# Persistence of Deltamethrin in Baled Alfalfa Hay†

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Deltamethrin was applied to alfalfa at 12.5 g/ha, and residues were determined after 0, 7, and 14 days. The crop was cut and baled after 19 days. Residues in the bales were monitored using a $^{63}$Ni-ECD GC method to analyze core samples from replicate stacks. Residue decline in the standing crop was first-order with a half-life of 9.0 days. Deltamethrin residues were carried over into the bales. Two days after baling, 0.64 ppmd (d = dry weight basis) residues were detected. Residue decline during the 0–16-week period after baling was also first-order but extremely slow with a projected half-life of 77 weeks. Residue levels 16 weeks after baling were 0.55 ppmd. There was no residue decline during the 16–52-week winter/spring period. The sampling errors from taking core samples were investigated. There was negligible sampling error between bale ends (0%) or among sites on the bale ends (0.5%) compared with 2.5% error among replicate stacks and 7.4% error for laboratory analyses.

## INTRODUCTION

Deltamethrin [(*S*)-α-cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] is registered in Canada for the control of alfalfa weevil and lygus bug on alfalfa used for seed production only. The foilage from the treated seed alfalfa plants must not be fed to animals because the deltamethrin residues may appear in the meat and milk. This feeding restriction is currently under review. It has been proposed that, given sufficient time after spraying, the deltamethrin residues in the alfalfa should decline to acceptable levels which would not be transferred to the animals' meat or milk. We have previously investigated the decline of deltamethrin residues in standing alfalfa crops (Hill et al., 1989). When deltamethrin was applied at 14 g/ha to both actively growing and mature crops, the 2.9–4.2 ppmd (d = dry weight basis) initial residues declined biphasically with a $DT_{50}$ of 5.1–7.7 days and a $DT_{90}$ of 24–26 days (disappearance time for first 50 and 90% of residue). We estimated that, on the basis of a minimum detectable level of 0.03 ppmd, 45–48 days would be required for residues to decline to nondetectable levels. In the case of forage alfalfa or seed alfalfa cut for forage, the alfalfa would be cut and baled 7–30 days after spraying. Therefore, some deltamethrin residues would be carried over into the bales. If and when the treated bales could be fed to animals would then depend on how long the deltamethrin residues persist in the baled alfalfa. With the onset of winter, most producers would not wait much more than 16 weeks before feeding the treated bales.

Although there have been several reports on deltamethrin residues in standing crops (L'Hotellier, 1982; Westcott and Reichle, 1987; Hill and Johnson, 1987; Hill et al., 1989), to our knowledge there are no published studies on the persistence of deltamethrin, or any other pesticide, in dried or baled hay.

On a related topic, Smith and Willis (1985) reported the disappearance of the pyrethroid fenvalerate from sugarcane leaf trash. In a laboratory incubation of field-treated trash containing 28% moisture, held at 25 °C under aerobic conditions for 12 weeks, residue decline was first-order with a half-life of 10 weeks. Substantial evidence of microbial activity was presented.

In a study on deltamethrin aerially applied to pastures of crested wheatgrass, Hill and Johnson (1987) determined the persistence of deltamethrin on the litter (dead stems and leaves) covering the soil surface. Residue decline was biphasic with a $DT_{50}$ of 27 days and was attributed to microbial activity similar to that found on soil. This rate of decline was slower than the $DT_{50}$ of 12 days observed for the residues on the crop.

The objective of this study was to determine the rate of deltamethrin dissipation in baled alfalfa held in stacks under typical western Canadian conditions. This information will be required if a wait period is to be established between spray application and the feeding of treated bales to livestock. We also investigated the sampling errors involved in taking core samples to estimate the pesticide concentration in a stack of bales.

## MATERIALS AND METHODS

**Field Plot Procedures.** The alfalfa bales were obtained from a 0.85-ha area of a producer's field located near Lethbridge, AB. The alfalfa (cv. Maxim) had been seeded 4 years earlier mixed with orchardgrass (14:1 alfalfa/grass).

The plots consisted of 10.1 × 425 m untreated control area adjacent to a 10.1 × 425 m treated area. A Decis 5.0 EC formulation was applied at 12.5 g of ai/ha (maximum label rate) using a self-propelled plot sprayer equipped with a 10.2-m boom and Delavan LF-1.5 80° nozzles. Water volume was 112 L/ha, and pressure was 275 kPa. The spray application was made on June 8, 1990, while the alfalfa was still growing (crop height 43 cm, 2 weeks prior to bloom).

