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

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

LITERATURE CITED

Glomot, R. Toxicity of Deltamethrin to Higher Invertebrates. In *Deltamethrin Monograph*; Rousel-Uclaf: Paris, 1982; pp 109–137 (translated by B. V. de G. Walden).

Hill, B. D.; Schaalje, G. B. A Two-Compartment Model for the Dissipation of Deltamethrin on Soil. *J. Agric. Food Chem.* **1985,** *33,* 1001–1006.

Hill, B. D.; Johnson, D. L. Persistence of Deltamethrin and its Isomers on Pasture Forage and Litter. *J. Agric. Food Chem.* **1987,** *35,* 373–378.

Hill, B. D.; Charnetski, W. A.; Schaalje, G. B.; Schaber, B. D. Persistence of Fenvalerate in Alfalfa: Effect of Growth Dilution and Heat Units on Residue Half-Life. *J. Agric. Food Chem.* **1982,** *30,* 653–657.

L'Hotellier, M. Deltamethrin Residues in Food Crops and Some Animals Products. In *Deltamethrin Monograph*; Roussel-Uclaf: Paris, 1982; pp 285–319 (translated by B. V. de G. Walden).

Ruzo, L. O.; Holmstead, R. L.; Casida, J. E. Pyrethroid Photochemistry: Decamethrin. *J. Agric. Food Chem.* **1977,** *25,* 1385–1394.

Tessier, J. Structure, Synthesis and Physical-Chemical Properties of Deltamethrin. In *Deltamethrin Monograph*; Roussel-Uclaf: Paris, 1982; pp 37–66 (translated by B. V. de G. Walden).

Westcott, N. D.; Reichle, R. A. Persistence of Deltamethrin and Cypermethrin on Wheat and Sweetclover. *J. Environ. Sci. Health* **1987,** *22,* 91–101.

Persistence and Fate of Deltamethrin Sprayed on a Pond

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

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

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

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

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that (i) deltamethrin rapidly partitioned from water into suspended solids, plants, and sediment, with a half-life of 2–4 h in water, (ii) half-lives for disappearance from sediment were 5–14 days, (iii) some of the injected deltamethrin did volatilize from water, and (iv) major products were cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DBCA) and 3-phenoxybenzoic acid (PBacid). However, the analytical methods used did not differentiate between the parent deltamethrin and its less toxic (to insects and mice at least) isomers, which can be produced by photochemical reaction or α-proton exchange in a (dark) chemical reaction (Ruzo et al., 1977; Hill, 1983; Hill and Inaba, 1987; Hill and Johnson, 1987). Moreover, the significance of volatilization may have been obscured by their method of introduction of deltamethrin to the ponds. The addition of deltamethrin just below the water surface (0–2 cm) likely reduced volatilization losses compared to the more realistic agricultural situation in which spray drift would settle on the surface microlayer of natural waters. We report here the persistence and fate of deltamethrin sprayed aerially on a pond and stream in Prince Edward Island, Canada. This work extends that of Muir et al. (1985) by (i) assessing the importance of volatilization from the surface microlayer in laboratory experiments and (ii) determining the concentrations of the four sets of enantiomers resulting from sunlight photolysis of deltamethrin, as well as concentrations of DBCA, PBacid, 3-phenoxybenzaldehyde (PBald), and 3-phenoxybenzyl alcohol (PBalc), which are major, but certainly not the only, products of the photolysis of deltamethrin (Ruzo et al., 1977), its degradation on and in plants (Ruzo and Casida, 1979; Khan et al., 1984; Akhtar and Khan, 1985) and in soil (Khan et al., 1988), and its metabolism by mammalian and other enzyme systems (Ruzo et al., 1978, 1979; Shono et al., 1979; Akhtar, 1984; Akhtar et al., 1985, 1986). It should be noted that as far as acute toxicity to mice is concerned, none of the common degradation products exhibits significant toxicity relative to deltamethrin (Ruzo et al., 1977).

METHODS AND MATERIALS

Materials. Analytical standards of deltamethrin and DBCA were provided by Hoechst Canada Inc. DECIS 2.5 EC emulsifiable deltamethrin concentrate in xylenes from Hoechst (Lot No. DEREHE0101) was bought locally and found, by GC-ECD, to contain only one peak corresponding to (1+1')-deltamethrin at the nominal concentration of 25 g/L, which was stable 1.5 year after purchase. It was assumed that only the parent enantiomer 1 was present, but since the analytical method could not indicate otherwise, the designation (1+1')-delatmethrin was used in this paper.

3-Phenoxybenzaldehyde (PBald), 3-phenoxybenzyl alcohol (PBalc), 3-phenoxybenzoic acid (PBacid), and pentafluorobenzyl bromide (PFBBr) were obtained from Aldrich Chemical Co., Milwaukee, WI. Pesticide-grade dichloromethane, pentane, hexane, acetone, methanol, benzene, and toluene were all obtained from Caledon Laboratories, Georgetown, ON.

