Behavior of Phenthoate (Cidial) Deposits and Residues on and in Grapefruits, Lemons and Lemon Leaves, Oranges and Orange Leaves, and in the Soil beneath Orange Trees

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Phenthoate residues on and in orange rind dissipated rapidly during the 4-week period after spraying. The degradation half-life during the initial weathering period was about 14 days and the persistence half-life during the last 30 days of the study was about 50 days. Dissipation from lemon rind was qualitatively similar but slower than that on oranges while dissipation from grapefruit rind was faster. Low-volume application left more rind residues on oranges and lemons than the corresponding dilute application. Phenthoate residues above 0.01 ppm were not detected in the pulp of the three fruits. Little residue reduction occurred from laboratory washing of oranges and lemons but 50% was removed from 3-day posttreatment grapefruits. Dried orange pulp cattle feed contained up to 2.5 times more residue than the ground rind on a weight basis. The foliar dislodgable residue level decreased from 1.7 (maximum) to 0.05 $\mu g/cm^2$ in 14 days for all three fruits. Field washing of trees effectively removed about 70% of the phenthoate dislodgable residues on orange leaves at 3- and 10-days posttreatment while vigorous shaking of trees had no measurable effect on dislodgable residues. At least 85% of the particulate matter dislodged during shaking was larger than would enter the human trachea. Phenthoate residues were quite persistent on dry soil.

Phenthoate [*O,O*-dimethyl *S*-(α-(carboethoxy)benzyl)phosphorodithioate, Cidial, Elsan] is a broad-spectrum scalicide/thripsicide/acaricide that may have wide use on citrus in southern California. Dissipation rates of the parent compound on and in oranges and orange leaves and lemons and lemon leaves in the field were determined to assist in making recommendations for use in setting fruit tolerances and worker reentry intervals. Dislodgable and penetrated residues were determined separately on the fruit and leaves and water washing of the trees with a high-pressure, high-volume spray was evaluated as a means for reducing residue levels. A less comprehensive study on bearing grapefruit trees was made to establish that the degradation pattern on this substrate approximated that for oranges.

Magnitude and rate of dissipation of phenthoate in the soil beneath sprayed orange trees were also determined. Laboratory studies on the behavior and alteration of radiolabeled phenthoate on and in Valencia oranges and leaves, in water, and upon exposure to air and sunlight (Takade et al., 1977) and the metabolism of phenthoate in the white mouse and housefly (Takade et al., 1976) have been reported. The degradation of radiolabeled phenthoate in soil was investigated by Iwata et al. (1977). Published residue methodology was reviewed by Bazzi (1976). Pertinent background literature is cited in these publications.

EXPERIMENTAL DESIGN

Field Plot Treatments. Mature Valencia orange trees and mature bearing lemon trees located on the Irvine Ranch, Tustin, Calif., and grapefruit trees located on the Citrus Research Center, Riverside, Calif., were sprayed on June 29, 1973, April 12, 1974, and July 6, 1973, respectively, with a phenthoate emulsifiable concentrate (EC) formulation containing 4.0 lb of AI (active ingredient)/gal. Treatments are given in Table I. Plots D and IV (low-volume applications) were treated with an air-blast sprayer (FMC-E200-TR) while the others were treated with an oscillating boom spray rig. Plots A through D and I through IV were designed for residue dissipation rate (persistence) studies; each plot was replicated three times with buffer trees separating individual replicates. Plots C and II were oversprayed 56 and 46 days, respectively, after the initial treatment to determine the effect of multiple applications on residue levels. Plots E, F, V, and VI were used for field tree-washing tests and plots G and H were used for tree-shaking tests (Westlake et al., 1973). Each plot contained a minimum of ten trees, of which five (eight for grapefruits) in each plot were used for fruit samples and eight for leaf samples.

Field Sampling. Orange fruit and leaf samples were collected as described by Gunther et al. (1973) and Westlake et al. (1973). Plots were sampled at 3-, 10-, 17-, 24-, 31-, 45-, and 56-day intervals after spraying. Leaf samples were discontinued after the 17-day sampling in plots B and C and after the 31-day sampling in plots A and D as the dislodgable residue levels had reached the lower limit of reliable measurement at these times and were therefore considered insignificant. Double samples of fruit were taken at the 10-, 24-, and 45-day intervals and one-half of each sample was washed in the laboratory prior to further processing to simulate packing house practice (Gunther, 1969). Four-hundred oranges were collected from plot A at the 24-day interval and from plot D at the 45-day interval for preparing dried citrus pulp cattle feed.

Lemon plots were sampled at 4, 11, 18, 33, 46, 61, and 67 days after spraying with the exception of plot II which was oversprayed after the 46-day sampling and was then sampled 3, 15, 21, and 28 days after the second treatment.

Grapefruit samples were selected, using the Gunther (1969) method, at 4, 11, 18, 25, 32, and 46 days after spraying. Duplicate samples were taken at all sampling times and one was washed in the laboratory before processing.

