# Fate of the Pyrethroid Insecticide Deltamethrin in Small Ponds: A Mass Balance Study

Derek C. G. Muir,* Gary P. Rawn,[1] and Norbert P. Grift

The fate and distribution of $^{14}C$-radiolabeled deltamethrin (1(*R*)[1a(*S**),3a]-cyano-(3-phenoxyphenyl)methyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate) were monitored for 306 days, following a single application at 10 g/ha to two small outdoor ponds (17 $m^2$ surface area). Initial concentrations of the insecticide in filtered water ranged from 1.28 to 2.50 $\mu g/L$. Deltamethrin ([$^{14}C$]cyclopropyl acid or benzyl alcohol labeled) rapidly partitioned into suspended solids, plants, sediment, and air, with a half-life of 2–4 h in water. Duckweed (*Lemna* sp.) and a submerged pondweed (*Potamogeton berchtoldi*) accumulated deltamethrin concentrations ranging from 253 to 1021 ng/g, respectively, at 24 h posttreatment. Sediments were the major sink for radioactivity at 306 days posttreatment, and intact deltamethrin was present at concentrations ranging from 3 to 5 ng/g. Deltamethrin levels in air above the water ranged from 10–100 $ng/m^3$ during a 48-h monitoring period following application. Fathead minnows (*Pimephales promelas*) accumulated levels of extractable radioactivity 248–907-fold higher than concentrations in water at 24 h posttreatment, but no fish mortality was observed.

## INTRODUCTION

Deltamethrin (1(*R*)[1a(*S**),3a]-cyano-(3-phenoxyphenyl)methyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate) (Figure 1), like other synthetic pyrethroid insecticides, may be applied to control insect pests in large acreage crops such a cereals, tobacco, and cotton. Contamination of water bodies in agricultural areas, from runoff (Carroll et al., 1981) or spray drift, may result from widespread use of the insecticides. Pyrethroid insecticides are extremely toxic to aquatic organisms in laboratory studies with 96 h $LC_{50}$'s in the low parts per billion range for fish (Spehar et al., 1983; McLeese et al., 1980) and in the parts per trillion range for aquatic invertebrates (Anderson, 1983; Stephenson, 1982). Under field conditions, the impact of synthetic pyrethroids such as cypermethrin, deltamethrin, and permethrin, applied to the surface of small ponds or to nearby crops, is generally less than expected, on the basis of laboratory data, due to rapid dissipation of the compounds (Mulla et al., 1981; Crossland, 1982; Crossland et al., 1982). It is apparent, from conflicting laboratory and field observations on the effects of synthetic pyrethroids, that a better understanding of the environmental dynamics of the compounds in aquatic environments is needed.

The rapid disappearance of the synthetic pyrethroids, following application to small ponds, has made it difficult to establish a mass balance of the insecticides. Field studies with small ponds have demonstrated rapid disappearance of cypermethrin (Crossland, 1982), permethrin (Rawn et al., 1982), and deltamethrin (Tooby et al., 1981) in water with half-lives of <1 day. Crossland (1982) could account for only 8–16% of cypermethrin, in the subsurface water, 48 h after application to a pond surface, while deltamethrin could not be detected in water (detection limit 0.5 $\mu g/L$) 24 h after a similar treatment (Tooby et al., 1981). Only 56% of [$^{14}C$]permethrin could be accounted for 24 h after direct addition to the water column (Rawn et al., 1982). Major losses of the pyrethroids have been attributed to volatilization from water (Rawn et al., 1982) or surface films (Crossland, 1982), but have not been measured directly. The purpose of the present study was to determine, quantitatively, the relative importance of various pathways, such as volatilization, degradation in water and sediment, and uptake by fish and plants, following application of $^{14}C$-labeled deltamethrin to water under field conditions.

## MATERIALS AND METHODS

**Aquatic System.** Two artificial outdoor ponds (5.3 $m^3$ water volume, 17 $m^2$ area, and 0.5 m depth) were selected for the study. The ponds had been constructed two years previously, as described by Corbet (1983). An identical pond nearby was used as an untreated control. The ponds were eutrophic with abundant aquatic macrophytes, duckweed (*Lemna* sp.), and a submerged pondweed (*Potamogeton berchtoldi* Fieber *var. acuminatus* Fieber). Pond 1 contained a greater biomass of macrophytes than pond 2. A filamentous green algae (*Spirogyra* sp.) was observed in pond 1 following addition of the insecticide. Fathead minnows (*Pimephales promelas*) were added to the ponds 7 days prior to treatment. Bottom sediments consisted of 77% clay and 23% silt, with a 3.5% organic carbon content. Containers (6 cm diameter and 3 cm depth), filled with sediments from a control pond, were placed on the pond bottom 21 days prior to the addition of insecticide to provide sediment samples.

**Chemicals.** Deltamethrin, [$^{14}C$]deltamethrin (cyclopropyl acid labeled or benzyl alcohol labeled) (Figure 1), and the hydrolysis product IR cis acid (IR *cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid) were obtained from Hoechst Canada Ltd. (Regina, Sask.). PB acid (3-phenoxybenzoic acid) was obtained from I.C.I (Jealotts Hill, U.K.). The two $^{14}C$-labeled deltamethrin standards were purified before use by preparative thin-layer chromatography with a solvent system of chloroform–ethyl acetate–methanol (6:3:1). Analysis by HPLC indicated the [$^{14}C$]deltamethrin was >99% radiochemically pure. The purified products were diluted with a deltamethrin formulation (Decis, 25 g/L emulsifiable concentrate, Hoechst Canada Ltd.) to a final specific activity of 12.2 DPM/ng.

**Pond Treatment and Sampling.** The ponds were treated at a rate of 10 g a.i./ha (or 17.06 mg per pond) on July 7, 1982. The application rate was that recommended for agricultural use by ground rig application. Acetone solutions (0.65 mL) of each $^{14}C$-label were applied, in the

Department of Fisheries and Oceans, Freshwater Institute, Winnipeg, Canada R3T 2N6.

[1]Current address: Commercial Chemicals Branch, E.P.S., Environment Canada, Ottawa, Canada K1A 1C8.

