)$^{-1}$ acre^{-1}; B, 7.50 lb of AI (100 gal)$^{-1}$ acre^{-1} (low volume). [c] Pretreatment samples contained no determinable residues (>0.05 ppm) of phenthoate or its oxygen analogue. Control samples contained <0.4, <0.3, <0.3, <0.06 and <0.02 ppm of phenthoate, respectively, for the five sampling dates and <0.03 ppm of oxon for all sampling dates. Chopped samples were frozen for ~4–10 weeks prior to analysis.

safety were obtained at that time. Reported here are additional fruit residue data to assist in setting legal tolerances and more extensive dislodgeable residue data to assist in setting worker reentry intervals.

Fruit Residues. *Oranges.* Rind residue data for the 1978 application for fruit sampled 10, 19, and 39 days postapplication are given in Table I. Rind residue data for the 1979 application for fruit sampled 3, 10, 19, and 39, and 59 days postapplication are shown in Figure 3. In the previous report on phenthoate (Iwata et al., 1977a), residue dissipation was shown as being composed of two first-order processes, the first giving way to a slower second dissipation process at ~28 days postapplication. The description, of course, was a means of bringing order to the residue data as the actual processes responsible for residue dissipation were likely a result of multiple factors. The 1979 residue data shown in Figure 3 can be described by a single line. No explanation can be given for this different residue behavior.

For the 1979 data for the low-volume application at 7.5 lb of AI (100 gal)$^{-1}$ acre^{-1}; dissipation was described by the line $\ln y = -0.048t + \ln 7.4$ with a correlation coefficient (r) of 0.99 and half-life ($t_{1/2}$) of 14 days. The dilute application data for the 7.5 lb of AI and 3.75 lb of AI (1500 gal)$^{-1}$ acre^{-1} were described by $\ln y = -0.044t + \ln 4.6$ with $r = 0.99$ and $t_{1/2} = 16$ and $\ln y = -0.046t + \ln 3.5$ with $r = 0.99$ and $t_{1/2} = 15$, respectively. The mean $t_{1/2}$ value for phenthoate dissipation for the three 1979 treatments was 15 ± 1 days. The phenthoate oxygen analogue was sought in the two applications by using 7.5 lb of AI/acre. Data are given in Table II. The maximum level found was 0.09 ppm.
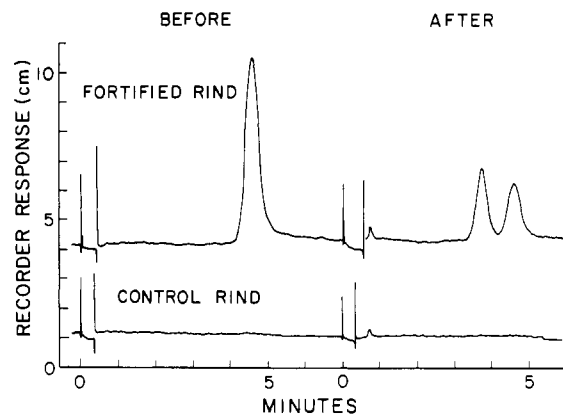

Figure 2. Gas chromatograms of extracts from control orange rind and rind fortified at 1.0 ppm of phenthoate, before and after oxidation with sodium hypochlorite solution. Phenthoate (4.6 min) is partially converted to its oxygen analogue (3.7 min). Chromatograms represent injection of extractives from 8.0 mg of rind. A 5% OV-17 column and a flame photometric detector were used.

A sample chromatogram for the analysis of a 39-day rind sample is shown in Figure 4 for phenthoate and in Figure 5 for phenthoate oxon.

Two field samples collected from each of the three treatment rates at each of the three sampling dates (10, 19, and 39 days postapplication) for the 1978 application were analyzed for phenthoate in the edible portion (pulp) of the fruit after rind removal. No determinable residues (>0.02 ppm) were found. Three field samples collected from each of the three treatment rates at each of three

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Table III. Lemon Rind Residues (ppm) of Phenthoate Resulting from a 1978 Field Application[a]

appli-cation[b]	days after spraying	plot[c]						mean	SD
		1		2		3			
		A	B	A	B	A	B		
A	10	1.2	1.3	1.4	1.7	1.5	1.6	1.5	0.2
	19	0.9	1.2	0.6	0.9		0.9	0.9	0.2
	38	0.41	0.37	0.51	0.47	0.51	0.57	0.47	0.07
B	10	3.0	2.7	2.6	2.4	3.1	3.1	2.8	0.3
	19	1.7	1.6	1.6	1.9	1.7	1.6	1.7	0.1
	38	0.88	0.76	0.73	0.76	0.68	0.84	0.78	0.07
C	10	2.6	3.7	3.4	3.7	3.9	5.6	3.8	1.0
	19	2.8	3.3	2.1	3.0	5.1	3.2	3.3	1.0
	38	1.5	1.8	1.1	1.2	3.8	3.5	2.2	1.2
none	10	<0.05	<0.05					<0.05	
	19	<0.05	<0.05					<0.05	
	38	<0.05	<0.05					<0.05	