Field Washing for Residue Reduction. The orange trees (124 trees/acre) in the field-washing tests were sprayed either 3 or 10 days after application with 3000 gal/acre of water containing 16 ml/100 gal of Sur-Ten (70% sodium dioctylsulfosuccinate) wetting agent, using an oscillating boom sprayer. Samples of fruit and leaves were collected immediately before washing and as soon as the leaves were dry after washing. Pans of orchard soil (see later section) were placed under the trees immediately before washing and were removed for analysis when the

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Table I. Plot Treatments

Plot designation			Application			
				gal of spray/acre		
Orange	Lemon	Grapefruit	lb of AI/acre	Orange	Lemon	Grapefruit
A, E, F, G, H	I, V, VI		7.50	1500	1250	
B	II	None	3.75	1500	1250	1500
C	III		1.88	1500	1250	
D	IV		7.50	100	100	

fruit and leaf samples were taken. Lemon trees (180 trees/acre) were similarly washed with a wetting agent spray either at 4 or 11 days after application with 2500 gal/acre using an oscillating boom sprayer.

Tree Shaking. Samples of orange leaves and fruit were taken from the trees in this test immediately before shaking. The shaking was done with a commercial OMC "Shock-Wave" shaking machine of the type used for shaking some fruits and nuts from trees for harvest. Each of five trees per test was vigorously shaken for 1 min, during which time air samples were taken at several locations in and around each tree. Leaf and fruit samples were collected after the shaking was completed.

Air Sampling. An Andersen eight-stage particulate matter sampler (Andersen 2000 Inc.) drawing 28.3 l. of air/min was operated under each tree near the trunk for 1 min during shaking. Three minipersonnel samplers (Medi-Comp R & D, 4 stage impinger plus filter attached to a Micronair Permissible Air Sampling Pump) were also used; these were held at the desired positions for the same time intervals while drawing 1.4 l. of air/min. Five trees were shaken per test; the total sampling time was 5 min.

Three-liter evacuated stainless steel cylinders were employed to secure "grab" samples of air before and during shaking (Westlake et al., 1973). The cylinders were fitted with micropore filters to retain particulate matter (>0.3 μm) and these filters and the cylinder contents were analyzed for phenthoate levels in the particulate matter and filtered air. The cylinders were allowed to fill with air in about 2 s either before the trees were shaken or 5 s after shaking had commenced.

Ambient air was sampled for phenthoate in the vapor phase with Greenburg-Smith impingers. Two units, each consisting of two impingers connected in tandem, were used during each sampling period and were operated at an air flow rate of 5 l./min for 2 h. Ethylene glycol (200 ml) was used in each impinger to retain the pesticide.

Soil Sampling. Orchard soil samples were exposed in 9 × 1.25 in. aluminum cake pans placed underneath the orange trees before spraying in plot A and just before washing in the washing test plots. Pans were filled with pretreatment orchard soil and the surfaces were leveled with the tops of the pans. This use of pans eliminated the almost impossible task of obtaining suitable samples from the soil beneath sprayed trees. Filled pans were positioned at 0° (side within the row), at 90° (side between the rows), and at 45°, with one pan halfway between the trunk and drip line and one at the drip line at each of the three positions. Thus, 36 pans were placed under 6 trees in plot A. Six were removed at each sampling interval, one per tree taken from a different position from each tree; each sampling represented all pan positions and all six trees.

Laboratory Processing. The leaf samples were collected in 8-oz wide-mouth jars (Gunther et al., 1974). One-hundred milliliters of water and 4 drops of a 1:50 dilution of Sur-Ten wetting agent were added to each sample and the bottles were then capped and shaken end-to-end at 200 cycles/min for 20 min on a reciprocating shaker. This solution was decanted into a 500-ml separatory funnel or a temporary holding bottle and the shaking and decanting procedure was repeated two more times using 100 ml of water–detergent solution each time and combining the three strippings. The total stripping solution from each sample was shaken for 30 s with 50 ml of mixed hexanes (63–76 °C boiling range, Standard Oil of California) in the separatory funnel, the aqueous layer was discarded, and the hexane solution was washed 2× with 50 ml of water and then stored in a cold room at about 4 °C over a few grams of anhydrous Na_2SO_4.

Orange, lemon, and grapefruit samples were peeled (Gunther, 1969) and the rinds were chopped in a Hobart food cutter to pieces 5 mm in diameter or smaller. Duplicate 100-g subsamples were then extracted by blending them at high speed for 2 min with 300 ml of acetonitrile. Each acetonitrile–water solution was filtered and a 150-ml aliquot was transferred to a separatory funnel. Fifty milliliters of mixed hexanes and 10 ml of saturated NaCl solution were added and the funnel contents were mixed thoroughly. Then 700 ml of water was added, the funnel was shaken vigorously for 1 min, and the aqueous layer was discarded. The hexane solution was then washed and stored as described above.