The sodium sulfate, silica gel, aluminum foil, glass fiber filters, and disposable pipets were heated to 500 °C for 24 h before use. All glassware was rinsed with pesticide-grade solvents before use, as were the 40-L extraction vessels in the field work. Hydrochloric acid was reagent grade but was extracted with pentane before use. Organic-free water was distilled water purified by carbon adsorption and reverse osmosis. Gas chromatography with electron capture detection of hexane extracts of this water revealed no contamination, even with 1000-fold concentration.

There are eight possible stereoisomers of deltamethrin. We have used the numbering system given by Ruzo et al. (1977) in which the parent deltamethrin is designated as 1 and the only other isomer toxic to insects (Tessier, 1982) or mice (Ruzo et al., 1977), although to a lesser extent in each case, is designated as 3. On achiral gas chromatographic phases there are thus four pairs

of enantiomers that can be separated: (1+1'), (2+2'), (3+3'), and (4+4'). Of these, only the (1+1') and (3+3') pairs appear to be of insecticidal and mammalian toxicological importance. It is recognized that each of these pairs is potentially the sum of an active and inactive enantiomer. There is no information on the toxicity of deltamethrin isomers to aquatic organisms. Although deltamethrin is marketed as solely the active isomer 1, for the purposes of this paper we have designated the parent insecticide as (1+1')-deltamethrin since chiral chromatographic phases were not used in the analyses.

A mixture of the (1+1'), (2+2'), (3+3'), and (4+4') diastereomers of deltamethrin was prepared from the (1+1') analytical standard by the procedure given by Hill and Johnson (1987). Deltamethrin, as a thin film (15 $\mu g/cm^2$) on glass, was irradiated outdoors with bright summer sunshine for 4 days, and the photoisomers were recovered from the glass with hexane. The mass spectra of all four sets of diastereomers were identical. The electron capture responses of all diastereomers were assumed to be identical with that of the (1+1') analytical standard.

Spray Site Location. The study site, Kelvin Grove, is located in a potato growing area of Prince Edward Island 5 km south of Kensington. The pond was about 0.4 ha in area and was bordered on the northeast by a 10-ha grain field and on the southwest by a 20-ha potato field. The area to the southeast and the northwest was primarily bullrushes (*Typha sp.*) and alders (*Alanus sp.*), which were ca. 4 m in height. The pond was 2 m deep at its deepest point. The pond was fed by a stream (ca. 0.25 m^3/s), but was not a direct flow-through system. The temperature of the pond and stream water at the time of spraying was 9 °C, and the pH was 7.7. The pond and adjacent potato field were sprayed directly in a number of swaths at 07:30 July 10, 1986, at a rate of 6.2 g of active ingredient/ha.

Sampling. (i) *Subsurface Water.* Samples of 40 L were collected from a depth of 0.5 m and immediately pressure-filtered through 0.45-μm glass fiber filters using compressed N_2 and modified pressurized beverage containers, pressure filters, and Teflon transfer lines (Fox, 1986). The filters containing the suspended solids were frozen for shipment to the laboratory. The filtrate was immediately acidified to pH 1 and extracted twice with dichloromethane (1 L each time, with stirring for 10 min) in the 40-L containers. After phase separation, the dichloromethane extracts were transferred to dark brown solvent bottles for shipment to the laboratory. Some of the extracted water was added to each bottle to retard volatilization of the dichloromethane. Passage through a 0.45-μm filter is only an operational definition of the "dissolved" phase, and chemicals such as deltamethrin may still be absorbed to colloidal material that passes the filter.

(ii) *Sediment.* The top 2 cm was collected with a scoop from an area at which the water depth was 0.3 m, and the sediment was transferred to darkened 500-mL glass jars with aluminum foil lined screw caps. The sediment jars were then frozen for transport to the laboratory.

(iii) *Surface Microlayer.* A rotating drum sampler with ceramic coating was used, similar to that designed by Harvey (1966). The radius was 15 cm and the length 48 cm. The operation of the drum was calibrated so that in the collection of 4 L of microlayer in 10 min at 12 rpm the thickness of the microlayer sampled was estimated to be 75 μm.

The 4-L surface microlayer samples were collected as soon as possible after the spray and were not filtered; i.e., they were analyzed as bulk water. The samples in dark brown solvent bottles were acidified to pH 1 for preservation, and 200 mL of dichloromethane was added to start extraction. The contents were shaken several times and then transported to the laboratory where they were more thoroughly extracted with dichloromethane.

Extraction and Analysis. The methods used for the extraction, cleanup, and analysis of the water, sediment, and suspended solids were developed or adapted for deltamethrin isomers and the four degradation products DBCA, PBald, PBalc, and PBacid.

