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Foliar Washoff of Oil-Applied Malathion and Permethrin as a Function of Time after Application

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Understanding pesticide foliar washoff is important in environmental modeling and in pest management. Malathion [diethyl (dimethoxyphosphinothioyl)thiobutanedioate] and permethrin [(3-phenoxyphenyl)-methyl (1*R*,*S*)-*cis*,*trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] were applied in oil to mature cotton plants with an ultra-low-volume (ULV) applicator. Simulated rainfall (51 mm in 1 h) was applied to the plants at times ranging from 2 to 146 h after insecticide application to determine washoff characteristics. Residues appeared to become increasingly resistant to washoff with time. Most of the washoff occurred early in each rainfall event. ULV-oil application in this study did not appear to improve insecticide rainfastness compared to a conventional application in a previous study.

INTRODUCTION

It has long been known that rainfall can sometimes reduce the efficacy of field-applied pesticides, especially foliar-applied pesticides (Gaines and Mistric, 1951; Hopkins et al., 1952; Weaver et al., 1946). The amount of elapsed time between foliar pesticide application and the initial rainfall event can be critical to pesticide persistence and efficacy (Bryson, 1987; Pick et al., 1984; McDowell et al., 1985). An understanding of the effects of rainfall on pesticide washoff is necessary for developing (a) models to predict the movement of foliar-applied pesticides, (b) integrated management strategies that permit acceptable crop yields and reduce or alleviate environmental pollution, (c) models to predict the effect of pesticides on pest populations, and (d) guidelines for respraying for pest control following natural rainfall or overhead irrigation.

Oil carriers for pesticide application have been reported to increase rainfastness of pesticides on foliage (Wheeler et al., 1967; Nemac and Adkisson, 1969; Mayo, 1984; Omar and Matthews, 1990). However, Hatfield et al. (1983) found a slight decrease in rainfastness for oil-applied permethrin [(3-phenoxyphenyl)methyl (1*R*,*S*)-*cis*,*trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate], while Baker and Shiers (1989) found no difference in washoff of water-applied and water–oil-applied herbicides from corn residue.

This paper reports the washoff of ultra-low-volume (ULV) oil applied malathion [diethyl (dimethoxyphosphinothioyl)thiobutanedioate] and permethrin from cotton foliage as functions of time between application and initial rainfall. Malathion (MAL) and permethrin (PER) have been used for cotton insect control in the mid South.

MATERIALS AND METHODS

The study was conducted on the S. F. Johnson farm near Oxford, MS, in August and early September of 1984. MAL and PER were tank-mixed with once-refined soybean oil (7.4 L ha^{-1}) and applied at respective rates of 0.986 and 0.112 kg of active ingredient ha^{-1} to cotton plants (1.25-m mean height, 0.97-m-wide rows, 5.0 ± 0.7 stalks m^{-1} of row, 100% canopy cover) by an 8-row sprayer equipped with a rotary-atomizer controlled-droplet-applicator (CDA) for each row. The CDAs were set at 0.38 m above the mean canopy surface and adjusted to deliver droplets with volume medium diameters of 135 μm (based on CDA product information tables). Separate areas, 8 rows wide and about 50 m long, were sprayed for each of three replicates. Replicate sprayings were made 1 week apart. Each pesticide application was made at 10:00 a.m. (CDT), after the dew had dried. At insecticide application times the wind speed was 1.43 ± 0.15 m s^{-1} and the air temperature at canopy height was 30.0 ± 2.1 °C. At night and prior to potential natural rainfall events, portable shelters (lightweight tarps stretched over wheel-mounted metal frames) were placed over the rainfall plots and the adjacent plants that were used to determine insecticide load on plants.

A multiple-intensity rainfall simulator (Meyer and Harmon, 1979) was used to apply 51 mm of rain in 1 h to the cotton plots 2, 6, 29, 50, 98, or 146 h after the insecticides were applied. A new test plot (not previously rained on) was used for each simulated rainfall event. This nozzle-type simulator applies rain with drop sizes, velocities, and impact energies very similar to those of natural rainfall in the mid South. Natural rainfall events of 51 mm h^{-1} for 1-h duration have a return period of less than 2 years at Meridian, MS (U.S. Department of Commerce, 1955).