The pulp (edible portion after peeling) was sampled as described by Gunther (1969) and 100-g subsamples were blended with 200 ml of acetonitrile and thereafter treated in the same manner as the rind.

Citrus pulp cattle feed was prepared as described by Gunther (1969), and the ground rind, limed and pressed rind, and dried rind were processed for analysis in the same manner as the rind samples except that 4 ml of acetonitrile/g of sample was used for the dried cattle feed.

Each soil sample was mixed by tumbling in a Twin-Shell blender. Duplicate 50-g samples were taken and each placed in an 8-oz wide-mouth jar. Each sample was shaken at 200 strokes/min with 100 ml of acetone for 1 h. Each sample was filtered and stored as described above. No cleanup was necessary.

Analysis. Samples were analyzed by GLC using either a flame photometric detector (FPD) operated in the phosphorus mode or an alkali flame phosphorus detector (AFID). The glass column for the FPD was 210 cm in length × 4 mm i.d., packed with 3% OV-1 on 60/80 mesh Chromosorb W, and operated at 220 °C with a nitrogen carrier gas flow rate of 80 ml/min. Injector and detector temperatures were 235 and 225 °C, respectively. The glass column for the AFID was 90 cm in length × 2 mm i.d., packed with 3% DC-200 on 60/80 mesh Gas-Chrom Q, and operated at 165 °C with a nitrogen carrier gas flow rate of 30 ml/min. Injector and detector temperatures were 230 and 220 °C, respectively. A third instrument fitted with an AFID was used for some of the analyses: the column was stainless steel, 175 cm in length × ~2 mm i.d., and packed with a 1:1 mixture of 10% DC-200 and 15% QF-1 each coated on 60/80 mesh Gas-Chrom Q. The nitrogen carrier gas flow rate was 30 ml/min and column, injector, and detector temperatures were 220, 235, and 200 °C, respectively. Chromatograms shown in Figure 1 were taken with this instrument. Phenthoate retention times

Table II. Recovery of Phenthoate from Fortified Extracts

Substrate		Fortification,[a] ppm	Found,[b] ppm	% recovered
Fruit				
Orange	Rind	0.25	0.19 ± 0.01	76
		1.27	1.05 ± 0.03	83
		6.33	5.74 ± 0.18	91
Orange	Pulp	0.014	0.013 ± 0.003	93
		0.14	0.12 ± 0.02	86
Lemon	Rind	0.25	0.22 ± 0.01	88
		1.27	1.07 ± 0.10	84
		6.33	5.47 ± 0.28	86
Lemon	Pulp	0.014	0.015 ± 0.004	107
		0.14	0.13 ± 0.02	92
Grapefruit	Rind	0.25	0.22 ± 0.01	88
		1.27	1.06 ± 0.06	83
		6.33	6.13 ± 0.30	97
Grapefruit	Pulp	0.014	0.013 ± 0.002	93
		0.14	0.13 ± 0.01	93
Foliage				
Lemon	Dislodgable	0.01[c]	0.01 ± 0.00[c]	100
		0.50[c]	0.51 ± 0.04[c]	102
Lemon	Penetrated	1.0	0.96 ± 0.10	96
		10.0	8.3 ± 0.3	83
Soil				
		0.10	0.10 ± 0.01	100
		10.0	11.5 ± 0.07	115

[a] Phenthoate was added to acetonitrile extracts of rind, pulp, and leaves (penetrated), to water washes of leaves (dislodgable), and directly to soil. [b] All values are a mean of four replicates. No phenthoate or interferences were present in control samples. [c] $\mu g/cm^2$, not ppm.

for the three instruments, in the order named, were approximately 2, 3, and 3 min. Quantitation was by peak height measurement. No cleanup was required for the orange rind, leaf, air, or soil samples. When cleanup was required (for orange pulp samples where residues were searched for at the 0.01-ppm level, and for grapefruit rind which contained interfering material), a 2-cm diameter column containing a 5-cm height of Florisil deactivated with 5% water was used. After prewetting the column with hexane, the sample was introduced in about 5 ml of hexane and the sample container and the sides of the column were then rinsed with 10 ml of benzene. After these rinsings had entered the column, 40 ml of benzene was used to complete the elution. The benzene was removed using a rotary vacuum evaporator and the residue was dissolved in hexane for GLC analysis.

Figure 1 shows AFID chromatograms for orange rind and pulp whose acetonitrile extracts were fortified at 0.25 and 0.014 ppm, respectively. Table II gives the recovery data from fortified soil, fortified acetonitrile extracts of rind, pulp, and leaves (penetrated), and fortified water washes of leaves (dislodgable residues). The FDA acetonitrile blending procedure (Pesticide Analytical Manual, 1971) was adopted for the rind, pulp, and leaf samples and its actual effectiveness was not explored. The recovery data in Table II for soil and water give a good indication of the effectiveness of the procedure for these samples. Recovery data from fortified acetonitrile extracts only indicate the procedural recovery. Three-day posttreatment samples of orange rind processed with acetonitrile gave 1.70 and 1.38 ppm for samples from plots I and II, respectively. An alternate method, often used for citrus rind (Gunther, 1969), involving blending 150 g of rind with 450 ml of 2:1 hexane–2-propanol for 1 min, tumbling the mixture for 50 min, filtering the extract, and washing out the 2-propanol with water gave 1.86 and 1.33 ppm, respectively. Both procedures gave the same results.

