LONGEVITY OF ULTRA-LOW-VOLUME SPRAYS OF FIPRONIL AND MALATHION ON COTTON IN MEXICO

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ABSTRACT

In 1996, fipronil and malathion residues were evaluated after four ultra-low-volume (ULV) spray applications in northeastern Tamaulipas, Mexico. Sprays were applied at 0.88 L/ha. Fipronil was applied at 28 and 56 g A.I./ha and malathion at 840 g A.I./ha. Four applications were made beginning 23 May at four, five and six day intervals. Leaf surface residues of malathion accumulated with each application. Leaf surface residues of fipronil applied at both rates dissipated >90% after 2 to 4 d after all applications.

INTRODUCTION

Probably the most extensive use of ultra-low-volume (ULV) insecticides in crop production has been in the Boll Weevil Eradication Program which began in 1978. From the beginning, ULV application of insecticides has been used to great effectiveness. The labor and money saved by using ULV application has helped to keep the cost of the program at an affordable level. Vast acreage can be most expeditiously treated with ultra-low-volumes of insecticides because aircraft are able to spend more time spraying and less time filling and ferrying to and from the airstrip.

Technical malathion is the insecticide of choice for area-wide eradication programs against the boll weevil, *Anthonomus grandis grandis* Boheman, in the United States. It is effective against this insect as an ultra-low volume (ULV) spray (Jones et al. 1996, 1997).

Fipronil (as Regent® from Aventis Environmental Science, Research Triangle, NC) is a phenyl pyrazole (Colliet et al. 1992) that has been demonstrated to be effective as a high volume spray at 0.056 kg A.I./ha against the boll weevil in field plots (Burris et al. 1994). Four applications of ULV sprays of malathion and fipronil in cottonseed oil at 0.88 L/ha were effective against the boll weevil in a field test (Reed et al. 1998).

How long an insecticide remains effective on the plant surface is an important factor in determining the optimum spray interval for controlling boll weevils. Costly over-treating can be avoided if the longevity of the insecticide being used to control a pest is known.

The objective of this test was to compare the longevity of ULV sprays of fipronil and malathion on cotton leaves after multiple applications.

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MATERIALS AND METHODS

The test was conducted in a 30-ha field of cotton planted on 18 February 1996 near Nuevo Progreso, in northeastern Tamaulipas, Mexico. The field was irrigated prior to planting and twice during the test. No rain fell during the test period.

Fipronil, as a 300 g/liter or 2.5 lbs/gallon emulsifiable concentrate, was tested at 28 or 56 g A.I./ha. Crude cottonseed oil (Olete de Monterrey, Nuevo Leon, Mexico) was used as a diluent of fipronil. Technical malathion (95%) (Chemica Lucava, Monterrey, N.L., Mexico) was tested at 840 g A.I./ha.

Applications of each treatment were made at 202 km/hr with a single-winged Ag-Cat airplane fitted with an eight-meter boom calibrated to deliver 0.88 L/ha through nine 8002 flat fan TeeJet nozzles (Spraying Systems, Wheaton, IL.). Applications were made on 23, 27 May and 1 and 7 June 1996. Boom pressure of all sprays was 1.75 kg/cm^2. The airplane made applications 1.0 m above the plant canopy and along the north to south rows. Applications were directly into or with a prevailing south to southeast wind at about 07:00 hours. Wind gusts did not exceed 24.1 km/hr during the applications.

The test field consisted of 383 rows on 1.0-m centers that averaged 750 m in length. Treated plots were replicated four times and were 28 rows wide with one swath/replicate. Treatments were randomly assigned to the plots.

Leaves were collected for residue analysis from the second or third nodes below the first fully expanded terminal leaf on each of 16 plants (four/plot) in row 15 of each plot. Leaves were sampled 0, 1, and 2 d after the first application and 0, 1, and 4 d after the second and fourth application, respectively. Leaves were not collected after the third application because the field was furrow irrigated.

Sixteen leaves (four leaves/plot) collected on each date were placed in 946-ml plastic bags, sealed, and placed in a cold box. The bags were placed in a freezer at 0 °C within 2 h after collection and held until residues were extracted. Within 3 to 7 d, residues of fipronil and malathion were washed from the upper and lower surface of each leaf using dual-side leaf washers (Carlton 1992) with 95% ethanol as a solvent.

Samples of both insecticides were transported in refrigerated containers to the USDA Laboratory in Stoneville, Mississippi, for analysis. Samples of fipronil were evaporated to dryness under a slow stream of ultra high purity (UHP) grade nitrogen. The dried samples were then reconstituted in 1 ml acetonitrile-methanol for analysis.