0021-8561/85/1433-0603$01.50/0 Published 1985 by the American Chemical Society

**Table I. Water Chemistry Parameters Monitored during the Field Study**[a]

| time, days | pond no. | pH | Chloro-*a*, μg/L | TSS, mg/L | susp N, μg/L | susp C, μg/L | DOC, μmol/L | OC/TSS, % |
|---|---|---|---|---|---|---|---|---|
| −1 | 1 | 8.1 | 48.0 | 23 | 1126 | 6540 | 2860 | 4 |
| | 2 | 7.65 | 22.2 | 11 | 673 | 3300 | 2390 | 3 |
| | C[b] | 7.80 | 26.4 | 15 | 608 | 3020 | 2860 | 3 |
| 1 | 1 | 8.86 | 94.5 | 22 | 1398 | 6890 | 2550 | 4 |
| | 2 | 8.44 | 49.5 | 11 | 814 | 3920 | 2610 | 2 |
| 8 | 1 | 9.40 | 52.5 | 9 | 775 | 3280 | 2990 | 3 |
| | 2 | 9.27 | 157.0 | 23 | 1812 | 9400 | 3020 | 7 |
| 21 | 1 | 9.91 | 86.5 | 24 | 1198 | 9410 | 2710 | 8 |
| | 2 | 9.96 | 48.0 | 14 | 1096 | 5230 | 3180 | 5 |
| 35 | 1 | 7.48 | 27.2 | 7 | 477 | 2500 | 2830 | 2 |
| | 2 | 7.48 | 47.5 | 14 | 736 | 3430 | 2550 | 3 |
| 56 | 1 | 10.18 | 21.2 | 5 | 407 | 2450 | 2830 | 2 |
| | 2 | 9.92 | 27.0 | 7 | 605 | 2760 | 3020 | 2 |
| 112 | 1 | 8.10 | 7.9 | 5 | 201 | 1870 | 2390 | 1 |
| | 2 | 8.30 | 12.3 | 7 | 219 | 2420 | 2230 | 2 |

[a] Chloro-*a* = chlorophyll-*a*; TSS = total suspended solids (>greater 1.0 μm); susp N = suspended nitrogen; susp C = suspended carbon; DOC = dissolved organic carbon; OC/TSS = percent organic carbon in suspended solids. Determined by using the methods of Stainton et al. (1977). [b] Control pond.

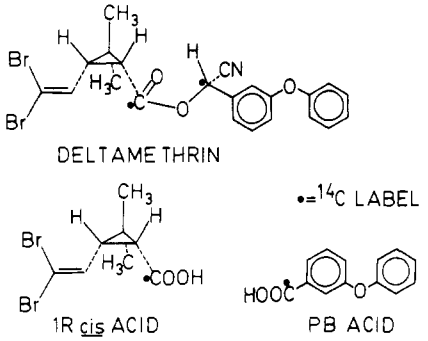


**Figure 1.** Structures of deltamethrin and hydrolysis products.

0–2 cm depth, with a Pasteur pipette in such a way that most of the water surface was covered. Pond 1 received [$^{14}$C]cyclopropyl acid-labeled insecticide and pond 2 the [$^{14}$C]benzyl alcohol-labeled compound. Surface (0–5 cm) and subsurface (5–50 cm) water (1 L) was collected at 1, 2, 4, 8, 12, 18, 24, and 48 h posttreatment by using a depth integrated sampling technique. After 48 h, samples integrated over the entire depth were collected (in duplicate) at 3, 4, 5, and 7 days and then at weekly intervals to 112 days. Water samples were immediately filtered through glass fiber paper (Whatman GFA grade). Extraction of filtered water was begun immediately by adding ethyl acetate to each sample. Water was then stored at 4 °C until further analysis. Suspended solids were air-dried and stored at −18 °C.

Sediment was sampled at 12 and 24 h, 2, 5, and 7 days, and at two-week intervals to 112 days by removing containers (in duplicate) from the pond bottom and recovering the 0–2-cm layer. Fish, aquatic plants, and filamentous algae samples were sampled on a similar schedule. All samples were stored at −50 °C until analyzed. Additional water, sediment, and algae samples were collected at 306 days posttreatment.

Air was sampled (10 L/min), with polyurethane foam plugs (5 cm diameter × 7 cm length) held in glass tubes, at three heights (5, 12.5, and 17.5 cm) above each pond. Polyurethane foam was prepared for use as described by Grover and Kerr (1981). The foam plugs were changed every 2 h during the initial 36 h after treatment. A final 12-h sample was taken from 36 to 48 h after treatment.

Water chemistry (Table I), wind speed, and air temperature were monitored throughout the study.

**Analytical Procedures. (a) Water.** Aliquots of filtered and unfiltered water (4 mL) were assayed directly by liquid scintillation counting (LSC) before and after filtration. Water samples were transferred to a separatory funnel and extracted with ethyl acetate. Ethyl acetate extracts were dried over anhydrous sodium sulfate, evaporated on a rotary evaporator, and taken up in chloroform–methanol (1:1) for HPLC and TLC–autoradiographic analysis. Aliquots of extracted water were analyzed by LSC.

**(b) Sediment and Suspended Solids.** Sediment (25 g wet wt) was extracted with a procedure similar to that described by Rawn et al. (1982). A portion of each sample was oven-dried (80 °C in vacuo) to constant weight to determine moisture content. Unextractable radioactivity was determined by LSC after combustion of portions of the extracted sediment on a Packard 306 oxidizer. Sediment extracts were cleaned up, prior to HPLC analysis, by chromatography on Sep-Pak C-18 cartridges (Waters Scientific). Suspended solids were extracted by shaking with acetone–hexane (1:1). Aliquots of the suspended solids extracts were assayed directly by LSC and HPLC.

**(c) Plants, Algae, and Fish.** Plant samples were blotted dry and a portion of the sample (10 g wet wt) was extracted by ball-milling with hexane–acetone (1:1), as described by Rawn et al. (1982). The extracts were cleaned up with Sep-Paks, prior to HPLC analysis. Fish were weighed and lyophilized (48 h). The dried whole fish was placed in a ball-mill centrifuge tube and extracted with hexane–acetone (8:2), as described for vegetation. Aliquots of the hexane–acetone phase were assayed by LSC to determine extractable radioactivity.

**(d) Polyurethane Foams.** Foams were extracted on a Soxhlet apparatus with hexane (2 h). The hexane extract evaporated and taken up in chloroform–methanol (1:1) for HPLC analysis.

