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Persistence of Residues of the Insecticide Phosphamidon on and in Oranges, Lemons, and Grapefruit, and on and in Orange Leaves and in Dried Citrus Pulp Cattle Feed

William E. Westlake,* Monika Ittig, Daniel E. Ott, and Francis A. Gunther

The dissipation rates of phosphamidon on and in oranges, lemons, and grapefruit were determined; the degrading deposit half-lives were 3–5 days and the persisting residue half-lives were 10–12 days. Dosages from 0.5 to 1.5 lb a.i./acre yielded maximum initial deposits of about 1.5 ppm (rind basis), which decreased to about 0.1 ppm (rind basis) after 28 days. Residues declined slightly more rapidly on leaves than on fruit. The persisting residues on all varieties of fruit and on orange leaves remained largely on the surface for as long as 28 days after application, *i.e.*, they were largely dislodgable residues. There was indication of only slight, if any, translocation into the edible portion of any of these fruits; the highest level detected was 0.02 ppm in lemon juice sacs 1 day after application. The cis isomer of phosphamidon disappeared slightly more rapidly than the trans isomer. *N*-Desethylphosphamidon was not detected in any sample (*i.e.*, <0.01 ppm). About 90% of the phosphamidon in orange rind (0.04 ppm, 14-day sample) was lost in processing the rind into dried citrus pulp cattle feed.

Phosphamidon (2-chloro-*N*,*N*-diethyl-3-hydroxycrotonamide dimethyl phosphate) is a broad spectrum systemic insecticide that has been found useful for the control of some insects and mites on citrus in Southern California. Technical grade phosphamidon is a mixture of cis and trans isomers in the proportion of 73:27 (Anliker and Beriger, 1971) plus approximately 1% each of dechlorophosphamidon (*cis-* and *trans-*) and γ-chlorophosphamidon (*cis-* and *trans-*). The cis isomers of phosphamidon and of *N*-desethylphosphamidon (a metabolite formed in plant tissues) have high biological activity, while that of the trans isomers is low.

This study was designed to obtain data on deposit and residue levels and their rates of dissipation to enable state, federal, and other regulating agencies to establish tolerances and conditions for use of the compound in the area of citrus pest control. Residue levels on and in foliage were also determined in one Valencia orange plot for comparison with similar data for fruit. Dried citrus pulp cattle feed was prepared and analyzed to determine the effect of this processing on the persisting residue levels.

Although not directly comparable due to differences in amounts applied and numbers of applications, the data reported here agree well with earlier work (Voss and Geissbühler, 1971) which showed a persisting residue half-life of 7–15 days for phosphamidon on and in oranges, compared with our 10–12 days.

EXPERIMENTAL DESIGN

Plots of mature, furrow-irrigated Valencia orange trees were sprayed with phosphamidon in April of 1971 for the purpose of determining deposit and residue dissipation rates on and in fruit and leaves and the extent of penetration into the edible part of the fruit. The compound was applied at rates of 0.5, 1.0, or 1.5 lb/acre (0.5, 1.0, or 1.5 pt of a formulation containing 8 lb of technical grade phosphamidon/gal) in 200 gal of water (plots 1, 2, and 3, respectively). Plots of furrow-irrigated grapefruit trees were sprayed in July of 1971 with 0.5 or 1.0 pt/acre and furrow-irrigated lemon trees were sprayed in April of 1972 at these same rates (plots 1 and 2, respectively, for each). All plots were replicated three times. Samples of orange fruits were collected for analysis before treatment and at intervals of 1, 3, 7, 14, 21, 28, and 42 days after treatment. Double samples were taken at the 3-, 14-, and 28-day intervals and one-half of each sample was washed in a manner simulating commercial practice before processing for analysis. Pulp (edible portion) of the fruit was analyzed at the 1-, 7-, and 21-day intervals. Leaves from plot 2 were sampled at the same intervals as fruit and analyzed for surface (dislodgable) and total (dislodgable plus penetrated) residues. At the 14- and 28-day intervals, samples of oranges were taken from plot 3 for conversion into dried citrus pulp cattle feed.

The field plot arrangement and the sampling procedure for fruit and the preparation of cattle feed prior to analysis were as described by Gunther (1969). Leaf samples consisted of 40 1-in. disks punched from the approximate centers of that number of leaves with a specially designed punch that deposited the disks in an attached 4-oz wide-mouthed jar (Gunther *et al.*, 1973). Preliminary tests showed that the calculated total leaf residues (as $\mu g/cm^2$) using the leaf-punch method agreed very well with values obtained by using the entire leaf.

