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Comparison of Dislodgable and Total Residues of Three Pyrethroids Applied to Cotton in Arizona

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Recent studies comparing several pyrethroid insecticides for residual life and efficacy against first-instar tobacco budworm (TBW), Heliothis virescens (F.), larvae revealed a drastic drop in dislodgable residue from cotton, Gossypium hirsutum L., leaves while still killing over 80% of the TBW larvae. In some instances toxicity occurred for as long as 21 days after application of the insecticides (unpublished 1984-1987). Bioassay of these cotton plants with adult worker honey bees, Apis mellifera L., indicated that the cotton leaves were safe for foragers in 3 - 7 days after application and the honey bee mortality followed a trend which reflected the results of chemical analyses for dislodgable residues (Waller et al. 1988). Dislodgable residue levels were indicative of a pyrethroid's toxicity to honey bees, but were not a good measure of the insecticide's efficacy against TBW. This is not unexpected considering honey bees contact only leaf surfaces while budworms ingest the leaves. In previous work (unpublished 1984-1986) we compared various insecticides for dislodgabe residues, efficacy against TBW larvae and toxicity to honey bees with no regard for the relationship between dislodgable and total residues in the cotton leaves. It was the purpose of this study to compare dislodgable and total insecticide residues from cotton leaves immediately after spraying and at various time intervals up to 21 days after spraying.

METHODS AND MATERIALS

Test plots located in a field of McNair 220 short staple cotton at the Campus Agricultural Center, Tucson, Arizona, consisted of 8 rows, with 102 cm spacing, 30.5 m long. Two rows of untreated cotton served as buffers between plots. Cotton plants had an average height of 74 cm the day of the pyrethroid applications, September 2, 1987, and averaged 79 cm 14 days after application.

The aqueous sprays were applied between 7:45 and 8:25 am at 122 L/ha at 4.4 km/h using a shop-built, two-row, manually-drawn, boom-type sprayer as described by Ware et al. (1983). Insecticide formulations and recommended rates applied were cyhalothrin 0.028 kg ai/ha (Karate™ 1E, ICI Americas, Goldsboro, NC), flucythrinate 0.067 kg ai/ha (Pay-Off®, American Cyanamid, Wayne, NJ) and s-fenvalerate 0.045 kg ai/ha (Asana®

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Insecticide, E. I. duPont de Nemours, Wilmington, DE). The cotton was flood-irrigated according to schedule during the study. Light rain fell September 4, 5 and 20 with an accumulation of 0.38, 0.33 and 0.18 cm, respectively. High temperatures during the study ranged from 30.5-38.2°C and lows ranged from 12.2 - 23.3°C.

Triplicate samples of 100 leaves were collected from the upper 30 cm of leaf canopy from the 6 inner rows in each treated plot and from an untreated control plot immediately and up to 21 days after treatment. One hundred discs (2.54 cm diameter) were cut from each sample, one disc per leaf. The discs were weighed and the dislodgable residues were extracted from the discs by shaking with 100 mL redistilled hexane for 1 min. The extracts were stored in the freezer and the discs were discarded. The remainder of the leaves (minus the discs) from each sample were chopped in a Hobart® food chopper and frozen. Twenty-g subsamples of the frozen chopped leaves were extracted with 200 mL redistilled hexane:isopropanol (3:1) by blending 5 min in an Omni-mixer®. The isopropanol was washed out with 3 rinses of distilled water and the hexane layer (total residues extract) was dried through anhydrous Na_2SO_4 and stored in the refrigerator. Fortified control samples, recovery samples, and reagent blanks were run each time a group of samples was extracted.

Ten-mL aliquots of sample extracts were cleaned in 22-mm id columns containing 2.5 cm activated Florisil® (120°C for 24 h) covered with 1.2 cm Na_2SO_4 after prewetting with 50 mL hexane. The pyrethroids were eluted with 100 mL eluant at a flow of 2 drops/sec. Eluants used were 4, 6 and 10% ethyl acetate in hexane for s-fenvalerate, cyhalothrin and flucythrinate, respectively. The cleaned extracts were analyzed using a Micro Tek MT-220™ gas chromatograph equipped with a ^{63}Ni electron capture detector and a 33 cm x 4 mm id Pyrex® column packed with 5% SE-30 on 100/120 mesh Chromosorb® W (H.P.). Nitrogen carrier flow was 80 mL/min. Detector and inlet temperatures were 250 and 220°C, respectively. Column temperature was 200°C for flucythrinate and s-fenvalerate and 190°C for cyhalothrin. Retention times were 2.9, 3.6 and 4.7 min for cyhalothrin, flucythrinate and s-fenvalerate, respectively. Quantitation was by peak area using a Hewlett Packard 3392A Integrator.

