

# Dissipation of Deltamethrin Applied to Forage Alfalfa<sup>1</sup>

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When deltamethrin was applied at 14 g/ha to immature, actively growing alfalfa, initial residues of 4.2 ppm (d = dry-weight basis) declined rapidly and biphasically. A two-compartment model was fitted to the residue data to calculate a DT<sub>50</sub> of 3.4 days and a DT<sub>90</sub> of 14 days (disappearance time for first 50% and 90% of residue). When deltamethrin was applied at 14 g/ha to more mature alfalfa in bloom, initial residues of 2.9 ppm declined with a DT<sub>50</sub> of 4.1 days and a DT<sub>90</sub> of 22 days. The isomeric nature of the "deltamethrin" residues was investigated. Small amounts of the ( $\alpha$ R)-deltamethrin isomer (maximum 0.08 ppm on day 0) were detected. *trans*-Deltamethrin isomers were not detected on day 0 but increased rapidly to 0.21 ppm by day 4 and then slowly declined. A multicompartment model is proposed to explain the fate of deltamethrin and its isomers on alfalfa.

Deltamethrin [(S)- $\alpha$ -cyano-3-phenoxybenzyl (1R,3R)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropane-carboxylate] is registered in Canada for the control of alfalfa weevil and lygus bug on alfalfa used for seed production only. The foliage from the treated seed alfalfa plants must not be fed to animals. The removal of this feeding restriction and the use of deltamethrin on alfalfa grown for forage are currently under review. With an acute oral LD<sub>50</sub> of 129 mg/kg for deltamethrin in male rats (Glomot, 1982), the concern is not that the animals would be poisoned by the treated foliage but the possibility that deltamethrin residues could appear in the meat and milk.

Published reports on the persistence of deltamethrin residues on forage crops are limited. In one summary, L'Hotellier (1982) reported that residues in oat straw were <0.05 ppm 1 month after treatment at 12.5 g/ha. In alfalfa, residues were 0.10-0.15 ppm 2-3 weeks after treatment at 17.5 g/ha. Westcott and Reichle (1987) found 0.05 ppm residues in wheat herbage 27 days after application at 6 g/ha. Five days after application at 5 g/ha, the same authors reported 0.04 ppm residues in sweet clover herbage. From these reports, one could expect residue levels of 0.05 ppm 1 month after deltamethrin application to forage crops.

Hill and Johnson (1987) determined the persistence of deltamethrin on pastures of crested wheatgrass. Residue decline was biphasic with a DT<sub>50</sub> of 12 days. Twenty-eight days after application at 7.2 g/ha, the mean residue level was 0.73 ppm (d = dry-weight basis) or 0.48 ppm (f = fresh-weight basis). These residue levels were considerably higher than the 0.05 ppm reported above.

The purpose of this study was to determine the rate of deltamethrin dissipation on forage alfalfa grown under western Canadian conditions. This information will be required if a wait period is to be established between spray application and the feeding of treated alfalfa to animals. We also investigated the isomeric nature of the deltamethrin residues and have proposed a multicompartment model to explain the fate of deltamethrin and its isomers in alfalfa.

## MATERIALS AND METHODS

**Field Studies.** Experiments 1 and 2 were conducted within the same field located near Lethbridge, Alberta. The alfalfa (cv. Beaver) had been seeded 3 years earlier as a forage crop with 17.8-cm row spacing. In both experiments, plots were 12.2 × 4.88 m arranged in a randomized complete block design with four

**Table I. Recovery of Deltamethrin from Fortified Alfalfa**

fortificn level, <sup>a</sup> ppm	% rec (std dev) <sup>b</sup>	fortificn level, <sup>a</sup> ppm	% rec (std dev) <sup>b</sup>
10	97.0 (2.3)	0.1	87.6 <sup>c</sup> (4.4)
1	96.1 (3.3)	0.03	94.2 <sup>c</sup> (5.3)

<sup>a</sup>Parts per million, dry-weight basis. On a fresh-weight basis, fortification levels were 2, 0.2, 0.02, and 0.006 ppm. <sup>b</sup>Each value is a mean of three or four replicates. <sup>c</sup>Recoveries were corrected for naturally occurring interferences by subtracting the 0.018 ppm "background residues" detected in unfortified controls.

replicates. Plots were not irrigated during these experiments. The Decis 2.5 EC formulation was applied at 14 g of AI/ha with a tractor-mounted plot sprayer with TeeJet 65015 nozzles. Water volume was 112 L/ha, and pressure was 275 kPa. In experiment 1, spray application was made on May 31 while the alfalfa was actively growing. In experiment 2, application was made on June 25 at the start of alfalfa flowering.

