Dissipation of *lambda*-Cyhalothrin on Fallow vs Cropped Soil†

Bernard D. Hill* and Dan J. Inaba

Agriculture Canada Research Station, P.O. Box 3000 Main, Lethbridge, Alberta T1J 4B1, Canada

Soil in pans was treated with *lambda*-cyhalothrin at 15 g/ha using an indoor track sprayer, and the pans were dug into adjacent fallow and cropped areas of a field. Overall, the initial *lambda*-cyhalothrin residues (0.032 ppm or 11.8 g/ha) dissipated biphasically with a DT_{50} of 1.3 weeks and a DT_{90} of 14.5 weeks (disappearance time for first 50% and 90% of residue). Among treatments, residues in the soil pans shaded by the crop canopy declined faster (DT_{90} of 12.8 weeks) than residues in the fallow area (DT_{90} of 16.2 weeks). Compared with bare fallow, soil surface temperatures on warm, summer days were 8–16 °C cooler within the crop canopy. Also, the surface 0–2.5 cm of soil within the canopy took longer to dry out after a rainfall. It is postulated that the more ideal soil temperature and moisture conditions within the crop canopy increased the microbial degradation of *lambda*-cyhalothrin. One year after application, only 3.2% of the initial residues were recovered in the fallow area.

INTRODUCTION

Field studies to determine the dissipation of pesticides on Canadian soils are mandatory for Canadian registration. A small plot method using an accurate application is recommended to minimize variation in the dissipation curve (Agriculture Canada, 1987). One continuing dilemma is whether the experiment should be conducted on bare, fallow soil or in the presence of a growing crop. The presence of a crop represents the normal field situation but makes results more variable. It is extremely difficult to accurately and evenly apply a pesticide through a growing crop onto the soil. Variation arises from sampling residue "hot" and "cold" spots on the soil. However, pesticide dissipation on bare soil may not represent the real field situation because the soil beneath a crop canopy is often more shaded, cooler, and wetter. In some instances, uptake by the crop may contribute to pesticide dissipation in the soil.

We investigated the dissipation of pyrethroid insecticides on soil by conducting large and small plot experiments on bare, fallow soil (Hill, 1981, 1983; Hill and Schaalje, 1985). More recently, we developed a soil-pan method in which pans are accurately sprayed indoors and then are moved outdoors and dug into a fallow field (Hill et al., 1991). This soil-pan method also gives the researcher the option of placing the treated pans between the rows of a growing crop. As the canopy develops, the treated soil will then be shaded by the crop as in the real field situation.

The pyrethroid *lambda*-cyhalothrin (Karate, formerly PP321), a 50:50 mixture of (*S*)-α-cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-dimethyl-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)cyclopropanecarboxylate and (*R*)-α-cyano-3-phenoxybenzyl (1*S*,3*S*)-*cis*-2,2-dimethyl-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)cyclopropanecarboxylate, is currently under development to control grasshoppers, cutworms, flea beetles, and alfalfa weevil in western Canada. The objective of this study was to use the soil-pan method to compare the dissipation of *lambda*-cyhalothrin on fallow vs cropped soil.

MATERIALS AND METHODS

Soil. The Lethbridge sandy clay loam (Typic Haploboroll, fine loamy, mixed, mesic) contained 24.2% clay, 20.5% silt, and 55.3% sand with a cation-exchange capacity of 20.1 mequiv/100 g. The organic matter content was 2.2%, the pH was 7.9 as a 1:1 soil–water slurry, and the moisture-holding capacity was 18.8% at 30 kPa.

Field Experiment. This study was conducted on adjacent fallow and cropped (barley) areas of the same field. Use of the soil-pan method (Hill et al., 1991) was judged appropriate because *lambda*-cyhalothrin does not leach in soil (Chipman, 1988).

The main experiment consisted of three sprayed treatments: (1) soil pans placed in the fallow area, (2) soil pans placed within the barley crop, and (3) soil pans containing seeded barley also placed within the barley crop. A total of 12 soil pans were used, 4 per treatment, to follow the 0–16-week dissipation of *lambda*-cyhalothrin. Untreated soil pans (one per treatment) were placed in the fallow and cropped areas as controls. In addition, four treated pans were placed in the fallow area to monitor the long-term (0–52 week) residue dissipation of *lambda*-cyhalothrin. Within the fallow and cropped areas, the location of the various treatment pans was randomized within a lattice of three rows of six pans.