(i) *Extraction.* Dichloromethane extracts of the filtered subsurface water samples and the unfiltered surface microlayer samples were dried by passage through sodium sulfate and concentrated to 10 mL.
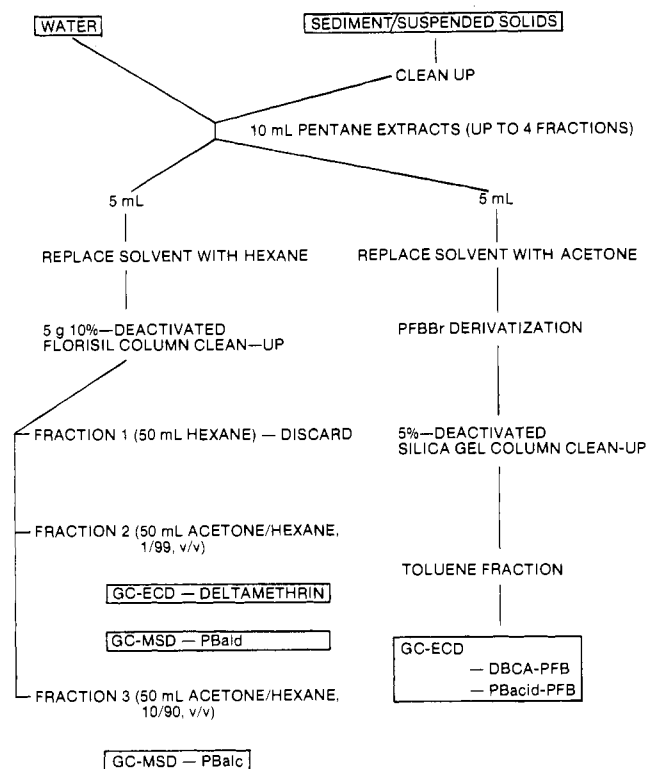
Figure 1. Analytical scheme for deltamethrin isomers and some degradation products in extracts of water, sediment, and suspended solids.

Frozen sediment and suspended solids samples were freeze-dried and extracted in a Soxhlet apparatus with dichloromethane for 24 h at 8 cycles/h. Ten grams of sediment and the total suspended solids sample were extracted. The extracts were passed through sodium sulfate and concentrated to 10 mL.

Some sediment samples, which had been extracted with dichloromethane, were mixed with 6 N HCl at 50 °C for 24 h to release any bound or conjugated residues of (1+1')-deltamethrin and its isomers and degradation products, but no such residues were found.

(*ii*) *Preliminary Cleanup of Sediment and Suspended Solids Extracts.* The 10-mL dichloromethane extracts from above were solvent-exchanged with pentane by addition of pentane and careful evaporation to 0.5 mL with a gentle flow of nitrogen. This procedure was done three times to remove traces of dichloromethane. The extract was then made up to 1 mL of pentane. At this point there was usually some precipitation in the test tube, but all material was transferred to the cleanup column as described below.

The 1-mL pentane extracts were cleaned up on activated silica gel columns of length 40 cm and diameter 2.5 cm, with a layer of sodium sulfate for drying. Four 100-mL fractions were eluted from the columns. Fraction 1 was pentane; fraction 2 was dichloromethane/pentane (20/80, v/v); fraction 3 was dichloromethane/pentane (60/40, v/v); fraction 4 was 50 mL dichloromethane followed by 50 mL methanol. At each solvent change, a little solvent was used to rinse the test tubes containing the original extract, and in this way even the precipitated material was transferred to the cleanup column. All four fractions were solvent-exchanged with pentane and reduced to 10 mL. The deltamethrin isomers and degradation products usually eluted in fractions 1–3. The fractions were split and analyzed as described below.

(*iii*) *Analytical Scheme.* The extracts of water and the cleaned-up extract fractions from sediment and suspended solids were analyzed according to the scheme shown in Figure 1. Deltamethrin isomers, PBald and PBalc, were determined by gas chromatography with an electron capture detector (GC-ECD) or a mass spectrometric detector (GC-MSD), and the DBCA and PBacid were determined as their pentafluorobenzyl derivatives by GC-ECD. All sample extracts were concentrated to 1.0 mL before analysis.

Derivatization of the samples with pentafluorobenzyl bromide

involved concentrating the sample to 4.0 mL in acetone, adding 30 μL of 30% K_2CO_3 and 100 μL of 5% PFBBr solution in acetone, and heating for 3 h at 60 °C. After the reaction, acetone was replaced with hexane and the reaction mixture was cleaned up on a 5-cm 5% deactivated silica gel column made with a disposable pipet. A 10-mL portion of hexane was passed through the column and discarded. Then, 10 mL of toluene or benzene was passed through the column and collected. This fraction contained the DBCA-PFB and PBacid-PFB derivatives.