At each of six sampling dates after spraying, 40 representative stems were collected from 20 sites within each plot by cutting the alfalfa at ground level. Samples were immediately transported to the laboratory, weighed, and chopped on a Hobart 84181-D food cutter. Subsamples were taken for moisture determination (10 g, oven-dried at 110 °C for 48 h) and for residue analysis (20 g fresh weight, stored at -40 °C).

**Residue Analysis.** The alfalfa samples were analyzed by a previously reported residue method (Hill and Johnson, 1987). Briefly, samples were blended with acetone-hexane, liquid-liquid partitioned into hexane, cleaned up on alumina and silica gel microcolumns, and quantitated by <sup>63</sup>Ni GC. A 6% OV-210 column (Hill et al., 1982) was used in the GC analysis of sample extracts from experiment 1. Because this column did not adequately separate deltamethrin from its isomers (three partially resolved peaks were obtained with retention times of 13.3, 15.2, and 16.8 min), residues were determined on a total isomer basis, i.e., deltamethrin plus its isomers. Sample extracts from experiment 2 were analyzed on a DB-1 capillary column (Hill and Johnson, 1987), which resolved deltamethrin and its isomers into four peaks with retention times of 22.6, 24.0, 24.4, and 25.3 min. Residues from this experiment were determined on both a total isomer basis and an individual GC peak basis.

Method recoveries were estimated by analysis of fortified samples. Blank alfalfa samples (20 g fresh weight, 4 g dry weight) were fortified with 4 mL of 10, 1, 0.1, and 0.03 ppm deltamethrin-hexane solutions, equilibrated for 1 h at room temperature, and then stored for 3 days at 5 °C. Fortified samples were then frozen at -40 °C and held for 1-60 days before extraction. The fortified samples were withdrawn one or two at a time and analyzed at the same time as a set of field samples.

## RESULTS AND DISCUSSION

**Residue Analysis Method.** Recoveries of deltamethrin from the fortified alfalfa samples were generally >90% with good reproducibility (Table I). Thus, field residues were not corrected for apparent method losses. There was

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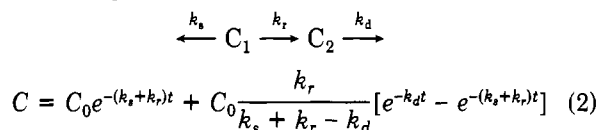
a small background interference in the alfalfa that co-chromatographed with the deltamethrin peak. This interference became a factor at the 0.1 ppm level, and thus residues detected in the day 28 field samples were background-subtracted using unsprayed controls. Residues from the other sample dates did not require this correction. The minimum detectable limit ( $2\times$  background) for residues in the field samples was 0.03 ppm.

**Modeling Residue Decline.** Unless otherwise stated, the terms "deltamethrin residues" or "residues" refer to deltamethrin determined on a total isomer basis. Deltamethrin residue data are expressed on both a ppm (micrograms per gram dry weight) basis and a tugs (total micrograms per 40-stem sample) basis. Residue decline on a ppm basis includes both dissipation of the chemical plus any effect from crop growth dilution. Residue decline on a tugs basis indicates dissipation of the chemical without growth dilution.

Either the first-order model (FOM)

$$C \xrightarrow{k} C_0 e^{-kt} \quad (1)$$

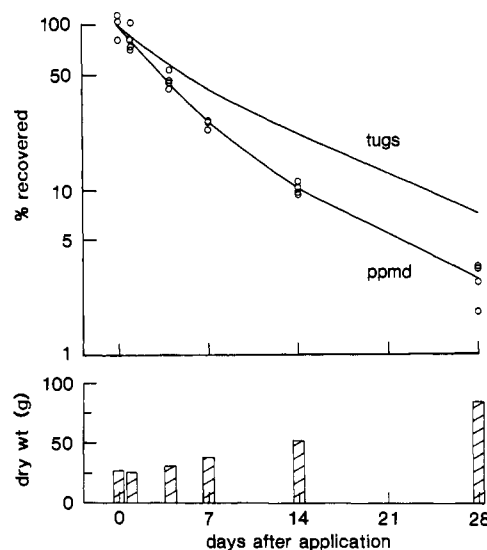
or a two-compartment model (2CM)