[a] Applied Oct 6, 1978, to trees located on the Citrus Research Center, Riverside, CA. [b] A, 3.75 lb of AI (1500 gal)$^{-1}$ acre^{-1}; B, 7.5 lb of AI (1500 gal)$^{-1}$ acre^{-1}; C, 7.5 lb of AI (100 gal)$^{-1}$ acre^{-1}. [c] All pretreatment residue values were below 0.03 ppm.
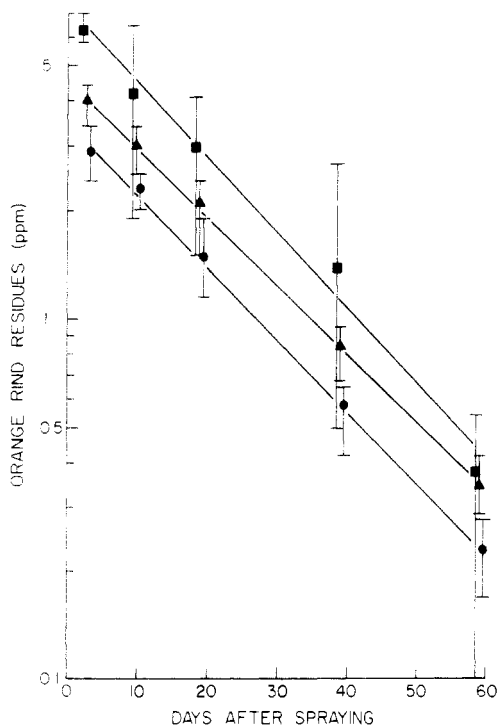
Figure 3. Phenthoate orange rind residues after low-volume application at a rate of 7.5 lb of AI (100 gal)$^{-1}$ acre^{-1} (■) and at 3.75 (●) and 7.5 (▲) lb of AI (1500 gal)$^{-1}$ acre^{-1}. Vertical lines indicate the range of values found for six replicate field samples. Applied April 20, 1979, to trees located on the Citrus Research Center, Riverside, CA. Pretreatment samples contained no determinable residues (>0.05 ppm) of phenthoate.

Figure 4. Sample chromatograms obtained with a nitrogen/phosphorus flame ionization detector. A 3% OV-101 column was used; arrows indicate the phenthoate peak. (A) Orange rind sample obtained 39 days posttreatment. The sample was found to contain 0.90 ppm of phenthoate. (B) Standards of 1.6 ng each of phenthoate and its oxon used to quantitate (A). (C) Untreated sample which was found to contain "apparent" residues of 0.06 ppm of phenthoate. (D) Standards of 0.1 ng each of phenthoate and its oxon used to quantitate (C). (A) and (C) each represent injection of extractives from 1.8 mg of rind.

sampling dates (10, 19, and 39 days postapplication) for the 1979 application were also analyzed for phenthoate in the pulp. No determinable residues (>0.02 ppm) were found. In addition, the 19-day samples for the 1979 application were analyzed for phenthoate oxon. No determinable residues were found (>0.02 ppm). Residues are generally not found in the pulp unless the insecticide has some systemic properties. Residues on a whole-fruit basis are about one-fifth the values for rind as Valencia oranges are 18.7 ± 6.3% rind by weight (Gunther, 1969) and since no determinable residues were present in the pulp.

Lemons. Rind residue data for fruit sampled 10, 19, and 38 days postapplication are given in Table III for the 1978 application and in Table IV for the 1979 application. Rind residue values for the 1979 application (Table IV) were
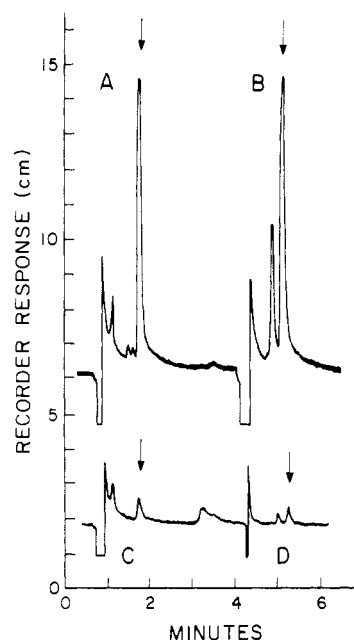
anomalously high. The data of Iwata et al. (1977a) indicate a phenthoate dissipation involving two first-order processes, an initial process giving way to a slower second process. Thus, the data in Tables III and IV are insufficient for calculation of $t_{1/2}$ values. However, for purposes of comparison, semilogarithmic plots of the data (three points) were made for each field treatment. Perhaps fortuitously, all plots were linear with $r = 0.99$. The mean $t_{1/2}$ value for phenthoate residues was 16 ± 1 days for the four dilute applications, and the $t_{1/2}$ values were 35 and 22 days for the low-volume applications. The overall $t_{1/2}$ value was 20 ± 8 days. For both application years, two samples from each of three replicate treatment plots for each of the three application rates were collected at each of the three sampling dates (10, 19, and 38 days postap-