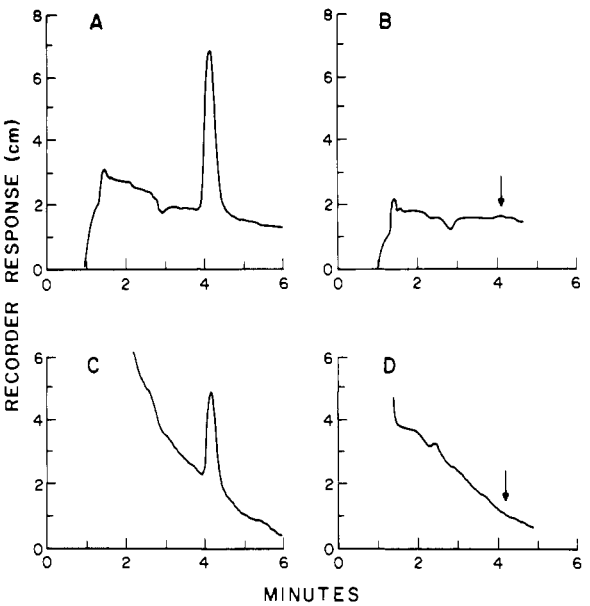

Figure 1. Gas chromatograms (AFID) for: (A) orange rind fortified at 0.25 ppm; (B) untreated rind; (C) orange pulp fortified at 0.014 ppm; and (D) untreated pulp. Extract injected was equivalent to 47 mg of rind and 97 mg of pulp.

RESULTS AND DISCUSSION

Fruit Residues. The phenthoate residue data for unwashed orange rind obtained from the fruits taken from the persistence plots A through D are shown in Figure 2. Residues on and in orange rind dissipated rapidly during the 4-week period after spraying and at a slower rate during the next 4 weeks. The degradation half-life during the initial weathering period was about 14 days and the persistence half-life during the last 30 days of the study was about 50 days. As both plots A and D received 7.5 lb of AI/acre, the dissipation curves show the effect of dilute and low-volume applications on residue levels. Residues resulting from the low-volume treatment were twice those for the dilute spray application during the initial 4 weeks and 2.5 times more during the next 4 weeks. The low-volume application is a more economical method as less water/acre is required and more pesticide is deposited on

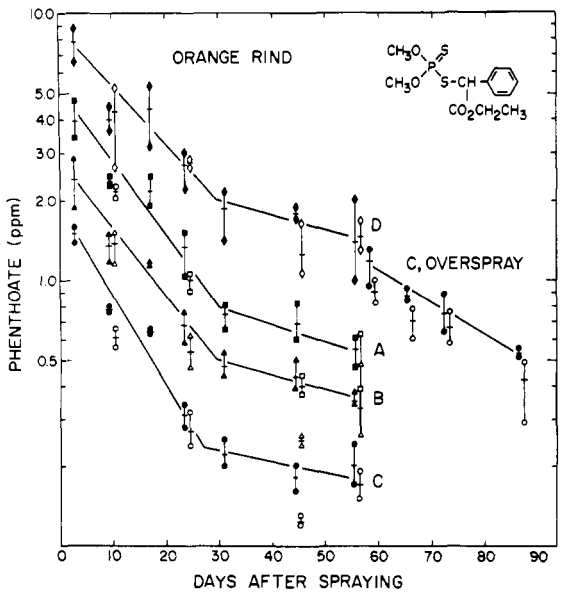

Figure 2. Dissipation of phenthoate residues on and in orange rind. Plots A, B, and C were treated at 7.5, 3.75, and 1.88 lb of AI/1500 gal per acre, respectively, and plot D at 7.5 lb of AI/100 gal per acre (low volume). Ranges of values for three plot replicates are shown by vertical lines and averages are shown by horizontal dashes. Open symbols represent values for fruit washed in the laboratory to simulate packing house procedures.