was fitted to the residue data. In the FOM, different dissipation processes are represented by one concerted process with rate constant  $k$ . The amount of residue  $C$  remaining after elapsed time  $t$  is a function of the initial residue  $C_0$ , the rate constant, and the elapsed time (eq 1). In the 2CM, two distinct dissipation processes are proposed: surface losses ( $k_s$ ) of residues (physical, volatilization, photolysis, hydrolysis, oxidation) from compartment  $C_1$  versus retention ( $k_r$ ) of the residues into compartment  $C_2$  with subsequent metabolic and chemical degradation ( $k_d$ ). The 2CM is fitted to residue data by iteratively solving for  $C_0$ ,  $k_s$ ,  $k_r$ , and  $k_d$  (eq 2). The FOM and 2CM models and the criterion for choosing between them have been previously described in detail (Hill and Schaalje, 1985; Hill and Johnson, 1987).

**Field Studies.** Temperatures during experiment 1 were moderate (mean max/min = 22.9/7.2 °C) with sufficient sunshine (10.8 h/day) and rainfall (24.3 mm) to promote crop growth. The mean alfalfa sample weight on day 28 was 3.2 times that on day 0 (Figure 1). Deltamethrin dissipation was biphasic, and the 2CM gave the best fit to both the ppm and tugs data (Figure 1). Because of the large growth dilution effect, residue decline on a ppm basis was rapid. Residue decline on a tugs basis, i.e., deltamethrin dissipation with growth dilution effects removed, was considerably slower. This difference is most evident between 7 and 28 days after application (Figure 1) when alfalfa growth was greatest. The time required for 50% and 90% of the initial residue to dissipate, i.e., the  $DT_{50}$  and  $DT_{90}$  (Table II), was calculated by iteration of eq 2. The  $DT_{90}$  of 24 days on a tugs basis versus 14 days on a ppm basis indicates the magnitude of the crop growth dilution effect.

The weather during experiment 2 was warm (mean max/min = 26.9/10.4 °C), sunny (11.4 h/day), and dry (2.6 mm of rainfall). Because the alfalfa was sprayed at the flowering stage, crop growth during this experiment was minimal and was restricted to the first 7 days after spraying (Figure 2). The mean alfalfa sample dry weight on day 28 was only 1.3 times that on day 0. The 2CM gave



**Figure 1.** Experiment 1. Dissipation of deltamethrin and growth of alfalfa. Using a log scale, the best fit residue decline is indicated on both a ppm (micrograms per gram dry weight) and a tugs (total micrograms per 40-stem sample) basis. Residue data are shown for the ppm basis only. The ppm basis includes deltamethrin dissipation plus growth dilution; the tugs basis removes growth dilution effect. Alfalfa growth is indicated by mean dry weight of 40-stem samples.

**Table II.** Dissipation of Deltamethrin Applied to Alfalfa

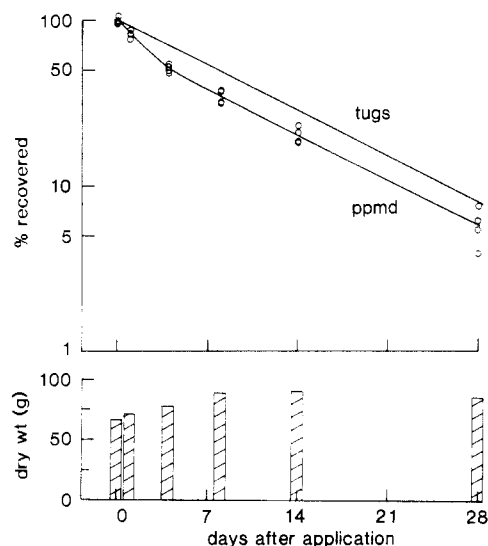
expt	init res <sup>a</sup>	best-fit decline model	$DT_{50}$ days	$DT_{90}$ days	days until ND res <sup>b</sup>
1	4.2 ppm <sup>c</sup>	2CM	3.4	14	46
	103 tugs	2CM	5.1	24	
2	2.9 ppm <sup>c</sup>	2CM	4.1	22	48
	176 tugs	FOM	7.7	26	