Soil pans were prepared 8 days before they were sprayed by filling metal flats (50 × 35 × 9 cm with bottom drainage holes) with soil from the 0–9-cm layer of the fallow field. The pans were then equilibrated under greenhouse conditions with light watering to settle the soil, encourage microbial activity, and crust the soil surface. Two days before the pans were sprayed, barley (2 rows of 16 plants) was seeded into four of the soil pans. The *lambda*-cyhalothrin (EC formulation) was applied June 24 at 15 g/ha, 125 L/ha volume, using an indoor spray chamber equipped with a single, traveling nozzle (T-Jet 8001E). Immediately after the pans were sprayed, the treated soil pans were moved outdoors and dug into the adjacent fallow and cropped areas. The cropped area had been seeded a month earlier and the barley crop was at the two-leaf stage. Pans were set in level with the rest of the field surface. Barley in the treated pans (treatment 3) emerged 3–5 days after the pans were sprayed. Barley in the surrounding cropped area grew quickly and provided a canopy over the treated soil pans within 2 weeks of *lambda*-cyhalothrin application.

Soil residue samples were taken at 0 (2 h), 1, 2, 5, 10, 13, and 16 weeks after application. To sample four strata were visually identified across the length of the pan and one 0–2.5-cm core sample (2.38 cm i.d.) was taken at random within each stratum. The four soil cores were then combined to form one composite sample from each pan. (In separate laboratory trials, *lambda*-cyhalothrin did not leach out of the top 2.5 cm of soil after application of 102 cm of water, i.e., 2 times the annual rainfall). The holes left by sampling were not filled in but were marked with a small stake so that they could be avoided on subsequent samplings. All soil samples were stored at −40 °C for 4–7 months until analysis. The barley crop was cut and removed after the week 10 sampling. The pans set into the fallow area to monitor

* Author to whom correspondence should be addressed.
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Table I. Recovery of *lambda*-Cyhalothrin from Fortified Soil

fortification level,[a] ppmd	recovery,[b] % (SD)
0.1	95.2 (6.0)
0.01	93.9 (2.0)
0.003	90.3 (4.1)
0.001	81.6 (26.1)

[a] Parts per million, dry-weight basis. [b] Each value is a mean of four replicates. Residues were corrected for naturally occurring interferences by subtracting the background residues detected in unfortified controls.

the long-term dissipation of *lambda*-cyhalothrin were sampled at 0, 16, 24, 40, and 52 weeks.

Residue Analysis Method. The residue analysis method was adapted from those previously reported for fenvalerate and deltamethrin in soils (Hill, 1981, 1983). The four-core composite samples (approximately 60 g each) were thawed and analyzed without subsampling or further preparation. The samples, contained in 500-mL Erlenmeyer flasks, were equilibrated with 20 mL of 0.1 N acetic acid for 1 h (resultant soil slurry pH 6.5) and then were extracted on a rotary platform shaker at 220 rpm according to the following regime: 100 mL of acetone for 1.5 h, 75 mL of 1:1 v/v hexane–acetone for 1.5 h, 75 mL of 1:1 v/v hexane–acetone for 15 min, followed by a 5-min rinse with 100 mL of hexane. Between solvent changes, the soil was allowed to settle and the liquid extract decanted through prewashed glass wool. Combined extracts were liquid–liquid partitioned with 550 mL of 2% NaCl, the hexane layer was separated, and the aqueous layer was reextracted with a fresh 100 mL of hexane. Combined hexane extracts were dried over 10 g of anhydrous Na_2SO_4, rotary evaporated (<40 °C) to a small volume, and adjusted to 10–25 mL in a volumetric flask.

Extracts were then cleaned up on acid alumina microcolumns (14.5 × 0.75 cm i.d. disposable pipets). The alumina (6% deactivated, 2.8 g per column) was wet packed to 5-cm height using hexane and 2.0 mL of extract (4.8–12 g of soil equivalent) applied. The extract was washed in with 2 mL of hexane and *lambda*-cyhalothrin eluted with 12 mL of 1:6.7 v/v ether–hexane. The eluate was evaporated to near dryness using a stream of dry nitrogen and adjusted to final volume (5–10 mL) with hexane.