Analyses for deltamethrin and its isomers were performed with a Varian 3400 gas chromatograph and an electron capture detector. A 30 m × 0.2 mm (i.d.) DB-1 column with 10:1 split was programmed from 220 to 235 °C at 0.5 °C/min followed by a 10-min hold. The inlet temperature was 200 °C. With these conditions partial separation of the four sets of enantiomers was achieved similar to that described by Hill and Johnson (1987). Because the DB-1 column was achiral and did not separate enantiomers, each of the four chromatographic peaks potentially represented one or both of the possible enantiomers. With the numerical designation of Ruzo et al. (1977), the retention times and peak identities were assigned in the same way as Hill and Johnson (1987): 21.9 min, (2+2'); 22.9 min, (4+4'); 23.3 min, (1+1'); 24.0 min, (3+3').

Analyses for the DBCA-PFB and PBacid-PFB derivatives were performed with a Hewlett-Packard 5880A gas chromatograph and an electron capture detector. A 12 m × 0.2 mm (i.d.) OV-1 column was used under the following conditions: initial temperature, 70 °C for 0.5 min; programming rates, (1) 30 °C/min (70–200 °C), (2) 5 °C/min (200–280 °C), with final hold for 15 min. Under these conditions the retention times of the PFB esters of DBCA and PBacid were about 8.9 and 12.1 min, respectively. Some analyses for these compounds were also done with the Varian 3400 gas chromatograph with a 30-m DB-1 column under similar conditions.

For PBald and PBalc, analyses were done with a Hewlett-Packard 5880A gas chromatograph and 5970B mass selective detector and data system. A 30 m × 0.25 mm (i.d.) SPB-5 column was directly interfaced to the electron-impact ion source for maximum sensitivity. Electron energy was 70 eV. Operating temperatures: injection port, 275 °C; interface, 280 °C, column head pressure, 4 psi, helium carrier gas. Gas chromatographic conditions: initial temperature, 70 °C for 0.5 min; programming rates, (1) 25 °C/min (70–180 °C), (2) 2 °C/min (180–220 °C). The ions selected for monitoring for PBald and PBalc were 198 and 200, respectively, and the retention times were 10.2 and 11.5 min, respectively. Other, less sensitive, analyses for these two compounds were performed by GC-ECD on highly concentrated (ca. 10-μL) samples under similar conditions.

In experiments in all-glass containers, recoveries of (1+1')-deltamethrin, DBCA, PBald, PBalc, and PBacid from water at spiked levels of 5 ng/L were in the range 88–115%. From sediment, recoveries for these compounds were in the range 65–109%. It was assumed that recoveries of other isomers of deltamethrin would be the same as for the (1+1')-deltamethrin. Recoveries of deltamethrin and degradation products from water with the modified pressurized beverage containers were not determined but were assumed to be the same as recoveries from all-glass containers. Using the beverage containers, Fox (1986) demonstrated recoveries in the range 56–118% for a variety of chlorinated hydrocarbons spiked at <1 ng/L in Lake Ontario water. The concentrations reported in this paper have not been corrected for recovery. The limits of quantitation (Keith et al., 1983) for the compounds of interest in water and sediment, respectively, were as follows: (1+1')-deltamethrin, 0.1 ng/L and 0.5 μg/kg dry weight; DBCA, 0.2 ng/L and 1 μg/kg; PBald, 0.5 ng/L and 2 μg/kg; PBalc, 0.5 ng/L and 2 μg/kg; PBacid, 0.2 ng/L and 1 μg/kg.

(*iv*) *Laboratory Tests of Deltamethrin Stability and Volatilization.* The stability of (1+1')-deltamethrin in sterilized pond water was assessed in the laboratory. Its volatilization from subsurface-injected water samples and from surface-sprayed water samples was also measured indirectly.

In one set of experiments, a DECIS formulation was injected 2 cm below the surface of azide-poisoned pond water (0.5 g of NaN_3/100 mL) in filled, uncapped, 125-mL jars. The initial deltamethrin concentration was 2 μg/L. Duplicate samples were extracted at intervals over 1 month, and the deltamethrin isomers,

Table I. Concentrations (ng/L) of Deltamethrin and Transformation Products in Bulk Subsurface Pond Water after the Spray

time, h	[(1+1′)]	[(2+2′)]	[DBCA]	[PBald]	[PBalc]	[PBacid]	[total], mol/L × 10^{10}	% of [total] at t = 0.7 h
0.2	4.1 × 10	6.0 × 10^{-1}	9.0				1.1	
0.7	3.1 × 10^2	1.4 × 10	3.6	0.6	2.4		6.7	100
1.2	1.2 × 10^2	7.3		1.9	7.5	6.2	1.1	17
1.7	8.3 × 10	8.6		0.8	1.7		2.0	30
3.2	4.6 × 10	1.2 × 10	6.8				1.4	20
4.7	2.0 × 10	6.4	6.6				0.8	11
6.2	1.1 × 10	4.9	2.7				0.4	6
7.7	1.2 × 10	5.9					0.4	5
9.2	5.3 × 10	2.8				0.9	1.2	17
10.7	7.2	2.8		0.6	3.5		0.5	7
25.4	3.9	2.7					0.1	2
32.0	3.3	1.2				10.0	0.7	10
55.0	2.0	1.2					0.1	1
271.0								0

