Dissipation of Cyhalothrin Residues on Apple Foliage and Apples at Harvest†

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A method to quantify cyhalothrin (Karate) residues by gas chromatography on apple foliage and fruit is described in detail. Two models are proposed to describe the dissipation pattern on foliage. According to these models, cyhalothrin residues would be half their initial concentration 10 days following a treatment. When two treatments are carried out, there is some carry-over and accumulation of residues from the first treatment to the second. Thirty-nine days past treatment, residues could not be detected in the pulp, but very low levels were detected in the peel and a whole apple at harvest. In high-density dwarf apple orchards spray drift from one row to the other can be completely eliminated with the use of a screen, mounted on a trailer and pulled along by a second tractor, running parallel to the sprayer in the adjacent passageway.

The presence of lepidopterous pests such as the eye-spotted bud moth, *Spilonota ocellana* (Denis & Schiffermüller), obliquebanded leafroller, *Choristoneura rosaceana* (Harris), and plant bugs necessitates the prebloom use of synthetic pyrethroid insecticides in Quebec apple orchards. A second insecticide treatment is also applied at petal fall to obtain commercially acceptable control of these pests and others, such as the plum curculio, *Conotrachelus nenuphar* (Herbst).

An understanding of the weathering process of an insecticide is useful for the development of integrated pest management (IPM) programs based on the use of that product. The literature is full of references showing the residues of a particular insecticide on the finished commodity. However, in recent years few studies have monitored the degradation of a product systematically in the field. In apples, Bostanian and Bélanger (1985) reported that residues of permethrin, fenvalerate, and cypermethrin had dissipated to one-third and one-fourth their original dose 8 and 14 days posttreatment. With multiple treatments, Bostanian et al. (1985) reported carry-over residues from one treatment to the other, and among the several pyrethroids evaluated, deltamethrin was the most persistent. Earlier, Shwe Yin Tan (1983) had shown that fenvalerate was more persistent than *trans*-permethrin which in turn was more persistent than *cis*-permethrin. Bellows et al. (1985) reported that in citrus dimethoate dissipated rapidly from the foliage, and it had a half-life of 2.2 days, whereas acephate had a half-life of 8.2 days. More recently, Hill et al. (1989) showed that the degradation of deltamethrin on alfalfa was biphasic.

In this study, we report the degradation of cyhalothrin (Karate), a third-generation synthetic pyrethroid, on apple foliage and fruit at harvest, when this product is applied once (prebloom) or twice (prebloom and postbloom) per season.

MATERIALS AND METHODS

Field Procedures. The field work was conducted according to a nested design at the Agriculture Canada experimental orchard at Frelighsburg, Quebec. The experimental site consisted of three separate orchards, each 0.24 ha of high-density dwarf cv. Jersey Mac apple trees. Each orchard was divided into two sections of equal size. One section was treated, the other was not treated (check plot). The treated section of the first orchard received a cyhalothrin treatment when the buds were at pink. The treated section of the second orchard received a cyhalothrin treatment at pink and at petal fall. The treated section of the third orchard received a cyhalothrin treatment only at petal fall. Cyhalothrin [10 g of active ingredient (ai)/ha] was applied with a Swanson airblast sprayer calibrated to deliver 560 l/ha at 1034 kPa (150 psi) pressure. Spray drift to adjacent rows was eliminated by a corrugated plastic screen. The screen (12 × 16 ft) was mounted on a trailer and pulled along by a second tractor running parallel with the sprayer in the adjacent passageway.