Table IV. Lemon Rind Residues (ppm) of Phenthoate Resulting from a 1979 Field Application[a]

appli- cation[b]	days after spraying	plot[c]						mean	SD
		1		2		3			
		A	B	A	B	A	B		
A	10	3.2	3.3	3.8	3.9	3.6	4.2	3.7	0.4
	19	2.5	2.3	2.6	2.6	3.4	2.5	2.7	0.4
	38	1.2	1.0	1.1	1.0	1.1	1.0	1.1	0.1
B	10	7.1	7.5	6.4	7.1	7.3	6.5	7.0	0.4
	19	5.1	5.2	4.3	4.6	3.8	4.2	4.5	0.5
	38	2.1	2.1	1.8	1.8	1.7	1.7	1.9	0.2
C	10	15	11	11	16	16	13	14	2
	19	8.5	11.7	9.8	8.6	15.9	10.2	11	3
	38	6.1	5.1	5.2	3.1	·4.8	9.8	5.7	2.2

[a] Applied Oct 26, 1979, to trees located on the Citrus Research Center, Riverside, CA. [b] A, 4.5 lb of AI (1800 gal)$^{-1}$ acre^{-1}; B, 9.0 lb of AI (1800 gal)$^{-1}$ acre^{-1}; C, 9.0 lb of AI (100 gal)$^{-1}$ acre^{-1}. [c] All pretreatment samples contained no determinable residues (>0.01 ppm) of phenthoate.
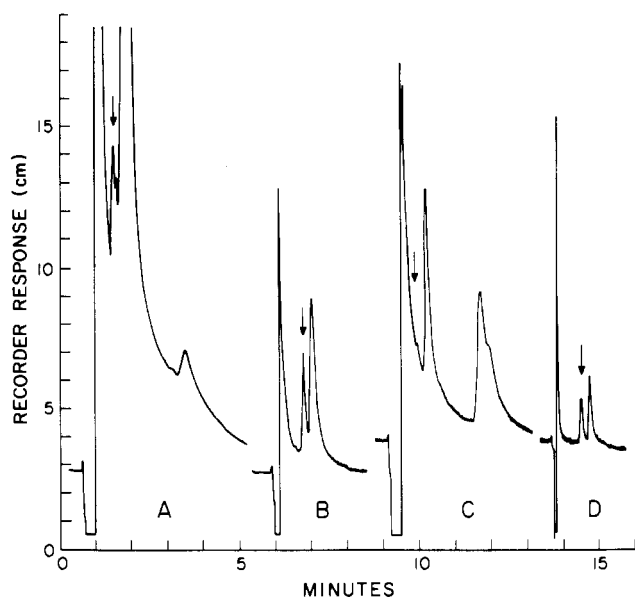
Figure 5. Sample chromatogram obtained with a nitrogen/ phosphorus flame ionization detector. A 3% OV-101 column was used; arrows indicate the phenthoate oxon peak. (A) Orange rind sample obtained 39 days posttreatment. The sample was found to contain 0.06 ppm of oxon. (B) Standards of 0.2 ng each of phenthoate and its oxon used to quantitate (A). (C) Untreated sample which was found to contain <0.03 ppm of oxon. (D) Standards of 0.1 ng each of phenthoate and its oxon used to quantitate (C). (A) and (C) represent injection of extractives from 1.8 and 4.0 mg of rind, respectively.

plication) and analyzed for phenthoate residues in the edible portion of the fruit. No determinable residues (>0.03 ppm) were found. Residues on a whole-fruit basis are about one-third the value of the rind as lemons are 30.0 ± 8.5% rind by weight (Gunther, 1969) and since no determinable residues were found in the pulp.

Grapefruit. For the July 1978 study, fruit samples were collected 10, 19, and 38 days postapplication, and fruits were laboratory washed prior to further processing. Residue data are shown in Figure 6. Dissipation of phenthoate in rind over the 30-day interval examined appeared to be a first-order process. For the 3.0 lb (1200 gal)$^{-1}$ acre^{-1} application, the semilogarithmic plot was described by ln y = −0.024t + ln 1.2 with r = 0.99 and $t_{1/2}$ = 29. For the 6.0 lb (1200 gal)$^{-1}$ acre^{-1} application, the plot was described by ln y = −0.032t + ln 2.9 with r = 0.99 and $t_{1/2}$ = 22. For the 3.0 lb (100 gal)$^{-1}$ acre^{-1} low-volume application, the plot was described by ln y = −0.036t + ln 5.3 with r = 0.99 and $t_{1/2}$ = 19. These results are in good

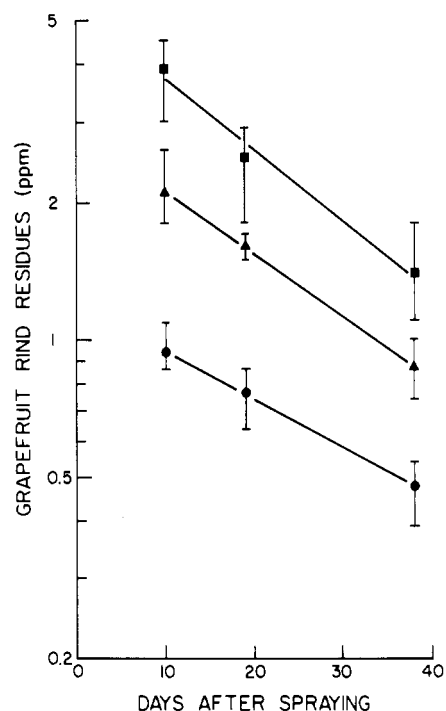**Figure 6.** Phenthoate residues in laboratory-washed grapefruit rind after low-volume application at a rate of 3.0 lb of AI (100 gal)$^{-1}$ acre^{-1} (■) and dilute application at rates of 6.0 (▲) and 3.0 (●) lb of AI (1200 gal)$^{-1}$ acre^{-1}. Vertical lines indicate the range of values found for six replicate field samples. Applied July 14, 1978, to trees located on the Citrus Research Center, Riverside, CA. All samples collected from an untreated control plot contained less than 0.05 ppm.

agreement with the data of Iwata et al. (1977a) for washed fruit; data were described by ln y = 0.038t + ln 1.5 with r = 0.99 and $t_{1/2}$ = 18 for a 3.75 lb (1500 gal)$^{-1}$ acre^{-1} application with samples collected 4, 11, 18, 25, 32, and 46 days postapplication.