**HPLC and TLC Analysis of Deltamethrin.** HPLC was performed with a column (30 cm × 4.6 mm i.d.) of μBondapak C-18 (Waters Scientific) and a solvent system of methanol–chloroform–water–formic acid (42:2.5:5.0:0.5) at 1.5 mL/min (Lam and Grushka, 1978). The column eluate was monitored at 254 nm with a UV detector. Fractions of eluate were collected every 0.3 min in scintillation vials, diluted with scintillation fluor, and assayed by LSC. $^{14}$C-Containing peaks were identified by comparison with retention times of standards of deltamethrin and degradation products. Retention times of deltamethrin, IR *cis*-acid, and PB acid were 4.2, 2.5, and 2.8 min, respectively. Water, sediment, vegetation and foam extracts were analyzed by this procedure. Detection limits for deltamethrin with this technique were about 20 DPM/20 μL injection or 0.01 μg/L in water, 10 ng/g (10

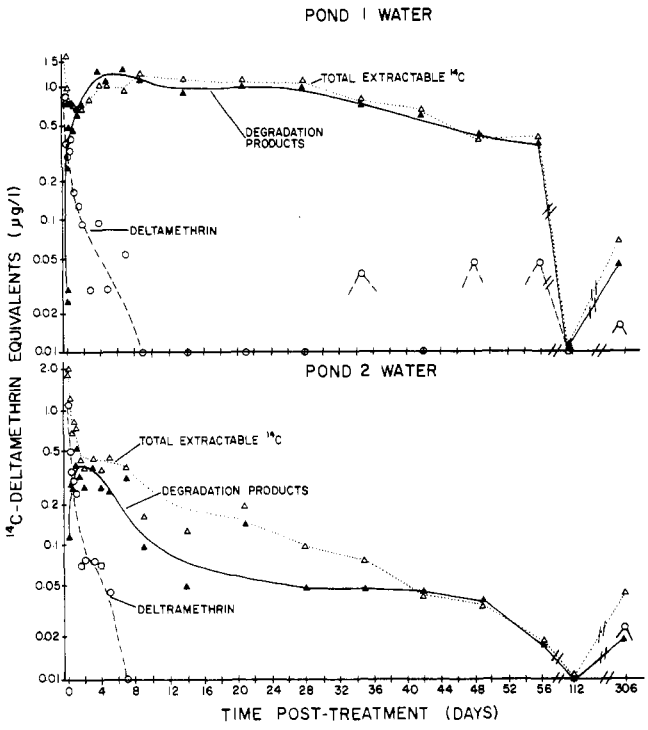


**Figure 2.** Concentrations (μg/L) of deltamethrin and cyclopropyl acid or benzyl alcohol labeled degradation products in water from treated ponds. Each point is the average of duplicate samples.

g wet weight) in vegetation and fish samples, and 1 ng/g in sediment.

Water sample extracts were spotted on silica gel plates (Whatman K6F) and the plates developed with a solvent system of chloroform–ethyl acetate–methanol (6:3:1) (Rawn et al., 1982). Radioactive spots were then located by exposing the plates to X-ray film (Kodak NS-5T) for 1–2 weeks. $R_f$ values for deltamethrin, IR *cis*-acid, and PB acid, were 0.75, 0.40, and 0.23, respectively.

**Laboratory Studies. (a) Henry's Law Constant Determination.** Water (HPLC grade) containing $^{14}C$-labeled deltamethrin was sparged with $N_2$ at 120 mL/min for 24 h. Henry's law constant was determined from the slope of a plot of ln concentration vs. time, as described by Mackay et al. (1979).

**(b) Bioavailability of Radioactivity in Sediment.** Sediments (0–2 cm) from each pond (50 g wet wt in duplicate) were collected at 360 days posttreatment, placed in 500-mL jars, flooded with 250 mL of dechlorinated water, and allowed to equilibrate for 24 h under gentle aeration. *Chironomus tentans* larvae (mean wt 10 mg) were added to each container and removed (5 each time) from sediment at intervals over a 5-day exposure period. Individual larvae were solubilized with NCS (Amersham Radiochemicals) for 24 h and then assayed by LSC to determine total $^{14}C$ in each animal. Radioactivity in water and sediment was analyzed as described.

## RESULTS

**Water and Suspended Solids.** Deltamethrin residues, in filtered water samples, decreased rapidly in both ponds with half-lives of between 2 and 4 h (Figure 2). Deltamethrin persisted at >0.01 μg/L levels until 7 days posttreatment. In pond 1 ([$^{14}C$]-cyclopropyl acid labeled) deltamethrin residues were detected at 35, 49, 56, and 306 days posttreatment, at levels ranging from 0.01 to 0.05 μg/L (Figure 2). These results were confirmed by TLC–autoradiography. Residues of the intact insecticide ([$^{14}C$]benzyl alcohol labeled) were also observed in water from pond 2 at 306 days (0.02 μg/L). The presence of low levels of deltamethrin in filtered water, 35 days or more after application, coincided with the death of algae, duckweed, and pondweed during cooler weather and reduced chlorophyll and suspended solids levels (Table I).

Total $^{14}C$-radioactivity in filtered water (expressed as deltamethrin equivalents), at 4 h posttreatment, ranged from 2.14 to 2.50 μg/L (0–5 cm depth) and 1.29 to 1.33 μg/L (5–50 cm depth) in ponds 1 and 2. Stratification of the applied chemical was expected because only the top 0–2 cm depth was treated. Total $^{14}C$-concentrations were in the range expected from the complete mixing of 17.06 mg of the compound in each pond (volume 5.3 $m^3$). By 36 h posttreatment, levels of radioactivity in upper and lower depth samples were similar; therefore, it was decided to collect duplicate samples over the entire depth. As much as 50% of the radioactivity in each water sample was sorbed to suspended solids and was removed by filtration on glass fiber paper. After 4–5 days, concentrations of [$^{14}C$]deltamethrin were similar in filtered and unfiltered water, indicating little association of radioactivity with suspended solids.

Following an initial decrease between 2 and 4 h posttreatment, total radiocarbon, in filtered and unfiltered water, remained relatively constant for 35 days in pond 1 (containing the [$^{14}C$]cyclopropyl acid label) and 7–9 days in pond 2 (containing the [$^{14}C$]benzyl alcohol label). Recoveries of radioactivity from filtered water, by solvent extraction, averaged 70.0 ± 19.4% of the cyclopropyl acid label (pond 1) and 48.1 ± 26.4% of the benzyl alcohol label (pond 2) over the entire sampling period. The identity of the unextractable radioactivity in water was not investigated. Within 8–12 h after addition of deltamethrin, the major forms of radioactivity, in extracts of the filtered water from both ponds, were $^{14}C$-labeled polar compounds (Figure 2) having HPLC retention times similar to IR *cis*-acid (pond 1) and PB acid (pond 2). PB acid was identified on the basis of its identical TLC and HPLC behavior with an analytical standard of the compound. In pond 1, HPLC analysis revealed a single peak with the retention time of IR *cis*-acid, but TLC of the same extracts revealed three spots with the major product ($R_f$ 0.54) having a greater $R_f$ than the IR *cis*-acid standard. Low levels of these products prevented further identification. The polar products are reported as total [$^{14}C$]cyclopropyl acid products, based on HPLC results. Concentrations of the cyclopropyl acid products increased to a maximum of 1.44 μg/L at 4 days posttreatment and persisted at levels of 0.9–1.2 μg/L for 4 weeks (Figure 2). PB acid differed considerably from the cyclopropyl acid products; after maximum concentrations at 24 h posttreatment, levels of the products had declined 50% by 3–5 days (Figure 2).

