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Residues of Malathion and Methidathion on and in Fruit After Dilute and Low-Volume Spraying of Orange Trees

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Because of high labor costs and the use of highly toxic insecticides, fully mechanized spraying of citrus trees has been developed and used extensively in California and other citrus producing areas. The most effective mechanical sprayers have been ground units. In general these units have been used to apply dilute sprays ranging in gallonage from several hundred to over 3500 gallons of dilute spray/acre, depending primarily on tree size, tree density, nature of the pest control problem, and material being used. The current trend has been toward the increasing use of low-volume applications wherein much more concentrated sprays are applied at rates of about 100 gal of spray/acre. Legally permissible residue levels for fruit have been established in the past on the basis of dilute insecticide applications. Thus, there is a need to examine residue levels in and on fruit after low-volume applications to determine if fruit harvested after such applications will still meet legal requirements or whether new post-application waiting intervals need to be considered.

Reported here are residue data for malathion and methidathion on and in oranges after low-volume and dilute applications to orange trees at typical rates in California.

MATERIALS AND METHODS

Application. Applications were made on October 17, 1977 to Valencia orange trees on the University of California Citrus Research Center, Riverside, CA. The tree planting was 18 (in-row) x 21 ft. Each plot consisted of 24 trees (6 x 4) and three replicate plots were used for each application.

Treatments were made using malathion 8-lb active ingredient (AI)/gal and Supracide 2-lb AI/gal emulsifiable concentrates. Low-volume sprays were made with a Kinkelder machine equipped with an air tower. The vehicle speed was 1.5 mph and the spray was delivered at 3.2 gal/min and 100 gal/acre. Dilute treatments were made with an oscillating boom sprayer. The vehicle speed was 1.4 mph and the boom making 66 oscillations/min delivered 47 gal/min and 1550 gal/acre. Application rates for both dilute and low-volume sprays were 9.3 lb AI/acre for malathion and 3.9 lb AI/acre for Supracide.

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Sampling. At each sampling date four fruits, one from each quadrant of the tree, were picked from each of 8 trees into paper bags. Thus, a 32-fruit sample was obtained from each of the three replicate plots. The rind was removed from the unwashed fruit and chopped in a Hobart food chopper and two 100-g subsamples frozen for later processing. When pulp (edible fruit) samples were taken, the fruits were first washed and dried and then peeled. Core samples of the pulp were removed and 100-g subsamples were frozen for later processing. Both the total sample weight and the total rind weight were determined for each sample so that the final residue data could be expressed as ppm whole fruit.

Extraction and cleanup procedure. A 100 g sample of chopped rind or pulp was macerated with 300 mL of acetone for 5 min in a Waring blender jar. The extract was filtered through a Büchner funnel using a gentle vacuum. A 50 mL aliquot of the extract was placed in a 125-mL separatory funnel. Then, 50 mL of benzene (for methidathion) or hexane (for malathion) was added and the separatory funnel was gently shaken for 30 s. The lower layer was discarded and the upper layer was passed through a funnel containing Na_2SO_4 into a flask. The Na_2SO_4 and funnel were rinsed with 25 mL of fresh solvent. The solvent was removed. The residue was dissolved in 5 mL of hexane and the solution was transferred to a 330 x 22 mm ID column (Kontes K-420600) filled with 10 g of Florisil (used without additional activation) and topped with 1 cm of Na_2SO_4. The flask was rinsed with a second 5 mL portion of hexane and the rinse was added to the column. The column was eluted with 150 mL of 25% acetone in hexane for methidathion or with 100 mL of 5% acetone in hexane for malathion. The solvent was removed from the eluate. The residue was dissolved in acetone for GLC analysis. Calculations assumed that the total acetone extract volume was 380 mL (300 mL acetone plus 80 mL of water from 100 g of substrate).

The above procedure was initially developed in anticipation of encountering samples containing low residue levels and hence requiring sample cleanup prior to analysis. Since actual field samples contained relatively high residue levels and oxygen analogues of the parent insecticide were not sought, Florisil column cleanup was unnecessary and this step was omitted. Since the overall methodology may be useful to residue analysts, the entire procedure is given.

Method validation. Chopped untreated rind samples were each fortified in the blender jar prior to the addition of the acetone and the procedural recoveries determined. For methidathion, average recoveries for three replicate samples fortified at 0.10, 1.0, and 10 ppm were 97±5, 99±4, and 100±3%, respectively. For methidathion oxygen analog or "oxon", recoveries for samples fortified at 0.05, 0.10, and 1.0 ppm were 91±5, 84±7, and 86±4%, respectively; interferences did not permit accurate quantitation at the 0.01 ppm level. For malathion, recoveries for samples fortified at 0.10, 1.0, and 10 ppm were 89±15, 94±3, and 91±9%, respectively; use of benzene instead of hexane gave 98±4, 99±5, and 97±10%, respectively, but a Florisil column cleanup could generally not be omitted.