For the June 1979 study, fruit samples were collected 10, 19, and 34 days postapplication and fruits were not washed prior to processing. Residue data are shown in Figure 7. Based on the data of Iwata et al. (1977a) and of the 1978 study, the 1979 data were plotted on semilogarithmic paper although the first-order nature of the dissipation was not clear-cut over the 25 days examined. The data for the 0.5 pt of Cidial 4EC/100 gal of spray fit the line ln y = −0.043t + ln 1.3 with r = 0.98 and $t_{1/2}$ = 16 days. The data for the 1.0 pt of Cidial 4EC/100 gal of spray fit the line ln y = −0.044t + ln 2.3 with r = 0.91 and $t_{1/2}$ = 16 days. The mean $t_{1/2}$ value for phenthoate dis-
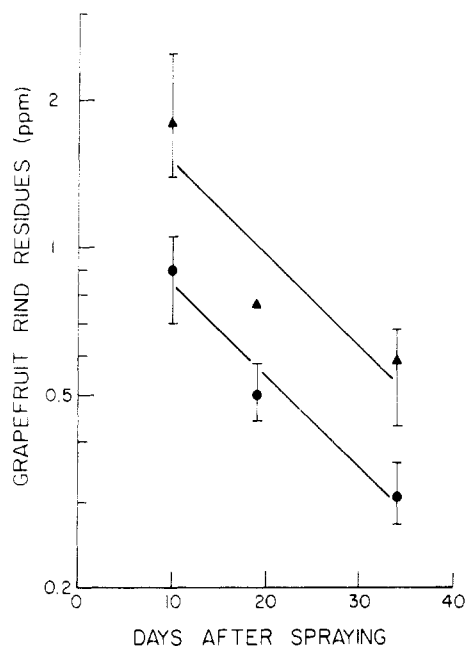
Figure 7. Phenthoate residues on and in grapefruit rind after manual full-coverage treatment using spray mixtures of 1.0 (▲) and 0.5 (●) pt of Cidial 4EC formulation/100 gal of water. Vertical lines indicate range of values from three replicate field samples. Applied June 1, 1979, to trees located on the Citrus Research Center, Riverside, CA. No determinable residues (>0.02 ppm) were found in pretreatment samples.
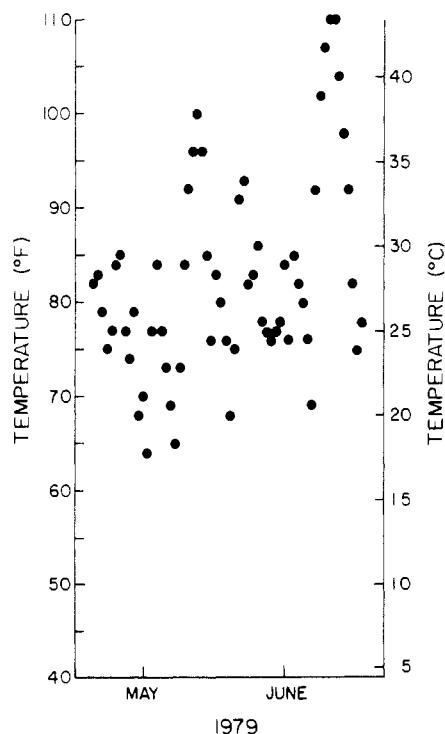

Figure 8. Daily maximum air temperature and rainfall (none) at the University of California during the 1979 dislodgeable residue study with orange trees. Data are supplied through the courtesy of the U.S. Department of Commerce, National Weather Service Office, Riverside, CA.

sipation for both the 1978 and 1979 studies was 20 ± 5 days.

No determinable residues (>0.03 ppm) of phenthoate were found in the edible portion of the fruit for both the 1978 and 1979 studies. Residues on a whole-fruit basis are one-fourth the rind values as grapefruits are 23.0 ± 3.2% rind by weight (Gunther, 1969) and since no determinable
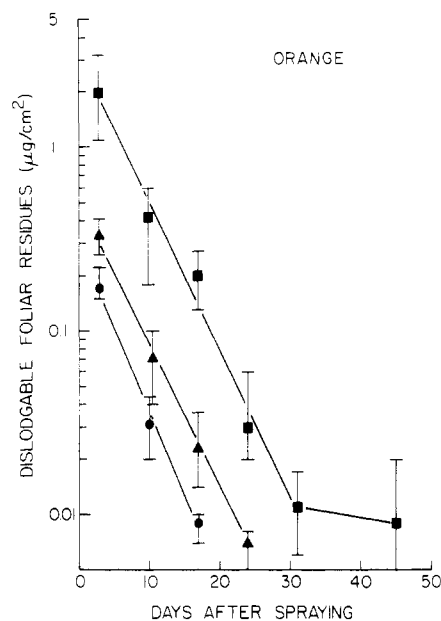