Extracts were analyzed using a ^{63}Ni-ECD GC with DB-1 capillary column (30 m × 0.25 mm i.d., 0.1-μm film thickness) operated isothermally at 200 °C with helium carrier gas flow of 1.3 mL/min and nitrogen makeup gas at 19.4 mL/min. Responses were linear over the 1–40 pg/μL range of *lambda*-cyhalothrin standards injected (2-μL injections), and unknowns were quantified by alternate injections of appropriate standards.

Method recoveries were estimated by analysis of fortified samples. Blank soil samples (50 g of dry weight, sieved to 16 mesh) were fortified with 10 mL of *lambda*-cyhalothrin–acetone solution and then slurried with 20 mL of 0.1 N acetic acid (resultant pH 6.5) and air-dried overnight at room temperature. To simulate field-treated samples, fortified samples were held frozen at −40 °C for 1–4 months before extraction.

lambda-Cyhalothrin residues were calculated on a total micrograms per four-core sample basis (i.e., μg/17.8 cm^2). Residues were not corrected for apparent method losses but were background subtracted using unsprayed controls. Dissipation curves were fitted using the NLIN procedure (SAS Institute, 1985), and a likelihood ratio test (Gallant, 1987) was used to test for differences among dissipation curves.

RESULTS AND DISCUSSION

Residue Analysis Method. Recoveries of *lambda*-cyhalothrin from the 0.003–0.1 ppmd (d = dry-weight basis) fortified soil samples were >90% with good reproducibility (Table I). Recoveries were lower and more variable at the minimum quantifiable limit (2× background) of 0.001 ppmd. Background interferences became significant only at the 0.001–0.003 ppmd levels.

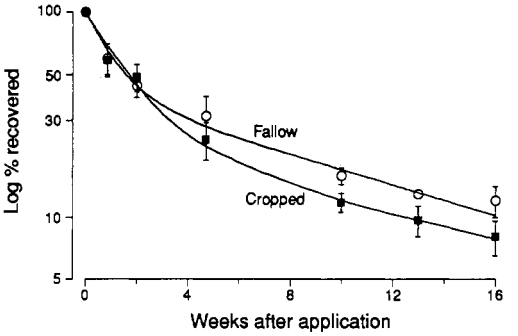

Figure 1. Dissipation of *lambda*-cyhalothrin, applied at 15 g/ha, on Lethbridge soil in fallow (treatment 1, DT_{90} = 16.2 weeks) vs cropped areas (treatment 2, DT_{90} = 12.8 weeks). Treatment 3 dissipation (DT_{90} = 12.2 weeks, not shown) was essentially the same as treatment 2. Each value is a mean of four replicate pans ± SD; 100% recovery at week 0 was 0.032 ppmd (11.6 g/ha) on the fallow soil and 0.031 ppmd (11.9 g/ha) on the cropped soil.

Field Experiment. Weather conditions over the 0–16 weeks were as follows: mean maximum temperature, 22.7 °C; mean minimum temperature, 8.0 °C; mean sunshine = 9.1 h/day, with 243 mm of rainfall occurring in 23 events. As previously observed for deltamethrin (Hill and Schaalje, 1985), the dissipation of *lambda*-cyhalothrin (mean initial residues 0.032 ppmd or 11.8 g/ha) on Lethbridge soil was biphasic (Figure 1). We have proposed that the rapid initial residue decline (0–2 weeks) is caused by initial surface losses (evaporation, photolysis, chemical hydrolysis, and physical loss) combined with microbial degradation, followed by a period of slow steady decline (2–16 weeks) mainly due to microbial degradation. A two-compartment model (Hill and Schaalje, 1985) was fitted to the data combined over all three treatments (R^2 = 0.953), and an overall DT_{50} = 1.3 weeks and DT_{90} = 14.5 weeks were calculated.