Table III. Phenthoate Residues in Ground Rind, Limed and Pressed Rind, and Dried Citrus Pulp Cattle Feed

Days after spraying	Plot[a]	ppm: Ground rind	ppm: Limed and pressed rind	ppm: Dried feed	Loss during processing,[b] %
24	A	0.71	0.78	1.36	58
45	D	0.91	1.25	2.28	44

[a] Plot A = 7.5 lb of AI/1500 gal per acre (dilute); plot D = 7.5 lb of AI/100 gal per acre (low volume). [b] Based on theoretical increase by reducing water content from ~80 to ~10%.

the tree (Carman et al., 1972). Plot C shows the residue pattern resulting from overspraying 56 days after the initial application. Plot C had a rind residue of 0.53 ppm 31 days after the overspray treatment and plot B, which received the equivalent amount of material as plot C in a single application, had 0.47 ppm after 31 days. Residues appear to be declining to the same level in both plots. No phenthoate was detected in the pulp samples at any time. Takade et al. (1976b) found less than 1% of applied radioactivity in the pulp 14 days after radiolabeled phenthoate was applied to the rind. Residues on a whole-fruit basis are approximately one-fifth the values for rind as Valencia oranges are 18.7 ± 6.3% rind by weight (Gunther, 1969). At the 15-day interval after spraying, therefore, the residues on a whole fruit basis would range from approximately 0.8 ppm (plot D) to 0.1 ppm (plot C). The residues after laboratory washing of the fruit to simulate packing house treatment are also shown in Figure 2; although the data are erratic, the overall trend indicates that little if any residue reduction occurred.

The phenthoate levels found in the ground rind, the limed and pressed rind, and the dried cattle feed are in Table III. The increase in residue levels due to water removed in pressing and drying was less than the approximate 4.5-fold theoretical increase showng an approximate 44 to 58% loss during processing and drying.

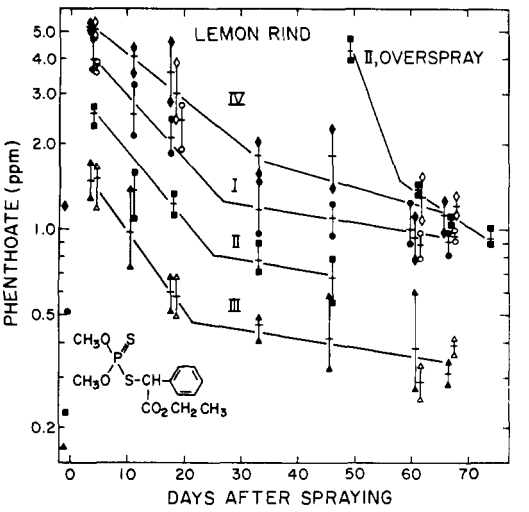

Figure 3. Dissipation of phenthoate residues on and in lemon rind. Plots I, II, and III were treated at 6.25, 3.12, and 1.56 lb of AI/1250 gal per acre, respectively, and plot IV at 6.25 lb of AI/100 gal per acre (low volume). Plot II was oversprayed at the same rate 46 days after the first treatment. Ranges of values obtained for three plot replicates are shown by vertical lines and averages are shown by horizontal dashes. Open symbols represent values for fruit washed in the laboratory to simulate packing house procedures.

The phenthoate residue data for unwashed lemon rind obtained from the fruits taken from the persistence plots I through IV are shown in Figure 3. The trees were sprayed on Nov 14, 1973 but due to rain the residue study was terminated. The same application was repeated 147 days later on April 12, 1974. Plots I through IV, therefore, had pretreatment rind values of 0.51, 0.23, 0.17, and 1.2 ppm, respectively. The phenthoate applied to the lemon plots was 83% of that applied to the corresponding orange plots. The dissipation from the lemon rind was qualitatively similar to that from orange rind but somewhat slower.

Degradation and persistence half-lives for lemon rind are from 11, 19, and about 100 days, respectively. As both plots I and IV received 6.25 lb of AI/acre, the dissipation curves show the effect of dilute and low-volume applications on residue levels. Low-volume resulted in 1.25 to 1.75 more phenthoate residues than the corresponding dilute application. Plot II shows the residue pattern resulting from overspraying 46 days after the initial application. The 3-day deposit was somewhat higher than anticipated. Plot II had a rind residue of 1.04 ppm 67 days after the initial treatment; plot I, which received the equivalent amount of material as plot II in a single application, had 1.12 ppm 67 days after treatment. Pulp samples (the entire fruit less the rind) were analyzed at the 19- and 61-day intervals from plot I and at 15 and 28 days after overspray from plot II and residue levels were all less than 0.01 ppm. Residues on a whole-fruit basis are approximately one-third the value for the rind as lemons are 30.0 ± 8.5% rind by weight (Gunther, 1969). The residues after laboratory washing of the fruit to simulate packing house treatment are also shown in Figure 3. As for oranges, residues were not removed from lemons by washing, indicating phenthoate penetration into the rind waxes and oils.

The phenthoate residue data for unwashed and washed grapefruit rind are shown in Figure 4. Residues on and in grapefruit dissipated more rapidly than on and in oranges or lemons, due to a short persistence half-life followed by short degradation half-life (about 15 days).

