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Disappearance of Acephate, Methamidophos, and Malathion from Citrus Foliage*

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Acephate and malathion were materials used extensively in the citrus blackfly eradication attempt which was conducted in several southeastern Florida counties during 1976 to 1979 (LOTORTO 1979). Treatments were applied to the citrus of individual homes in a generally heavily urbanized area. The purpose of this study was to determine the disappearance rates of acephate, its hydrolysis product, methamidophos, and malathion total residues from citrus foliage under simulated eradication application conditions.

MATERIALS AND METHODS

A random design with four replicates per chemical treatment, including four no spray blocks, was utilized in the first study (Table 1). Each replicate was one city block. Within each city block, eight subsamples were taken. One subsample was taken each from 'Temple' or 'Valencia' oranges, 'Hamlin' or'Pineapple' oranges, grapefruit, tangerine or tangelo, and lime or lemon and the three remaining subsamples consisted of the dominant citrus in the block. Each subsample consisted of 10 leaves picked at the petiole. For the second experiment (Table 2), a random design with six replicates was used. Each replicate comprised seven trees with one tree treated with each insecticidal treatment. Only trees that were spaced at least 15 m apart were chosen. Samples of 10 leaves per tree were taken in this study. Leaves for both studies were frozen at -20°C for 21 to 35 days prior to analysis. The effect of storage on residue levels was not determined.

Acephate was applied at 3-week intervals at 0.6 g active ingredient per liter (AI/L) (0.5 lb AI/100 gal) (ca. 38 L or 10 gal/tree) with a high-pressure handgun at 14 kg/cm^2 (200 psi) and at 2.4 g AI/L (2 lb AI/100 gal) by mist blower (ca. 0.8 L/tree or 0.2 gal/tree). Malathion was applied at 1.5 g AI/L (1.25 lb AI/100

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gal) by high-pressure handgun at 14 kg/cm^2.

The method of LEARY (1974) was modified for extraction and analysis of acephate and methamidophos. Samples were removed from storage, cut immediately into fine pieces with stainless steel scissors, and a 10 g sample weighed for analysis. The 10 g sample of leaves was homogenized in 100 ml of ethyl acetate and 15 g of anhydrous sodium sulfate for 5 min in a Sorvall blending cup in an ice bath. The blender cup top was loosened upon removal and allowed to sit 1 min for particulate matter to settle. A 20 ml aliquot was taken, evaporated to dryness at 40°C under N_2, and transferred to brown glass bottles over sodium sulfate in 10 ml of methyl isobutyl ketone for gas-liquid chromatography (GLC) analysis. Malathion samples were similarly processed except that methylene chloride was substituted for ethyl acetate and the final solvent was benzene. Extracts were stored at -20°C prior to analysis. Between samples all equipment was washed with copious amounts of soapy hot water, rinsed in tap water, deionized water, isopropanol and finally in deionized water.

For acephate and methamidophos, GLC was conducted in a Hewlett-Packard 5730A gas chromatograph equipped with dual nitrogen-phosphorus detectors. Operating conditions were: 0.8 m x 2 mm I.D. silanized glass column packed with 1% Reoplex 400 on Gaschrom Q (GCQ), 80/100 mesh (Applied Sci. Lab., State College, PA 16801); He 30 ml/min, detector temp 300°C, injector 210°C, temperature program 150°C to 200°C at 8°C/min, 8 min in final hold and 45 sec delay after injection. Quantification was by comparison of peak height of standard materials chromatographed at the same attenuation. Standards were chromatographed every fourth injection. All injections were 5 µl.

Malathion and malaoxon were analyzed on a Tracor 550 GLC with phosphorus flame photometric detection. Operating conditions were: 0.8 m x 2 mm I.D. silanized glass column packed with 5% SP 2100 on 100/120 mesh GCQ (Supelco., Inc., Bellefonte, PA 16823), N_2 60 ml/min, detector 200°C, injector 210°C, and oven 190°C isothermal.

All solvents were from Burdick and Jackson. One hundred ml of each solvent was evaporated to 1 ml and injected to check for interfering materials. Standard acephate and methamidophos were provided by Chevron Chemical Co., Richmond, California; malathion and malaoxon by American Cyanamid, Princeton, New Jersey.