Analytical Procedures. *Foliage.* In each treated section four groups (replicates) of three trees in a row were selected at random. From each group 24 leaves (8 leaves/tree) were collected from the flower or fruit cluster at different intervals of time. Each sample of 24 leaves was weighed (leaves and flowers) and the insecticide was extracted within 24 h with 100 mL of glass-distilled acetone in a 250-mL Erlenmeyer flask. After 1 h of passive extraction, the flask was shaken for 1 h with a wrist-action shaker. The acetone extract was filtered (Whatman No. 1), and the filtrate was collected in a round-bottom flask. The extraction procedure was repeated twice with 50 mL of acetone and shaken for 10 min each time. The solvent extract was then concentrated to 25 mL with a rotary evaporator in a water bath set at 25 °C. The extract was then transferred to a 500-mL separatory funnel with 50 mL of distilled water. The extract was then partitioned between 50 mL of hexane and water, and the aqueous layer was extracted three more times with 35 mL of hexane before being discarded. The combined hexane extracts were dried over anhydrous sodium sulfate and concentrated to near dryness with a rotary vacuum evaporator. The dry residue was dissolved in 2 mL of acetone in a test tube to which 8 mL of hexane was added. The concentrate was then poured into a Florisil (14 g) column (16-mm diameter) wet-packed with hexane. The test tube was rinsed with 4 mL of 20% acetone in hexane and the rinsate poured into the column. Cyhalothrin was eluted with 100 mL of 25% redistilled diethyl ether in hexane. The eluate was collected in a 250-mL round-bottom flask and evaporated to near dryness (ca. 1 mL). The dried concentrate was quantitatively transferred to a test tube with several rinses of acetone–hexane (4:1). The volume of the dried concentrate was then reduced under a gentle stream of nitrogen to less than 1 mL. The residue was redissolved in an appropriate volume of acetone and injected into the gas chromatograph. One-microliter

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Table I. Parameter Estimation for Two Models Describing Cyhalothrin Dissipation on Apple Foliage

Figure 1	tree phenology		model 1							model 2					
			C_{max}	k_s	k_r	k_d	R^2	df	RMS	α	β	k_2	R^2	df	RMS
A	pink	1988	4.05408	0.19807	0.29800	0.02429	0.95	51	0.35211	0.85239	2.93071	0.10244	0.95	52	0.35484
D	pink	1987	5.18398	0.31813	0.57732	0.07221	0.91	35	0.86374	0.22820	4.73505	0.12603	0.90	36	0.90614
G	pink	1986	3.72949	0.38949	0.95369	0.02497	0.88	43	0.83633	0.00000	3.19745	0.03491	0.86	44	0.91875
B	pink and petal fall	1988	5.23750	0.06146	0.06146	0.00000	0.98	24	0.30732	1.10608	4.13141	0.07792	0.98	25	0.29503
E	pink and petal fall	1987	4.06536	0.19051	0.03886	0.01382	0.94	16	0.32794	0.42681	3.62642	0.19862	0.94	17	0.31590
H	pink and petal fall	1986	4.49374	0.10361	0.01323	0.00000	0.94	15	0.58573	0.50899	3.98475	0.11684	0.94	16	0.54913
C	petal fall	1988	1.63138	0.08292	0.02188	0.00000	0.91	20	0.10496	0.34100	1.29064	0.10473	0.91	21	0.09996
F	petal fall	1987	1.73000	0.10485	0.00064	0.00000	0.94	16	0.06557	0.00000	1.72833	0.10387	0.94	17	0.06174
I	petal fall	1986	1.28458	0.28228	0.48623	0.03293	0.98	23	0.01455	0.26626	0.93887	0.10205	0.97	24	0.01678

aliquots were analyzed in triplicate, and all values were calculated in parts per million.

Pulp and Peel. An apple from each of the four compass cardinal points was harvested from each of the three trees in replicate (12 apples/replicate). A total of 48 apples were harvested per treatment. The apples were weighed and peeled. The weight of the peel was recorded separately. The pulp (one-eighth of an apple) and all peel were transferred separately to Mason jars (500–1000 mL), 150 mL of acetone was added to the jars, and the contents were homogenized for 4 min. A Polytron homogenizer with a saw-toothed knife was used. The homogenate was filtered with two Whatman No. 4 filter papers in a Büchner funnel, and the filtrate was collected in a 1000-mL round-bottom flask. The residue from the Büchner funnel was returned to the Mason jar and the extraction repeated three more times with the addition of 100 mL of acetone. The extracts were combined and concentrated with a rotary evaporator. The concentrate was transferred to a 1000-mL separatory funnel by using 150 mL of distilled water followed by 25 mL of acetone and 100 mL of hexane. After 1 min of shaking, the extract was partitioned between hexane and water. The aqueous layer was extracted five more times with hexane. The first time the extraction was carried out with 100 mL of hexane and the remaining four times with 35 mL of hexane each time. The combined hexane extracts were dried over anhydrous sodium sulfate and concentrated to near dryness with a rotary evaporator. The dried residue concentrate extracted from the apple peel was dissolved in 6 mL of acetone and 4 mL of hexane in a test tube. The residue concentrate extracted from the apple pulp was dissolved in 8 mL of acetone and 2 mL of hexane in a test tube. The concentrate was then poured into a Florisil (14 g) column (16-mm diameter) wet-packed with hexane. The test tube was rinsed with 4 mL of 60% acetone in hexane for the peel and with 4 mL of 80% acetone in hexane for the pulp. Cyhalothrin was eluted with 50 (peel) and 100 mL of hexane (pulp). The eluate was collected and evaporated to near dryness (ca. 1 mL) in a 250-mL round-bottom flask. The dried concentrate was quantitatively transferred to a test tube with several rinses of the round-bottom flask with acetone–hexane (4:1). The contents of the test tube were then evaporated to dryness with nitrogen gas. The concentrate was redissolved in an appropriate volume of acetone and injected into the gas chromatograph.