Table II. Distribution of (1+1′)-Deltamethrin in Subsuface Pond Water between Dissolved Phase and Suspended Solids[a]

| time after spray h	[(1+1′)-deltamethrin] dissolved, ng/L	suspended solids, μg/kg dry weight	assoc with susp solids, ng/L	K_p	% dissolved	% in susp solids
0.2	2.9 × 10	2.4 × 10^3	1.2 × 10	8.3 × 10^4	71	29
0.7	1.3 × 10^2	2.2 × 10^4	1.8 × 10^2	1.7 × 10^5	41	59
1.2	7.5 × 10	7.0 × 10^3	4.4 × 10	9.3 × 10^4	63	37
1.7	3.9 × 10	9.6 × 10^3	4.4 × 10	2.5 × 10^5	47	53
3.2	3.1 × 10	2.2 × 10^3	1.5 × 10	7.1 × 10^4	68	32
4.7	7.2	2.9 × 10^3	1.3 × 10	4.0 × 10^5	36	64
6.2	2.8	8.5 × 10^2	8.6	3.0 × 10^5	25	75
7.7	2.8	8.7 × 10^2	9.0	3.1 × 10^5	24	76
9.2	4.9	7.9	0.4	1.6 × 10^3	92	8
10.7	7.0	2.5 × 10^3	0.2	3.6 × 10^5	97	3
25.4	2.5	4.1 × 10^2	1.4	1.6 × 10^5	64	36
32.0	1.8	1.1 × 10^2	1.5	6.1 × 10^4	55	45
55.0	0.8	8.0 × 10	1.2	1.0 × 10^5	39	61

[a] The concentration of (1+1′)-deltamethrin associated with suspended solids in nanograms per liter of water was derived from its concentration in suspended solids (μg/kg dry weight) and the concentration of suspended solids in water (mg/L). K_p is the ratio of concentration in suspended solids (μg/kg) to concentration in dissolved phase (μg/L).

but not degradation products, were determined. In addition, to assess isomerization in the absence of volatilization, two jars were sealed full and analyzed after 1 month. In the analysis, the whole volume of water in the jars was extracted, and care was taken to rinse the sides of the jars to minimize adsorptive loss of deltamethrin.

In the other set of experiments, a DECIS formulation was sprayed (using a sprayer of the type used to develop thin-layer chromatograms) at a nominal 6.2 g of AI/ha (the spray rate in the field) over jars filled with azide-poisoned pond water (0.5 g of NaN₃/100 mL) to determine whether volatilization from the surface microlayer was significant. Duplicate samples were extracted at intervals over 1 month, and the deltamethrin isomers, but not degradation products, were determined. Both sets of experiments were performed at 20 °C in darkened fume hoods to eliminate photolytic transformation and were also performed in azide-poisoned organic-free water as well as azide-poisoned pond water.

RESULTS

Subsurface Water. (1+1′)-Deltamethrin disappeared quickly from bulk subsurface water (i.e., water plus suspended solids) as shown in Figure 2. A maximal concentration of 320 ng/L was reached 0.7 h after the spray, and the concentration declined with a half-life of about 1 h. The concentration declined to 1% of its initial maximum after 1 day and measurable concentrations were still found 2–3 days after the spray. Table I shows the concentrations of the parent (1+1′)-deltamethrin as well as those of the transformation and degradation products detected. Low recoveries at t = 0.2 h were probably due to the time it took for the sprayed deltamethrin to diffuse to a depth of 0.5 m. The less toxic (2+2′)-deltamethrin was the only isomer found. Its concentration never ex-
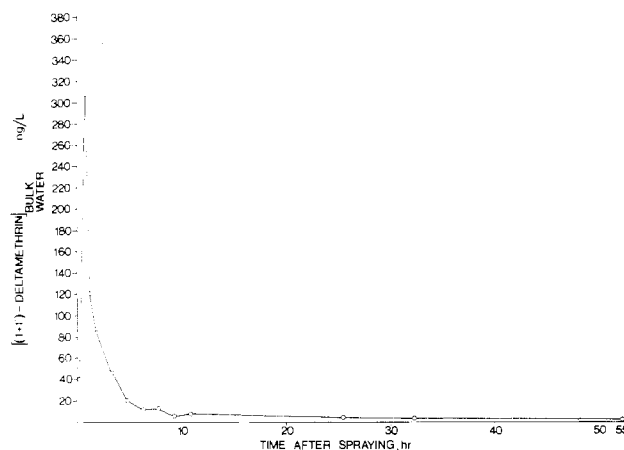
Figure 2. Concentration of (1+1′)-deltamethrin in bulk subsurface pond water.

ceeded 14 ng/L, but over 2–3 days it became a major contributor to the total deltamethrin concentration. At 25.4 h after the spraying its concentration was 69% of that of the (1+1′) isomer. DBCA, PBald, PBalc, and PBacid were all detected occasionally, sometimes at appreciable concentrations relative to the (1+1′)-deltamethrin (e.g., at 32 h). After 24 h, the concentration of the deltamethrin isomers plus the four products accounted for only ca. 10% of the original deltamethrin recovered.