Figure 9. Dislodgeable residues of phenthoate on orange foliage after application at 7.5 lb of AI (100 gal)$^{-1}$ acre^{-1} [(■) low volume] and at 3.75 (●) and 7.5 (▲) lb of AI (1500 gal)$^{-1}$ acre^{-1}. Vertical lines indicate the range of values found for six replicate field samples. Applied April 20, 1979, to trees located on the Citrus Research Center, Riverside, CA. All pretreatment values were below 0.002 μg cm^{-2} phenthoate.

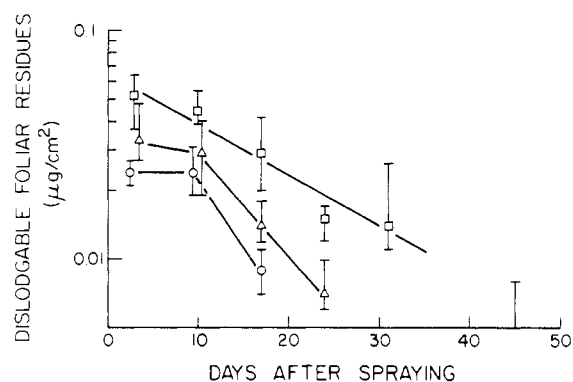**Figure 10.** Dislodgeable residues of phenthoate oxon on orange foliage after application at 7.5 lb of AI (100 gal)$^{-1}$ acre^{-1} [(□) low volume] and at 3.75 (○) and 7.5 (△) lb of AI (1500 gal)$^{-1}$ acre^{-1}. Vertical lines indicate range of values found for six replicate field samples. Applied April 20, 1979, to trees located on the Citrus Research Center, Riverside, CA. All pretreatment values were below 0.004 μg cm^{-2} oxon.

residues were present in the edible portion of the fruit.

Dislodgeable Residues. *Oranges.* Figure 8 shows the maximum daily air temperature recorded over the 45-day sample collection period; there was no rainfall. The data are presented as it may subsequently be possible to use these data in coming to an understanding of the effects of weather on foliar residue decay. Dislodgeable foliar residue data are shown in Figures 9 and 10. The mean $t_{1/2}$ value for phenthoate dissipation for the three treatments was 3.6 ± 0.3 days.

Residues dissipated rapidly from foliage of orange trees treated with an oscillating boom. Dissipation appeared to be first-order from the limited data obtained. The curve (three points) for the 3.75 lb of AI (1500 gal)$^{-1}$ acre^{-1} treatment was described by ln y = $-0.21t$ + ln 0.30 with r = 0.99 and $t_{1/2}$ = 3.3 days. Mean phenthoate levels reached 0.1 and 0.01 μg/cm^2 at about 5 and 16 days, respectively; the maximum value for the oxon was 0.031 μg/cm^2 for a 10-day sample. The curve (four points) for

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Table V. Dislodgeable Foliar Residues ($\mu g/cm^2$) of Phenthoate Oxon after Application of Phenthoate to Lemon Trees[a]

compd	appli-cation[b]	elapsed days	plot[c] A 1	A 2	B 1	B 2	C 1	C 2	mean	SD
oxon	A	0	0.006	0.007	0.005	0.005	0.005	0.004	0.005	0.001
		3	0.017	0.016	0.016	0.014	0.013	0.016	0.015	0.002
		10	0.010	0.010	0.010	0.013	0.012	0.014	0.012	0.002
		17	<0.003	<0.003	0.003	0.003	0.004	<0.003	<0.003	
	B	0	0.008	0.009	0.005	0.006	0.005	0.004	0.006	0.002
		3	0.018	0.019	0.018	0.017	0.018	0.017	0.018	0.001
		10	0.017	0.018	0.019	0.020	0.018	0.015	0.018	0.002
		17	0.004	<0.003	0.003	0.004	0.003	0.003	0.003	0.001
	C	0	0.037	0.057	0.021	0.026	0.027	0.024	0.032	0.013
		3	0.049	0.062	0.042	0.045		0.052	0.050	0.008
		10	0.038	0.048	0.037	0.042	0.042	0.070	0.046	0.012
		17	0.005	0.005	0.007	0.006	0.008	0.011	0.007	0.002

[a] Applied Oct 6, 1978, to trees located on the Citrus Research Center, Riverside, CA. [b] A, 3.75 lb of AI (1500 gal)$^{-1}$ acre^{-1}; B, 7.50 lb of AI (1500 gal)$^{-1}$ acre^{-1}; C, 7.50 lb of AI (100 gal)$^{-1}$ acre^{-1} (low volume). [c] All pretreatment residue values were below 0.001 $\mu g/cm^2$. Untreated samples from control plots had residue values of 0.007 and 0.005 $\mu g/cm^2$ phenthoate for 0- and 3-day samples, respectively, possibly due to pesticide spray drift. All other residue values for control samples were <0.003 $\mu g/cm^2$ for both phenthoate and its oxon.
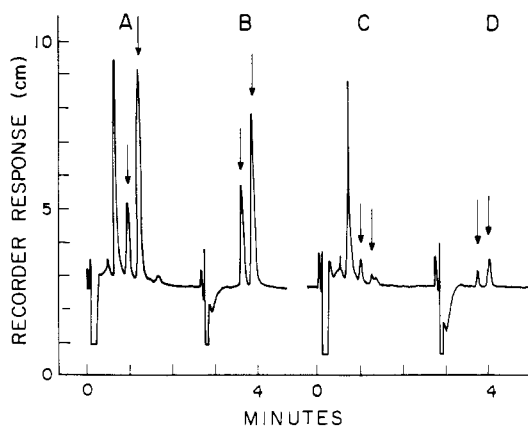