Gas Chromatography. A Varian gas chromatograph (Model 3700) was used. Cyhalothrin was detected with a ^{63}Ni electron capture detector and chromatographed on a megabore capillary column (DBI-15 m, 1.5-μm film for the leaves and 30 m for the pulp and the peel). A guard column (2 mm i.d.) packed with 7 cm of 5% OV-101 on 80–100-mesh Gas Chrom Q was placed between the injector and the capillary column. Inlet, column, and detector temperatures were 240, 220 (210 °C for pulp and peel), and 270 °C, respectively. The nitrogen carrier gas flow was 18 mL/min. A makeup gas was also used, and it consisted of nitrogen at 35 mL/min. The retention time for cyhalothrin was 3.077 min on the DBI-15 m and 19.00 min on the DBI-30 m. One-microliter aliquots were analyzed in triplicate, and all parts per million values were calculated on a fresh weight basis (w/w). The values reported in the tables are the mean of triplicate subsamples taken from each experimental unit. Standard cyhalothrin solutions were analyzed to establish a standard curve. The standard curve related surface area under the peak to the concentration of cyhalothrin. Prior to analyses, all samples were kept under refrigeration at 4 °C. Total residues in an apple were estimated using the following summary expression of separately determined residues in the peel and the pulp.

total residues in an apple (ppm) = [residues in peel (ppm) × peel wt (g) + residues in pulp (ppm) × pulp wt (g)]/total wt of apple (g)

Modeling Residue Dissipation. Cyhalothrin residues are expressed in parts per million (ppm). The two-compartment model (model 1) of Hill and Schaalje (1985) was used to describe the dissipation pattern.

$$\overset{k_s}{\leftarrow} C_1 \overset{k_r}{\leftrightarrow} C_2 \overset{k_d}{\rightarrow}$$

model 1

$$C_t = C_{max}e^{-(k_s+k_r)t} + C_{max}\frac{k_r}{k_s + k_r - k_d}[e^{-k_d t} - e^{-(k_s+k_r)t}]$$

where C_1 is a deposited residue compartment, C_2 is a residue retained compartment, C_t is the total residue remaining after time t (t = day), C_{max} is the maximum residue present at time $t = 0$, k_s is a rate constant for surface losses of residue from C_1, k_r is a rate constant for movement of residues into C_2, and k_d is a rate constant for degradation of residues in C_2.

When $k_d = 0$, the model of Hill and Schaalje may be simplified to

model 2

$$C_t = \alpha + \beta e^{-k_2 t}$$

where C_t equals the amount of insecticide residues (ppm) at time t. The parameter β is related to the position of the "intercept" on the Y axis (i.e., the ppm value corresponding to $t = 0$, the time of maximum residue present). The parameter α is related to the concentration of residues at the time of the last observation. The maximum concentration C_{max} is $\beta + \alpha$. The parameter k_2 is the rate per unit t of insecticide degradation, as it is related to the value at which the response changes from its "initial" value (determined by the magnitude of β) to its "final" value (determined by the magnitude of α).