Table II demonstrates that (1+1′)-deltamethrin was found in both suspended solids and dissolved phases, but in general from the mass balance viewpoint it exhibited no consistent preference for one phase over the other. The

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Table III. Concentrations (ng/L) of Deltamethrin and Transformation Products in Bulk Surface Microlayer of the Pond after the Spray

| time, h	[(1+1')]	[(2+2')]	[PBald]	[PBalc]	[total], mol/L × 10⁷	% of [total] at t = 0.1 h
0.1	4.9 × 10⁴	6.1 × 10³	6.2 × 10	6.7 × 10	1.11	100
0.3	1.9 × 10⁴	8.0 × 10²	5.1 × 10		0.40	36
0.4	3.0 × 10³	9.2 × 10	1.9 × 10		0.06	5
0.6	1.7 × 10³	8.9 × 10	7.7		0.04	3
0.7	8.6 × 10²	9.6 × 10	6.6		0.02	2
0.9	7.2 × 10²	8.0 × 10			0.02	2
1.7	3.7 × 10²	4.1 × 10	1.0 × 10		0.01	1
3.3	6.8 × 10²	7.6 × 10			0.02	2
4.2	6.0 × 10²	7.4 × 10			0.01	1
4.8	2.3 × 10²	5.7 × 10	7.2		0.01	1
6.4	8.1 × 10	2.0 × 10				
7.8	9.9 × 10	2.5 × 10				
9.3	2.0 × 10²	4.2 × 10				
10.7	6.9 × 10	2.1 × 10				
26.0	1.5 × 10	9.4	1.1 × 10			
32.0						
55.0	4.2 × 10	8.7				

same was true of (2+2')-deltamethrin. These results agree with those of Muir et al. (1985) for total deltamethrin. By contrast, the four degradation products were only found in the suspended solids phase. The apparent suspended solids to water partition coefficient (K_p) of the (1+1') isomer did not exhibit a consistent trend with time. The average value was (1.8 ± 1.3) × 10⁵ μg/kg solids per μg per L, which was roughly equal to that of the (2+2') isomer. This K_p value is 6–9 times greater than the value reported by Muir et al. (1985). This difference in K_p values probably reflects differences in the nature of the suspended solids, and organic carbon content, in the two studies. Muir et al. (1985) determined values of 1–8% for organic carbon in suspended solids, and we determined (only once) a value of 14% for suspended solids sampled before the spray. Using a value of 2 μg/L for the aqueous solubility of deltamethrin, Muir et al. (1985) calculated a K_p value 5–7 times lower than their observed value. The K_p value can also be estimated by Karickhoff's (1981) regression equation

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346 \quad (1)$$

where K_{ow} is the octanol–water partition coefficient (2.5 × 10⁶; Briggs et al., 1983) and K_{oc} is the organic carbon normalized partition coefficient, equal to K_p divided by the fractional organic carbon content of suspended solids (0.14 before the spray and assumed to be constant). The resulting estimate for K_p was 1.3 × 10⁵ μg/kg per μg per L, which is between the value reported here and that of Muir et al. (1985). As Karickhoff (1981) noted, large experimental errors in solubility measurements in the microgram per liter range and in K_{ow} measurements in the 10⁶ range can lead to inaccurate estimates of K_{oc} (hence K_p). Since deltamethrin has these properties, the difference between values of K_p (or K_{oc}) estimated from solubility and K_{ow} measurements and those determined experimentally is not surprising.

(2+2')-Deltamethrin can be produced from (1+1')-deltamethrin by photochemical and dark chemical reactions (Ruzo et al., 1977; Hill and Johnson, 1987). Experiments conducted in the laboratory with (1+1')-deltamethrin formulations injected below the surface of sterile pond water showed the production of (2+2')-deltamethrin in water in the dark. Figure 3 shows that even after a few hours the concentration of the (2+2') isomer in water forms a significant percentage of the total isomer concentration. In these experiments the first half-life of disappearance of the parent (1+1')-deltamethrin was about 2 days. (2+2')-Deltamethrin disappeared at a similar rate after
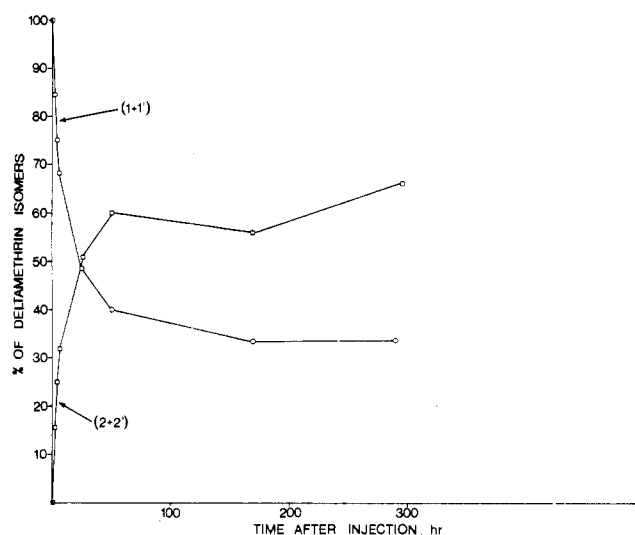
Figure 3. Percentage of deltamethrin isomers in sterile pond water in the dark after subsurface injection.