Washoff from the plant canopy was sampled throughout each rainstorm by the use of a collection pan placed on the soil surface between two rows and under the canopy to intercept and route the flow into 1-L glass jars. The collection pan (86.4 cm wide by 244 cm long by 5 cm deep) was made of aluminum and had a drain pipe at one end. About 15 min before rainfall initiation, the pan was carefully placed under the canopy with the pan's upper end raised to create a 4% slope. A small pit was dug at the pan's lower (drain) end to facilitate washoff collection. The pan collections were 89.6 ± 1.2, 89.5 ± 1.9, 85.9 ± 3.9, 89.0 ± 0.2, 91.4 ± 2.8, and 88.6 ± 1.7% of the applied rain, respectively, at the 2-, 6-, 29-, 50-, 98-, and 146-h sampling times. The uncollected rain was assumed to be lost through stem flow, wind drift, evaporation, and plant hold-up. Insecticide washoff amounts were not corrected for sample collection efficiency. Instantaneous washoff samples were collected according to the protocol listed in Table I. After washoff collection, each sample was weighed to measure water discharge, 100 mL of hexane was added, and the samples were stored at 4 °C. Insecticides were extracted from the samples in the laboratory by mixing (magnetic stirrer) the hexane and water for 1 h. Extraction efficiencies were 96 ± 3% for MAL and 99 ± 2% for PER as determined from laboratory studies with fortified water samples.

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Table I. Washoff Sample Collection Protocol for a 60-Min Simulated Rainstorm

storm time,[a] min	no. of samples collected	individual sample collection time, min	interval between individual sample collections, min
0.00–2.00	4	0.25	0.25
2.00–3.50	2	0.25	0.50
3.50–7.25	3	0.25	1.00
7.25–14.0	3	0.25	2.00
14.0–27.0	4	0.25	3.00
24.0–44.0	4	0.25	4.00
44.–60.0	4	0.25	5.00

[a] Simulated rainfall was applied at a rate of 51 mm h^{-1} for 60 min. Collection of sample 1 began the instant washoff flowed from the sample collection pan and continued for 0.25 min. Following a 0.25-min delay, collection of sample 2 began and lasted for 0.25 min, followed by a 0.25-min delay. This sample collection frequency continued until sample 5 was collected, at which time there was a 0.50-min delay before sample 6 was collected. The same sampling pattern was continued throughout the 60-min storm with the delay time between sample collections becoming progressively longer (1 min following sample 7, 2 min following sample 10, 3 min following sample 13, 4 min following sample 17, and 5 min following sample 21). A total of 24 samples (0.25-min collection time each) were collected during the 60-min rainstorm.

Cotton plants adjacent to the rainfall plots were collected immediately after insecticide spraying and just before each simulated rainstorm to determine insecticide load on the plants as a function of time. The plants were severed at the soil surface along a 1.5-m length of a single row and placed in a 114-L steel drum (prerinsed with methanol). Four separate rows were sampled for each simulated storm (i.e., quadruplet samples for each rainstorm for each replicate). Methanol was immediately added to each drum and the drum heads were replaced to prevent solvent–insecticide evaporation. Care was taken to ensure that the plant material was completely covered with methanol. After the plants had soaked in the methanol at ambient temperatures for a minimum of 4 h, the methanol was thoroughly mixed and a 125-mL aliquot was removed and stored in an amber bottle at 4 °C until analysis. Extraction efficiencies were 94 ± 4% for MAL and 96 ± 3% for PER as determined from laboratory studies with fortified plant samples.

The extracts were adjusted to volumes appropriate for gas chromatographic analysis [the hexane extracts (water samples) were adjusted with additional hexane; the methanol extracts (plant samples) were adjusted with benzene]. The gas chromatograph was equipped with a ^{63}Ni electron-capture detector, glass columns (1.8 m long by 2 mm i.d.) packed with 50 g kg^{-1} (5%) OV-1 (MAL) or 30 g kg^{-1} (3%) SP-2401 (PER) on 100/120 Supelcoport, and an electronic integrator to compare retention times and areas of sample peaks to standard peaks. General operating conditions were as follows: carrier gas, filter-dried N_2, 99.995% minimum purity; flow rate, 90 mL min^{-1}; inlet temperature, 240 °C; detector temperature, 350 °C; column oven temperature, 170 (MAL) or 210 °C (PER). Under these conditions the lower limits of detection were 0.01 and 0.2 g ha^{-1}, respectively, for MAL and PER on cotton plants and 0.0001 mg L^{-1} for both MAL and PER in water.

Storm insecticide losses and storm runoff amounts were calculated by integrating the area under the insecticide and washoff discharge rate curves.