Grapefruit samples were taken before spraying and at intervals of 3, 6, 10, 20, and 31 days after treatment, and lemons were sampled before spraying and at 1-, 3-, 7-, 14-, and 21-day intervals afterward. Pulp of the grapefruit

Department of Entomology, University of California Citrus Research Center and Agricultural Experiment Station, Riverside, California 92502.

samples from the plot sprayed at the higher rate was analyzed for all but the 31-day sample. Lemon pulp samples from both dosages were analyzed for all but the 21-day sample.

There was no rainfall between these applications and final samplings for the three varieties of citrus trees.

METHODS

Extraction Procedures. The samples of rind and cattle feed were extracted as described by Voss *et al.* (1971), and the chloroform extractives were stored at about 4° pending analysis. The pulp samples were prepared as described by Gunther (1969), using chloroform as the solvent, and the chloroform extractives were stored as above. Leaf disk samples were surface-stripped (Gunther *et al.*, 1973) by shaking for 1 hr at 120 cpm on a reciprocating shaker with 50 ml of water to which two drops of a 1:50 dilution of Sur-Ten wetting agent (American Cyanamid) had been added. This solution was decanted and another 50 ml of fresh solution was added and the samples were shaken for 30 min. This solution was decanted, added to the first, and the samples were shaken with 10 ml of water, by hand, for 30 sec and this washing was added to the previous washes. The total aqueous stripping solution was shaken for 20 sec with 50 ml of chloroform in a separatory funnel. The chloroform layer was drawn off into a sample storage bottle and the extraction was repeated two more times, adding these extracts to the first. About 20 g of anhydrous sodium sulfate was added to each sample, which was then stored at about 4°.

Each stripped leaf disk sample from above was transferred to a stainless steel semi-micro Waring Blendor container and about 10 g of anhydrous sodium sulfate and 100 ml of chloroform were added, rinsing the sample jar in the process. The sample was blended at high speed for 3 min and the chloroform extract was decanted onto a Whatman No. 1 filter paper, retaining as much of the leaf tissue as possible in the blender container. The tissue was again blended with another 100 ml of chloroform for 30 sec at high speed and the resulting extract was added to the first. After the addition of 20 g of anhydrous sodium sulfate, this extract was stored as described above.

Cleanup. Aliquots of the chloroform solutions equivalent to 20 g of rind or cattle feed or 50 g of pulp were used for analysis. The extractives in a sample were first transferred to hexane by adding 30 ml of mixed hexanes and concentrating to about 5 ml using a rotary vacuum evaporator, and then repeating the process two more times. After the third evaporation, 30 ml of water was added and the hexane was completely evaporated. This aqueous solution was transferred to a separatory funnel using an additional 20 ml of water, and then shaken with two successive 10-ml portions of hexane (discarded) to remove oils and some colored matter. The extractives still present were then partitioned into chloroform by shaking with three successive 50-ml portions and the chloroform extract was concentrated to about 5 ml using a rotary vacuum evaporator.

Three centimeters of alumina (neutral, activity grade V) was poured into a chromatographic column 22 mm in diameter, the column was washed with 25 ml of chloroform, and the concentrated sample was introduced. Phosphamidon was eluted with 50 ml of chloroform and the solvent was completely removed on the rotary vacuum evaporator, evaporating the last traces with a gentle current of air. The oily residue was dissolved in 0.5 ml of ethyl acetate and brought to a suitable volume with hexane for gas chromatography.

Stripping solutions from and extracts of leaves required no cleanup and were prepared for analysis by removing the chloroform, taking the residues up in 0.5 ml of ethyl acetate, and bringing them to the desired volume with hexane.

Gas Chromatography. An Aerograph 1740 gas chromatograph fitted with an alkali flame phosphorus detector and a 2.5 ft × 2 mm i.d. glass column packed with 5% Carbowax 20M on 60/80 mesh Gas Chrom Q was used. The temperatures were: column, 210°; detector, 220°; and injection port, 235°. Helium was used as the carrier gas at 30 ml/min. Under the conditions of use, this column completely separated the cis and trans isomers of phosphamidon and *N*-desethylphosphamidon (retention times of 5.1, 3.3, and 5.9 min, respectively). Phosphamidon was quantitated in the 1- and 3-day samples of orange rind and leaves by measuring the peak height for the cis isomer. After the first week a change in the ratio of these isomers was observed, the cis isomer apparently being metabolized slightly faster than the trans isomer. In all subsequent samples both isomers were measured and their sum was reported as the total phosphamidon residues.