RESULTS AND DISCUSSION

The results of these comparisons are shown in Figure 1, expressed as $\mu g/cm^2$ (1 surface only) dislodgable residues and parts per million (ppm) total residues remaining immediately and up to 21 days after application. Dislodgable residues remaining 1 day after application were 85, 89 and 100% of initial deposit for flucythrinate, cyhalothrin and s-fenvalerate, respectively. These dislodgable residues are similar to what we've observed in past studies with pyrethroids in 1977 - 1984 where 70 - 100% of initial deposits were present 1 day after August and September applications (Estesen et al. 1979; Buck et al. 1980; Ware et al. 1980; Waller et al. 1988). Three days after application, the dislodgable residue levels dropped to 28 - 36% of initial residue and 5 days after application the dislodgable residue was 20 - 24% of initial deposit. These values agree closely with dislodgable residues remaining 3 and 5 days after a 1985 September application in which flucythrinate, fenvalerate and

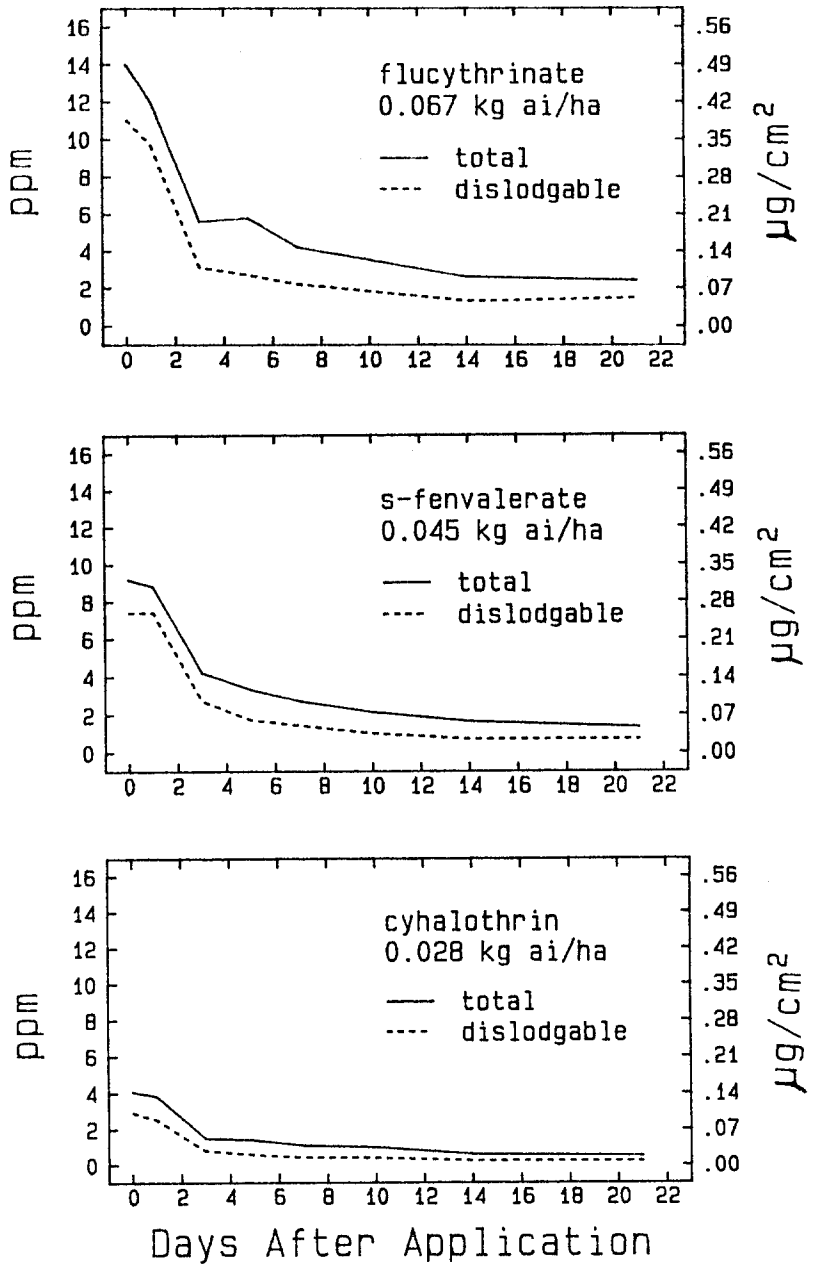

Figure 1. Total and dislodgable insecticide residues, expressed as ppm and $\mu g/cm^2$, respectively, from cotton leaves following application by ground rig of pyrethroids to cotton in Tucson, Arizona, September 2, 1987.