Deltamethrin residues, on suspended solids, reached maximum concentrations of 85 000 ng/g at 12 h in pond 1 and 47 000 ng/g at 8 h in pond 2 (Figure 3). Maximum levels of $^{14}C$-labeled polar degradation products, having HPLC retention times similar to IR *cis*-acid (pond 1) and PB acid (pond 2), were also observed during the first 24 h posttreatment. Hexane–acetone (1:1) extraction recovered 90–100% of the $^{14}C$ from suspended solids samples taken from 4 to 24 h posttreatment. Levels of deltamethrin on suspended solids decreased rapidly during the 0–7-day period, with half-times of about 30 h in pond 1 and 24 h in pond 2 (Figure 3). At 14 days, deltamethrin residues had reached detection limits (350 ng/g) in pond 1 and 2000 ng/g in pond 2. Beyond 14 days posttreatment levels of radioactivity in suspended solids were near detection limits and actual levels of deltamethrin were not determined. Suspended solids levels ranged from 9 to 24

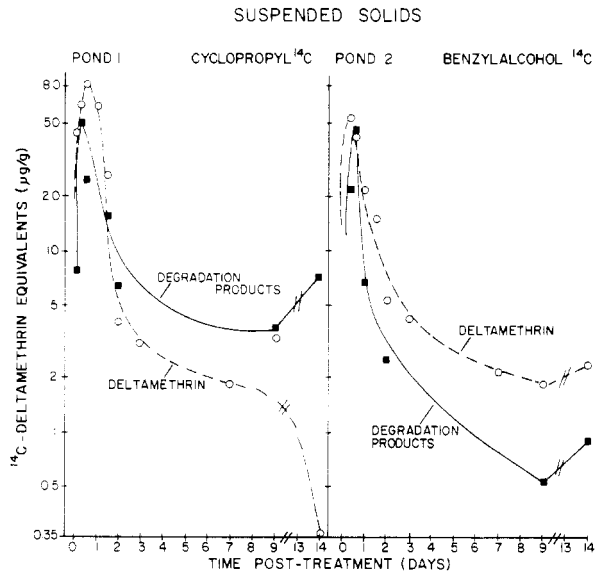


**Figure 3.** Concentrations (μg/g) of deltamethrin and extractable degradation products in suspended solids. Each point is the average of duplicate samples.

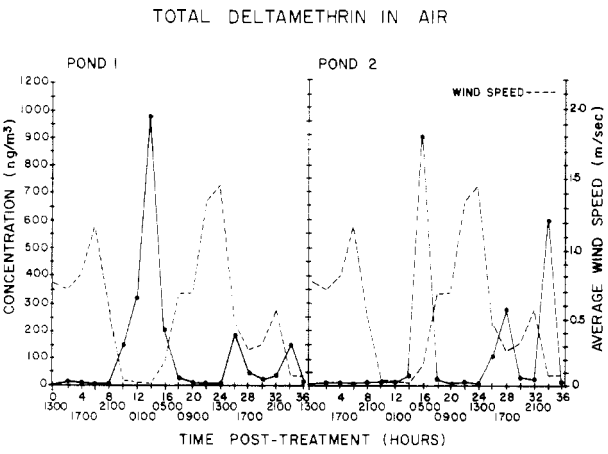


**Figure 4.** Total concentrations (ng/m$^3$) of deltamethrin trapped by polyurethane foams at 5, 11.5, and 17.5 cm above treated ponds.

mg/L during the first 21 days after insecticide application and dropped to 5–7 mg/L at 56 and 112 days posttreatment (Table I).

**Volatilization from Water.** Deltamethrin concentrations in air above the treated ponds, during the first 36 h posttreatment, ranged from 10 to 100 ng/m$^3$ (Figure 4). Deltamethrin accounted for all the radioactivity extracted from the foams. Recovery efficiency of the foams for deltamethrin in air was not determined, but efficiencies of 80–90% for 1,3,6,8-tetrachlorodibenzodioxin and 2,4-D esters have been reported (Corbet, 1983; Grover and Kerr, 1981). Maximum concentrations of deltamethrin were observed at 14 h posttreatment (Figure 4) when wind speeds above the ponds were negligible (0.01 m/s) (Table II). A concentration gradient was generally observed for the foams at 5, 12.5, and 17.5 cm above the water, but in some cases, levels of deltamethrin were higher at the 12.5 and 17.5 cm heights than at 5 cm. The results in Figure 4 are for total deltamethrin in the three foams at each 2-h sampling interval.

**Residues in Sediment.** Deltamethrin in sediment reached maximum concentrations at 48 h posttreatment in both ponds (Figure 5), then decreased to less than 50% of the maximum level by 5 days in pond 1 and by 7–14 days in pond 2. Deltamethrin was detected in sediments at 112 days (prior to freeze-up) (0.6–2 ng/g dry wt) and

Table II. Predicted Total Flux of Deltamethrin from Two-Film Theory

| time, h | av wind[a] speed, m/s | water concn, 0–5 cm, μg/L | | predicted flux, μg/m$^2$h, two-film theory[b] | |
|---|---|---|---|---|---|
| | | pond 1 | pond 2 | pond 1 | pond 2 |
| 0–2 | 1.42 | 0.95 | 1.73 | 3.5 | 6.4 |
| 2–4 | 2.92 | 0.72 | 1.34 | 2.7 | 5.0 |
| 4–8 | 0.70 | 0.44 | 0.42 | 1.6 | 1.5 |
| 8–12 | 0.10 | 0.35 | 0.37 | 1.3 | 1.4 |
| 12–18 | 0.06 | 0.40 | 0.34 | 1.57 | 1.3 |
| 18–24 | 0.13 | 0.34 | 0.34 | 1.3 | 1.3 |
| 4–36 | 0.23 | 0.19 | 0.22 | 0.7 | 0.8 |
| 36–48 | 0.10 | 0.16 | 0.09 | 0.6 | 0.3 |
| total over 48 h, μg/m$^2$ | | | | 56.2 | 63.2 |
| total μg/pond (17 m$^2$) | | | | 953.7 | 1074.4 |

[a] Average wind speed at 44 cm height over the time interval. [b] Calculated using the eq 2.