After gas chromatographic analysis, some orange rind sample extractives were also analyzed by cholinesterase inhibition determination using the automated procedure described by Ott (1968). Aliquots of the solutions used for gas chromatography, usually equivalent to 8 g of rind, were concentrated to solvent dryness in 45-ml glass vials. Five milliliters of water and a boiling chip were added to each and the vials were capped with a double layer of aluminum foil and placed in an oven at 110° for 15 min to solubilize the phosphamidon residues from the oily material. Aliquots from a standard solution of technical grade phosphamidon, added to either pretreatment or control orange rind extractives, were similarly treated for quantitation purposes. All solutions were individually filtered, while warm, through 4.25-cm diameter Whatman No. 1 filter papers directly into polystyrene sample cups for the AutoAnalyzer (Technicon Instruments Corp.).

RESULTS AND DISCUSSION

Definitions. Specific terminology should be used in pesticide residue evaluations with citrus fruit and leaves, for "deposit" and "residue" are not synonymous (Gunther and Blinn, 1955). The following distinctions (Gunther, 1969; Westlake *et al.*, 1973) apply to the present discussion: "degradation curve" refers to the time-dependent transformation of the initial deposit to a decreased but mechanically reasonably stable residue still largely on the surface of the fruit or leaf; "degrading deposit" and "degrading deposit half-life" refer to this deposit or surface residue before it becomes a true residue largely embedded or dissolved in surface waxes beginning to penetrate subsurface tissues and thus not further dislodgable by desiccation, wind, rain, and abrasion; "persistence curve" refers to the time-dependent disappearance or other loss of identity of this so-stabilized deposit; "persisting residue" and "persisting residue half-life" refer to this so-stabilized deposit and its subsequent behavior with time; on the same plot, both degradation and persistence behaviors follow first-order reaction kinetics (for nonsystemic pesticides) and intersect in a necessarily poorly defined transition zone; precise terminology would distinguish between "persisting surface residue" and "persisting subsurface (or penetrated) residue," but the former residue plus the persisting deposit have now been termed "dislodgable residue" (Westlake *et al.*, 1973) to designate pesticide-bearing material transferrable by contact to workers brushing against fruit and foliage or capable of becoming airborne when fruit and foliage are vigorously disturbed; and "residues on and in fruits and leaves" refers to dislodgable residues as "on" and penetrated residues as "in."

Ratios of Phosphamidon Isomers. The difference in the rates of disappearance of the cis and trans isomers of

Table I. Ratios of Cis-Trans Isomers of Phosphamidon in Aging Deposits on and in Orange Rind and Leaves[a]

Plot[b]	Sample	Cis-trans ratio after, days				
		7	14	21	28	42
1	Rind	68:32	64:36	63:37	60:40	
2	Rind	68:32	64:36	61:39	59:41	
3	Rind	71:29	67:33	63:37	61:39	58:42
2	Leaves (surface)	70:30	66:34	61:39	59:41	
	(penetrated)	76:24	74:26			

[a] The cis-trans ratio in technical grade phosphamidon is approximately 73:27. The individual isomers were measured by comparing their peak heights with those of standards prepared from the pure isomers and the sum of the isomers is used as the amount of technical grade phosphamidon present. The ratio of the isomers was determined by the relative weights as calculated from the peak heights. [b] Plot 1 = 0.5 lb, plot 2 = 1.0 lb, and plot 3 = 1.5 lb of a.i./200 gal/acre.

