mixture of 2 (0.1 g), sodium carbonate (51.5 mg, 1.275 equiv), and methanol-$d_4$ (1.96 g) in a 10-mm NMR tube was monitored according to the same methodology used for 10. The results are shown in Table VI. The conversion percentage was calculated on the basis of the integration ratio of the methoxy group of 10 (at $\delta$ 3.98) and 27c (at $\delta$ 3.71).

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# Persistence of Deltamethrin and Its Isomers on Pasture Forage and Litter

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The deposition, persistence, and isomeric conversion of deltamethrin [(*S*)-$\alpha$-cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] were measured after a 7.2 g/ha aerial application to control grasshoppers in two pastures. Mean deposition was 75.9% of applied, with initial deltamethrin residues of 2.06 ppmd (d = dry-weight basis) on the forage and 146 $\mu g/m^2$ on the litter. Deltamethrin dissipation was biphasic, and a two-compartment model was fitted to the residue data. The $DT_{50}$ was 5.9 days for deltamethrin residues on forage and 17 days on litter. Small amounts of the $\alpha R$ diastereomer of deltamethrin were detected on the forage (0.06 ppmd) and on the litter (0.65 $\mu g/m^2$). The concentration of the trans isomers increased exponentially until, within 14 days after application, asymptotic levels of 0.26 ppmd on the forage and 22.7 $\mu g/m^2$ on the litter were reached.

The synthetic pyrethroid deltamethrin is registered for the control of grasshoppers in cereal crops in western Canada with the restriction that fields must not be treated within 40 days of harvest. Deltamethrin also has potential for controlling grasshoppers in pastures (Johnson et al., 1986).

There have been few published reports on the persistence of deltamethrin in field crops or forage. Ruzo and Casida (1979) reported that, under greenhouse conditions, [$^{14}$C]deltamethrin had a half-life of 1.1 weeks on cotton and a time for 90% loss of 4.6 weeks. Cole et al. (1982) found that less than 50% [$^{14}$C]deltamethrin remained on cotton and beans after 4–5 days outdoors. Khan et al. (1984) investigated the formation of bound residues of deltamethrin in bean plants. Ten days after treatment with [$^{14}$C]deltamethrin, 3–10% of the $^{14}$C label was in the form of bound residues. In summarizing deltamethrin residue levels found in various crops, L'Hotellier (1982) reported that residues in oat straw were less than 0.05 ppm 1 month after treatment at 12.5 g/ha. Two to three weeks after treatment at 17.5 g/ha, the residue levels in fresh or dried alfalfa were 0.10–0.15 ppm.

**Table I. Name, Numbering, and Structures of Deltamethrin Isomers**[a]

| common name | numerical designation | stereochemical configuration: $\alpha$-cyano C | stereochemical configuration: $C_1$,$C_3$ of cyclopropane |
|---|---|---|---|
| deltamethrin | 1 | *S* | 1*R*,3*R*-cis[b] |
| | 1′ | *R* | 1*S*,3*S*-cis |
| ($\alpha R$)-deltamethrin | 2 | *R* | 1*R*,3*R*-cis |
| | 2′ | *S* | 1*S*,3*S*-cis |
| *trans*-deltamethrin | 3 | *S* | 1*R*,3*S*-trans[b] |
| | 3′ | *R* | 1*S*,3*R*-trans |
| | 4 | *R* | 1*R*,3*S*-trans |
| | 4′ | *S* | 1*S*,3*R*-trans |

[a] As designated by Ruzo et al. (1977). [b] Most biologically active isomers.

The purpose of this study was to obtain residue data for the establishment of a minimum time interval between treatment of pastures and grazing by cattle. We were particularly interested in the isomeric nature of the "deltamethrin" residues. There are eight possible isomers that may be found after chemical transformations of

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deltamethrin in the environment (Table I). Of these, ($\alpha R$)-deltamethrin can originate from $\alpha$ proton exchange, whereas the *trans*-deltamethrin isomers can be formed by photochemical reactions (Ruzo et al., 1977). Significant amounts of *trans*-deltamethrin (5–8% of applied), but little if any ($\alpha R$)-deltamethrin, have been found on cotton leaves (Ruzo and Casida, 1979). This pattern of substantial amounts of *trans*-deltamethrin (9–29% of applied), with little ($\alpha R$)-deltamethrin (0–2% of applied), was confirmed in a later study with cotton and bean leaves (Cole et al., 1982). It has been reported that only deltamethrin and the trans isomer 3 (Table I) are highly active against insects (Tessier, 1982), and only deltamethrin is of high acute toxicity to mammals (Ruzo et al., 1977). There could also be differences in the chronic effects of the isomers. Thus, it may be important to determine the isomeric nature of "deltamethrin" residues found in the environment.