All further tests were conducted with laboratory-treated fruit. Oranges were treated by individually immersing each whole fruit for about 10 s in a solution of 1.0 mL of Supracide 2 lb/gal EC and 38 mg of methidathion oxon or 0.6 mL of malathion 8 lb/gal EC in 800 mL of water. The methidathion and malathion concentrations were equivalent to a tank spray mixture of 1.0 pt 2EC/100 gal and 0.6 pt 8EC/100 gal, respectively. Fruits were air-dried after treatment for 1 day before processing.

Some fruits were water-washed prior to peeling and processed to determine if residues were on or in the rind. Water-washing decreased methidathion residues from 3.1 ± 0.2 to 2.1 ± 0.3 ppm or about 32%, decreased oxon residues from 0.10 ± 0.01 to 0.06 ± 0.02 ppm or about 40%, and decreased malathion residues from 1.8 ± 0.2 to 1.2 ± 0.1 ppm or about 33%.

To estimate the extraction efficiency of the acetone blending procedure, the pulp remaining after filtering the acetone rind macerate was Soxhlet-extracted using 1:9 methanol:chloroform. The Soxhlet extraction (no thimble, only glass wool) was conducted for 2 h and then again for another 2 h with fresh solvent. Residues obtained for the second 2 h extractions were always negligible (<0.01 ppm). Using rind from unwashed fruit, the acetone blending procedure yielded 3.1 ± 0.2 ppm methidathion and 0.10 ± 0.01 ppm oxon. The recoveries from the Soxhlet extraction was an additional 0.49 ± 0.06 ppm methidathion and <0.01 ppm oxon. Thus, extraction efficiency was about 86% for methidathion and over 90% for the oxon. Using rind from washed and unwashed fruit, acetone blending gave residues of 1.1 ± 0.2 and 1.8 ± 0.2 ppm, respectively, for malathion. The recoveries from the Soxhlet extraction was an additional 0.17 ± 0.02 and 0.29 ± 0.03 ppm, respectively. Thus, extraction efficiency was about 85% in both cases. No corrections for extraction efficiency or other possible losses were made to the data for actual field samples.

Fruit samples brought in from the field often cannot be processed immediately. Therefore, laboratory-treated fruits were stored at 8°C for 2 and 7 days to determine if residue levels would be adversely affected. After 0, 2, and 7 days of storage, methidathion residues were 3.1 ± 0.2, 2.9 ± 0.2 and 2.5 ± 0.1 ppm, respectively, or a decline of 6 and 19% after 2 and 7 days, respectively, of storage. The corresponding methidathion oxon residues were 0.10 ± 0.01, 0.11, and 0.08 ± 0.01 ppm, respectively, or a decline of 0 and 20% after 2 and 7 days, respectively, of storage, The corresponding malathion residues were 1.7 ± 0.1, 1.5 ± 0.1, and 1.1 ± 0.0 ppm, respectively, or a decline of 12 and 35% after 2 and 7 days, respectively, of storage. Thus, fresh fruit samples should not be stored beyond 2 days.

Rind was chopped in a Hobart food chopper and 100 g subsamples were stored for 14 and 21 days in a freezer to determine if residue levels would be affected. Residues after 0, 14, and 21 days of storage were for methidathion 3.1 ± 0.2, 3.0 ± 0.3, and 3.1 ± 0.1

ppm, respectively, for the oxon 0.10, 0.11, and 0.11 ppm, respectively, and for malathion 1.7 ± 0.1, 1.7 ± 0.0, and 1.5 ± 0.1 ppm, respectively. Residues are relatively stable under frozen storage of substrate. Thus, if fruits cannot be peeled, chopped, and extracted within a day or two, they should be peeled, chopped, and frozen.

Finally, acetone extracts of orange rind were stored for 14 and 21 days. Residues after 0, 14, and 21 days of storage were for methidathion 3.1 ± 0.2, 3.4 ± 0.3, and 3.3 ± 0.3 ppm, respectively, for the oxon 0.10, 0.11, and 0.11 ppm, respectively, and for malathion 1.7 ± 0.1, 1.8 ± 0.1, and 1.5 ± 0.1 ppm, respectively. Thus, no problem with short-term storage of extracts was evident.

RESULTS AND DISCUSSION

Figures 1 and 2 show the whole fruit residues found on and in mature, unwashed citrus fruit picked from trees that were treated using a dilute application of 1550 gal/acre or a low-volume application of 100 gal/acre. At both gallonage levels malathion was applied at a rate of 9.3 lb AI/acre and methidathion was applied at a rate of 3.9 lb AI/acre. All residue values were below the tolerance level of 8 ppm malathion and 2 ppm methidathion (FEDERAL REGISTER 1975).