Figure 11. Sample chromatograms obtained with a nitrogen/phosphorus flame ionization detector. A 3% OV-101 column was used and arrows indicate elution of phenthoate oxon and phenthoate. (A) Dislodgeable foliar residue sample obtained 24 days posttreatment. The sample was found to contain residues of 0.013 $\mu g/cm^2$ oxon and 0.020 $\mu g/cm^2$ phenthoate. (B) Standards of 2.0 ng each of the oxon and phenthoate used to quantitate (A). (C) Untreated sample which was found to contain "apparent" residues of <0.005 $\mu g/cm^2$ of both the oxon and phenthoate. (D) Standards of 0.3 ng each of the oxon and phenthoate used to quantitate (C).

the 7.5 lb of AI (1500 gal)$^{-1}$ acre^{-1} treatment was described by ln y = -0.18t + ln 0.51 with r = 0.99 and $t_{1/2}$ = 3.9 days. Mean phenthoate levels reached 0.1 and 0.01 $\mu g/cm^2$ at about 9 and 22 days, respectively; the maximum oxon level found was 0.048 $\mu g/cm^2$ for a 3-day sample.

The curve (five points) for the 7.5 lb of AI (100 gal)$^{-1}$ acre^{-1} low-volume treatment was described by ln y = -0.19t + ln 3.3 with r = 0.99 and $t_{1/2}$ = 3.6 days. Mean phenthoate levels reached 0.1 and 0.01 $\mu g/cm^2$ at about 19 and 31 days, respectively; the maximum oxon level found was 0.063 $\mu g/cm^2$ for a 3-day sample.

Figure 11 shows a typical gas chromatogram for the analysis of phenthoate and its oxon after removal from orange foliage collected 24 days posttreatment.

Dislodgeable residues on orange fruit were determined for the 7.5 lb of AI (1500 gal)$^{-1}$ acre^{-1} plot and data are shown in Figure 12. Samples of fruit and foliage collected the same day as the spray application had dislodgeable residues of 0.91 ± 0.06 and 1.0 ± 0.1 $\mu g/cm^2$ phenthoate, respectively. After the initial 10 days, the residue dissi-

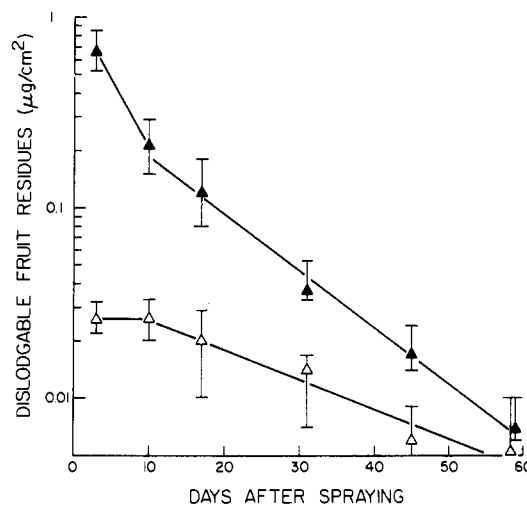**Figure 12.** Dislodgeable residues of phenthoate (▲) and its oxon (△) on orange fruit after application at 7.5 lb of AI (1500)$^{-1}$ acre^{-1}. Vertical lines indicate the range of values found for six replicate field samples. Applied April 20, 1979, to trees located on the Citrus Research Center, Riverside, CA. Pretreatment residues were <0.001 μg cm^{-2} for both phenthoate and its oxon.

pation was described by ln y = -0.069t + ln 0.38 with r = 0.99 and $t_{1/2}$ = 10 days for phenthoate and ln y = -0.036t + ln 0.037 with r = 0.96 and $t_{1/2}$ = 19 days for the oxon. Phenthoate appears to persist longer on fruit surfaces ($t_{1/2}$ = 10) than on foliar surfaces ($t_{1/2}$ = 3.9 days). This observation was noted by Iwata et al. (1979) for methidathion on orange fruit and foliage. Since the fruit is partially protected from sunlight and air movements by the outer foliar canopy, these factors may have played an important role in residue persistence.

Lemons. Figure 13 gives the maximum daily air temperature and rainfall data over the 59-day sample collection period. Dislodgeable residue data for phenthoate are shown in Figure 14 and data for the oxon are given in Table V. The mean $t_{1/2}$ value for phenthoate dissipation for the three treatments was 3.1 ± 0.3 days.