Table IV. Dislodgable Phenthoate Residues ($\mu g/cm^2$) on Orange Foliage

Days after last spraying	Plot[a]											
	A			B			C			D		
	Min	Max	Av[b]	Min	Max	Av	Min	Max	Av	Min	Max	Av
3	0.35	0.40	0.38	0.13	0.14	0.14	0.04	0.06	0.05	1.1	2.3	1.7
10	0.05	0.08	0.06	0.01	0.03	0.02	0.01	0.01	0.01	0.16	0.36	0.25
17	0.03	0.04	0.03	0.01	0.02	0.01		<0.01	<0.01	0.03	0.04	0.04
24	0.01	0.02	0.02							0.02	0.05	0.03
31		<0.01	<0.01								0.01	<0.01
3							0.09	0.11	0.10			
10							0.03	0.04	0.03			
17							0.01	0.02	0.01			

[a] Plots A, B, and C were treated at 7.5, 3.75, and 1.88 lb of AI/1500 gal per acre, respectively, and plot D at 7.5 lb of AI/100 gal per acre (low volume). Plot C was oversprayed on day 56. [b] The minimum, maximum, and average residue found for the three replicate field plots.

Table V. Phenthoate Residues on and in Lemon Foliage

Days after spraying	Plot[a]											
	I			II			III			IV		
	Min	Max	Av[b]	Min	Max	Av	Min	Max	Av	Min	Max	Av
	Dislodgable Residues ($\mu g/cm^2$)											
Pretreatment			<0.01			<0.01			<0.01			<0.01
4	0.06	0.17	0.11	0.05	0.06	0.05	0.02	0.06	0.04	0.20	0.50	0.38
11	0.01	0.02	0.02	0.01	0.02	0.01		0.01	<0.01	0.04	0.10	0.07
19		0.01	0.01		<0.01	<0.01		<0.01	<0.01	0.01	0.02	0.02
33		<0.01	<0.01							0.01	0.01	0.01
46											<0.01	<0.01
	Penetrated Residues (ppm)[c]											
Pretreatment[d]			3.0			1.6			0.7			5.7
4			13			8.1			4.4			36
11			6.9			3.3			2.1			17
19			4.0			2.7			1.4			11
33			5.3			3.0			1.6			11
46			5.6			2.4			1.4			9
61			7.3						3.0			12
67			6.8						2.9			12

[a] Plots I, II, and III were treated at 6.25, 3.12, and 1.56 lb of AI/1250 gal per acre, respectively, and plot IV at 6.25 lb of AI/100 gal per acre (low volume). [b] The minimum, maximum, and average residues found for the three replicate field plots. [c] One-hundred leaf disks with a total surface area of 1010 cm^2 weighed 16.6 g. [d] Trees were sprayed 147 days earlier but the experiment was terminated due to rain.

Laboratory washing of the grapefruit removed about 50% of the residue at the 3-day sampling period and from about 25% to less than 10% thereafter. Phenthoate was not detected in any grapefruit pulp samples. Therefore, the residues on a whole fruit basis are one-fourth the rind values as grapefruits are 23.0 ± 3.2% rind by weight (Gunther, 1969).

Foliage Residues. The phenthoate residue data for orange foliage taken from the persistence plots A through D are in Table IV. Dislodgable residues on the leaf surface dissipated rapidly, especially down to the 0.05-$\mu g/cm^2$ level. Analyses were discontinued when the dislodgable residue levels reached 0.01 $\mu g/cm^2$ as this was considered a negligible level. The time required to reach this point was 10 days for the lowest application rate (plot C) and 30 days for the low-volume treatment (plot D).

Takade et al. (1977) using acetone rinses to remove surface residues from leaves found in two different experiments that, after 14 days, 1 and 13% of the phenthoate remained. The difference was attributed to outdoor temperature. The maximum amount of phenthoate oxon formed was equivalent to 0.5% of the initially applied phenthoate. The overall data indicated that phenthoate was lost from leaf surfaces by volatilization.

To determine the effectiveness of field washing of orange trees in reducing foliar dislodgable residues, trees were spray washed with 3000 gal/acre of water containing 16 ml of Sur-Ten wetting agent/100 gal. The residues before and after washing were 0.34 and 0.11 $\mu g/cm^2$, respectively, for trees washed 3-days posttreatment and 0.07 and 0.02 $\mu g/cm^2$, respectively, for trees washed 10-days posttreatment. Thus, approximately 70% of the dislodgable residues was removed each time. Field washing was ineffective in removing phenthoate from the fruit, as supported by the data (Figure 2) for laboratory-washed fruit.

The phenthoate residue data for lemon foliage taken from the persistence plots I through IV are in Table V. The dislodgable residue levels were less than 0.01 $\mu g/cm^2$ at 11, 19, 33, and 46 days after spraying for plots III, II, I, and IV, respectively. The rapid dissipation from the leaf surface is very desirable from the worker safe-reentry standpoint. Dislodgable residues on grapefruit leaves were 0.05, 0.01, and <0.01 $\mu g/cm^2$ 4, 11, and 18 days, respectively, after spraying.