## MATERIALS AND METHODS

**Site.** The experiment was conducted on two ungrazed pastures (block 1, 38 ha; block 2, 47 ha) located 1 km apart near Claresholm, Alberta, Canada. The forage in block 1 was mainly crested wheatgrass (93%) interspersed with alfalfa (7%), with a crop height of 20–25 cm. Block 2 was essentially 100% crested wheatgrass, with a crop height of 25–30 cm. The ground was covered with considerable amounts of litter (271 g dry wt/m$^2$) consisting of dead crested wheatgrass stems and leaves.

**Chemicals.** Deltamethrin analytical standard (purity ≥99%) was obtained from Roussel Uclaf (Romainville, France), and the formulated product, 50 g/L emulsifiable concentrate (EC), was supplied by Hoechst Canada Inc., Regina, Saskatchewan. Aluminum oxide 504-C acidic from CAMAG (Switzerland) and Silicar CC-4 Special from Mallinckrodt, Inc., were deactivated to 6% moisture and equilibrated overnight before use.

**Treatment.** On June 23, 1983, between 9:00 and 9:50 a.m., a Grumman Ag Cat 164 aircraft applied the deltamethrin EC at 7.2 g/ha using 8.9 L/ha water volume. The water volume had been precalibrated on an "actual loss basis", and samples from the spray tank were analyzed to confirm the deltamethrin concentration. The aircraft was equipped with 43 TeeJet 4664 nozzles fitted with #5 tips and #25 cores and tilted 157° to the rear. The aircraft flew at 145 km/h and sprayed at 138 kPa pressure from a 3-m height. From these spray parameters, the volume median drop diameter was estimated to be 250 $\mu$m. Meteorological conditions during the spray treatment: wind, NNW at 13–18 km/h; RH, 71% at 2-m height; temperatures, 18.1, 18.2, 15.5, and 14.5 °C (slightly lapse condition) at 0.01-, 0.1-, 1-, and 3-m height.

In each block, a control area of about 9 ha was left unsprayed.

**Sampling.** An 8 × 8 grid (30 m between grid lines) was laid out on a treated area of 210 × 210 m within each block. Residue samples from 16 sites, chosen from the 64 grid intersections in a stratified random design, were combined to form one composite sample. A second composite sample was also taken from 16 different random sites within each block. At each site, the forage and litter from within a 25 × 25 cm area were sampled separately. The standing forage was cut at ground level, and then the litter was hand picked down to the bare soil. The soil was not sampled because only about 5% of the original sampled area was bare soil. The treated areas were sampled −1, 0.2, 1, 4, 7, 14, 21, and 28 days after spraying.

The unsprayed control areas were sampled as described above except that only five randomly chosen sites were used for each composite.

All forage and litter composite samples were placed on dry ice as collected and were then stored at −40 °C until analysis.

**Residue Analysis.** The method was a modification of procedures previously used to determine fenvalerate residues in alfalfa (Hill et al., 1982).

*Sample Preparation.* Before analysis, the forage samples were weighed, chopped on a Hobart Model 84181-D food cutter, mixed, and subsampled: 20 g for residue analysis and 10 g for moisture determination (dried at 110 °C for 48 h). The litter samples were prepared in the same manner except that any soil collected with the litter was first removed by sieving through a 20-mesh screen.

*Extraction and Cleanup.* The forage and litter samples were extracted on a Waring Blendor by the following solvent regime: 200 mL of acetone–hexane (1:1), 150 mL of acetone–hexane (1:2), and then 150 mL of hexane, followed by a final rinse of the Blendor and residuum with 50 mL of acetone–hexane (1:1). The combined extracts were partitioned with 350 mL of 2% NaCl solution, and the hexane layer was separated. The remaining acetone–aqueous salt solution was reextracted with 100 mL of fresh hexane. The hexane layers were combined, dried over anhydrous $Na_2SO_4$, rotary evaporated (35 °C) to near dryness, and adjusted to 25- or 50-mL volumes with hexane. The extract was then cleaned up by alumina and silica gel column chromatography. The columns were disposable Pasteur pipets (14.6 × 0.75 cm i.d.) packed with 5 cm of adsorbent. A 1- or 2-mL aliquot of extract (0.4–1.6-g sample equivalent) was applied to the alumina column and washed in with 2 mL of hexane and then with 10 mL of ether–hexane (1:19), and the deltamethrin fraction was eluted with 10 mL of ether–hexane (1:9). This fraction was evaporated to near dryness under a stream of dry nitrogen and quantitatively transferred onto the silica gel column with hexane. The column was developed with 5 mL of ether–hexane (1:19), and then the deltamethrin fraction was eluted with 10 mL of ether–hexane (1:9). This fraction was concentrated as before and adjusted with hexane to an appropriate final volume (5–25 mL) for GC analysis.