Table II. Phosphamidon Residues on and in Unwashed Valencia Orange Rind by a Gas Chromatographic Method

Days after spraying	Residue, ppm, rind basis[a]								
	Plot 1 (field replicate)			Plot 2 (field replicate)			Plot 3 (field replicate)		
	A	B	C	A	B	C	A	B	C
1	1.10	0.70	0.50	0.70	0.70	0.70	1.10	1.50	1.40
3	0.30	0.40	0.10	0.50	0.40	0.50	0.60	2.30	1.40
3 W[b]	0.06	0.10	0.05	0.30	0.10	0.10	0.10	0.30	0.20
7	0.20	0.20	0.10	0.20	0.10	0.30	0.30	0.50	0.50
14	0.10	0.10	0.10	0.20	0.10	0.20	0.10	0.30	0.20
14 W[b]	0.02	0.06	0.02	0.06	0.02	0.03	0.04	0.06	0.06
21	0.05	0.05	0.06	0.09	0.05	0.15	0.20	0.02	0.20
28	0.04	0.05	0.04	0.04	0.03	0.05	0.05	0.09	0.08
28 W[b]	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.03	0.02
42							0.03	0.04	0.02

[a] Each value = average of eight analytical replicates. Residue levels on the basis of weights of entire fruit are 18.7 ± 6.3% of those reported for rind only. All values have been corrected for 92% recovery of phosphamidon added to the extractives from untreated control samples. No background correction was necessary. Forty-two samples fortified at levels from 0.03 to 1.0 ppm were analyzed to determine the mean recovery value of 92 ± 8%. Plot 1 = 0.5 lb, plot 2 = 1.0 lb, and plot 3 = 1.5 lb of a.i./200 gal/acre. [b] Sample washed in laboratory in simulated packinghouse procedure (Gunther, 1969) before processing. The difference between washed and unwashed samples represents a dislodgable residue.

Table III. Phosphamidon Residues on and in Valencia Orange Leaves from Field Replicates in Plot 2

Days after spraying	Residue, μg/cm²[a]					
	Replicate A		Replicate B		Replicate C	
	Surface[b]	Interior	Surface[b]	Interior	Surface[b]	Interior
1	1.40	0.30	1.10	0.10	1.00	0.10
3	0.80	0.10	0.70	0.10	0.70	0.10
7	0.60	0.02	0.40	0.01	0.40	0.02
14	0.06	0.01	0.04	<0.01	0.03	<0.01
21	0.06	Tr	0.04	Tr	0.06	Tr
28	0.08	Tr	0.03	Tr	0.06	Tr

[a] Tr = peak too small to measure (<0.005 μg/cm²). As no cleanup was required for leaf samples, laboratory recovery was 100%. Each value = average for duplicate field samples. Plot 2 = 1.0 lb of a.i./200 gal/acre. [b] Represents dislodgable residue.

phosphamidon was not great enough to permit establishing different residue half-lives but was, nevertheless, a measurable one as illustrated for oranges in Table I (from 70:30 initially to 60:40 after 28 days). There is a suggestion, in the limited leaf data, that the ratio changed more rapidly on the surface than in the penetrated residues. *N*-Desethylphosphamidon was not found in the field-treated samples (*i.e.*, <0.01 ppm, fruit or leaves).

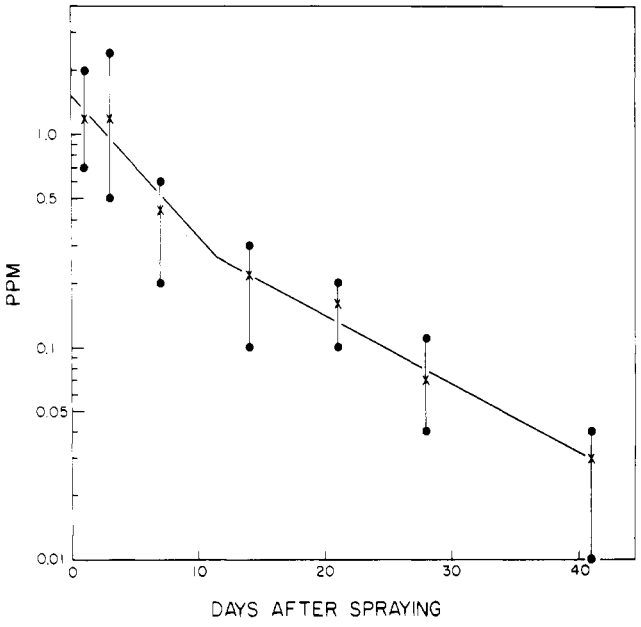

Figure 1. Phosphamidon residues on and in Valencia orange rind for 1.5 lb of a.i./200 gal/acre: ⁞ = range of analytical and plot replicates and × = average.