Field washing was ineffective in reducing residues on the lemon fruit. Rind residues before and after washing were 3.5 and 4.0 ppm, respectively, at the 4-day interval, and 2.6 and 2.8 ppm, respectively, 11 days after spraying. The corresponding lemon foliar dislodgable residue values were 0.07 and 0.06 $\mu g/cm^2$ at the 4-day interval and 0.03 and 0.02 $\mu g/cm^2$ at the 11-day interval. Residue reduction was not as great as anticipated but due to the low residues

Table VI. Phenthoate ($\mu g/m^3$) in Particulate Matter Collected in Andersen Air Samplers[a]

Sampler type	No.[b]	Minimum particle size, μm 11	7.0	4.7	3.3	2.1	1.1	0.65	0.43	<0.65	Total
					3-Day Interval						
Standard		81.0	1.3	0.3	ND	ND	ND	ND	ND		82.6
Mini	1			74.0	11.0	11.0		ND			96.0
Mini	2			63.0	10.0	ND		ND		ND	73.0
Mini	3			50.0	11.0	ND		ND		ND	61.0
					10-Day Interval						
Standard		42.0	1.3	0.4	ND	ND	ND	ND	ND		43.7
Mini	1			14.0	ND	ND		ND		ND	14.0
Mini	2			29.0	ND	ND		ND		ND	29.0
Mini	3			7.0	ND	ND		ND		ND	7.0

[a] The standard sampler had eight stages with no filter. The mini samplers had four stages plus a filter. [b] Number 1, 6 ft above ground in center of tree; number 2, 4 ft above ground at periphery of tree; number 3, 8 ft above ground at periphery of tree.

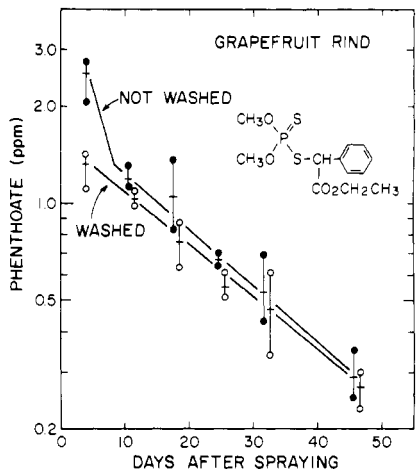

Figure 4. Dissipation of phenthoate residues on and in unwashed and laboratory washed grapefruit rind. Trees were sprayed with 3.75 lb of AI/1500 gal per acre. Ranges of values obtained for three plot replicates are shown by vertical lines and averages are shown by horizontal dashes.

present the data are difficult to interpret.

Airborne Residues. To simulate worker activity, orange trees were shaken for 1 min with an OMC "Shock-Wave" tree shaker. The foliar dislodgable residues before and after shaking were 0.39 and 0.37 $\mu g/cm^2$, respectively, for trees shaken 3-days posttreatment and 0.08 and 0.07 $\mu g/cm^2$, respectively, for trees shaken 10-days posttreatment. The deposits, although sufficiently loosely adhering to permit their ready removal by washing, were not shaken off in significant quantities. They could probably be readily brushed off by workers, however.

The data for the Andersen particulate matter samplers operated while trees were shaken with an OMC "Shock-Wave" tree shaker are in Table VI. Over 80% of the phenthoate recovered from the particulate matter collected was in the largest particles (above 11 μm in the standard sampler; above 4.7 μm in the mini-type). The data for all the minisamples show that less than 15% of the dislodged particulate matter could reach the alveoli of the human respiratory system (Brown et al., 1950). It is evident that shaking the trees dislodged only the larger loosely adhering particles and is probably not a good indication of the exposure encountered by a worker moving about in a tree, vigorously brushing against the foliage.

The data for the grab samples are in Table VII. The insecticide found on the filters was considered to be that contained in the particulate matter of larger particle sizes that fell upon the filters during shaking. These filters were exposed, in an upright position, for an undetermined

Table VII. Phenthoate Levels in Air-Borne Particulate Matter and in Air in Grab Samplers 3 Days after Spraying[a]

Sampling position[b]	Sampled	$\mu g/m^3$ Filter	Cylinder
Tree center	Before shaking	20	73
		55	100
Periphery	Before shaking	ND	110
		ND	180
Tree center	During shaking	200	120
		220	110
Periphery	During shaking	240	240
		260	130

[a] Sprayed with 3.75 lb of AI/1500 gal per acre. [b] Samples taken 6 ft above ground.