BLINN et al. (1959) reported a "degradation" half-life of 7 days and a "persistence" half-life of 32 days for malathion. In Figure 1, the "degradation" half-life was 5.5 days and the "persistence" half-lives were 38 (low-volume treatment) and 50 (dilute treatment) days for malathion. In Figure 2, the "degradation" half-life was about 30 days for methidathion.

Both Figures 1 and 2 show less residue variation for dilute spray treatments. This is consistent with a more uniform spray coverage achieved by using dilute sprays. Residue levels after spraying are governed by the initial amount of pesticide deposited on the fruit.

Samples of pulp (edible portion of the fruit after rind removal) were taken 7 and 30 days post-application from the low-volume treated plots. Malathion residues for the three plots were 0.01, 0.03, and 0.02 ppm after 7 days and were all less than 0.01 ppm after 30 days. Methidathion residues at 7 and 30 days were all less than 0.01 ppm. Thus, essentially all residues are on or in the rind.

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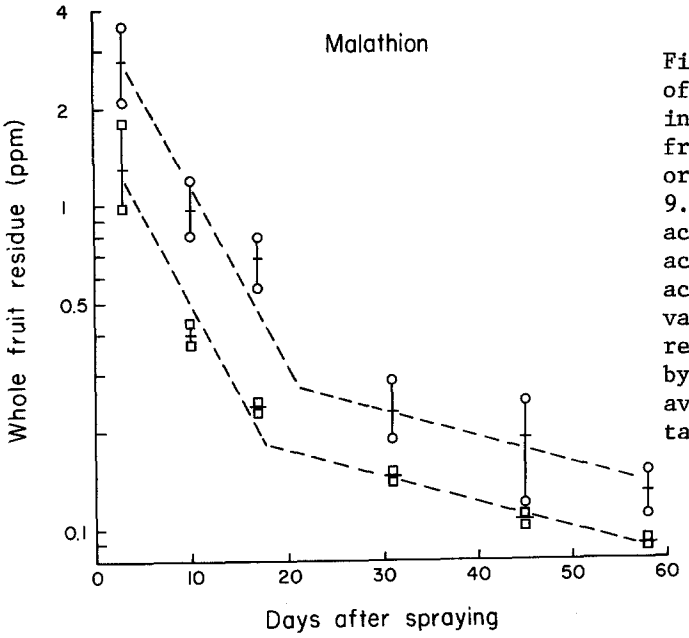

Figure 1. Residues of malathion on and in mature whole fruit after spraying orange trees with 9.3 lb AI malathion/acre using 1550 gal/acre (□) or 100 gal/acre (○). Ranges of values for three plot replicates are shown by vertical lines and averages by horizontal dashes.

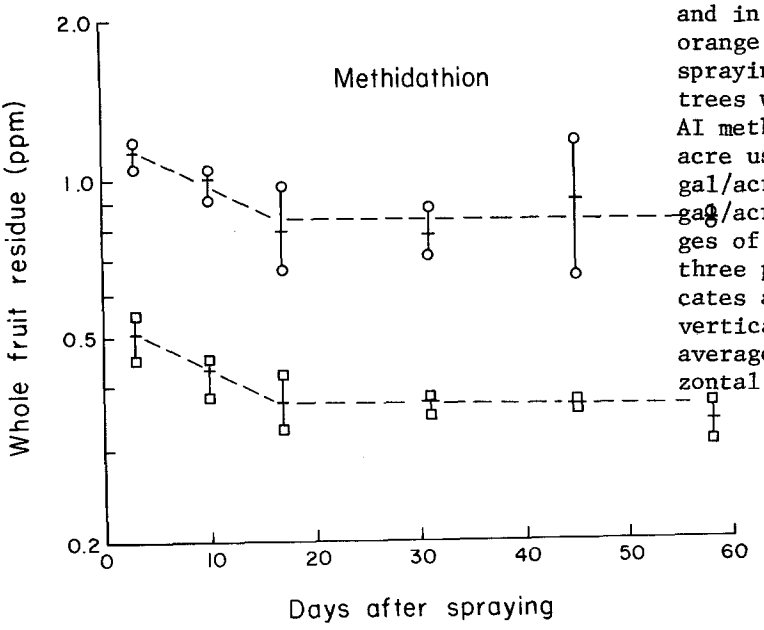

Figure 2. Residues of methidathion on and in mature whole orange fruit after spraying orange trees with 3.9 lb AI methidathion/acre using 1550 gal/acre (□) or 100 gal/acre (○). Ranges of values for three plot replicates are shown by vertical lines and averages by horizontal dashes.