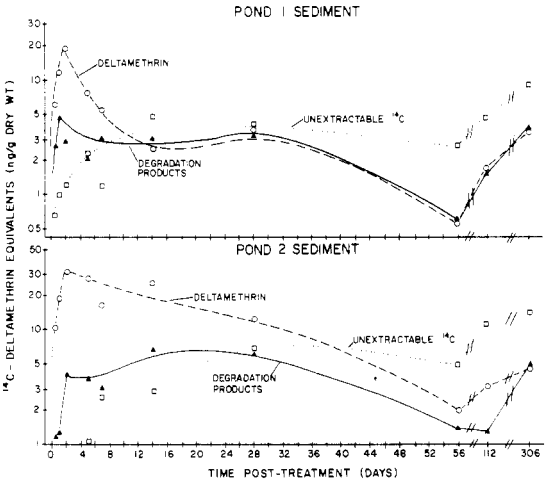


**Figure 5.** Concentrations (ng/g dry wt) of deltamethrin, degradation products identified by HPLC and unextractable radioactivity (deltamethrin equivalents) in bottom sediments from treated ponds. Each point is the average of duplicate samples.

at higher concentrations (3.5–5 ng/g) at 306 days posttreatment (Figure 5). The higher concentrations, at 112 and 306 days, coincided with the death of macrophytes and algae due to cold weather in September and early October.

$^{14}$C-Labeled degradation products, having similar retention times to cyclopropyl acid products (pond 1) and PB acid (pond 2), were observed by HPLC analysis of sediment extracts. Further identification of these products was not pursued because of the large amount of coextractive pigments in the extracts. Unextractable $^{14}$C in sediments represented <20% of total radioactivity in sediments for the first 7 days in pond 1 and 14 days in pond 2 (Figure 5). After 28 days, higher unextractable levels were observed and, at 306 days, >50% of radioactivity in sediments was unextractable by refluxing with acetone–hexane. The identity of the unextractable residue was not investigated further.

**Residues in Plants.** Duckweed rapidly accumulated high levels of deltamethrin, during the initial 24 h posttreatment, reaching 253 and 308 ng/g in ponds 1 and 2, respectively (Table III). Concentrations in duckweed dropped to less than 50% of the maximum levels by 3 days posttreatment. Degradation products in duckweed extracts were tentatively identified on the basis of HPLC retention times as PB acid (pond 2) and cyclopropyl acid products (pond 1).

Levels of deltamethrin in pondweed were 4–5-fold higher than those in duckweed at 1 day posttreatment (Table III) and were detectable in samples taken at 56 days (pond 2)

**Table III. Extractable Deltamethrin Residues in Vegetation As Determined by HPLC and by Combustion of Extracted Material**

| | concn (ng/g) wet wt in each type of plant | | | | | |
|---|---|---|---|---|---|---|
| | duckweed | | pondweed | | algae | |
| time | deltam | dgn prod[a] | deltam | dgn prod[a] | deltam | dgn prod[a] |
| | Pond 1 (Cyclopropyl Acid Label) | | | | | |
| pretreatment | <10 | <10 | <10 | <10 | *b* | *b* |
| 1 | 253 | 25 | 1021 | 40 | *b* | *b* |
| 3 | 87 | 11 | 160 | 14 | *b* | *b* |
| 4 | 68 | 12 | 503 | 25 | *b* | *b* |
| 7 | 109 | 28 | 184 | 21 | *b* | *b* |
| 14 | <10 | <10 | 14 | <10 | 50 | <10 |
| 28 | *b* | *b* | 18 | <10 | 13 | <10 |
| 42 | *b* | *b* | <10 | 10 | 10 | 10 |
| 56 | *b* | *b* | *b* | *b* | 13 | 11 |
| 306 | *b* | *b* | <10[c] | 10[c] | <10 | 12 |
| | Pond 2 (Benzyl Alcohol Label) | | | | | |
| pretreatment | <10 | <10 | <10 | <10 | *b*[2] | *b* |
| 1 | 308 | 57 | 1728 | 87 | *b* | *b* |
| 3 | 132 | 20 | 841 | 39 | *b* | *b* |
| 4 | 107 | 17 | 126 | 18 | *b* | *b* |
| 7 | 142 | 15 | 270 | 25 | *b* | *b* |
| 14 | 12 | <10 | 16 | <10 | *b* | *b* |
| 28 | 16 | <10 | <10 | <10 | *b* | *b* |
| 56 | *b* | *b* | 42 | 26 | *b* | *b* |
| 306 | *b* | *b* | <10 | <10 | *b* | *b* |

[a] Retention times of degradation products corresponded to IR *cis*-acid (acid label) and to PB acid (alcohol label). Concentrations of degradation products and unextractable were obtained by dividing DPM/g by specific activity to yield deltamethrin equivalents. [b] Not sampled. [c] Decayed vegetation mainly pondweed from previous season.

when levels of the insecticide in water were <0.01 μg/L. The proportion of the radioactivity in pondweed tissue unextractable with hexane–acetone was high, ranging from 60% (cyclopropyl acid label) to 75% in samples taken after 35 and 42 days. Low levels of radioactivity (10 ng/g wet wt) were present in decayed vegetation, which consisted mainly of pondweed found on the pond bottom at 306 days posttreatment.

Deltamethrin concentrations in filamentous algae, which was found in pond 1 at 14 days posttreatment, were higher than those in duckweed or pondweed sampled at the same time. Low levels of radioactivity continued to be found in algae at 56 and 306 days posttreatment (Table III).

**Residues in Fish.** Highest levels of extractable radioactivity were observed in fathead minnows sampled at 4 days in pond 1 and at 8–24 h in pond 2 (Table IV). Levels of radioactivity declined to <50% of the maximum concentrations by 7 days in both ponds. The actual identity of the extracted radioactivity was not determined, however, extraction with acetone–hexane (4:1) was likely to be highly efficient for deltamethrin and less efficient for the acidic degradation products. Concentration factors of 906 in pond 1 and 278 in pond 2 were calculated by dividing concentrations of extractable radioactivity in the fish (Table IV) by water concentrations of deltamethrin at the 5–50-cm depth observed at the same time posttreatment. No fish mortality was observed following addition of deltamethrin to each pond.