Table VIII. Phenthoate Residues in Soil beneath Sprayed Orange Trees[a]

Pan position[b]	ppm at days after spraying 0	3	10	17	45	59
0° P	0.9	0.4	8.4			1.6
0° 1/2	1.2	5.9	8.0	5.3	3.7	2.5
90° P	3.7	1.7	7.9	7.9	4.1	7.3
90° 1/2	1.8	3.5		3.7	3.6	3.2
45° P	3.5	4.3	3.3	5.8	4.5	
45° 1/2	7.4	4.1	3.6	6.0	3.6	2.9
Av	3.1	3.3	5.2	5.4	3.3	2.9

[a] Sprayed with 7.5 lb of AI/1500 gal per acre. [b] 0°, position on side within the row; 90°, position on side between the rows; 45°, position halfway between 0 and 90°; P, position at perimenter of tree canopy; 1/2, position halfway between perimeter and trunk.

period during which the cylinders were allowed to fill with air. The phenthoate found in the filtered air in the cylinders in approximately the same amounts, whether collected before the tree was disturbed or during shaking, appears to indicate a high vapor concentration; yet the Greenburg-Smith impinger samples from the same general area show extremely low levels as discussed below.

Ambient air was sampled with Greenburg-Smith impingers immediately after the spray was applied and at the 3- and 10-day intervals. The impingers were placed with air intakes 45 cm above the ground inside the tree canopies, one on the north side and the other on the south side of trees in plot D. The vapor-phase levels of phenthoate detected in the samples from the north sides of the trees were 13.5, 3.2, and 1.8 $\mu g/m^3$ for the 0-, 3-, and 10-day intervals, respectively; on the south sides they were 29.0, 4.8, and 2.2 $\mu g/m^3$. Air temperatures (in the shade) ranged between 75 and 85 °F during the 2-h sampling periods.

Soil Residues. Table VIII gives the residues found in the soil in pans after spraying. The pans were placed under the trees before they were sprayed. Amounts found

Table IX. Phenthoate in Soil beneath Field-Washed Trees[a]

Pan position[b]	ppm at days after spraying	
	3	10
0° P	1.1	1.4
0° 1/2	1.5	1.5
90° P	2.7	0.5
90° 1/2	1.5	1.1
45° P	0.4	1.9
45° 1/2	1.9	0.9
Av	1.5	1.2

[a] Sprayed with 7.5 lb of AI/1500 gal per acre, then washed with 3000 gal/acre of water-detergent solution at 3 and 10 days post-application. [b] Pans of soil placed under trees immediately before washing and removed as soon as trees were dry. Positions as shown in Table VIII.

were approximately the same for the various pan positions, showing very uniform spray coverage of the tree. Except for the initial wetting, the soil remained dry as there was no rain throughout the experimental period. The average residue for all the pan positions remained relatively constant and indicates that the phenthoate present is strongly sorbed to the soil and does not undergo extensive degradation. Iwata et al. (1975) found that when phenthoate was added to moist soil at 500 ppm, 50% of the pesticide was degraded within 10 days and over 95% within 30 days. Thus, the field residues would also be expected to degrade rapidly when the soil is wetted by irrigation or rain.

Pans of soil were placed under the field-washed trees just prior to washing at the 3- and 10-day intervals and removed for analysis as soon as the trees had dried to provide an estimate of the amount of insecticide carried into the soil by washing. These data are in Table IX. Approximately the same amount was recovered from the soil at each interval and these levels were about half of those resulting from runoff when the spray was applied.

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A Rapid Spectrophotometric Method for the Simultaneous Determination of Intact Benomyl and Its Degradation Product, Methyl 2-Benzimidazolecarbamate (MBC), in Organic Solvents and Water

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A rapid ultraviolet (UV) spectrophotometric method for determining benomyl and its degradation compound, methyl 2-benzimidazolecarbamate (MBC), has been developed. Maximum absorbances of a solution containing benomyl and MBC occur at 294 nm (A) and 286 nm (B), and, from the ratio A/B, the proportion of intact benomyl and MBC in the solution can be obtained from a standard curve. After determining the proportion of benomyl and MBC in organic solvents, n-butyl isocyanate (BIC) is added to the same solution to determine the total quantity of benomyl in the solution. With a nonscanning spectrophotometer, absorption of the sample is measured at 294 nm before and after adding BIC, and both intact and total benomyl concentrations are determined. BIC stabilizes benomyl in most common organic solvents except methanol and ethanol.

Benomyl, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, is one of the most widely used systemic fungicides for the control of plant diseases, but its mode of action is not yet clearly understood. Because its breakdown product, methyl 2-benzimidazolecarbamate (MBC), is also fungitoxic (Peterson and Edgington, 1969; Clemons and Sisler, 1969), studies to elucidate its mode of action became complicated.

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The greatest problem in elucidating the mode of action has been in the lack of suitable analytical methods for intact benomyl and MBC. Methods available to determine intact benomyl per se to date include a colorimetric method in the milligram range (Miller et al., 1974), a TLC technique (Clemons and Sisler, 1969; Peterson and Edgington, 1969), and a radioactive technique (Upham and Delp, 1973; Baude et al., 1973), but these are rather impractical for routine quantitative analyses at microgram levels. There are many other methods to determine MBC and further degradation compounds, including fluorometric and colorimetric methods (Pease and Gardiner,