Recoveries of standard materials from blank leaf

homogenates were: 73 ± 17% methamidophos and 78 ± 15% acephate at 1 ppm; 83 ± 5% methamidophos and 85 ± 6% acephate at 5 ppm for the four technical staff who performed the extractions. Recoveries of malathion and malaoxon were 98 ± 3% and 94 ± 4%, respectively. No varietal differences in recovery of standard materials were noted. Results were not corrected for recoveries.

Statistical methods for treatment of these data have been previously detailed (STAMPER et al. 1979).

RESULTS AND DISCUSSION

No malaoxon was detected in any sample. Disappearance rates of individual pesticides from all leaf varieties were not significantly different (95% level) and data were combined (Table 1). These data show that residues did not accumulate from treatment to treatment. We find that a ln-ln representation of Table 1 data is superior to first-order (see R^2, Table 1).

Malathion disappeared significantly faster than acephate and acephate disappeared at least as rapidly as methamidophos (Table 1). The mist blower application resulted in disappearance at a faster rate than the handgun. This result is consistent with an evaporative disappearance mechanism, as the mist blower yields greater droplet surface area per gram of pesticide (STAMPER et al. 1979, NIGG and STAMPER 1980).

The first-order half-lives of the chemicals in this study compare favorably with previous studies. From the data of Table 1, malathion had a half-life of 5.2 days. NIGG et al. (1979) previously found a half-life of about 8 days in the rind of 4 citrus varieties. The California 'Valencia' orange rind data of BLINN et al. (1959) indicated a half-life of 13.9 days for malathion. In this study, acephate had a half-life of 6.8 days (mist blower) and 12.6 days (handgun). These compare with an 8.9 day half-life on citrus foliage (FITZPATRICK and BOGAN 1980) and 10.3 days and 15 days in citrus rind and pulp of 4 citrus varieties, respectively (NIGG et al. 1979). Studies of acephate in Douglas fir (Pseudotsuga menziesii) found half-lives of 3 days (SETO et al. 1978) and 5 days (RICHMOND et al. 1978). Here, methamidophos had half-lives of 9.5 days (mist blower) and 13.6 days (handgun). These compare with 8.4 days in/on citrus foliage (FITZPATRICK and BOGAN 1980), 10.5 days and 6.1 days in citrus rind and pulp (NIGG et al. 1979), and 3 days (SETO et al. 1978) and 5 days (RICHMOND et al. 1978) in Douglas fir.

TABLE 1

Acephate, methamidophos, and malathion total citrus leaf residues (ppm) (Ft. Lauderdale, FL)

Day post application	21 (1st Treat.)	21 (2nd Treat.)	1 (3rd Treat.)	3	5	7	14	28
Malathion (HG)[a] 1.5 g AI/L	2.3[c] ± 0.6	2.9 ± 0.5	120.0 ± 15.1	73.5 ± 55.2	39.0 ± 34.2	8.8 ± 6.5	3.8 ± 1.9	3.1 ± 1.6
Acephate (MB)[b] 2.5 g AI/L	1.3 ± 0.6	1.2 ± 1.0	25.7 ± 15.3	9.9 ± 8.6	3.7 ± 3.4	4.2 ± 3.0	2.7 ± 1.0	0.9 ± 0.8
Methamidophos	0.2 ± 0.1	0.2 ± 0.1	1.9 ± 0.4	1.2 ± 0.2	0.7 ± 0.4	0.7 ± 0.4	0.5 ± 0.6	0.2 ± 0.2
Acephate (HG) 0.6 g AI/L	7.1 ± 1.1	11.4 ± 1.4	72.5 ± 24.7	82.7 ± 15.1	17.9 ± 6.1	28.2 ± 4.6	22.4 ± 4.7	13.5 ± 3.4
Methamidophos	1.1 ± 0.2	1.0 ± 0.2	5.3 ± 3.2	5.0 ± 1.6	2.3 ± 0.7	3.5 ± 1.9	2.2 ± 1.0	1.2 ± 0.5

Statistical analyses: Least squares fit to $\ln (C_1/C) = A + B \ln (t/t_1)$ with t_1 = 1 day post application; C_1 = 3rd treatment, 1 day post application