RESULTS AND DISCUSSION

Insecticide loads on the cotton plants and the amounts washed from the plants when the initial rainfall occurred at various times after application are given in Table II. Respective MAL and PER plant loads immediately after application were 55 ± 10 and 57 ± 12% of the nominally applied amounts. The ULV oil application did not appear to substantially improve insecticide interception by target plants compared to literature reports for conventional (hydraulic nozzle, water carrier) emulsifiable concentrate (ec) applications for insecticides in general (Willis and McDowell, 1987). The MAL load on the plants decreased logarithmically with time (Table III). The PER plant load data were scattered; the best-fit curve was linear, but since the r^2 was only 0.33, strict conclusions should be avoided. The DT_{50} for MAL was smaller than most reported $t_{0.5}$ values (a mean value of 2.2 days for conventional ec applications; Willis and McDowell, 1987). The DT_{50} for PER was larger than reported $t_{0.5}$ values for conventional ec applications to cotton in Arizona [G. W. Ware and associates as summarized in Willis and McDowell (1987)]. Since DT_{50} values and $t_{0.5}$ values are not the same thing, the contrasts given above are presented as nonrigorous comparisons of foliar disappearance time estimates based on application methodology.

The mean amounts of MAL and PER washed from the plants decreased with increasing time between application and initial rainfall (Table II) and were, in general, related to the mean insecticide loads on the plants. On the average, about 60 and 49%, respectively, of the MAL and PER plant loads were washed from the plants. However, the fractions washed from the plants decreased with time after 50 h (Table II), which suggests that the insecticides became progressively harder to wash from the plants with time; i.e., the fraction of the plant load washed from the plants became smaller with time. The decrease in mean fractions of MAL and PER washed from the plants with time is shown in Figure 1.

On the basis of the equations in Table III and Figure 1, about 48% of the original MAL plant load would still be on the foliage 6 h after application, and 51 mm of rain 6 h after application would wash about 64% of the plant load (i.e., about 31% of the original MAL plant load) from the plants to the soil surface. Similar calculations show that about 24, 19, 12, and 6% of the original MAL plant loads would be washed from the plants by 51 mm of rain at 12, 25, 48, and 96 h after application. Analogous calculations for PER show that 51 mm of rain would wash about 61, 58, 52, 41, and 24% of the original PER plant loads from the plants, respectively, at 6, 12, 24, 48, and 96 h after application.

Cumulative fractional MAL and PER losses in plant washoff as functions of cumulative rain applied to different plots 2, 6, 29, 50, 98, or 146 h after application are presented in Figures 2 and 3, respectively. Most of the washoff loss occurred early in the washoff event, especially for MAL. The steepness of the initial slope segments decreased with increasing time intervals between insecticide application and rainfall. This trend suggests a decrease in the fraction that is easily washed from the plants with increasing time. Some insecticides begin to penetrate leaf surfaces soon after application, e.g., permethrin applied to cotton with either water or oil carriers (Southwick et al., 1983a,b). Leaf penetration would reduce the amount of easily removable pesticide available for washoff.

On the basis of the equations in Figures 2 and 3 for the fractional amounts washed from the plants for all times combined, the first 4.8 and 6.5 mm of rain removed 50% of the MAL and PER washed from the plants. In an earlier study under similar conditions, 50% of the conventional ec applied PER washed from the plants 2 h after application was removed by 1.2 mm of rain (Willis et al., 1986). In the current study, 50% of the ULV oil applied PER washed from the plants 2 h after application was removed by 0.9 mm of rain (calculated from data used to develop the 2-h curve in Figure 3). Thus, the use of oil as the insecticide carrier did not appear to improve rainfastness for PER.

Table II. Malathion and Permethrin Washed from Cotton Plants at Various Times following Insecticide Application

		insecticide		
insecticide[a]	time after application, h	load on[b,c] plants, mg m^{-2}	washed off, mg m^{-2}	fraction[c,d] of load washed off, %
MAL	0	54.2 ± 9.86		
	2	29.3 ± 2.65	17.1 ± 3.58	59 a,b
	6	28.7 ± 4.51	17.0 ± 3.49	62 a,b
	29	16.7 ± 1.56	11.7 ± 2.40	70 a
	50	12.3 ± 2.98	7.07 ± 2.15	58 a,b
	98	5.87 ± 1.15	2.27 ± 0.12	39 b
	146	4.40 ± 2.23	1.30 ± 0.30	34 b
PER	0	6.38 ± 1.34		
	2	6.27 ± 1.80	4.17 ± 0.31	70 a
	6	7.30 ± 3.00	3.47 ± 0.42	55 a,b
	29	6.53 ± 3.70	3.17 ± 0.47	59 a,b
	50	5.37 ± 0.81	2.67 ± 0.91	52 a,b
	98	3.73 ± 1.32	0.93 ± 0.23	27 b
	146	3.23 ± 0.90	0.80 ± 0.26	25 b

[a] MAL, malathion; PER, permethrin. [b] Load m^{-2} of land surface at the time rainfall (51 mm) was initiated. [c] Mean of three replications ± 1 standard deviation. [d] Values of % washed off values followed by a common letter within insecticide groups are not significantly different ($P = 0.05$). MAL LSD = 0.287; PER LSD = 0.388.