Dissipation for the proportion p residues can be solved easily for model 2 by substituting p for C_t/C_{max} and solving for t.

$$DT_p = t = \ln\left[\frac{1}{\left(\frac{\alpha+\beta}{\beta}\right)\left(p - \left(\frac{\alpha}{\alpha+\beta}\right)\right)}\right]/k_2$$

These models were fitted by least squares to residue data by iteratively solving for every parameter using the simplex algorithm of Wilkinson (1990), with the restriction that all parameters were equal to or greater than zero.

RESULTS AND DISCUSSION

In fortified leaves, total recovery at 1 ppm was 96.2 ± 2.4%, and at 0.1 ppm it was 94.3 ± 3.2%. In apples, total recovery at 0.1 ppm was 71.9 ± 1.8% in the pulp and 103.6 ± 2.4% in the peel. At 0.01 ppm, total recovery was 72.0 ± 2.4% in the pulp and 98.2 ± 3.7% in the peel. At 0.001

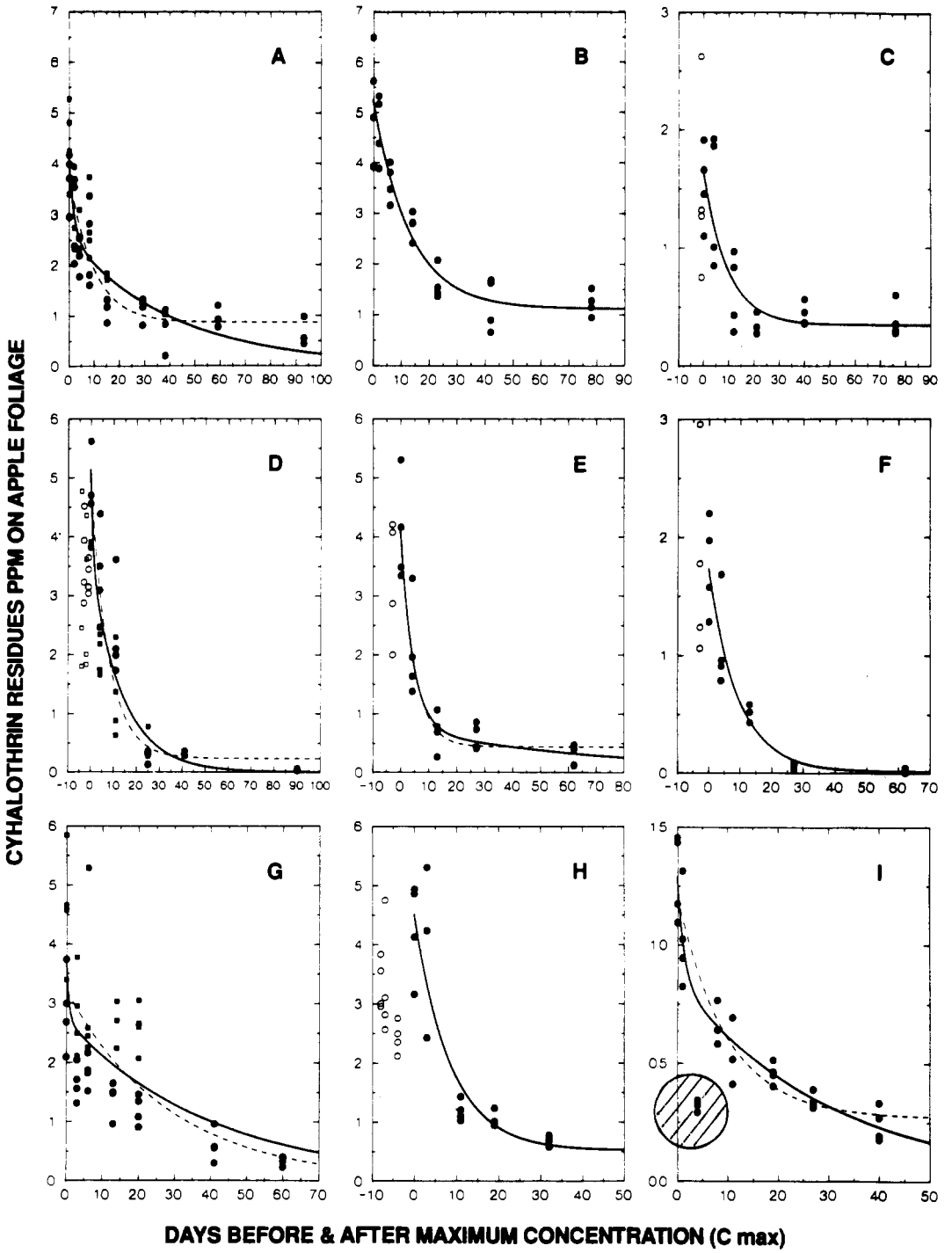

Figure 1. Dissipation of cyhalothrin on apple foliage. Parts A, D, and G indicate residue levels after apple foliage was treated at the pink stage in 1988, 1987, and 1986, respectively. Parts B, E, and H indicate residue levels after a petal fall treatment preceded by a pink stage treatment in 1988, 1987, and 1986, respectively. Parts C, F, and I indicate residue levels after apple foliage was treated at petal fall in 1988, 1987, and 1986, respectively. Residue levels depicted by model 1 are shown by a solid line, whereas residue levels depicted by model 2 are shown by a dashed line. The open dots and squares show actual residue levels before maximum concentration, C_{max}, was reached, and they were not used in fitting either model. The open squares in part D are actual residue data (pink treatment) from part E treated at (pink and petal fall treatment). The solid dots and squares show actual residue data at $t \geq 0$, and they were used in fitting the two models. The solid squares in parts A, D, and G are actual residue data from the pink treatment in parts B, E, and H. In part I, where $t = 4$, the readings in the shaded area were not used to fit either model.

ppm, total recovery was 72.0 ± 2.1% in the pulp and 83.8 ± 2.6% in the peel. These values are an average of three replicates.