The standing alfalfa crop was sampled 2 h and 7, and 14 days after spraying by cutting, at ground level, all of the crop within a 12.5 × 12.5 cm (0.016 m$^2$) square. At each of four locations in the treated and untreated areas (chosen according to a stratified random design), two 12.5 × 12.5 cm samples were taken, and all eight subsamples were combined to form one composite sample. Four such composites (each using a different set of four locations) were collected from the treated area on each sample date. Two composites per date were collected from the control area. The standing crop samples were transported on ice to the laboratory, weighed, and then held frozen at −40 °C for 6 months. The samples were then chopped (while

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frozen) using a Hobart 84181-D food cutter and mixed and subsamples taken for moisture determination (10 g, oven-dried at 110 °C for 48 h) and residue analysis (20 g of fresh weight).

Fifteen days after spraying, the standing alfalfa was cut (2.44-m swaths) and rolled into windrows using a mower conditioner. Four days after cutting, the windrows were baled into conventional "small square" bales (40.6 × 45.7 × 91.4 cm, 30–35 kg). The bales were removed from the producer's field, transported to the Lethbridge Research Station, and stacked 1 day after baling.

The alfalfa had been irrigated earlier in the season but was not irrigated during the 15 days between spraying and cutting. During this time, total precipitation was 29.2 mm (28.0 mm fell 4-5 days after spraying) and the mean maximum/minimum temperature was 19.7/8.6 °C. No precipitation fell between cutting and baling.

**Bale Handling and Sampling.** The bales from the treated area were randomly assigned to four replicate stacks, each stack consisting of four rows of four bales. The bales were aligned side by side so that the bale ends were exposed and accessible for sampling. Bales from the control area were similarly arranged in two replicate stacks. The stacks were located outdoors and were unsheltered except for plastic and plywood sheets placed on top of the stacks to repel precipitation.

The stacks were sampled 2 days and 4, 12, 16, 37, and 52 weeks after baling using a stainless steel, hollow-core, sample probe (40.6 cm × 2.22 cm i.d.) attached to an electric drill. A sample consisted of a composite of 16 cores per stack, one core taken from the end of each bale. Both ends of the bales were used by first sampling eight bales at random from one side of the stack and then sampling the remaining eight bales from the other side of the stack. The specific location of the cores within the bale ends was chosen at random based on a choice of 12 possible sites. There was enough space for six cores to be taken between the two strings holding the bale together (17.8 cm apart) plus three more cores between the string and each side of the bale.

To evaluate sampling errors, two subsampling experiments were conducted. At the 2-day and 4-week samplings, the stack sampling error was determined by taking duplicate composite samples from each stack, each duplicate taken from the 16 bales using a different random order (and therefore different bale ends) and different sites on the bale ends. At the 12-, 16-, and 52-week samplings, the within-bale sampling error was determined by taking duplicate composite samples of each stack, the duplicates taken from the same ends of the same bales but from different sites.

The 16-core composite samples were weighed and then stored at −40 °C for 1–6 months. The samples were chopped, mixed, and subsampled for moisture determination and residue analysis (10 g of fresh weight) as before.

**Residue Analysis.** The standing crop and bale samples were analyzed using a previously reported method (Hill and Johnson; 1987, Hill et al., 1989). Briefly, samples were blended with 1:1 (v/v) acetone–hexane, liquid–liquid partitioned into hexane, cleaned up on alumina and silica gel microcolumns, and quantitated by $^{63}$Ni-ECD GC using a DB-1 capillary column. Deltamethrin residues were not separated in the GC analysis. Residues were determined on a total isomer basis, i.e., deltamethrin plus any isomers. Method recoveries for the standing crop samples have been previously reported (88–97% with minimum detectable limit of 0.03 ppmd; Hill et al., 1989). Method recoveries for the bale samples were estimated by analysis of fortified alfalfa hay. Blank bale samples (10 g of dry weight) were fortified with 4 mL of deltamethrin–hexane solution and then air-dried for 2 h at room temperature. To simulate field-treated samples, fortified samples were frozen at −40 °C and stored with the field samples. Sets of fortified samples were then removed from storage and analyzed with the field samples. Depending upon which set of field samples they were analyzed with, the fortified samples were in storage for 2–4 months before extraction.

Table I. Recovery of Deltamethrin from Fortified Alfalfa Hay

| fortification level,[a] ppmd | recovery,[b] % (SD) |
|---|---|
| 2 | 95.9 (8.0) |
| 0.2 | 93.9 (6.0) |
| 0.02 | 103 (9.0) |
| 0.02–bkg | 85.0 (9.0) |

[a] Parts per million, dry weight basis. [b] Each value is a mean of four or five replicates. At the 0.02 ppmd level, residues were corrected for naturally occurring interferences by subtracting the background residues detected in unfortified controls.