Oranges. The initial deposits and subsequent persisting residues on and in orange rind and leaves using the gas chromatographic method are collated in Tables II and III, respectively, and values for the rind from plot 3 are graphed in Figure 1 to demonstrate first-order dissipation kinetics. The overall range of values for the analytical replicates is plotted to show the field variation encountered. The data for orange rind by the automated cholinesterase inhibition procedure are in Table IV. Residue data show a rapid decline in residue levels (persisting residue half-life ~10 days) for both fruit rind and leaves, the levels in orange rind being in the range of 0.1 ppm (0.02 ppm on a whole fruit basis) 14 to 28 days after treatment. Previous work by Voss and Geissbühler (1971), although not directly comparable because higher rates of application and some multiple applications were used, also showed a persisting residue half-life on and in oranges as 7–15 days by cholinesterase inhibition assay; their data for lemons and grapefruit are too limited to permit calculations of half-lives. The values for washed *vs.* unwashed fruit and for surface *vs.* interior levels for leaves show that the persisting phosphamidon residues remain largely on the fruit and leaf surfaces for at least 28 days after application. Thus, the amounts removed from fruits by the washing averaged 77, 75, and 72% for the 3-, 14-, and 28-day samples, respectively. Analysis of the orange pulp of samples from plot 2 at the 1-, 7-, and 21-day intervals confirmed the lack of significant penetration into aqueous tissues, measurable (0.01 ppm) residues being found only at the 7-day interval. In contrast, Voss and Geissbühler (1971) found from <0.1 up to 0.5 ppm in "juice" up to 18 days after application of from 4.2 to 16.8 kg of a.i./ha; their "juice" may have been prepared in a manner that permitted contamination by rind residues.

There is good agreement between the average values for residues on and in orange rind obtained by the two present methods of analysis (Tables II and IV), lending added creditability to these data; under our conditions the gas chromatographic method was specific for phosphamidon isomers and the cholinesterase inhibition values corresponded to mixed-isomer activity.

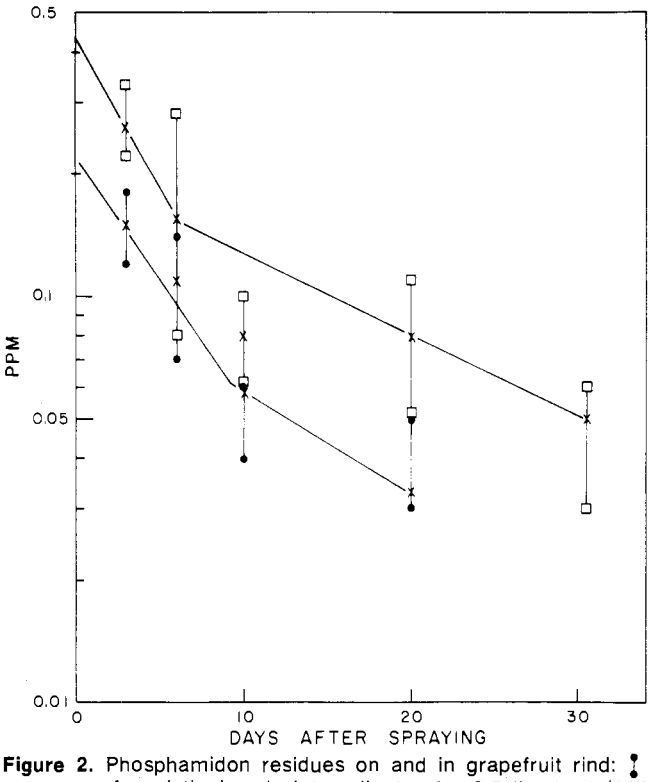

Figure 2. Phosphamidon residues on and in grapefruit rind: ⚫ = range of analytical and plot replicates for 0.5 lb of a.i./200 gal/acre; ☐ = range for 1.0 lb of a.i./200 gal/acre; and × = average.

The data for residues in the ground rind, the rind after liming and pressing, and in finished citrus pulp cattle feed (fruit from plot 3) are in Table V. As there is a potential increase in residue levels of 4.5 times in drying the rind from about 80 to 8–10% water content, the intial residues of about 0.04 ppm in the 14-day sample could theoretically result in a residue of about 0.2 ppm in the dried feed. The observed level was only one-tenth of this, or a loss of 90% of the phosphamidon during this processing. There was an increase in the residue level in the limed and pressed rind over the ground rind, indicating that most of the phosphamidon remained in the tissues rather than being removed in the water–oil press liquor. The principal loss occurred during the drying process.