Method recoveries were estimated by analysis of fortified forage samples. The forage, 20-g fresh weight, was fortified with 4 mL of deltamethrin–hexane solution, equilibrated for 1 h, and frozen at −40 °C to simulate field-treated samples.

*Gas Chromatography.* A Varian Model 3700 gas chromatograph equipped with a $^{63}$Ni detector was used. The column was a J&W fused silica capillary, 30 m × 0.25 mm, coated with DB-1 at 0.1-$\mu$m film thickness (Chromatographic Specialties Ltd., Brockville, Ontario, Canada). This column was operated isothermally at 221 °C with a helium carrier gas flow of 1.3 mL/min and nitrogen makeup gas at 19.4 mL/min. To generate the deltamethrin isomers and test for adequate GC resolution, deltamethrin, as a thin film (15 $\mu$g/cm$^2$) on glass, was irradiated outdoors with bright sunshine for 4 days (Ruzo et al., 1977). Photoproducts were recovered from the glass with hexane.

A Varian Model 8020 autosampler was used to inject 2-$\mu$L volumes onto a Varian 1085 direct capillary injector. Detector responses were linear over a 2–100-pg range of standards. Unknowns were quantified by alternate injections of these standards. Deltamethrin isomers were assumed to have the same response factor as deltamethrin.

*Confirmatory Methods.* The thin-layer chromatography (TLC) used Baker-flex silica gel IB2-F plates developed in either benzene–carbon tetrachloride (1:1) or hexane–

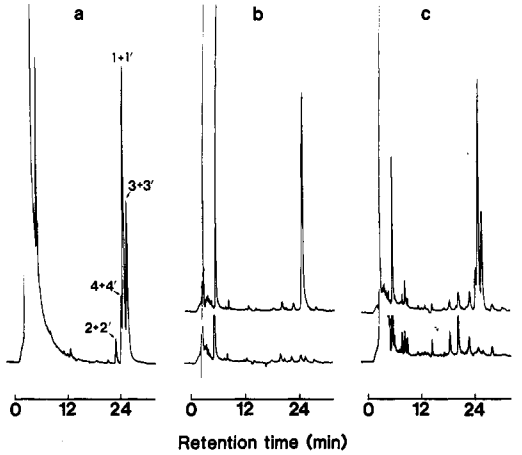


**Figure 1.** Typical chromatograms for the determination of deltamethrin and its isomers on forage: (a) isomeric photoproducts, as per Table I, recovered from the sunlight irradiation of deltamethrin on glass; (b) extract of forage sampled 0.2 day after application vs. extract of pretreatment forage (both are 2-μL injections of 0.4-g sample equivalent taken to 25-mL final volume); (c) extract of forage sampled 28 days after application vs. extract of pretreatment forage (both are 2-μL injections of 1.6-g sample equivalent taken to 10-mL final volume).

ether (4:1). The minimum detectable amount (visible spot with a 254-nm source) was 0.5 μg.

Combined gas chromatography–mass spectrometry (GC–MS) was conducted using a Hewlett-Packard 5985B instrument with an SPB-1 capillary column (30 m × 0.25 mm). Ten nanograms was required to obtain a confirmatory electron-impact spectrum.