Residues of fipronil were determined by high pressure liquid chromatography with ultraviolet detector at 280nM (Mulrooney et al. 1998). Analytical fipronil was provided by Rhone-Poulenc Ag Company, Research Triangle Park, NC. All solvents were HPLC grade. Retention time of fipronil was 7.50 min. Mulrooney and Goli (1999) recovered 92% of fipronil from the cotton leaf using ethanol. Minimum detection limit of fipronil was <50 ppb.

The concentration of malathion in washes of upper and lower leaf surfaces was determined by gas chromatography using a flame photometric detector in phosphorus mode (Mulrooney et al. 1997). Retention time of malathion was 5.44 min. Minimum level of detection was 0.12 ppm.

Analysis of variance ($P<0.05$) using PROC MIXED, SAS (1997) and subsequent mean separation (PDIFF option) were applied to residues of malathion and both rates of fipronil on upper and lower surfaces of leaves after each application. Residues of both insecticides were collected after the first, second, and fourth applications.

Curves of residues of malathion and fipronil were best fitted by $Y = AX^B$, or using linear regression, log (residue + 1) = intercept + slope (log time + 1). Analysis was made using PROC MIXED of SAS (1997). Contrasts of trends (intercept and slope) and slopes of the low and high rates of fipronil were made.

RESULTS AND DISCUSSION

Analysis of variance showed significant differences in residues of malathion and high and low rates of fipronil between days ($F=5.0; df=3,3; P<0.02$) and applications ($F=10.53; df=2,3; P<0.0001$).

Malathion residues on the upper surface of the leaf ranged from 398 to 4,391 ng/cm^2 and from 61 to 1367 ng/cm^2 on the lower surface (Table 1). After the first application, residues on upper or lower surfaces of leaves did not significantly decrease until two days after application. After applications two and four, there were no significant differences in residues on either the upper or lower leaf surfaces between day zero and day two sample dates. Malathion residues on the lower surface significantly decreased from day two to day four after applications two and four.

A ULV spray of technical malathion at 2.8 kg A.I./ha near Brownsville, Texas (Wolfenbarger and McGarr 1971) deposited 6,490 ng malathion/cm^2 on leaves. In our study, the first and fourth application of 0.84 kg A.I./ha deposited 2,105 and 3,381 ng malathion/cm^2 on leaves (Table 1). The 2.8 g A.I/ha of malathion applied in Brownsville, Texas, resulted in 2- to 3- fold greater deposition than the 0.84 g A.I./ha rate used in our study. Residues of malathion on upper leaf surfaces sampled on day zero after one (1,621 ng/cm^2), two (2,168 ng/cm^2) and four (2,576 ng/cm^2) applications show increasing residues after multiple applications. Residues collected immediately after applications two and four increased 35 to 60% from application one. Residues at 2 d after applications two and four were about 10 fold greater than application one. There was no significant difference in residues on the upper leaf surface between 0 and 4 d after application four.

Malathion residues on the upper and lower surfaces of the cotton leaves increased after the first and second application (Table 2). Intercepts of regressions of residues after the second and fourth application were equal.

The slope of regression of malathion residue on the upper leaf surface was negative after applications one and two and positive after application four (Table 2). This result seems to indicate a decrease in the rate of degradation of malathion on the leaf surface as the season progressed.

In contrast to malathion, residues of fipronil on the upper surface of the leaf on day zero did not accumulate after each of the three applications (Table 1). Fipronil is a short-lived insecticide compared to malathion. At both rates, residues of fipronil decreased an average of 95% 2 and 4 d after the three applications. Residues of the low rate of fipronil on the upper leaf surface decreased significantly on each of the days after application.

Residues of fipronil on the lower leaf surface decreased 98% 2 d after the first application at the high rate and 94% and 93% 4 d after the second and fourth application, respectively. Residues of fipronil were not significantly different on days 0 and 1 after the first application. The residues found on the lower leaf surface at the high rate after applications two and four were significantly different from each other on each of the sample days.

Fipronil residue declined on both surfaces of the leaf after all applications (Table 3). The loss of fipronil was always greater on the upper surface of the leaf than on the lower surface. The intercept, which is an estimate of the initial deposit on the leaf, of the high rate of fipronil was always greater than that for the low rate. The intercept decreased from application one to application four for the low rate of fipronil, especially on the upper surface of the leaf. At the high rate, the intercept was variable on both leaf surfaces. The intercept of fipronil at the high rate far exceeded the low rate after applications two and four.