reaching its maximal concentration 290 h after the experiment began. In neither case, however, was the decline in isomer concentration exponential over several half-lives. It is possible that some of the deltamethrin volatilized (cf. below). No traces of either isomer were found after 35 days. Degradation products were not investigated in this study. These results indicated that small quantities of (2+2')-deltamethrin can be produced between the time that an emulsifiable concentrate of deltamethrin is mixed with water in the spray tanks and the time that it is sprayed aerially.

Surface Microlayer. The initial concentration of (1+1')-deltamethrin of about 50 μg/L in the surface microlayer corresponded to roughly 30% of the deposit estimated with use of exposed glass fiber filters 30 cm above the surface of the water (Ernst, 1987), which is itself about 30% of the emitted dose of 6.2 g of AI/ha. (1+1')-Deltamethrin disappeared very quickly from the surface microlayer as shown in Table III. The half-life was about 5 min, and although less than 1% of the initial deposit remained after 5 h, 42 ng/L remained 55 h after the spray. Large concentrations of (2+2')-deltamethrin were also found shortly after the spray and, as discussed above, may have been produced in the spray tanks after the emulsifiable concentrate was mixed with water. Its concentration also declined quickly. In the surface microlayer, PBald was found frequently and PBalc was found only once.
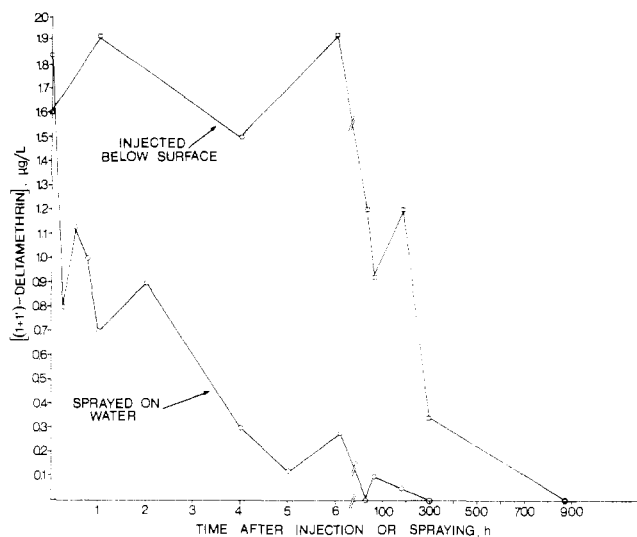
Figure 4. Disappearance of (1+1')-deltamethrin from sterile pond water in the dark in the laboratory after (i) spraying on surface and (ii) injection beneath surface.

PBacid and DBCA were not found.

Attempts to demonstrate the significance of volatilization of (1+1')-deltamethrin from the surfaces of sterile pond water in the laboratory were complicated slightly by the production of significant concentrations of (2+2')-deltamethrin. Nevertheless, the half-life of disappearance of (1+1')-deltamethrin from the whole volume of water after spraying on the surface was 2–3 h, compared with 2 days if deltamethrin was injected below the surface, as shown in Figure 4. Similar results were obtained with organic-free water in place of pond water. The half-life of disappearance of (1+1')-deltamethrin from subsurface water in these laboratory experiments (2 days) was much greater than that observed in subsurface water in the pond (1 h), probably because of the absence of photolysis and biological degradation in the laboratory experiment and the absence of sediment to which to adsorb. The observation of small quantities of (2+2')-deltamethrin in the water of jars that had been sealed for 1 month indicated that exposure to air was not necessary for the isomerization of the (1+1') isomer.

As noted in Methods and Materials, the (3+3') and (4+4') isomers of deltamethrin, as well as the (2+2') isomer, can be produced by the action of sunlight on (1+1')-deltamethrin. No (3+3') or (4+4') isomers were detected in any of the laboratory experiments or in any water or sediment sample.

Sediment. Table IV shows that the (1+1') and (2+2') isomers were infrequently detected in pond sediment. DBCA, however, was found in high concentrations relative to that of total deltamethrin, reaching a maximum of 0.4 mg/kg dry weight 3 h after the spray. PBald and PBalc were found at concentrations comparable to those of the deltamethrin isomers. No trace of deltamethrin isomers or degradation products was found in pond sediment 1 day after the spray.