## RESULTS AND DISCUSSION

**Gas Chromatography.** Sunlight irradiation of deltamethrin, as a thin film on glass, yielded diastereomers that were partially resolved by GC (Figure 1a). Because the capillary column was achiral and did not separate enantiomeric pairs, each GC peak potentially represents one or both of the possible enantiomers. With the numerical designation of Ruzo et al. (1977) (Table I), the retention times and tentative peak identities were as follows: 22.6 (2 + 2′), 24.0 (4 + 4′), 24.4 (deltamethrin + 1′), 25.3 min (3 + 3′). These isomeric assignments are based on TLC, GC, and GC–MS evidence. The photoproducts from the sunlight irradiation were first separated by TLC (benzene–carbon tetrachloride (1:1), developed three times) into cis ($R_f$ 0.61) and trans ($R_f$ 0.52) isomers. The cis and trans $R_f$ regions were recovered from the plates and were confirmed by GC and GC–MS. Further TLC (hexane–ether (4:1), developed three times) separated the cis isomers into 2 + 2′ ($R_f$ 0.79) and 1 + 1′ ($R_f$ 0.74) and the trans isomers into 4 + 4′ ($R_f$ 0.74) and 3 + 3′ ($R_f$ 0.69). The individual diastereomers were recovered from the plates and were confirmed by GC. The $R_f$ values of the diastereomers agreed with the $R_f$ values for authentic standards published by Ruzo et al. (1977). The mass spectra of the four diastereomers were essentially identical and agreed with the published spectrum (Tessier, 1982) for deltamethrin.

**Method Recoveries.** There were background interferences present in the forage (Figure 1b,c) that increased the apparent recovery of deltamethrin at the 0.01 and 0.03 ppmd (d = dry weight basis) fortification levels (Table II). When the GC response to these interferences was subtracted from the response to deltamethrin, method recoveries were greater than 90% at the 0.03 to 3 ppmd levels with acceptable variation (SD < 7%). To remove any possible effect of the background interferences on sample analyses, the GC responses of pretreatment (−1 day) blanks were deducted from the residues detected in the forage and litter samples. At the 0.01 ppmd fortification level, deltamethrin recovery was low and more variable. Because there were few residues less than 0.03 ppmd, the data were not corrected for the apparent method losses.

**Table II. Recovery of Deltamethrin from Fortified Forage**

| fortifcn level,[a] ppm (dry-wt basis) | % rec (SD), $n$ = 4 | adjusted % rec[b] (SD), $n$ = 4 |
|---|---|---|
| 3 | 90.7 (3.0) | 90.5 (3.0) |
| 0.3 | 92.3 (2.1) | 90.4 (1.9) |
| 0.03 | 109 (5.7) | 90.4 (6.4) |
| 0.01 | 120 (13) | 76.6 (13) |

[a] The mean moisture content of the forage was 34%. On a fresh-weight basis, the fortification levels were 2, 0.2, 0.02, and 0.007 ppm. [b] Blank deducted to remove the effect of background interferences.

**Table III. Deltamethrin Deposited on the Forage and Litter**

| block | composite sample | deposition,[a] % of applied: on forage[b] | on litter[b] | on forage + litter |
|---|---|---|---|---|
| 1 | 1 | 55.9 | 21.4 | 77.4 |
| | 2 | 61.3 | 25.9 | 87.2 |
| 2 | 1 | 53.8 | 19.3 | 73.1 |
| | 2 | 44.2 | 21.6 | 65.8 |
| overall means | | 53.8 | 22.1 | 75.9 |

[a] Deltamethrin applied was 722 μg/m². [b] Based on total deltamethrin isomers (μg/m²) per composite sample (ppmd × sample dry weight = μg/m²); each composite composed of 16 25 × 25 cm samples.

**Deltamethrin Deposition.** The 0.2-day residues (based on total deltamethrin isomers) were used to estimate spray deposition. The amount of deltamethrin deposited on the forage and litter was similar (±5%) between composites within blocks (Table III). The best estimate of total deltamethrin deposited is the overall mean of 75.9% of applied. Deposition must be considered if our data are used to predict residue levels for other field situations. There can be large differences in the deposition between different spray applications.

**Residues on Forage.** Contrary to many crop situations, there was no growth dilution of residues during this 28-day experiment. The mean forage density, estimated from 11 50 × 50 cm samples/block, was 182.5 g dry weight/m² (SE = 10.7 g/m²) on day 0 and 173.6 g dry weight/m² (SE = 15.3 g/m²) on day 28. The decrease in forage dry weight was attributed to grasshopper feeding because only 65% control was achieved by the deltamethrin treatment (Johnson et al., 1986).

The location of the 25 × 25 cm area sampled at each site on a given day was chosen at random. Because of this random selection, there were differences in stand density between subsequent samples at the same site, as well as among sites. The total dry weights of the composite samples were mostly within the range of 200–250 g. To compensate for differences in sample weights (i.e., stand density), residues are expressed on a ppmd basis.