**Bioavailability in Sediment.** *Chironomus tentans* larvae accumulated radioactivity from pond sediments, collected at 360 days posttreatment, reaching levels of 30–50 ng/g after 48 h exposure (Figure 6). The variation in levels of $^{14}C$ among larvae was high. The larvae, removed from sediment at each sampling time, exhibited normal undulating motion and no mortality was observed. Levels of intact deltamethrin in the sediment were similar

**Table IV. Extractable Radioactivity and Observed Concentration Factors in Fathead Minnows following Exposure in Ponds 1 and 2 (Expressed as Deltamethrin Equivalents)[a]**

| | pond 1 (cyclopropyl acid label) | | pond 2 (benzyl alcohol label) | |
|---|---|---|---|---|
| time | extractable, ng/g | CF | extractable, ng/g | CF |
| 2 h | 38.9 | 46 | 31.9 | 34 |
| 4 | 70.0 | 04 | 30.3 | 126 |
| 8 | 66.3 | 237 | 42.0 | 67 |
| 24 | 81.6 | 907 | 38.9 | 278 |
| 48 | 60.8 | 553 | 38.9 | 648 |
| 3 days | 86.1 | | 35.2 | |
| 4 | 100.2 | 1002 | 36.9 | 527 |
| 7 | 36.5 | 608 | 15.0 | |
| 14 | 18.8 | | 19.7 | |
| 28 | 12.9 | | 27.5 | |
| 56 | 15.3 | | 10.4 | |
| 84 | 12.2 | | 15.3 | |
| 112 | 17.1 | | 12.6 | |

[a] Extractable radioactivity in deltamethrin equivalents on a fresh weight whole fish basis. CF (concentration factor) calculated by dividing fish concentration by deltamethrin concentration in water at 5–50 cm depth if available.

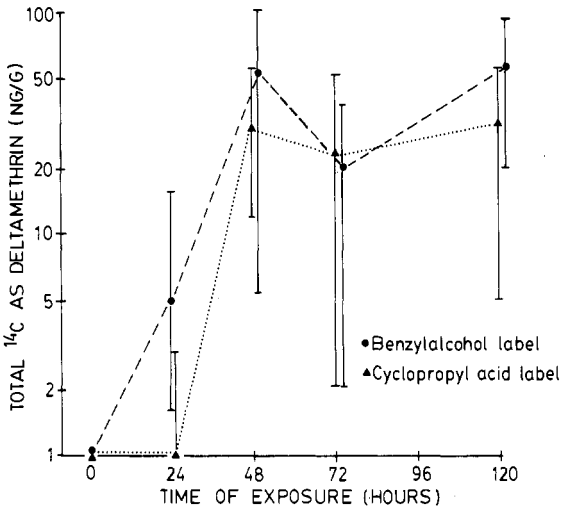


**Figure 6.** Concentrations (ng/g) of radioactivity (deltamethrin equivalents) in chironomid larvae exposed in the laboratory to bottom sediments collected at 360 days posttreatment. Each point is the average of 5–10 larvae; vertical bars represent standard deviation.

to those at 306 days, ranging from 3–5 ng/g (dry wt) in ponds 1 and 2, respectively.

## DISCUSSION

Total radioactivity remaining in each pond was estimated by multiplying the weight of each compartment (kg) by the level of $^{14}C$ (expressed as deltamethrin equivalents, μg/kg). At 24 h posttreatment, 87–98% of the $^{14}C$ could be accounted for. After 14 days, it was still possible to account for 59% of the added $^{14}C$ in pond 1 and 66% in pond 2. Losses of the radiolabel as $^{14}CO_2$ were not measured but could have been substantial, since both radiolabels were located on carboxylic acid groups on the molecule (Figure 1). $^{14}CO_2$ could have been absorbed by aquatic plants or remained in solution as carbonate. Microbial degradation of permethrin in soils resulted in evolution of 52–65% of carbonyl and benzyl alcohol labels as $^{14}CO_2$ after 27 days of incubation (Kaufman et al., 1977).

Water was a major compartment for $^{14}C$ in both ponds, exceeding all other phases analyzed throughout the study (except at 306 days) (Table V). Intact deltamethrin was detected in water in both ponds at 306 days and at several

**Table V. Mass Balance for Deltamethrin in Each Pond**

| time | deltamethrin equiv (mg) in each compartment | | | | | | |
|---|---|---|---|---|---|---|---|
| | water[a] | susp solids[b] | sediment[c] | duckweed[d] | pondweed | acct for mg | total,[e] % |
| | | | Pond 1 (Cyclopropyl Acid Label) | | | | |
| 4 h | 7.83 | 8.74 | *f* | *f* | *f* | *f* | *f* |
| 12 | 6.18 | 3.33 | 2.06 | *f* | *f* | *f* | *f* |
| 24 | 5.22 | 2.16 | 3.72 | 0.28 | 5.31 | 16.7 | 98 |
| 48 | 5.41 | 0.63 | 4.87 | *f* | *f* | *f* | *f* |
| 4 days | 6.19 | 1.26 | *f* | 0.08 | 2.64 | 13.7 | 80 |
| 7 | 7.17 | 0.39 | 2.15 | 0.14 | 1.03 | 10.9 | 64 |
| 14 | 7.39 | 0.17 | 2.28 | 0.006 | 0.11 | 10.0 | 59 |
| 28 | 5.39 | 1.19 | 2.36 | *f* | 0.15 | 9.1 | 53 |
| 56 | 3.84 | <0.01 | 0.96 | *f* | 0.09 | 4.9 | 29 |
| 112 | 3.81 | <0.01 | 1.72 | *f* | *f* | 5.6 | 33 |
| 306 | 0.68 | <0.01 | 5.74 | *f* | 0.06 | 6.5 | 38 |
| | | | Pond 2 (Alcohol) | | | | |
| 4 h | 7.71 | 6.44 | *f* | *f* | *f* | *f* | *f* |
| 12 | 6.26 | 1.23 | 2.60 | *f* | *f* | *f* | *f* |
| 24 | 4.95 | 1.17 | 4.36 | 0.36 | 4.32 | 14.8 | 87 |
| 48 | 5.01 | 1.11 | 7.70 | *f* | *f* | *f* | *f* |
| 4 days | 5.22 | 0.95 | *f* | 0.12 | 0.41 | 13.0 | 76 |
| 7 | 4.59 | 0.73 | 4.96 | 0.16 | 0.74 | 11.1 | 66 |
| 14 | 3.37 | <0.01 | 7.81 | 0.01 | 0.10 | 11.2 | 66 |
| 28 | 1.87 | <0.01 | 5.60 | 0.004 | 0.20 | 7.6 | 45 |
| 56 | 1.02 | 0.11 | 2.04 | 0.004 | 0.25 | 3.4 | 20 |
| 112 | 0.33 | <0.01 | 3.72 | *f* | *f* | 4.0 | 23 |
| 306 | 0.30 | <0.01 | 5.52 | *f* | 0.02 | 5.8 | 34 |