Grapefruit. Residues found on and in grapefruit rind are in Table VI and are graphed in Figure 2 to show the first-order dissipation kinetics; the overall range of all analytical samples per interval is plotted to show the full variation. The initial deposits as ppm were considerably less than those on oranges, probably due to the greater thickness of the grapefruit rind and a correspondingly lower surface-to-weight ratio, to the character of the fruit surface, and to other unknown variables (Gunther, 1969). The persisting residue half-life was ~12 days; rind residues resulting from the higher treatment (1 lb of a.i./acre) reached the 0.05-ppm level 31 days after spraying. No phosphamidon was detectable in the pulp of these fruits at any time (*i.e.*, <0.01 ppm). The degrading deposit half-life was ~4 days.

Lemons. Residues found in lemon rind are in Table VII and are graphed as before in Figure 3; the overall ranges of values for replicates are again shown. The residue levels were slightly higher than those in orange rind, but dissipated at about the same rate (persisting residue half-life ~10 days, degrading deposit half-life ~3 days). Rind residues were 0.5 ppm on the third day after spraying for the lower rate of application and reached that level in less than 14 days at the higher application rate. The maximum residue detected in the pulp of lemons was 0.02 ppm

Table IV. Phosphamidon Residues on and in Unwashed Valencia Orange Rind by a Cholinesterase Inhibition Method

Days after spraying	Residue, ppm, rind basis[a]								
	Plot 1 (field replicate)			Plot 2 (field replicate)			Plot 3 (field replicate)		
	A	B	C	A	B	C	A	B	C
1	0.7	0.6	0.4	0.8	0.6	0.4	0.6	1.6	1.2
3	0.5	0.6	0.3	0.5	0.6	0.6	0.7	1.1	1.4
3 W[b]	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.2
7	0.1	0.2	0.2	0.3	0.3	0.2	0.3	0.4	0.5
14	<0.1	0.1	0.1	0.1	<0.1	0.1	0.1	0.4	0.3

[a] All values have been corrected for an average apparent background of 0.3 ppm in untreated control samples and for 50% average recovery of phosphamidon added to the extractives of 15 untreated controls. Plot 1 = 0.5 lb, plot 2 = 1.0 lb, and plot 3 = 1.5 lb of a.i./200 gal/acre. [b] Sample washed in laboratory in simulated packinghouse procedure (Gunther, 1969) before processing.

Table V. Phosphamidon Residues in Ground Valencia Orange Rind from Plot 3, the Rind after Liming and Pressing, and in the Dried Citrus Pulp Cattle Feed

Days after treatment	Residue, ppm[a]		
	Ground rind[b]	Limed and pressed rind	Dried feed
14	0.04	0.07	0.02
28	<0.01	0.02	<0.01

[a] All values have been corrected for 92% recovery of phosphamidon added to the extractives from six untreated control samples. No background correction was necessary. Plot 3 = 1.5 lb of a.i./200 gal/acre. [b] Fruit was washed before juicing so these values are penetrated residues.

Table VI. Phosphamidon Residues on and in Unwashed Grapefruit Rind

Days after spraying	Residue, ppm, rind basis[a]					
	Plot 1 (field replicate)			Plot 2 (field replicate)		
	A	B	C	A	B	C
3	0.13	0.16	0.16	0.28	0.22	0.28
6	0.13	0.09	0.11	0.10	0.15	0.25
10	0.06	0.05	0.06	0.09	0.09	0.07
20	0.04	0.03	0.03	0.06	0.08	0.09
31				0.05	0.06	0.04

[a] Residue levels on the basis of weight of entire fruit are 23.0 ± 3.2% of those reported for rind only. Each value = average of eight analytical replicates. All values have been corrected for 98% recovery based on the analysis of 34 fortified control samples (98 ± 19%). Plot 1 = 0.5 lb and plot 2 = 1.0 lb of a.i./200 gal/acre.