Residues were first determined on a "total isomer basis" from the integrated area across all four GC peaks. When log concentration was plotted against time, residue decline was biphasic (Figure 2). The concept of biphasic dissipation of pesticides on and in plant parts was first introduced by Gunther and Blinn (1955) and then reiterated by Gunther (1969). They proposed an initial dissipation consisting of sloughing, codistillation, volatilization, pho-

**Table IV. Persistence of Deltamethrin and Isomers on Forage and Litter**

| substrate | compound[a] | best fit model[b] | $r^2$ | rate constants | | | $C_0$ or $C_{max}$, ppmd or $\mu g/m^2$[d] | $DT_{50}$ or $AT_{50}$,[e] days |
|---|---|---|---|---|---|---|---|---|
| | | | | $k_s$ | $k_r$ | $k_d$[c] | | |
| forage | total isomers | 2CM | 0.96 | 0.18 | 0.31 | 0.025 | 2.21 | 12 |
| | deltamethrin + 1′ | 2CM | 0.97 | 0.25 | 0.33 | 0.038 | 2.06 | 5.9 |
| | 2 + 2′ | 2CM | 0.74 | 0.13 | 0.08 | 0.001 | 0.06 | 8.3 |
| | 3 + 3′ | EAM | 0.79 | | | 2.53 | 0.21 | 0.3 |
| | 4 + 4′ | EAM | 0.91 | | | 0.27 | 0.05 | 2.6 |
| litter | total isomers | 2CM | 0.68 | 0.08 | 0.76 | 0.023 | 155 | 27 |
| | deltamethrin + 1′ | 2CM | 0.79 | 0.16 | 0.80 | 0.032 | 146 | 17 |
| | 2 + 2′ | FOM | 0.13 | | | 0.028 | 0.65 | 25 |
| | 3 + 3′ | EAM | 0.37 | | | 3.44 | 18.9 | 0.2 |
| | 4 + 4′ | EAM | 0.66 | | | 0.12 | 3.73 | 5.6 |

[a] Numbering as per Table I. [b] Key: 2CM = two-compartment model, EAM = exponential asymptotic model, FOM = first-order model. [c] $k_d$'s are only comparable within the same model. [d] $C_0$ for 2CM and FOM, $C_{max}$ for EAM. Units are ppm on a dry-weight basis for forage and $\mu g/m^2$ for litter. [e] Key: $DT_{50}$ = disappearance time for first 50% of residue, $AT_{50}$ = appearance time for first 50% of residue.

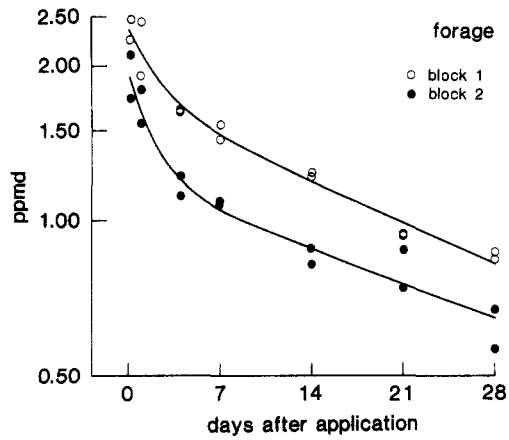


**Figure 2.** Dissipation of total deltamethrin isomers on forage (ppmd = ppm, dry-weight basis) plotted on a log scale. Regression lines are fitted by the two-compartment model.

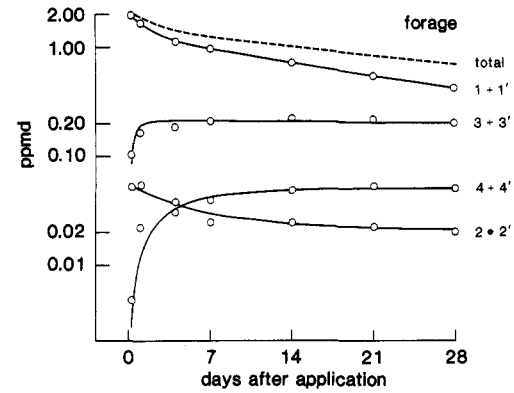


**Figure 3.** Dissipation of different deltamethrin isomers on forage (ppmd = ppm, dry weight basis) plotted on a log scale. Numbering and structures of the isomers are as per Table I. Each value is a mean of four composite samples. Regression lines are fitted by the best fit models for the different isomers as per Table IV.