[a] Water volume = 5.28 $m^3$. [b] Suspended solids based on difference between filtered and unfiltered water (4 h–3 days) or on extractable radioactivity. [c] Bottom surface area including sides = 18.3 $m^2$. Average sample depth = 2 cm, i.e., volume of sediment = 0.366 $m^3$. Density = 1.33 gm/mL wet wt. Weight of bottom sediment = 487.05 kg or 212.8 kg dry weight (43.7% solids). [d] Duckweed biomass estimated = 1 kg; Pondweed biomass estimated = 5 kg in pond 1 and 2.5 kg in pond 2. At 306 days, mass of decayed plant material is assumed to be the sum of duckweed and pondweed mass. [e] Treatment = 17.06 mg deltamethrin (formulation + $^{14}C$ standard). [f] No sample collected at this time.

earlier sampling times in pond 1. The death of algae and duckweed, in late August and in September (day 35–56) during cooler weather, may have contributed intact deltamethrin to the water column although levels of radioactivity in plants were low (Table III) by this time. Disturbance of the sediment, due to fluctuating water levels as well as freezing and thawing, may also have released deltamethrin into the water column. Most of the radioactivity was not in the form of intact insecticide but present as polar degradation products. The [$^{14}C$]cyclopropyl acid products could have been formed by both microbial hydrolysis or photolysis of deltamethrin in the water column. The high pH levels observed in water, from 8–56 days posttreatment (Table I), could also have resulted in direct chemical hydrolysis of deltamethrin. The high pH is indicative of intensive photosynthesis, which reduces dissolved $CO_2$, resulting in a shift in carbonate equilibrium (Wetzel, 1975). Photolysis of deltamethrin in aqueous solution has been shown to yield IR *cis*-acid and its debrominated analogue as well as PB acid as major products (Ruzo et al., 1977). Microbial degradation of pyrethroids in soils also result in ester cleavage (Kaufman et al., 1977). The rapid degradation of the parent compound suggests that photolysis was an important pathway; however, the relative importance of each transformation mechanism could not be determined. Photoisomerization of *cis*- and *trans*-permethrin isomers was observed in previous studies (Rawn et al., 1982), but in the present work, *trans*-deltamethrin was not separated from the cis isomer with the solvent systems used.

Suspended solids were a major compartment representing 38–51% of added $^{14}C$ at 4 h and 7–13% at 24 h after application. The high levels of radioactivity on suspended solids may be due in part to sorption of dissolved deltamethrin by the filter, as water passed through the filtering apparatus (Sharom and Solomon, 1981). Sorption partition coefficients (ng/g solids/ng/mL of $^{14}C$ in water) at 4 h ranged from 20 000–34 000, which are 5–7-fold higher than predicted for a compound of water solubility of approximately 2 μg/L (Kenaga and Goring, 1980).

Sedimentation of detrital material, which consisted mainly of decayed plants, appeared to be the major route by which radioactivity reached bottom sediments during the later sampling times. Quantities of [$^{14}C$]deltamethrin, at 112 and 306 days (Table V), increased relative to levels at earlier sampling times. At 306 days, residues in sediment accounted for 88% of the $^{14}C$ remaining in pond 1 and 95% in pond 2. The radioactivity in sediments was accumulated by *Chironomus tentans* larvae during short-term exposures, indicating that the residue was bioavailable. Whether the larvae accumulated intact deltamethrin, or other forms of radioactivity, was not clear because only total $^{14}C$ in the larvae was measured. The levels of radioactivity in larvae were similar to those obtained in laboratory studies in which larvae were exposed to deltamethrin, for 24 h, in silt sediments or water above silt (Muir et al., 1985). Maximum concentrations were not reached until 48 h exposure in the present work with field contaminated sediment, compared to 12–24 h in laboratory studies (Muir et al., 1985). The slower rate of accumulation may indicate that the radioactivity accumulated by the larvae was not intact deltamethrin or that accumulation occurred mainly by ingestion of sediment particulates to which the $^{14}C$ was tightly bound.

Aquatic macrophytes accounted for an estimated 27–32% of $^{14}C$ initially added to each pond at 24 h postapplication. Although much of the insecticide may have adsorbed onto the surface of the plants, as is observed in agricultural use of pyrethroids (Casida, 1980), some metabolism of deltamethrin is apparent from the levels of polar degradation products and the rapid depuration of radioactivity (Table III). The macrophytes may also have accumulated the degradation products from water, since

PB acid and cyclopropyl acid products were the major form of radioactivity in the water after 24 h posttreatment. Levels of degradation products, in duckweed and pondweed extracts, may be underestimates because the extraction solvent was designed to recover mainly nonpolar residues.

The quantity of deltamethrin volatilized (Table II) was estimated by use of the two-resistance model (Mackay and Leinonen, 1975; Thibodeaux, 1979). Mass transfer coefficients for $O_2$ ($k_w$) of 0.018 m/h and water ($k_g$) of 21 m/h for small ponds and lakes (Smith et al., 1981) were corrected by use of a molecular weight ratio (Liss and Slater, 1974) and substituted into the equation for overall mass transfer coefficient ($K_{ol}$) (Mackay and Leinonen, 1975):

$$K_{ol} = 1/k_w + RT/k_gH \quad (1)$$

where $H$ = Henry's constant (Pa $m^3$/mol), $R$ = gas constant, and $T$ = temperature (K). Henry's law constant for deltamethrin, obtained by the procedure of Mackay et al. (1979), was 12.6 ± 4.1 Pa $m^3$/mol. Substituting all the values into the equation yielded a $K_{ol} = 3.71 \times 10^{-3}$ m/h. The flux of deltamethrin was calculated from the Fick's law relationship:

$$\text{flux} = K_{ol}\Delta C \ (\mu g/m^2\ h) \quad (2)$$

where $\Delta C$ is the concentration gradient between water and air (essentially equal to the water concentration ($\mu g/m^3$)). Total losses (at 48 h), estimated by the two-resistance model, represented 5.6 and 6.3% of deltamethrin added to pond 1 and 2, respectively. A portion of the 20% of radiolabel unaccounted for in pond 1, and 24% in pond 2 (Table V), may thus be due to volatilization of intact deltamethrin.