Dislodgeable residues dissipated rapidly from foliage of lemon trees treated with an oscillating boom. Dissipation appeared to be first order from the limited data (three points) obtained. The curve for the 3.75 lb of AI (1500 gal)$^{-1}$ acre^{-1} treatment was described by ln y = -0.23t + ln 0.21 with r = 0.99 and $t_{1/2}$ = 3.0 days. Mean phenthoate
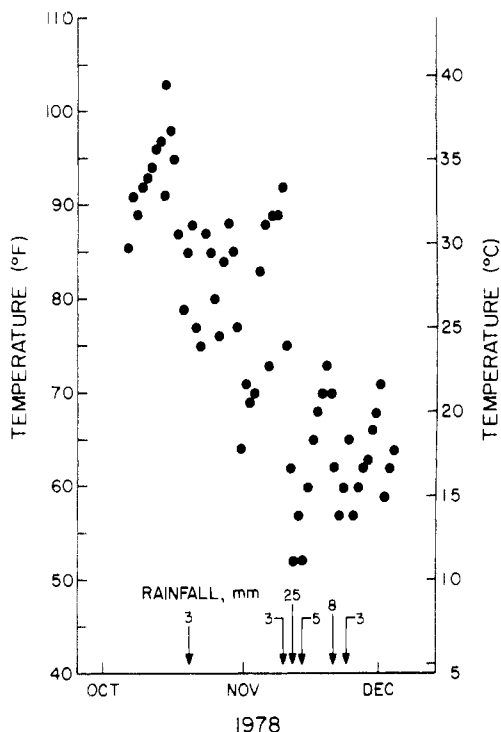
Figure 13. Daily maximum air temperature and rainfall at the University of California during the 1978 foliar dislodgeable residue study with lemon trees. Data are supplied through the courtesy of the U.S. Department of Commerce, National Weather Services Office, Riverside, CA.
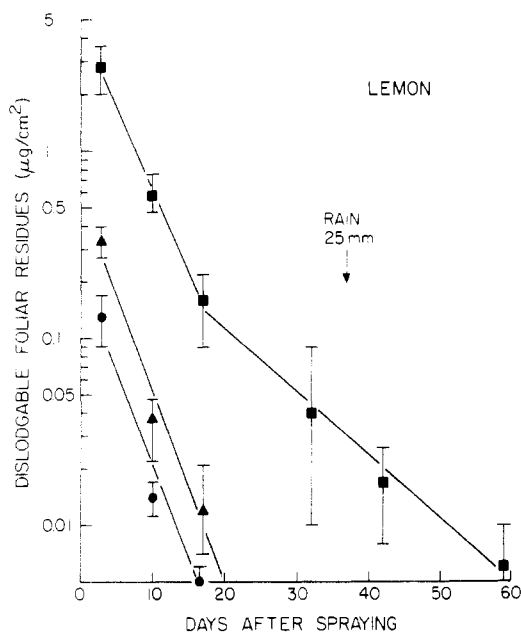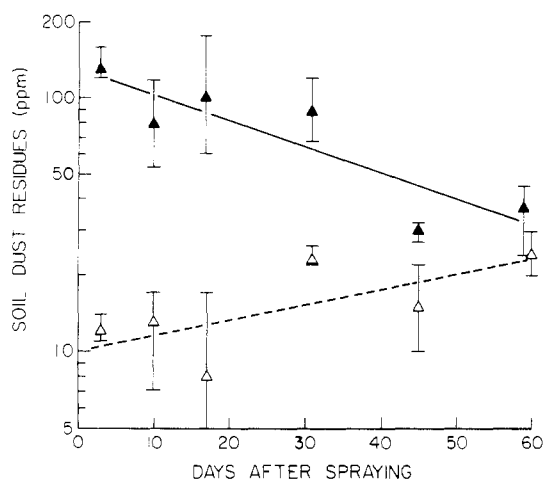

Figure 15. Residues of phenthoate (▲) and its oxon (△) in the mobile soil dust collected from an orange grove. Trees had been treated at 7.5 lb of AI $(1500 \text{ gal})^{-1}$ acre^{-1}. Vertical lines indicate the range of values for three replicate field samples. Applied April 20, 1979, to trees located on the Citrus Research Center, Riverside, CA. Pretreatment samples contained no determinable residues (>0.2 ppm) of phenthoate or its oxon.

Figure 14. Dislodgeable residues of phenthoate on lemon foliage after application at 7.5 lb of AI $(100 \text{ gal})^{-1}$ acre^{-1} [(■) low volume] and at 3.75 (●) and 7.5 (▲) lb of AI $(1500 \text{ gal})^{-1}$ acre^{-1}. Vertical lines indicate the range of values found for six replicate field samples. Applied October 6, 1978, to trees located on the Citrus Research Center, Riverside, CA. All pretreatment residue values were below 0.001 μg cm^{-2}.

levels reached 0.1 and 0.01 μg/cm^2 at about 3 and 13 days, respectively; the maximum value for the oxon was 0.017 μg/cm^2 for a 3-day sample. The curve for the 7.5 lb of AI $(1500 \text{ gal})^{-1}$ acre^{-1} treatment was described by ln $y = -0.24t$ + ln 0.56 with $r = 0.98$ and $t_{1/2} = 2.9$. Mean phenthoate levels reached 0.1 and 0.01 μg/cm^2 at about 7 and 17 days, respectively; the maximum oxon level found was 0.019

μg/cm^2 for one sample from day 3 and one from day 10.