todecomposition, hydrolysis, and oxidation (collectively classified as "weathering"), followed by a phase of metabolic and hydrolytic attack of the penetrated residue. The following two-compartment model (2CM) gave an excellent fit ($r^2$ = 0.96; Table IV) to the total isomer data

$$\overset{k_s}{\leftarrow} C_1 \overset{k_r}{\rightarrow} C_2 \overset{k_d}{\rightarrow} \quad (1)$$

from which the following expression can be derived

$$C = C_0 e^{-(k_s+k_r)t} + C_0 \frac{k_r}{k_s + k_r - k_d}[e^{-k_d t} - e^{-(k_s+k_r)t}] \quad (2)$$

where $C_1$ = a deposited residue compartment, $C_2$ = a retained residue compartment, $C$ = total residue remaining after time $t$, $C_0$ = initial residue deposited at time $t$ = 0, $k_s$ = rate constant for surface losses of residues from $C_1$, $k_r$ = rate constant for movement of residues into $C_2$, and $k_d$ = rate constant for degradation of residues in $C_2$. This 2CM has been previously described in detail to explain the biphasic dissipation of deltamethrin on soil (Hill and Schaalje, 1985). Although the best fit day 0 residue values, 2.51 ppmd for block 1 and 1.92 ppmd for block 2, were significantly different ($p < 0.001$), indicating more deposition on block 1, the plotted shapes and rates of dissipation for the two blocks were the same (Figure 2).

Residues were then determined on an "individual GC peak basis", and the log concentration of each enantiomeric pair vs. time was plotted (Figure 3). Deltamethrin + 1′ and 2 + 2′ both exhibited biphasic dissipation with a corresponding exponential increase in the trans isomers 3 + 3′ and 4 + 4′.

The 2CM was also the best fit model for the deltamethrin + 1′ and 2 + 2′ isomers (Table IV). Ruzo and Casida (1979) found that the dissipation of [$^{14}$C]deltamethrin topically applied to cotton leaves was essentially first order over the first 4 weeks. This first-order dissipation may have been a function of their method of application or of greenhouse conditions. In our study, it is important to note (Table IV) that the $DT_{50}$ = 5.9 days for deltamethrin + 1′ is considerably shorter than the $DT_{50}$ = 12 days for the total isomers ($DT_{50}$ = disappearance time for first 50% of residue). If the isomeric content of the "deltamethrin" residues had not been resolved by our GC analysis, the $DT_{50}$ of the total isomers would have greatly overestimated the "true" $DT_{50}$ for deltamethrin, per se. Our $DT_{50}$ agrees with the half-life of 1.1 weeks for [$^{14}$C]deltamethrin on cotton reported by Ruzo and Casida (1979) and the half-life of 5 days on cotton and 4 days on beans indicated by the data of Cole et al. (1982). In both previous metabolic studies, little or none of the 2 + 2′ isomers was detected. Our levels of 2 + 2′ were also low and may have originated in part from the formulation because 0.5% 2 + 2′ was detected in the spray tank samples.

The following exponential asymptotic model (EAM) gave the best fit ($r^2$ = 0.79 and 0.91; Table IV) to the residue data for the trans isomers

$$C = C_{max}(1 - e^{-k_d t}) \quad (3)$$

where $C$ = residue remaining after time $t$, $C_{max}$ = maximum residue (asymptote), and $k_d$ = degradation rate constant. There were no trans isomers detected in the spray tank samples, but by the 0.2-day sampling, substantial amounts of the trans isomers 3 + 3′ had been formed (Figure 3). Such a rapid formation of trans isomers suggests that a photochemical process was involved. Of

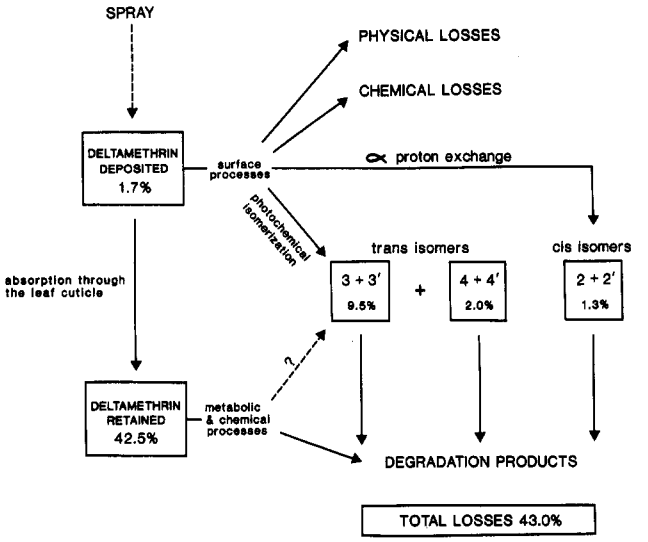


**Figure 4.** Proposed model for the dissipation of deltamethrin on forage. The day 7 amounts of each component are given as a percentage of the 2.21 ppmd deltamethrin deposited on the forage at day 0.

