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Weather-Dependent Residue Behavior of Malathion in Florida Citrus Varieties[1]

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Malathion (0,0-dimethyl S-[1,2-di(ethoxycarbonyl)ethyl] phosphorodithioate) is a recommended insecticide for the control of mealybugs, whitefly, and scale insects in commercial citrus. In 1976, malathion was used in an intensive eradication program for the citrus blackfly, Aleurocanthus woglumi Ashby (Homoptera: Aleyrodidae) in Broward, Dade, and Palm Beach Counties, Florida (REINERT 1976). In this program, malathion was applied three consecutive times at 3-week intervals to homeowner citrus and the homeowners were advised to wait 7 days after each treatment before consuming the treated fruit. No data was available on the environmental behavior of malathion (tolerance = 8 ppm) and its metabolite malaoxon (0,0-dimethyl S-[1,2-di(ethoxycarbonyl)ethyl] phosphorothiolate) in fruit rind and pulp of citrus varieties.

The purposes of this study were to determine the decay rate of malathion and malaoxon on/in common Florida citrus varieties and to determine if the decay rate could be related to Florida weather conditions.

MATERIALS AND METHODS

A completely randomized design with four replications per treatment including four unsprayed check blocks was utilized in this study. Each experimental plot consisted of one city block. Within each plot, three to ten trees of each citrus variety were used as source trees for an eight fruit sample of grapefruit, lemon, tangerine, Temple, and Valencia varieties on each sample date. Malathion was applied at 1.5 g AI/liter with a hydraulic sprayer at 29 kg/cm^2 (ca 38 liters/tree). Three applications were made at 3-week intervals and samples were taken after the third application.

Samples were taken on days 1, 3, 5, 7, 14, and 21, frozen at -20°C and transported frozen to Lake Alfred for analysis. Samples were stored approximately 1 month at -10°C prior to analysis. Dual samples were taken on days 1, 3, 5, and 7. One set was

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washed in a weak soap solution (liquid Ivory® [2]) to simulate homeowner washing.

For analysis, fruit were thawed, the rind removed from one half of each fruit, and the pulp sliced into a Waring blender. The pulp was blended for 3 min and a 10-g subsample removed for analysis. The rind was diced, blended for 3 min, and a 10-g subsample removed for analysis. The 10-g subsample of either rind or pulp was homogenized in 100 ml of methylene chloride and 15 g of sodium sulfate for 5 min in a Sorvall blending cup in an ice bath. The blender cup top was loosened upon removal and particulate matter allowed to settle for 1 min. A 20 ml aliquot was taken, evaporated to dryness at 40° under N_2 and transferred to brown glass bottles over sodium sulfate in 10 ml of benzene. Recoveries of malathion and malaoxon were 98 $\pm$ 3% and 94 $\pm$ 4%, respectively, from fortified pulp and rind homogenates. No varietal differences in recovery of standard materials were observed. Extractions were stored at -20°C prior to GLC analysis.

GLC analyses for malathion and malaoxon were performed on a Tracor 550 GLC with phosphorus flame photometric detection. Operating conditions were: 1.8 m x 2 mm ID glass column packed with 5% SP 2100 on 100/120 mesh GCQ (Supelco, Inc., Bellefonte, PA 16823), N_2 60 ml/min, detector 200°, injection port 210°, oven 190° isothermal. Quantification was by comparison with the peak height of standard materials chromatographed at the same attenuation. Standards were chromatographed every fourth injection. All injections were 5 µl. Solvents used were Burdick and Jackson. 100 ml of each solvent was evaported to 1 ml and 5 µl chromatographed to check for interfering materials. Standard malathion and malaoxon were provided by American Cyanamid Co., Princeton, NJ. The first-order time-based decay model used was

$$\ln\left(\frac{y}{y_o}\right) = -\lambda t \qquad (1)$$

and the first-order time-weather based decay model was

$$\ln\left(\frac{y}{y_o}\right) = a_o\int dt + a_1\int x_1 dt + \ldots.. + a_n\int x_n dt \qquad (2)$$

where y_o = initial pesticide residue, a = coefficient, $x_1,\ldots,x_n$ = environmental variables and t = ordinary time. Other statistics and computer programs have been described (NIGG et al. 1977, 1978a, b).

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[2]Mention of a trademark name does not constitute a guarantee or warranty of the product by the University of Florida and does not imply its approval to the exclusion of other products that may also be suitable.

RESULTS AND DISCUSSION

Malaoxon was not found in any sample. Only uninterpretable traces of malathion were detected in pulp. This lack of malathion in citrus pulp agrees with the results of BLINN et al. (1959). There was no difference ($P > 0.05$) between washed and unwashed fruit rind residues and these data were combined for statistical purposes. The lack of a measurable difference between these paired samples could have been due to sample handling.