Table I summarizes the estimates of the parameters for the two models, and Figure 1 presents graphically actual data and the expected residue level estimated by each model. Examination of Figure 1 shows that, irrespective of the time and number of treatments, residues of cyhalothrin decline with time. Further scrutiny of Figure 1 indicates that the highest residue level detected with a petal fall treatment (Figure 1C,F,I) is about half the level detected with a pink treatment (Figure 1A,D,G). Two factors are primarily responsible for this. First, at pink the foliage is small, and as the same volume of spray material was applied in both treatments, more material was deposited per unit area at pink than at petal fall. Leaf samples (96 leaves each) show that on the average the surface area of leaves collected at petal fall in 1987 was 1.75 times greater than the surface area of leaves collected at pink. In 1988, this factor increased to 1.81. The second

Table II. Cyhalothrin Residues in Jersey Mac Apples Treated at Pink and Petal Fall

treatment stage(s) and date	days after last treatment	residues, ppm					
		peel		pulp		whole apple	
		min	max	min	max	min	max
			1987				
pink (May 4)	58	ND[a]	0.0020	ND	ND	ND	0.0002
petal fall (June 3)	39	0.0031	0.0049	ND	ND	0.0003	0.0005
pink and petal fall	39	ND	0.0033	ND	ND	ND	0.0003
			1988				
pink (May 16)	58	ND	0.0008	ND	0.0001	ND	0.00010
petal fall (May 31)	42	0.0003	0.0015	ND	ND	0.00002	0.00012
pink and petal fall	42	0.0018	0.0022	ND	ND	0.00015	0.00018

[a] ND, inferior minimum detectable level: peel, 0.00109 ppm; pulp, 0.00003 ppm.

factor is the canopy; at petal fall, the canopy is far denser than at pink; therefore, less material may penetrate and be deposited on the inner leaves.

When we compare residue levels of a single treatment at petal fall (Figure 1C,F,I) with two treatments, one at pink and another at petal fall (Figure 1B,E,H), we note a carry-over and accumulation of residues from the first treatment at pink to the second treatment at petal fall. This is true not only at the highest residue levels (compare C_{max} values of C, F, and I to B, E, and H in Table I) but even toward the end of the study (50–80 days after the highest residue level). A similar observation was reported for cypermethrin, fenvalerate, and permethrin on apple foliage (Bostanian et al., 1985).

The R^2 and residual mean square (RMS) values reported in Table I indicate that both models describe adequately the data. When $K_d = 0$, the expected cyhalothrin residues predicted by models 1 and 2 are the same (Figure 1B,C,F,H).