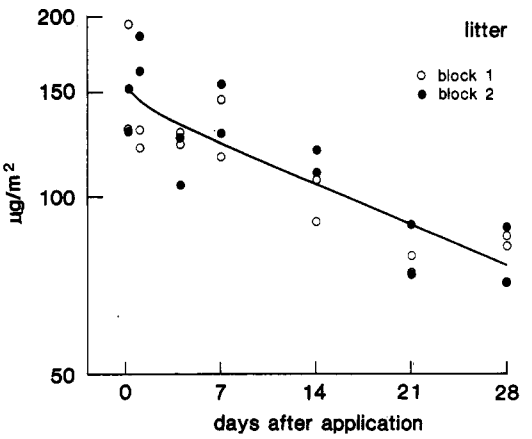


**Figure 5.** Dissipation of total deltamethrin isomers on litter ($\mu g/m^2$ plotted on a log scale). Regression line is fitted by the two-compartment model.

the total isomers detected on day 7, 20% consisted of the trans isomers 3 + 3′ and 4 + 4′. In their greenhouse study, Ruzo and Casida (1979) reported that by day 7 the trans isomers had increased to 7% of the total recovered $^{14}C$ radioactivity and then slowly decreased with time. The data of Cole et al. (1982) also showed an increase in trans isomers to 25–29% of recovered $^{14}C$ radioactivity by day 10, followed by a decrease to 13–15% by day 20.

Integrating our field results with previous metabolic studies (Ruzo and Casida, 1979; Cole et al., 1982) yields an overall model for deltamethrin dissipation on forage (Figure 4). For simplicity, we have not included all possible degradation mechanisms and we have excluded reversible reactions. Deltamethrin spray contacts the foliage and according to the 2CM is partitioned between "surface" and "retained" compartments. The surface deposits are photochemically isomerized to the trans isomers, which then slowly degrade. The cis isomers 2 + 2′ may also be formed, but this isomerization occurs via $\alpha$ proton exchange and is probably not a photochemical or metabolic reaction. Surface deltamethrin could also be lost via other chemical reactions and several authors (Ruzo and Casida, 1979; Cole et al., 1982; Khan et al., 1984) have suggested physical losses caused by volatilization, transpiration, and other weathering processes. In this study, the rate of dissipation due to surface processes was relatively fast ($k_s$ = 0.25), but by day 7 these processes should have subsided because most of the remaining deltamethrin had moved ($k_r$ = 0.33) into the retained compartment. The retained residues were then slowly degraded ($k_d$ = 0.038) by metabolic and chemical processes.

Experiments conducted by Miyamoto and Mikami (1983) on pyrethroid metabolism in plants support this model. They attributed a 20% loss of applied deltamethrin during the first week to evaporation from cotton leaves. They also found that 13–25% of applied pyrethroid had penetrated the plant during this time. Our model does not readily explain why, in our study, the concentration of trans isomers continued to increase past day 7 and had not declined by day 28 (Figure 3). It is possible (Figure 4) that either (1) the retained residues were also photochemically isomerized, (2) the retained residues were isomerized by metabolic and chemical processes, or (3) the degradation of the trans isomers was extremely slow. For (1) to occur, it may have been necessary for the retained deltamethrin to desorb through the cuticle to the leaf surface. McCall et al. (1986) recently reported this phenomenon for the herbicide tridiphane on giant foxtail. Evidence against (2) is found in the data of Cole et al. (1982) who recovered 8% [$^{14}C$]-*trans*-deltamethrin from bean plants held outdoors for 4 days, but none from plants held in the dark. Alternative (3) does not seem likely, especially since the trans isomers of other pyrethroids degrade faster on plants than the cis isomers (Gaughan and Casida, 1978; Miyamoto and Mikami, 1983). Although it seems reasonable to apply the 2CM to the biphasic deltamethrin dissipation, the EAM is probably an oversimplification of the processes affecting the trans isomers. The mathematical basis of the EAM is a zero-order or constant rate of formation ($dC/dt = a$) combined with a first-order loss process ($-dC/dt = kC$). In this study, the EAM was empirically fitted to the trans isomer data and did not provide a real insight into the nature of their formation or loss.