TABLE 1. Insecticide Residues (ng/cm^2) Recovered from the Upper and Lower Surfaces of Cotton Leaves.

	Application 1			Application 2			Application 4		
	Day after application			Day after application			Day after application		
Treatment	0	1	2	0	2	4	0	2	4
				Upper Surface					
Malathion	1621[a]a	1897a	398b	2168a	4053a	792b	2576a	4391a	3139a
Fipronil 28.0 g/ha	62.5a	7.8b	1.6c	30.6a	5.9b	0.9c	16.6a	0.9b	0.5c
Fipronil 56.0 g/ha	57.8a	8.0b	1.0c	78.9a	5.8b	1.4c	43.1a	2.4b	0.8b
				Lower Surface					
Malathion	484a	252a	61b	876a	1367a	389b	805a	935a	259b
Fipronil 28.0 g/ha	15.6a	3.4b	0.8c	14.4a	3.3b	1.3b	9.7a	5.6b	1.4b
Fipronil 56.0 g/ha	22.2a	14.7a	0.5b	39.2a	15.6b	2.3c	39.6a	8.8b	2.7c

[a]Means for each treatment over days within an application not followed by the same letter are significantly different ($P \leq 0.05$) as determined by PDIFF (SAS Institute, 1990).

TABLE 2. Equation (Residue= Intercept×Day^{Rate}) of Malathion, Applied at 0.88 l AI/ha, Residues as ng/cm^2 from Upper and Lower Surfaces of Cotton Leaves as a Function of Day (Application on Day 0).

Application	Intercept	Slope
	Upper Surface	
1	2080	-1.12
2	2893	-0.45
4	2864	0.12
	Lower Surface	
1	567	-1.77
2	1075	-0.36
4	1022	-0.61

TABLE 3. Equations (Residue = Intercept × Day^{Rate}) of Fipronil Residues from Upper and Lower Surfaces of Cotton Leaves as a Function of Day (Application on Day 0).

Rate (g A.I./ha)	Application	Intercept	Slope
		Upper Surface	
28.0	1	67	-3.51
56.1	1	68	-3.79
28.0	2	30	-2.13
56.1	2	80	-2.55
28.0	4	13	-2.24
56.1	4	41	-2.56
		Lower Surface	
28.0	1	16	-2.85
56.1	1	36	-3.23
28.0	2	15	-1.60
56.1	2	49	-1.71
28.0	4	9	-1.12
56.1	4	41	-1.71

Comparisons of trends, which includes both intercept and slope, of the low and high rates of fipronil indicated that greater degradation of fipronil on the upper leaf surface occurred after the second (F=4.85;df=2,75;P>F=0.0333) and fourth (F=7.56;df=2,75;P>F=0.0073) application of the high rate (Table 4). However, when only the slopes of each rate were compared, no significant differences were observed.

Comparisons of trends of the degradation of fipronil rates on the lower surface of leaves were significantly different for each of the three applications, with the greatest difference (F=15.57;df=2,80;P>F=0.0001) after the second application (Table 4). As with residues on the upper surface, comparisons of slopes showed no difference in degradation for any of the applications. Comparisons of trends, which include both the intercept (initial deposit) and the slope (rate of degradation), give a more complete picture of fipronil on the leaf surface.

TABLE 4. Contrasts of Trends and Slopes for Low and High Rates of Fipronil on Upper and Lower Surfaces of Cotton Leaves.

	Trend ($\beta_0 + \beta_1$)[a] Contrast		Slope (β_1) Contrast	
Application	F value	P>F	F value	P>F
		Upper Surface		
1	0.65	0.5225	0.55	0.4614
2	4.82	0.0333	1.86	0.169
4	7.56	0.0073	1.22	0.2722
		Lower Surface		
1	3.83	0.0256	0.68	0.4106
2	15.57	0.0001	0.13	0.7218
4	3.32	0.0574	2.69	0.1049

[a] β_0 = intercept, β_1 = slope.

Malathion has been effectively used in the eradication of the boll weevil. Its effectiveness along with its low cost will likely ensure its continued use in eradication. However, the EPA is carefully scrutinizing all organophosphorus insecticides for harmful effects on humans and the environment and their continued use could be questionable. If malathion was removed from the U.S. market, the eradication of the boll weevil could be accomplished with fipronil provided that it was labeled for use on cotton in the U.S. Substituting fipronil for malathion in an area-wide application program would have some consequences. Fipronil is highly toxic to aquatic organisms (Harmon et al. 1996) and being a relatively new insecticide, it would likely cost more than malathion.

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