In 1988 (Figure 1A) and 1986 (Figure 1G) C_{max} in a pink treatment was observed immediately following the insecticide application. On the other hand, in 1987 C_{max} was observed 4 days after treatment at pink (Figure 1D). Similarly for pink and petal fall treatments, C_{max} was observed at t = 0, 3, and 8 days following the second treatment in 1988, 1987, and 1986 (Figure 1B,E,H), respectively. Finally, for a petal fall treatment, C_{max} was observed at t = 2, 3, and 0 days following the treatment in 1988, 1987, and 1986 (Figure 1C,F,I), respectively. As cyhalothrin is a 1:1 mixture of S and R esters, we postulate that under different environmental conditions, from year to year, isomerization and epimerization take place at different rates and cause these differences in the timing of C_{max}. In this respect, Hill and Johnson (1987), reported that whereas total deltamethrin residues decreased on forage, there was a net increase in the 3+3′ and 4+4′ trans isomers.

The average 50% degradation of product following a pink treatment was 11.2 ± 1.8 (SEM) days after the treatment according to model 1 and 13.3 ± 3.3 days according to model 2. For a pink treatment followed by a petal fall treatment, the 50% degradation of product according to both models was 11.7 ± 2.4 days after the petal fall treatment. For only a petal fall treatment, the 50% degradation of product was 9.9 ± 0.9 days according to model 1 and 10.4 ± 0.5 days according to model 2.

Residue levels in the fruit are summarized in Table II. Virtually no residues could be detected in the pulp and low levels were noted in the peel and a whole apple in 1987 and 1988. In the untreated check plot, no residues could be detected on the foliage or the fruit at harvest. Thus, spray drift from one row to another was completely eliminated with the use of a corrugated screen, mounted on a trailer and pulled along by a second tractor, running parallel to the sprayer in the adjacent passageway. A severe frost during bloom in 1986 reduced the apple crop to such a low level that we could not carry out any residue studies in that year.

CONCLUSION

Cyhalothrin appears to dissipate at a reasonable rate, and irrespective of the time of treatment (pink or petal fall), only 50% of the material can be detected 10 days following a treatment. When two treatments are applied (pink and petal fall), there is some carry-over and accumulation of residues from the first treatment to the second treatment. Residues could not be detected in the pulp; however, very low levels were detected in the peel and a whole apple at harvest.

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LITERATURE CITED

Bellows, T. S., Jr.; Morse, J. G.; Hadjidemetriou, D. G.; Iwata, Y. Residual toxicity of four insecticides used for control of citrus thrips (Thysanoptera: Thripidae) on three beneficial species in a citrus agroecosystem. *J. Econ. Entomol.* **1985**, *78*, 681–681.

Bostanian, N. J.; Bélanger, A. The toxicity of three pyrethroids to *Amblyseius fallacis* Garman (Acari: Phytoseiidae) and their residues on apple foliage. *Agric. Ecosyst. Environ.* **1985**, *14*, 243–250.

Bostanian, N. J.; Bélanger, A.; Rivard, I. Residues of four synthetic pyrethroids and azinphos-methyl on apple foliage and their toxicity to *Amblyseius fallacis* (Acari: Phytoseiidae). *Can. Entomol.* **1985**, *117*, 143–152.

Hill, B. D.; Schaalje, G. B. A two-compartment model for the dissipation of deltamethrin on soil. *J. Agric. Food Chem.* **1985**, *33*, 1001–1006.

Hill, B. D.; Inaba, D. J.; Charnetski, W. A. Dissipation of deltamethrin applied to forage alfalfa. *J. Agric. Food Chem.* **1989**, *37*, 1150–1153.

Hill, D. H.; Johnson, D. L. Persistence of deltamethrin and its isomers on pasture forage and litter. *J. Agric. Food Chem.* **1987**, *35*, 373–378.

Shwe Yin Tan, C. Analyses persistence and degradation of synthetic pyrethroid insecticides permethrin and fenvalerate. M.Sc. thesis, Brock University, St. Catherines, ON, Canada, 1983.

Wilkinson, L. *Systat: The system for statistics*; Systat Inc.: Evanston, IL, 1990; 176 pp.

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