<sup>a</sup> Residue decline on a ppm (d = dry-weight) basis includes deltamethrin dissipation plus crop growth dilution; decline on a tugs (total micrograms per 40 stem sample) basis indicates deltamethrin dissipation without growth dilution. <sup>b</sup> Days until ND (nondetectable) residue based on the minimum detectable limit of 0.03 ppm. <sup>c</sup> Days estimated by supplying best-fit  $C_0$ ,  $k_s$ ,  $k_r$ , and  $k_d$  parameters to eq 2 and then solving for  $t$  iteratively until  $C = 0.03$  ppm. <sup>d</sup> Mean moisture contents of the alfalfa on day 0 were 79 and 72% for experiments 1 and 2. On a fresh-weight basis, initial residues were 0.88 and 0.81 ppmf, respectively.

the best fit for residue decline on a ppm basis, while the FOM gave the best fit on a tugs basis. Because there was some crop growth dilution early in this experiment, the  $DT_{50}$  on a ppm basis was 4.1 days versus 7.7 days on a tugs basis (Table II). With time after spraying, crop growth dilution became less of a factor; thus, the  $DT_{90}$ 's were similar (22 versus 26 days, Table II).

The initial residues on a tugs basis (Table II) were different between experiments 1 and 2 because the alfalfa was sprayed at different growth stages. The larger plants in experiment 2 trapped proportionately more micrograms of deltamethrin. Thus, on a ppm basis (see footnote c, Table II), the initial residues were nearly the same. The initial residues on a ppm basis (Table II) were not as similar because of the differences in moisture content of the alfalfa.

The rate of deltamethrin dissipation on alfalfa ( $DT_{50}$  of 5–8 days; Table II) was faster than the rate previously reported for deltamethrin on crested wheatgrass ( $DT_{50}$  of 12 days; Hill and Johnson, 1987). Also, the rate of deltamethrin dissipation in this study was faster than the rate previously observed for fenvalerate on alfalfa ( $T_{1/2}$  of 11–19 days; Hill et al., 1982). Because of the concern about feeding treated alfalfa to animals, the residue tolerance for



**Figure 2.** Experiment 2. Dissipation of deltamethrin and growth of alfalfa. Using a log scale, the best fit residue decline is indicated on both a ppmd (micrograms per gram dry weight) and a tugs (total micrograms per 40-stem sample) basis. Residue data are shown for the ppmd basis only. The ppmd basis includes deltamethrin dissipation plus growth dilution; the tugs basis removes growth dilution effect. Alfalfa growth is indicated by mean dry weight of 40-stem samples.

**Table III.** Name, Numbering, and Stereochemistry of Deltamethrin Isomers

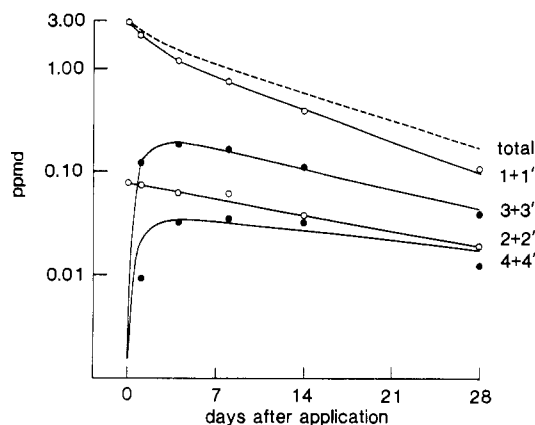
common name	numerical designation <sup>a</sup>	stereochemical configuration	
		$\alpha$ -cyano C	C1, C3 of cyclopropane
deltamethrin <sup>b</sup>	1	S	1R,3R-cis <sup>c</sup>
	1'	R	1S,3S-cis
( $\alpha$ R)-deltamethrin	2	R	1R,3R-cis
	2'	S	1S,3S-cis
trans-deltamethrin	3	S	1R,3S-trans <sup>c</sup>
	3'	R	1S,3R-trans
trans-deltamethrin	4	R	1R,3S-trans
	4'	S	1S,3R-trans

<sup>a</sup> As designated by Ruza et al. (1977). <sup>b</sup> [(S)- $\alpha$ -Cyano-3-phenoxycarbonyl (1R,3R)-cis-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate]. <sup>c</sup> Most insecticidally active isomers (Tessier, 1982).