Between treatments 2 and 3 within the crop, there was no significant difference ($P > 0.05$) in residue decline, but dissipation was faster ($P < 0.05$) on the soil within the crop canopy (treatments 2 and 3) than in the fallow soil (treatment 1). The increase in *lambda*-cyhalothrin dissipation within the crop did not become evident until after the canopy developed, i.e., 2 weeks after pesticide application (Figure 1). Most applications in western Canada are made in late June before the crop canopy has developed. In situations where the canopy is present at the time of pesticide application, *lambda*-cyhalothrin soil residues may dissipate at the increased rate over the entire 0–16-week period.

Previous studies have indicated that the dissipation of pyrethroids is mostly microbial (Kaufman et al., 1977; Williams and Brown, 1979; Chapman et al., 1981). Thus, the faster dissipation of *lambda*-cyhalothrin within the crop canopy probably was caused by more favorable temperature and moisture conditions stimulating microbial activity. Daytime soil temperatures near the surface (2-mm depth) were monitored on several occasions over the 0–16 weeks. As expected, temperatures were always cooler in the shade of the crop canopy than in the fallow area. The largest differences occurred on calm, warm, sunny days when the surface soil temperatures within the crop canopy were 8–16 °C lower than those in the fallow area (Table II). It has been reported that soil microbial activities increase with increasing soil temperatures up to a maximum of 30–35 °C and then activity decreases (Walker, 1978; Abou-Assaf and Coats, 1987; Choi et al., 1988). On warm, sunny days in this experiment, the crop canopy probably kept soil surface temperatures closer to

Table II. Soil Surface Temperatures in Fallow vs Cropped Areas

time of day	air temp,[a] °C	soil surface temp,[a] °C	
		on fallow	within canopy
8:15 a.m.	24.0	27.2	19.2
10:30 a.m.	28.1	41.5	26.3
11:30 a.m.	30.6	45.4	29.3
1:15 p.m.	32.5	46.6	34.5
3:15 p.m.	33.6	44.6	36.8
4:00 p.m.	33.2	46.7	34.7

[a] Each temperature is a mean of readings taken on July 13 and July 28, 1987 (both warm, sunny days). Soil temperatures were taken at 2-mm depth within the pans.

Table III. Soil Moistures at 0–16-Week Sample Dates

sample date, weeks after application	soil moisture within different treatments,[a] %		
	1	2	3
0	7.8	6.4	7.3
1	11.4	21.8	19.4
2	7.0	9.9	7.9
5	7.5	24.0	23.2
10	6.3	23.2	16.7
13	3.6	4.3	3.8
16	4.5	5.2	4.8

[a] Percent moisture in the 0–2.5-cm soil from pans in treatment 1 (fallow soil), treatment 2 (soil within crop canopy), and treatment 3 (seeded soil within crop canopy). Each value is a mean from duplicate pans.

the optimum for the microbial degradation of *lambda*-cyhalothrin.

It also was observed that the 0–5-cm soil in the pans within the canopy often was wetter than the fallow soil (Table III). This effect was especially noticeable after a rainfall when the soil within the canopy took longer to dry out. Although the effect of moisture on soil microbial activity is complex (Kowalenko et al., 1978; Schoen and Winterlin, 1987), activity is reduced if soil moisture is too low (Walker, 1978; Abou-Assaf and Coats, 1987; Choi et al., 1988). In this experiment, the crop canopy may have contributed to higher microbial activity by preserving critical soil moisture levels at the start of each drying period.

Residues recovered from the long-term dissipation study in the fallow area were 100 (0.030 ppmd or 11.8 g/ha), 11.2, 9.5, 8.8, and 3.2% at 0, 16, 24, 40, and 52 weeks, respectively. As in the fallow vs cropped soil study, residues declined steadily over the summer (0–16 weeks) and then declined very little over the winter (16–40 weeks), with a resumption of dissipation in the spring (40–52 weeks). There should be little or no carry-over of *lambda*-cyhalothrin soil residues into the next crop year.

Results of this research indicate that, for *lambda*-cyhalothrin, the rate of residue dissipation on soil depends on whether the experiment is conducted on fallow or cropped soil. Using the soil-pan method within a crop may be the best compromise between simulating real field situations and obtaining repeatable, precise results.

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