To facilitate comparisons, the crop and bale residues were both determined on a micrograms per gram of dry weight (ppmd) basis. Residues in the unknown crop and bale samples were not corrected for apparent method losses or for background interferences. Residue dissipation curves were fitted using the NLIN procedure (SAS Institute, 1989). Dissipation in the standing crop was calculated on both a ppmd basis, which includes dissipation of the chemical plus any crop growth dilution, and a total micrograms per sample basis, which determines dissipation of the chemical itself (Hill et al., 1982).

Bale sampling errors were determined using the following model of the sources of variation:

$$\text{ppmd} = \text{stacks, weeks, stacks} \times \text{weeks, subsamples within stacks and weeks, residual} \quad (1)$$

Analysis of variance (GLM procedure; SAS Institute, 1989) was used to obtain the root mean square errors and the residual maximum likelihood (VARCOMP procedure; SAS Institute, 1989) to separate the variance components. The laboratory analysis error was estimated using the mean variance from analyses of the 2 and 0.2 ppmd fortified samples.

## RESULTS AND DISCUSSION

**Residue Analysis Method.** Recoveries of deltamethrin from the alfalfa hay fortified at 2.0 and 0.2 ppmd were >90% with good reproducibility (Table I). Recoveries were slightly less at the minimum quantifiable limit (2× background) of 0.02 ppmd. Background interferences were significant at the 0.02 ppmd level only. Differences in the storage times (2–4 months) of the fortified samples had no effect on method recoveries as evidenced by the 6–9% standard deviations.

**Residue Decline in the Standing Crop.** The initial residue level of 2.0 ppmd declined rapidly until the alfalfa was cut 15 days later (Figure 1). The first-order model (FOM) was fitted ($R^2 = 0.97$) to this decline and a half-life of 8.7 days calculated. When calculations were made on a total micrograms per sample basis to remove any growth dilution (data not shown), the half-life was 9.0 days. The mean sample dry weights of 159 g (SD = 23) on day 0 and 178 g (SD = 35) on day 15 confirmed that there was only a slight crop growth dilution of the deltamethrin residues. The half-life of 9 days is slightly longer than the $DT_{50}$ of 5–8 days previously reported for deltamethrin dissipation on forage alfalfa (Hill et al., 1989). We attribute the reduced rate of dissipation in this experiment to cooler

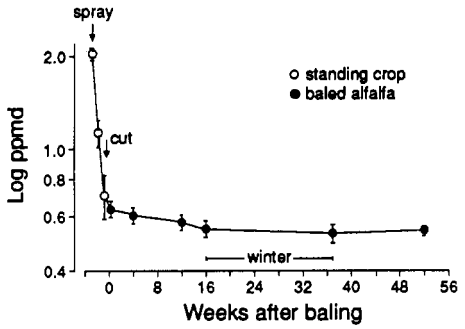


**Figure 1.** Dissipation of deltamethrin on a standing alfalfa crop and the subsequent persistence of residues carried over into the baled alfalfa. Crop was sprayed June 8 at 12.5 g/ha, cut June 23, and baled June 27. Residues are expressed on a ppmd (μg/g of dry weight) basis. Each value is a mean of four replicates ± SD.

temperatures (maximum/minimum 19.7/8.6 °C compared with 22.9/7.2 and 26.9/10.4 °C in the previous study).

**Residue Decline in the Stacked Bales.** The initial moisture level in the bales was 11.2% Two days after baling, deltamethrin residue levels of 0.64 ppmd were detected (Figure 1). These residue levels were reduced from the 0.71 ppmd detected in the standing crop just before cutting. However, once baled, the deltamethrin residues in the alfalfa hay declined extremely slowly. A projected half-life of 77 weeks was calculated by fitting the FOM ($R^2$ = 0.79) to the 0–16-week residue data. Sixteen weeks after baling, the residue levels were still 0.55 ppmd, which corresponds to a 14% loss of residues from time of baling.