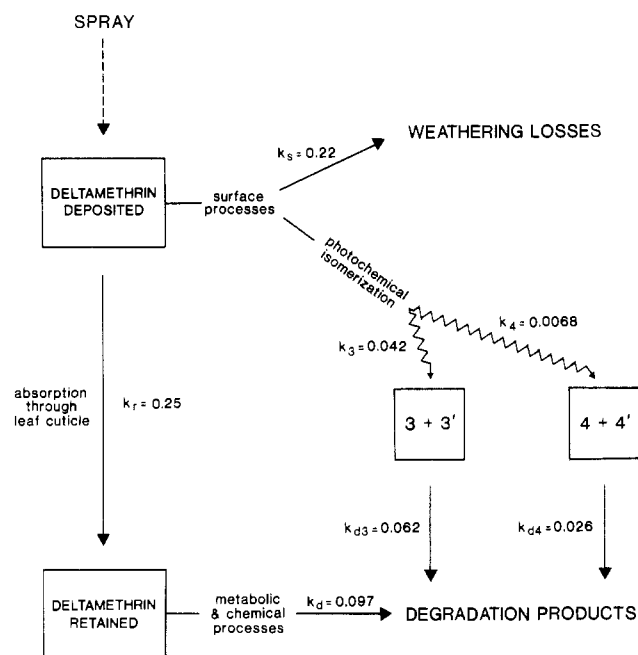
deltamethrin could be set at no detectable residues. The time required for deltamethrin residues to decline to our minimum detectable limit of 0.03 ppmd was estimated at 46–48 days (Table II).

**Isomeric Nature of Residues in Experiment 2.** As previously reported for deltamethrin on crested wheatgrass (Hill and Johnson, 1987), the DB-1 capillary column used in experiment 2 separated the "deltamethrin" residues into four diastereomers. Each GC peak represented one or both of a pair of enantiomers (Table III). Peak identities were tentatively assigned as follows: 2+2' for peak 1 at 22.6 min, 4+4' for peak 2 at 24.0 min, deltamethrin+1' for peak 3 at 24.4 min, and 3+3' for peak 4 at 25.3 min. To gain insight into the isomeric nature of the "deltamethrin" residues in experiment 2, residues were calculated on an individual GC peak basis.

The relative amounts of the different diastereomers changed with time after application (Figure 3). The cis isomers, deltamethrin+1' and 2+2', were at their highest concentrations on day 0 and then steadily declined. The decline of deltamethrin+1' was biphasic whereas the decline of the 2+2' isomers was first-order. The 2+2' isomers, initial concentration 0.08 ppmd or 3% of the total residue,



**Figure 3.** Experiment 2. Dissipation of deltamethrin isomers on alfalfa plotted on a log scale. Numbering and structures of the isomers are as per Table III. Each ppmd (micrograms per gram dry weight) value is a mean of four replicates. The best fit dissipation curves were calculated from the 2CM for total residues, the FOM for 2+2', and the MCM (Figure 4) for 1+1', 3+3', and 4+4'.



**Figure 4.** Proposed multicompartment model (MCM) for the dissipation of deltamethrin and its trans isomers on alfalfa. The  $k$  values are the best fit rate constants for the different processes determined by iterative, Basic language modeling.

probably originated from a formulation impurity or from a rapid chemical conversion ( $\alpha$ -proton exchange; Ruza et al., 1977) in the spray tank. Analysis of tank samples taken immediately after the spray operation revealed that there was 5% 2+2' in the spray solution.

The trans isomers, 3+3' and 4+4', rapidly increased from zero concentration on day 0 to maximum levels by day 4 and then slowly declined (Figure 3). There were no trans isomers detected in the spray solution. It appears that some of the deltamethrin+1' was initially converted to the trans isomers, this conversion eventually ceased, and then the trans isomers were slowly degraded.