Table VII. Phosphamidon Residues on and in Unwashed Lemon Rind

Days after spraying	Residue, ppm, rind basis[a]					
	Plot 1 (field replicate)			Plot 2 (field replicate)		
	A	B	C	A	B	C
1	0.8	0.6	0.7	1.7	1.8	1.6
3	0.5	0.5	0.5	1.0	1.1	0.9
7	0.3	0.3	0.3	0.8	0.7	0.7
14	0.2	0.2	0.2	0.3	0.3	0.3
21	0.1	0.1	0.1	0.2	0.2	0.1

[a] Residue levels on the basis of weight of entire fruit are 30 ± 8.5% of those reported for rind only. Each value = average of six analytical replicates. All values have been corrected for 96% recovery based on the analysis of 39 fortified control samples (96 ± 15%). Plot 1 = 0.5 lb and plot 2 = 1.0 lb of a.i./200 gal/acre.

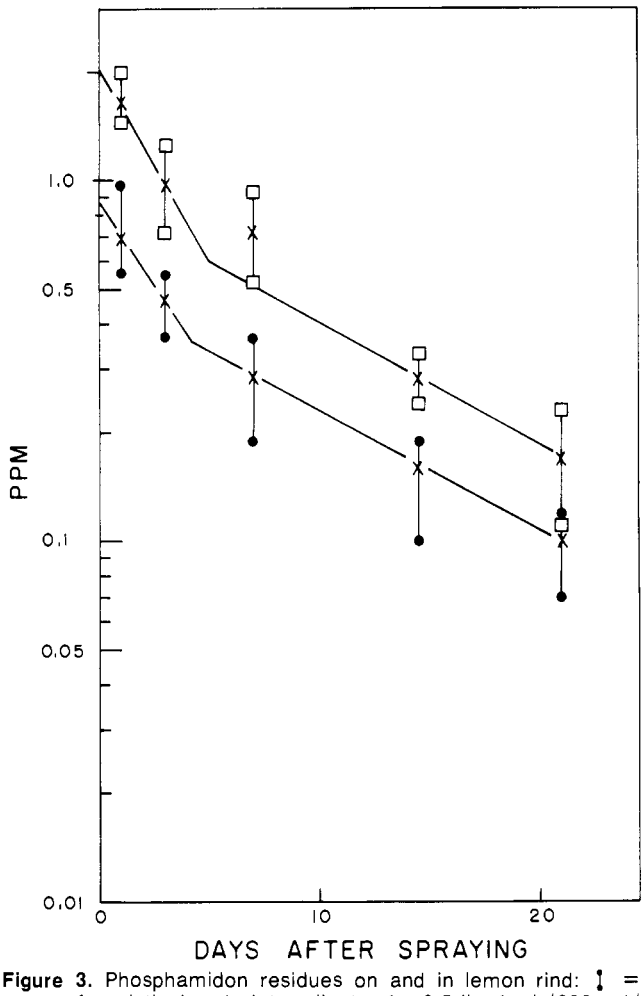

Figure 3. Phosphamidon residues on and in lemon rind: ⁞ = range of analytical and plot replicates for 0.5 lb of a.i./200 gal/acre; ⊟ = range for 1.0 lb of a.i./200 gal/acre; and × = average.

in samples taken 1 day after spraying; 3-day samples contained 0.01 ppm and none was detectable in later samplings.

CONCLUSIONS

The rates of dissipation of total phosphamidon deposits and residues were rapid on and in all three varieties of citrus fruits studied, the deposit half-life being 3–5 days and the residue half-life being 10–12 days. The initial deposits and succeeding residues were highest in lemons and lowest in grapefruit, but dissipation rates were almost identical.

A change in the ratio of the two isomers as both deposits and residues was observed with time, the cis isomer disappearing slightly more rapidly than the trans isomer. The individual isomers were measured from the 7- through the 42-day intervals and their sum was reported as total phosphamidon. The rate of change in the ratio of isomers was not rapid enough to permit the evaluation of their individual residue half-lives.

No desethylphosphamidon was detected in any of the samples analyzed, although trace amounts of less than the minimum detectable level (<0.01 ppm) could have been present.

Washing of orange fruits and leaves showed that most of the persisting phosphamidon was on the surfaces of both fruits and leaves throughout the duration of the study. Dislodgable residue half-lives on the orange fruits and leaves were 3–5 days for each. Between 7 and 14 days these dislodgable residues had decreased to 0.1 ppm or less and therefore would not represent a hazard for worker re-entry into a grove treated as specified herein. Conversion of orange rind to dried citrus pulp cattle feed destroyed 90% of the phosphamidon present (0.04 ppm) from 14 to 28 days after application.

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