**Residues on the Litter.** There was no apparent change in the amount of litter over the 28-day experiment. The mean dry weight/square meter was 228 g for block 1 and 314 g for block 2. Deltamethrin residues should not be a function of the litter weights because the spray contacts only the uppermost layer of litter. Thus, residues on the litter are expressed in micrograms/square meter. The litter residues were more variable than the corresponding forage residues because the amount of deltamethrin contacting the litter depended on the filtering effect of the forage and on how completely the litter covered the ground.

On a total isomer basis, residue decline was biphasic with no significant difference ($p > 0.2$) between blocks in either the predicted day 0 residues or rate of dissipation (Figure 5). The 2CM gave only an acceptable fit ($r^2$ = 0.68; Table IV) to the total isomer data because of the variability in residue values explained above. The first-order model (FOM) fitted the total isomer data almost as well ($r^2$ = 0.67).

When the litter residues were separated into the four enantiomeric pairs, the shape and relative magnitude of the log concentration vs. time plots (Figure 6) were similar to those for the forage residues (Figure 3). As expected, the best fit models accounted for less of the variation ($r^2$ = 0.13–0.79; Table IV) in the litter residues than in the forage residues ($r^2$ = 0.74–0.97).

The deltamethrin + 1′ degraded much slower on the litter than on the forage (Table IV). The 2CM predicted slower losses due to surface processes ($k_s$ = 0.16) and faster movement of litter residues into the retained compartment

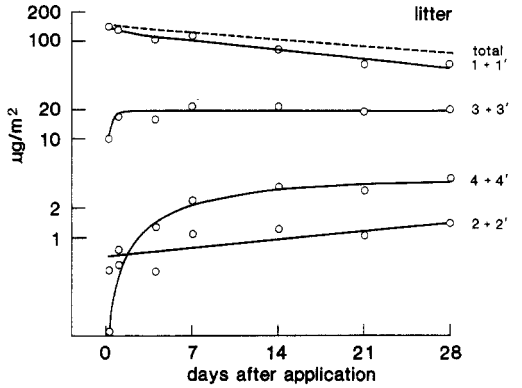


**Figure 6.** Dissipation of different deltamethrin isomers on litter ($\mu g/m^2$ plotted on a log scale). Numbering and structures of the isomers are as per Table I. Each value is a mean of four composite samples. Regression lines are fitted by the best fit models for the different isomers as per Table IV.

($k_r = 0.80$). It is conceivable that residues on the litter were more sheltered from physical losses and were absorbed faster than residues on the forage. The fitted rate of metabolic and chemical processes ($k_d = 0.032$) was similar to the rate ($k_d = 0.038$) previously fitted for the forage residues. On the litter, the source of metabolic and chemical processes could include microbial activity such as that proposed for the dissipation of deltamethrin on soil (Kaufman et al., 1977; Williams and Brown, 1979; Chapman et al., 1981). The $DT_{50}$ = 17 days for deltamethrin + 1′ on the litter (Table IV) is within the range of $DT_{50}$ = 11–30 days previously reported for the biphasic dissipation of deltamethrin on soil (Hill and Schaalje, 1985).

On the litter, the amount of **2** + **2′** isomers (Figure 6) appeared to slowly increase rather than decrease (Figure 3); however, the residue amounts were extremely low (equivalent to 0.002–0.008 ppmd). These levels were below the 0.01 ppmd limit for reliable method recoveries (Table II). Consequently, the FOM accounted for only 13% of the variability in the **2** + **2′** data (Table IV).

The trans isomers, **3** + **3′** and **4** + **4′**, were formed just as rapidly on the litter (Figure 6) as on the forage (Figure 3). Because the forage canopy was thin enough that much of the litter was exposed to sunlight, a photochemical process is again suggested. Of the total isomers detected on the litter on day 7, 17% consisted of the trans isomers. As previously observed on the forage, the levels of trans isomers on the litter continued to increase past day 7 and had not started to decline by day 28.

A model, analogous to that for forage (Figure 4), should apply to the dissipation of deltamethrin on the litter. However, deltamethrin deposits on the litter would be more protected from weathering, and with less surface loss, the overall rate of deltamethrin dissipation would be slower.

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