	R^2	B	A
Malathion (HG)	0.90 (0.72)[d]	1.3 ± 0.2[e]	-0.4 ± 0.4
Acephate (MB)	0.96 (0.79)	1.0 ± 0.1	-0.0 ± 0.2
Methamidophos (MB)	0.94 (0.90)	0.6 ± 0.1	-0.1 ± 0.2
Acephate (HG)	0.71 (0.55)	0.5 ± 0.2	-0.1 ± 0.4
Methamidophos (HG)	0.81 (0.82)	0.4 ± 0.1	-0.2 ± 0.2

Differences in B	
Malathion vs. acephate	0.7 ± 0.3[f] (HG)
Acephate vs. methamidophos	0.3 ± 0.1 (MB) 0.1 ± 0.2 (HB)
Mist vs. handgun	0.4 ± 0.2 (acephate) 0.2 ± 0.1 (methamidophos)

[a] HG = handgun

[b] MB = mist blower

[c] Each mean represents 4 replicates and 8 subsamples/replicate, i.e., 32 determinations (mean ± S. D.)

[d] () = first-order kinetics

[e] rms error in B from $[(1-R^2)\ \text{var}\ (y)/(n-2)\ \text{var}\ (x)]^{1/2}$

[f] rms error in $B_i - B_j$ from $[(\Delta B_i)^2 + (\Delta B_j)^2]^{1/2}$

TABLE 2

Total citrus leaf residues of acephate and methamidophos (ppm) (Ft. Lauderdale, FL)

	1st Treat. (7 days)	2nd Treat. (1 hr)	7 days	3rd Treat. (1 hr)	7 days	14 days
Mist blower						
1.2 g AI/L						
Methamidophos	0.4[a] ± 0.4	3.8 ± 3.0	0.9 ± 1.1	2.9 ± 2.7	1.6 ± 1.7	trace[b] ± 0.1
Acephate	2.5 ± 3.5	27.5 ± 11.0	5.9 ± 10.1	24.1 ± 12.1	29.8 ± 52.6	0.5 ± 0.5
1.8 g AI/L						
Methamidophos	0.5 ± 0.5	6.5 ± 1.3	3.3 ± 5.6	4.2 ± 3.2	2.8 ± 2.5	0.4 ± 0.4
Acephate	2.1 ± 2.2	49.9 ± 16.2	10.3 ± 6.5	39.7 ± 24.7	66.3 ± 55.9	0.9 ± 0.9
2.4 g AI/L						
Methamidophos	Missing	4.4 ± 2.3	2.8 ± 3.8	4.7 ± 3.3	2.0 ± 2.2	0.5 ± 0.1
Acephate		74.9 ± 10.8	19.5 ± 14.3	83.4 ± 67.1	48.8 ± 53.8	5.8 ± 2.7
3.0 g AI/L						
Methamidophos	0.2 ± 0.1	7.9 ± 2.4	1.1 ± 0.6	5.7 ± 3.2	2.3 ± 1.9	0.3 ± 0.2
Acephate	0.8 ± 0.8	37.5 ± 9.6	13.3 ± 13.6	88.6 ± 28.0	13.2 ± 15.7	1.7 ± 1.2
Handgun						
0.6 g AI/L						
Methamidophos	0.5 ± 0.2	5.2 ± 3.1	0.7 ± 0.3	6.6 ± 3.5	1.4 ± 0.4	Missing
Acephate	1.3 ± 1.2	65.1 ± 47.2	4.8 ± 2.5	78.7 ± 14.9	11.7 ± 7.7	
1.2 g AI/L						
Methamidophos	0.7 ± 0.3	5.9 ± 3.8	2.8 ± 1.2	5.9 ± 2.2	1.5 ± 0.4	Missing
Acephate	4.7 ± 0.9	141.7 ± 61.6	27.3 ± 18.4	178.3 ± 76.0	24.5 ± 7.2	

[a]Each mean = 32 determinations (mean ± S. D.)

[b]Trace = <0.01 ppm

All check samples were blank

Results of the rate experiment in Table 2 indicate that the handgun application gave better coverage, as the level of residue and rates were better correlated (see 2nd and 3rd treatment, 1 hr, Table 2). Again, there was no cumulative buildup of residue so that this treatment regimen is judged not dangerous to homeowners in contact with citrus foliage 7 days or more after application.

Inasmuch as the malathion and acephate were applied at the same time, the differences in disappearance rates observed could not have been due to different environmental conditions but rather to the chemistry of each compound. These differences in the behavior of applied pesticides could probably be explained by understanding the physicochemical parameters governing residue loss and environmental effects on these parameters.

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