cypermethrin residues were compared (unpublished). The dislodgable residue levels remaining 14 and 21 days after application were approximately 8, 9 and 12% initial deposit for cyhalothrin, s-fenvalerate and flucythrinate, respectively. Again, this agrees closely with the September 1985 study where 9 - 13% of initial deposit remained 14 days after application (unpublished).

For all 3 pyrethroids tested total residues, as expected, were greater than their corresponding dislodgable residues and in the majority of cases, the percent of initial residues remaining for total residues were greater than the corresponding percent of initial residues remaining for dislodgable residues. Total residues remaining 3 and 5 days after application were 37 - 46% and 34 - 41% of initial residues, respectively. These percentages drop to 13, 14 and 17 for cyhalothrin, s-fenvalerate and flucythrinate, respectively, 21 days after application.

No corrections were made in either total or dislodgable residues although recovery samples were run for both. Insecticide-fortified control leaf macerates averaged 95 - 113% and recoveries of insecticide standards from Florisil (dislodgable recoveries) averaged 86 - 92%. Total residue limits of detection were 0.12, 0.17 and 0.080 ppm for flucythrinate, s-fenvalerate and cyhalothrin, respectively. The limits of detection for dislodgable residues were 0.0039 $\mu g/cm^2$ for flucythrinate and 0.0020 $\mu g/cm^2$ for the others. All control samples were free of insecticide contamination and there were no chromatographic interferences in any of the analyses.

The relationship between dislodgable (expressed as ppm) and total residue for each insecticide was examined in several ways: the ratio dislodgable:total over time, the ln ratio dislodgable:total over time, and multiple regression equations relating the total residue to various independent variables. The ratio relationships were non-linear over time and these methods of comparison were abandoned. The original multiple regression equation estimated for each insecticide separately was:

$$\hat{y} = B_0 + B_1x_1 + B_2x_2 + B_3x_2^2 + B_4x_1x_2 + B_5x_1x_2^2$$

The main effects were: x_1 = dislodgable residue, x_2 = time (days) after application, and x_2^2 = time squared. The interactions were: time by dislodgable residue and time squared by dislodgable residue. Terms containing nonsignificant coefficients at the 0.05 level were eliminated from the equation and the final multiple regression equation became:

$$\hat{y} = B_0 + B_1x_1 + B_2x_2 + B_3x_1x_2$$

Table 1 presents the regression coefficients with standard errors and R^2 for each insecticide tested. The coefficients among insecticides were compared and no significant differences were found between s-fenvalerate and flucythrinate for any parameters. Cyhalothrin was significantly different from the other 2 pyrethroids in all coefficients except for the dislodgable by day interaction where no difference was seen at the 0.05 level.

This study indicates that knowledge of the dislodgable residue and the

time after application could provide an excellent basis for predicting total residue. However, the study also indicates that the coefficients may vary depending on the insecticide. Consequently, further tests would need to be conducted for each insecticide of interest and individual predictive equations would have to be derived from those studies.

Table 1. Regression coefficients and standard errors for equations predicting total residues in cotton leaves of three pyrethroids applied to cotton in Tucson, Arizona, September 2, 1987.

Insecticide	B_0 Intercept	B_1 Disl	B_2 Day	B_3 Day x Disl	R^2
s-fenvalerate	2.2[a]	0.93[a]	-0.040[a]	-0.059[a]	.99
	(0.34)	(0.046)	(0.021)	(0.030)	
cyhalothrin	0.55	1.1	-0.036	0.083[a]	.99
	(0.11)	(0.035)	(0.0067)	(0.033)	
flucythrinate	2.8[a]	0.99[a]	-0.079[a]	-0.013[a]	.98
	(0.56)	(0.055)	(0.048)	(0.038)	

[a]Coefficients within a column followed by the same letter are not significantly different at the 0.05 level.
Disl = Dislodgable residue
Day = Time after application

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