The curve for the dissipation of dislodgeable residues from low volume treated trees exhibited the normally observed two-sloped curve over the 59-day period studied. The first portion ("slope 1") was described by ln $y = -0.20t$ + ln 4.9 with $r = 0.99$ and $t_{1/2} = 3.5$. The second portion ("slope 2") was described by ln $y = -0.078t$ + ln 0.54 with $r = 0.99$ and $t_{1/2} = 8.9$. The two curves intersect at ~17 days. Mean phenthoate residues dropped below 0.1 and 0.01 μg/cm^2 at about 22 and 51 days, respectively; the maximum oxon level found was 0.070 on day 10. A 25-mm (1-in.) rainfall 37 days postapplication did not measurably reduce residue levels. The data of Iwata et al. (1977a), 0.38, 0.07, and 0.02 μg/cm^2 after 4, 11, and 19 days, fit the slope 1 curve equation ln $y = -0.20t$ + ln 0.74 with $r = 0.99$ and $t_{1/2} = 3.5$ days. Although the slopes of the two slope 1 curve lines are identical, the y-intercept values differ by ~7-fold, suggesting large losses in residues during the first 4 days posttreatment in the 1974 application reported by Iwata et al. (1977a).

Soil. A study of insecticides sorbed to dry soil is desirable for a number of reasons. The primary reason is that dislodgeable residues on fruit and foliar surfaces are thought to be predominantly associated with soil dust particles. Thus, a study of insecticides sorbed to air-dry dust may give some information about its behavior on foliar dust. Also, since insecticides 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 by using student picking crews in parathion-treated orange groves, Spear et al. (1977) concluded that the dermal dose data obtained indicated that soil dust played a relatively unimportant role in the immediate exposure process; since ~80% of the dermal paraoxon dose obtained by the volunteers appeared to be deposited above the waist, the foliar residue was considered the more appropriate indicator of worker hazard.

Residues on the mobile soil dust after application of phenthoate to orange trees at 7.5 lb of AI $(1500 \text{ gal})^{-1}$ acre^{-1} were determined and data are shown in Figure 15. The soil dust was collected at the drip line of the tree canopy.

Phenthoate appeared to dissipate by first order and fit the line described by ln y = -0.024t + ln 130 with r = 0.88 and $t_{1/2}$ = 29 days. The highest phenthoate level found was 180 ppm. Although Figure 15 shows that oxon levels increased over the entire 60-day period sampled, the correlation for the line (r = 0.69) is poor. The maximum oxon level encountered was 30 ppm for one sample.

Air. Two polyurethane foam plug samples were placed under a lemon tree located in the center of a plot treated by low volume in the 1978 application. Since the low volume treated trees always have the highest levels of dislodgeable foliar residues, it was thought that these trees would yield the most insecticide vapors. Phenthoate concentrations collected 3, 4, 5, 6, 7, and 10 days postapplication (Oct 6, 1978) between 9 and 11 a.m. were 10, 5.5, 3.8, 3.4, 5.1, and 0.75 $\mu g/m^3$, respectively. The data fit the line described by ln y = -0.32t + ln 24 with r = 0.91 and $t_{1/2}$ = 2.2 days. The dislodgeable foliar residues were dissipating with $t_{1/2}$ = 3.5 days for this plot. Due to the very small treatment plots involved, the data are only crude estimates of insecticide levels present in the air.

Repetition of the air sampling under an orange tree located in the center of a 1979 plot treated with a dilute spray at 7.5 lb of AI (1500 gal)$^{-1}$ acre^{-1} indicated only 3 $\mu g/m^3$ on day 3 postapplication and less than 2 $\mu g/cm^2$ thereafter.

ACKNOWLEDGMENT

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Degradation of Diazinon Encapsulated with Starch Xanthate

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The degradation of diazinon encapsulated with starch xanthate (SX) cross-linked by various reagents was studied under accelerated aging conditions at 70 °C in the presence and in the absence of reported stabilizers. Stability of diazinon was unchanged by most of these stabilizers. Acidity from the decomposition of SX-encapsulated diazinon decreased the stability. Stability was increased by adding water, keeping the xanthate degree of substitution low, increasing the diazinon loading, and adding alkaline substances to neutralize acidic decomposition products. Calcium oxide was particularly helpful in stabilizing the preparations.

Diazinon [O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate] is an organophosphorus insecticide with low soil persistency (Getzin and Rosefield, 1966). This compound is widely used in agriculture; however, due to its short persistence, treatments with the compound must be repeated periodically during the growing season to maintain effective control (Sethunathan and Pathak, 1972). By formulating diazinon in suitable polymeric matrices, it has been possible to apply diazinon in a granular form having greater persistency and effectiveness (Langbridge, 1963). Formulations that keep the pesticide where applied not only improve effectiveness but also reduce environmental pollution (Balassa, 1973; Nelson and Whitlaw, 1972).

An effective matrix used in this laboratory for encapsulating pesticides is starch xanthate (Shasha et al., 1976). Evaluation of starch matrix containing diazinon revealed that this formulation is more stable than the unencapsulated technical product (Feldmesser et al., 1976; Doane et al., 1977). The encapsulating material is based upon starch, and hence it is nonpersistent in the environment.

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