Table III. Equations Describing Fractional Insecticide Loads on Cotton Plants as a Function of Time after Application

insecticide	equation[a]	r^2	DT_{50},[b] h
MAL	FPL = 0.706 − 0.124 ln time	0.95	7.5
PER	FPL = 0.990 − 0.0034 time	0.33	144

[a] Developed from all measured values from triplicate plots: FPL, fraction of initial plant load remaining, time, elapsed time after insecticide application. [b] DT_{50}, 50% disappearance time, i.e., time required for 50% of the initial pesticide load on the plants to disappear.

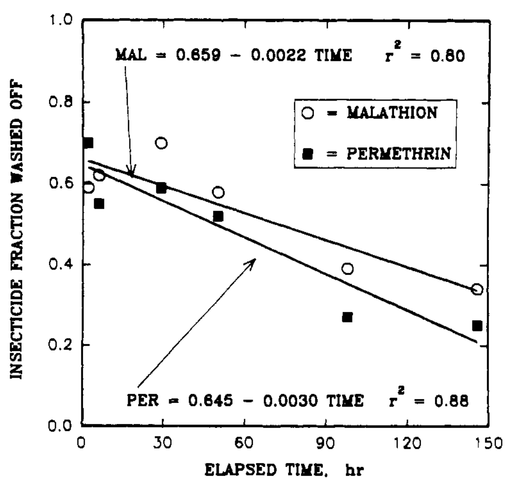

Figure 1. Fractions of malathion and permethrin plant loads washed from cotton plants when initial rainfall occurred at various times after insecticide application.

SUMMARY AND CONCLUSIONS

Malathion (MAL) and permethrin (PER) were ULV applied in oil by rotary-atomizer controlled-droplet applicators to mature cotton plants. The MAL load decreased logarithmically with time after application; the PER load decrease values were scattered. DT_{50}s for MAL and PER were 7.5 and 144 h, respectively. Initial rainfall (simulated, 51 mm in 1 h) was applied to the plants at times ranging from 2 to 146 h after insecticide application to determine washoff characteristics for both compounds. Residues appeared to become increasingly resistant to washoff with increased elapsed time between insecticide application and rainfall. The mean fraction of the MAL and PER plant loads washed from the plants decreased linearly as time between pesticide application and rainfall increased. Of the amounts of MAL and PER washed from the plants, 50% was removed by the first 4.8 and 6.5 mm of rain, respectively. Under the conditions of this study, the use of ULV oil application techniques did not appear to increase insecticide interception by plants or improve rainfastness compared to conventional ec applications in similar studies.

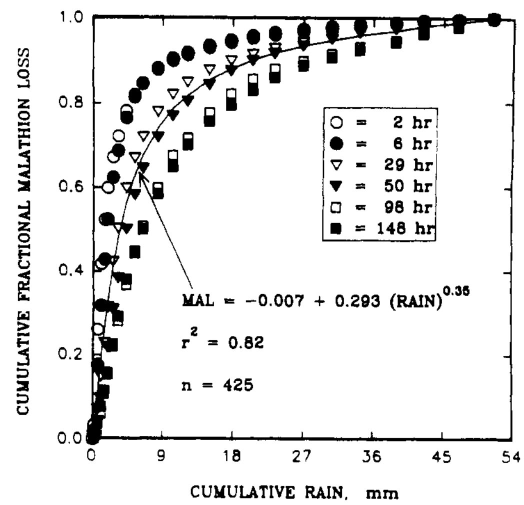

Figure 2. Cumulative fractional loss of malathion as a function of rain (51 mm in 1 h) applied at various times after insecticide application.

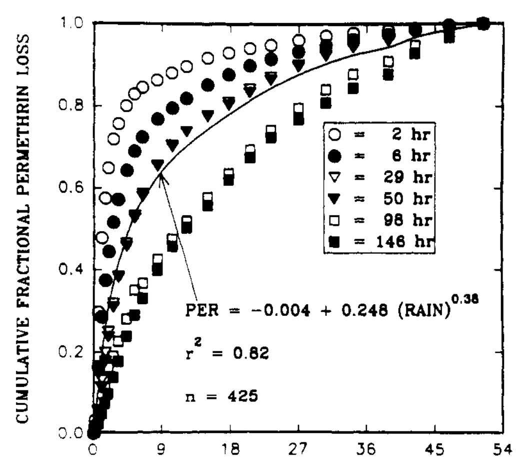

Figure 3. Cumulative fractional loss of permethrin as a function of rain (51 mm in 1 h) applied at various times after insecticide application.

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Registry No. Malathion, 121-75-5; permethrin, 52645-53-1.