The results with the two-resistance model suggested that volatilization loss of deltamethrin was primarily controlled by liquid-phase resistance ($k_w = 4.53 \times 10^{-3}$ m/h), rather than gas-phase resistance ($RT/Hk_g = 2.05 \times 10^{-2}$ m/h). Estimates of volatilization by this method could be improved by direct measurement of mass transfer coefficients for deltamethrin in laboratory studies (Smith et al., 1981) or of $O_2$ reaeration and water evaporation during the field experiment. Deliberate addition below the water surface likely reduced volatilization losses compared to the more realistic agricultural or forestry situation in which the insecticide would be introduced to an aquatic system by a surface spray. The high liquid mass transfer resistance of deltamethrin and low water solubility suggest that the surface applied chemical would tend to evaporate rather than dissolve (Thibodeaux, 1979).

The 3-fold lower concentration factor for extractable $^{14}C$ in fish in pond 2, at 24 h posttreatment compared with those in pond 1 (Table IV), may be the result of differences in rates of metabolism due to the location of the radiolabel. Synthetic pyrethroids are known to be rapidly metabolized and eliminated by fish (Glickman et al., 1981). Clearance of the cyclopropyl label was more rapid than the benzyl alcohol label. Ingestion of contaminated detritus may account for the persistence of extractable nonpolar residues in the fish, from both ponds, up to the last sampling time when residues in filtered water were <0.01 $\mu g/L$. The maximum levels of the insecticide in filtered water at the 5–50 cm depth, where the minnows were found, were about 2–3-fold lower than the LC-50's (24 h) for deltamethrin for four freshwater fish reported by Mulla et al. (1981). This, combined with the rapid dissipation of the chemical, may explain why no fish mortality was observed.

The results of this study confirm other published reports that pyrethroid insecticides are removed rapidly from the water column by degradation and sorption to lipophilic surfaces. Volatilization of the intact chemical, although difficult to quantitate precisely, was observed. Sediments were the major compartment for intact insecticide and the radioactivity in sediment was accumulated by sediment dwelling larvae in short-term laboratory studies. The tendency for deltamethrin and other pyrethroids to persist in sediments, following runoff or spray contamination of aquatic systems, deserves further study under conditions of actual use in view of the high toxicity of these compounds to aquatic organisms.

ACKNOWLEDGMENT

We thank A. Mychajlysyn for her assistance with analysis of samples.

**Registry No.** Deltamethrin, 52918-63-5.

LITERATURE CITED

Anderson, R. L. *Environ. Entomol.* **1983**, *11*, 1251.
Carroll, B. R.; Willis, G. H.; Graves, J. B. *J. Environ. Qual.* **1981**, *10*, 497.
Casida, J. E. *Environ. Health Perspect.* **1980**, *34*, 189.
Corbet, R. L. M.S. Thesis, 1983, University of Manitoba, Winnipeg, Canada.
Crossland, N. O. *Aquat. Toxicol.* **1982**, *2*, 205.
Crossland, N. O.; Shires, S. W.; Bennett, D. *Aquat. Toxicol.* **1982**, *2*, 253.
Glickman, A. H.; Hamid, A. R.; Rickert, D. E.; Lech, J. J. *Toxicol. Appl. Pharmacol.* **1981**, *57*, 88.
Grover, R.; Kerr, L. A. *J. Environ. Sci. Health Part B* **1981**, *B16*, 59.
Kaufman, D. D.; Haynes, S. C.; Jordon, F. G.; Kayser, A. J. *ACS Symp. Ser.* **1977**, No. *42*, 147.
Kenaga, E. E.; Goring, C. A. I. In "Aquatic Toxicology"; Eaton, J. G., Parrish, P. R., Hendricks, A. C., Eds.; American Society of Testing Material: Philadelphia, 1980; pp 78–115.
Lam, A.; Grushka, E. *J. Chromatogr.* **1978**, *154*, 318.
Liss, P. S.; Slater, P. G. *Nature (London)* **1974**, *247*, 181.
Mackay, D.; Leinonen, P. *Environ. Sci. Technol.* **1975**, *9*, 1178.
Mackay, D.; Shiu, W. Y.; Sutherland, R. P. *Environ. Sci. Technol.* **1979**, *13*, 333.
McLeese, D. W.; Metcalfe, C. D.; Zitko, V. *Bull. Environ. Contam. Toxicol.* **1980**, *25*, 950.
Muir, D. C. G.; Rawn, G. P.; Townsend, B. E.; Lockhart, W. L.; Greenhalgh, R. *Environ. Toxicol. Chem.* **1985**, *4*, 51.
Mulla, M. S.; Darwazeh, H. A.; Dhillon, M. S. *Bull. Environ. Contam. Toxicol.* **1981**, *26*, 689.
Rawn, G. P.; Webster, G. R. B.; Muir, D. C. G. *J. Environ. Sci. Health, Part B* **1982**, *B17*, 463.
Ruzo, L. O.; Holmstead, R. L.; Casida, J. E. *J. Agric. Food Chem.* **1977**, *25*, 1385.
Sharom, M. S.; Solomon, K. R. *J. Agric. Food Chem.* **1981**, *29*, 1122.
Smith, J. H.; Bomberger, D. C., Jr.; Haynes, D. L. *Chemosphere* **1981**, *10*, 281.
Spehar, R. L.; Tanner, D. K.; Nordling, B. R. *Aquat. Toxicol.* **1983**, *3*, 171.
Stainton, M. P.; Capel, M. J.; Armstrong, F. A. J. "The Chemical Analysis of Fresh Water"; *Fish. Environ. Canada. Misc. Special Publ. No. 25*, **1977**.
Stephenson, R. R. *Aquat. Toxicol.* **1982**, *2*, 175.
Thibodeaux, L. J. "Chemodynamics. Environmental Movement of Chemicals in Air, Water and Soil"; J. Wiley: New York, 1979.
Tooby, T. E.; Thompson, A. N.; Rycroft, R. O.; Black, I. A.; Hewson, R. T. "A Pond Study To Investigate the Effects on Fish and Aquatic Invertebrates of Deltamethrin Applied Directly to Water"; U. K. Ministry of Agriculture, Fisheries and Food, Burnham-on Crouch: Essex, England, 1981.
Wetzel, R. G. "Limnology"; W. B. Saunders: Toronto, 1975.

Received for review July 19, 1984. Revised manuscript received February 25, 1985. Accepted March 4, 1985. The authors would like to thank Hoechst Canada Ltd. (Industrial Division—Agriculture) for financial support.