The rate of deltamethrin decline in the baled alfalfa is much slower than the rate reported for the disappearance of fenvalerate (half-life of 10 weeks) from sugarcane leaf trash (Smith and Willis, 1985). Conditions in their laboratory study, higher moisture (28%) and constant temperature (25 °C), were probably more conducive to residue decline. The projected half-life of 77 weeks in the present study is also very much longer than the $DT_{50}$ of 27 days we previously observed for the dissipation of deltamethrin on litter from crested wheatgrass (Hill and Johnson, 1987). In that study, the deltamethrin was deposited onto the surface of the litter, whereas in this experiment the deltamethrin was applied to live crop tissue and may have been incorporated into the alfalfa during the 19 days between spraying and baling. We have previously reported on the rapid penetration of deltamethrin into wheat leaves (Hill and Inaba, 1990). Whether due to incorporation or simply physical location, the residues in the bales would not have been available for surface dissipation processes like photolytic degradation and weathering losses. Although incorporated and "aged", it is unlikely that the deltamethrin residues we detected were "bound" and unavailable for biological degradation. As pointed out by Khan et al. (1984), if these residues were truly bound residues, our conventional residue analysis method would not have detected them.

Conditions inside the bales were sufficiently aerobic to support plant metabolic processes. For example, the mean 16-core sample dry weight decreased from 415 g (SD = 11) 2 days after baling to 388 g (SD = 21) at 16 weeks. In spite of the low moisture levels, some enzyme activity and limited respiration probably occurred in the bales, which would account for the 6.5% loss in dry matter (Rode et al., 1986). Such activity would provide one mechanism for the slow dissipation of the deltamethrin residues in the bales.

The environment within the bales was relatively stable and represented a typical, low moisture, stacked bale situation. As expected, mositure levels in the bales decreased slightly from 11.2 to 10.0% at 16 weeks. Temperatures in the interior of the bales were monitored on several occasions. Daytime temperatures in the summer were consistently 21–24 °C compared with daily maximum/minimum air temperatures of 24–30/11–18 °C. Later in the season when the maximum/minimum air temperatures were 17–23/7–9 °C, bale temperatures were 14–17 °C. We found no excessive heating (40–60 °C) within the bales, which would have suggested extensive deterioration of the hay by molds or fungi (Wittenberg, 1991).

Because microorganisms are indigenous to most crop residues (Parr and Papendick, 1978) and from the incubation results of Smith and Willis (1985), one might expect some microbial activity in the baled alfalfa. The microbial activity would have been kept in check by the low moisture conditions; however, over time, it may have contributed to the slow dissipation of deltamethrin residues.

With the cooler temperatures, the deltamethrin residues did not decline during the 16–37-week winter period (Figure 1). The residues detected at 52 weeks (0.54 ppmd) also suggest that residue dissipation did not resume during the 37–52-week spring period.

We concluded that, given the current feeding restriction of no detectable residues (<0.02 ppmd), a 1-year holding period would not be sufficient for deltamethrin residues to decline to acceptable levels in baled alfalfa.

**Table II. Errors in Sampling Stacks of Bales for Residue Analysis**

| type of error | root mean square,[a] % | root variance component,[a] % |
|---|---|---|
| among stacks | 11.5 | 2.5 |
| experimental | 6.7 | 0 |
| between bale ends | 6.4 | 0 |
| among bale end sites | 9.9 | 0.5 |
| laboratory analysis | 7.4 | 7.4 |

[a] Expressed as percentage of the mean residue.

**Sampling Errors.** Because the deltamethrin spray treatment was applied to the standing crop, the highest residue levels would have been on the upper parts of the alfalfa plants. The residue distribution within the bales would then depend upon the orientation and mixing of the alfalfa stems in the bales as produced by the cutting and baling operations. There was potential for large variation in the residue levels detected in the bales from core-sampling different bale ends and different sites on the ends.

Analysis of the data from the bale subsampling experiments (Table II) indicated that the residues in the bales were fairly evenly distributed and that, by taking 16-core composite samples, the sampling errors were minimal. When the mean square errors were separated into the individual variance components, the bale sampling errors (0% between bale ends and 0.5% among bale end sites) were negligible compared with the 2.5% among different stacks and the 7.4% for laboratory analyses. We concluded that, for our sampling plan, it did not matter which end of the bales was sampled and minimal variation was introduced by randomly selecting 1 of 12 sites on the bale ends.

If the more dominant laboratory analysis error (which cannot be controlled by sampling) is ignored, recommendations can be made for future bale sampling. The 2.5% mean error among stacks (Table II), based on taking 1 core per bale to form a 16-core composite, translates to $2.5\% \times 16^{1/2} = 10\%$ error among different bales. Similarly, the 0.5% mean error within bales translates to $0.5\% \times 16^{1/2} = 2\%$ error within bales for a one core per bale sampling. Using the relative magnitude of these errors

and the relative costs of sampling multiple cores per bale vs sampling more bales (Steel and Torrie, 1989), it was determined that one core per bale was optimum. Therefore, when core-sampling a stack of bales for residue analysis, there is little benefit from sampling more than one core per bale; however, variation can be reduced by taking samples from more bales.

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