A multicompartment model (MCM) is proposed (Figure 4) to explain the biphasic dissipation of deltamethrin+1' on the alfalfa while at the same time accounting for the increasing then decreasing concentrations of the trans isomers. The MCM is based on the following scenario for the fate of the applied deltamethrin. The deltamethrin

spray contacts the foliage and, as per the 2CM, is partitioned between a surface compartment and a retained compartment. Some of the deltamethrin surface deposits are lost via weathering, and some are photochemically isomerized to the trans isomers which then slowly degrade. Eventually, the surface residues are depleted and the weathering and photochemical processes cease. The remaining retained residues degrade by metabolic and chemical processes. This MCM is similar to and supports the model previously proposed for deltamethrin dissipation on crested wheatgrass forage (Hill and Johnson, 1987). To test the feasibility of this MCM, it was simultaneously applied to the residue data for deltamethrin+1' and the trans isomers 3+3' and 4+4'. A Basic language program (available on request) was used to iteratively supply different  $k$  values and then visualize the resulting fit. With the optimized set of  $k$  values (shown in Figure 4), the dissipation curves predicted by the MCM gave an excellent fit to the residue data for the different isomers (Figure 3).

The significance of the isomeric content of the "deltamethrin" residues has not been established. In experiment 2, the amount of isomers other than deltamethrin increased from 3% of the total residue on day 0, to 19% on day 4, to 40% on day 28 (Figure 3). In the short term, this isomerization of deltamethrin may represent a detoxification process. Tessier (1982) reported that only deltamethrin and the trans isomer 3 possess insecticidal activity, while Ruzo et al. (1977) found that only deltamethrin was of high acute toxicity to mammals. Nevertheless, for forage alfalfa, it seems only prudent to consider the total residues (deltamethrin plus isomers) that could be fed to animals.

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## Persistence and Fate of Deltamethrin Sprayed on a Pond

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Deltamethrin sprayed on a pond in Prince Edward Island, Canada, disappeared quickly from water, with a half-life of about 1 h. Major routes of degradation or dissipation were (i) chemical and photochemical conversion to inactive (2+2')-deltamethrin stereoisomers and (ii) hydrolysis with subsequent oxidation of products. No residues of deltamethrin stereoisomers or any of the four major degradation products sought were found 11 days postspray. Laboratory experiments on the volatilization of deltamethrin formulations from sprayed water as opposed to subsurface-injected water indicated that volatilization from the surface microlayer was a very fast process that could be the major route of dissipation of deltamethrin sprayed on a pond.

The insecticidal properties of deltamethrin [(S)- $\alpha$ -cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] were first reported in 1974 (Elliot et al., 1974), and it was developed commercially in France by Roussel Uclaf (Lhoste, 1982). The *cis*-1*R*,3*R* configuration about the cyclopropane ring and the *S* configuration for the cyano group at the benzylic carbon atom are essential for its high toxicity. In Canada deltamethrin is marketed by Hoechst Canada Inc. under the trade name Decis and is registered for use on such crops as tobacco, pears, canola, mustard, potatoes, sun-

flowers, broccoli, cabbage, wheat, and barley. Contamination of streams and ponds near sprayed fields is undesirable because of the high toxicity of deltamethrin to aquatic organisms (Mulla et al., 1978; Zitko et al., 1979; Bocquet and L'Hotellier, 1985). For this reason buffer zones of 15 and 100 m are commonly used between sprayed areas and water when deltamethrin is sprayed from the ground or air, respectively. Despite these precautions some deltamethrin may drift to water, and it is necessary to characterize the aquatic persistence and fate of this highly toxic insecticide.

Very few reports are available on the aquatic environmental dynamics of deltamethrin. Tooby et al. (1981) found that the half-life of deltamethrin in pond water was <1 day. The most comprehensive work is that of Muir et al. (1985) who studied the distribution and fate of radio-labeled deltamethrin injected just below the surfaces of two small ponds. Among other things, they demonstrated

Rivers Research Branch (R.J.M., R.J.T.), Lakes Research Branch (J.H.C., J.H.H.), and Research and Applications Branch (H.-B.L.), National Water Research Institute, Department of Environment, Canada Centre for Inland Waters, Burlington, Ontario, Canada L7R 4A6.