The disappearance of malathion on and in the rind of each variety tended to show exponential decay (a first-order process) (Figure 1), except for lemon which showed a poor correlation of -.50 (Table I). The half-life of malathion was about 8 days for all varieties (Table I). This agrees with half-life of 7 days for malathion degradation behavior on and in California Valencia orange calculated from 1-14 day post application data ($r = -.98$) (BLINN et al. 1959). They reported a persistence behavior half-life of 32 days for malathion calculated from 21-62 day post-application data. Using BLINN et al. (1959) overall 1-62 day data, a 13.9 day half-life is obtained ($r = -.92$) which would indicate that malathion is about one half as persistent in Florida fruit compared to California fruit.

Malathion residues reached a level of 8 ppm or less in the rind of Florida citrus within 5 days after application during the relatively dry, cool Florida winter (Nov-Jan 1976-77) (avg. temp in Ft. Lauderdale: Nov '76, 21.5°C; Dec '76, 19.6°C; Jan '77, 15.5°C). Previous organophosphate residue data indicate that malathion residue levels <8 ppm would be reached in about 3 days for rind and less than 12 hours for pulp under relatively wet summer conditions (NIGG et al. 1977, 1978b).

Time-based half-life differences appear to be related to differences in weather (NIGG et al. 1977, 1978a, 1978b). The use of time plus weather is more accurate for modeling malathion residue decay compared to time alone (Tables I, II). For example, the correlation of the lemon data is significantly improved from an r of -.50 (time alone) to -.88 by modifying the first-order model base to include weather (Table I). As noted by NIGG et al. (1978a), a variety of weather sets is necessary to demonstrate significant differences between a time model and a time-weather model of first-order pesticide disappearance. Previous weather models for the disappearance of pesticides from leaf surfaces were highly accurate (NIGG et al. 1977, 1978b), and this approach has been suggested for preharvest intervals in food commodities (NIGG et al. 1978a). These fruit rind data for malathion indicate that the use of physical factors to predict the residue level on food-stuffs is a viable scientific approach.

TABLE I

Malathion first-order residue behavior in Florida citrus varieties based on time alone and time plus weather.

	% Variation explained (r^2 x 100)[a]		
Variety	Time alone	Time + HDD + Cum rainfall	t 1/2 (days)
Temple	78*	86**	7.7
Grapefruit	81**	93**	7.7
Valencia	96**	98**	6.9
Lemon	25	78*	8.7[b]
Tangerine	94**	98**	7.7
$\bar{X}$			7.7

[a] r = correlation to equation (1) for time alone and to equation (2) for time and weather.

[b] t 1/2 based on 7, 14 + 21 day data.

*$P < 0.05$ (MORRISON 1967).

**$P < 0.01$.

TABLE II

Variables used as base for first-order model of malathion residue disappearance.

Day post treatment	1	3	5	7	14	21
Variable						
Cum. time (days)	1	3	5	7	14	21
Cum. heating-degree days	15	30	41	59	157	294
Cum. rainfall (inches)	.63	.64	.64	.64	.73	.82

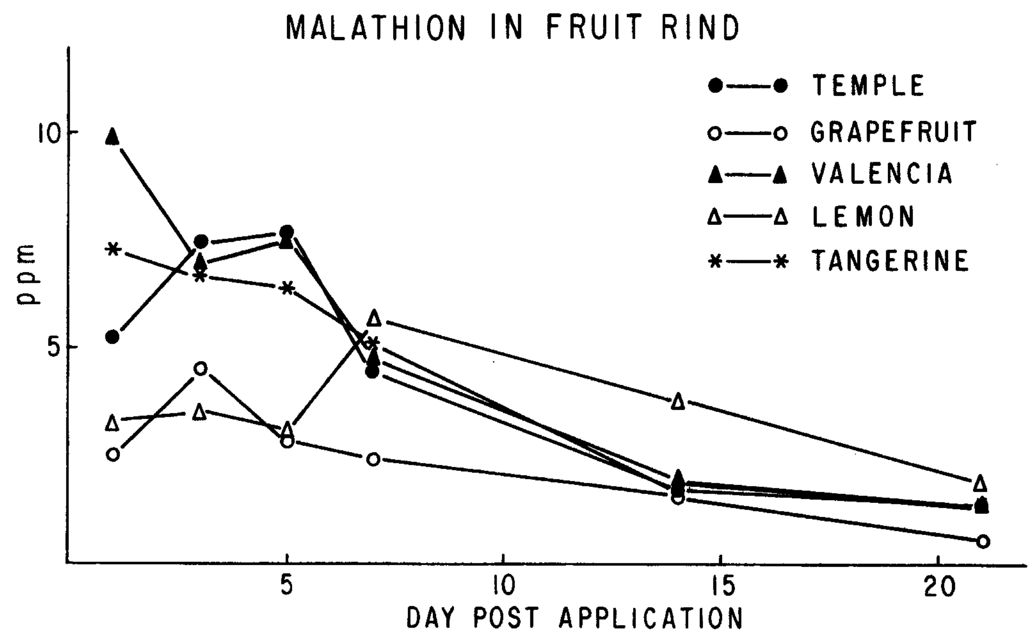

Figure 1. Malathion disappearance in the rind of Florida citrus varieties. Points for days 1 to 7 are averages of eight determinations while 14 and 21 day points are averages of four determinations.

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