DISCUSSION

The results of this study confirm the rapid disappearance from subsurface water of total deltamethrin, and (1+1')-deltamethrin in particular, with a half-life of about 1 h. Despite the poor mass balance on deltamethrin isomers and four degradation products, the (2+2') isomer and the four degradation products were significant products in the first few hours after the spray, and (2+2')-deltamethrin formed a significant part of total deltamethrin after that time. (1+1')-Deltamethrin partitioned rapidly from

Table IV. Concentrations (μg/kg Dry Weight) of Deltamethrin and Transformation Products in Pond Sediment (Top 2 cm Only) after the Spray

time, h	[(1+1')]	[(2+2')]	[DBCA]	[PBald]	[PBalc]
0.2					
0.7			5.7×10	3.8	
1.2	1.1×10	1.8		9.7	2.0×10
1.7				2.5	
3.2			4.3×10^2		
4.7			2.4×10^2		
6.2			1.6×10^2		
7.7			3.2×10^2		
9.2			1.3×10^2		
10.7	7.3	1.7			
25.4	8.1	0.9			
32.0					
55.0					

water to sediment, but after 1.2 h sediment analyses yielded no consistent pattern of appearance or disappearance of deltamethrin or degradation products. No trace of any of these compounds was found 32 h postspray. These results are in contrast to those of Muir et al. (1985), who found half-lives of 5–14 days for total deltamethrin in sediment and even observed deltamethrin residues up to 306 days posttreatment. Residues of deltamethrin in sediment observed at 306 days were ascribed to release from macrophytes and algae, into which the deltamethrin had partitioned. Such biota were not sampled at long times after the spray in this study.

The significance of volatilization of deltamethrin from water as a pathway of dissipation will probably depend to a large degree on its method of introduction to water. The Henry's law constant for deltamethrin *dissolved in water* is 95 Torr L mol^{-1} (Muir et al., 1985), which indicates a compound of low to medium volatility from water (Smith et al., 1980).

Muir et al. (1985) observed volatilization of deltamethrin from ponds after subsurface injection and estimated that volatilization losses were of the order of 6% over 2–4 days. Our laboratory results with sprayed vs injected formulations showed clearly that deltamethrin disappeared far faster from sprayed water than from subsurface-injected water. It is reasonable to assume that the kinetics of isomerization and degradation were similar in both sets of experiments. Indeed, similar results were obtained whether pond water or organic-free water was used. Therefore, we conclude that volatilization of deltamethrin from its formulation sprayed on the surface of water may be 1 order of magnitude faster than volatilization from subsurface water. We have made similar observations with regard to the insecticide fenitrothion sprayed on the surface of water as opposed to injected under the surface (Maguire and Hale, 1980). A loose terrestrial analogy of this proposed fast volatilization from the surface microlayer is provided by Hill and Schaalje (1985) who demonstrated a much faster loss of deltamethrin from soil if it were boom-sprayed compared to pipet-applied. They postulated that the high water volumes with pipet application washed the deltamethrin into the soil and, with less surface loss, dissipation was slowed. It may be that volatilization from the surface microlayer is the most important removal process for deltamethrin, or any insoluble pesticide, that settles on it.

Persistence and Fate of Deltamethrin

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LITERATURE CITED

Akhtar, M. H. Metabolism of Deltamethrin by Cow and Chicken Liver Enzyme Preparations. *J. Agric. Food Chem.* **1984**, *32*, 258–262.

Akhtar, M. H.; Khan, S. U. In Vitro Metabolism of Deltamethrin by Stem and Leaf Homogenates of Tobacco Plants. *Chemosphere* **1985**, *14*, 1037–1041.

Akhtar, M. H.; Hamilton, R. M. G.; Trenholm, H. L. Metabolism, Distribution and Excretion of Deltamethrin by Leghorn Hens. *J. Agric. Food Chem.* **1985**, *33*, 610–617.

Akhtar, M. H.; Hartin, K. E.; Trenholm, H. L. Fate of [^{14}C]-Deltamethrin in Lactating Dairy Cows. *J. Agric. Food Chem.* **1986**, *34*, 753–758.

Bocquet, J.-C.; L'Hotellier, M. The Effect of Deltamethrin on the Aquatic Environment. *Pestic. Sci.* **1985**, *16*, 198.

Briggs, G. G.; Elliott, M.; Janes, N. F. Present Status and Future Prospects for the Synthetic Pyrethroids. In *Pesticide Chemistry: Human Welfare and the Environment*; Miyamoto, J., Kearney, P. C., Eds.; Pergammon Press: New York, 1983; Vol. 2, pp 157–164.

Elliott, M.; Farnham, A. W.; Janes, N. F.; Needham, P. H.; Pulman, D. A. Synthetic Insecticide with a New Order of Activity. *Nature* **1974**, *248*, 710–711.

Ernst, W. R., Department of Environment, Dartmouth, NS, Canada, personal communication, 1987.

Fox, M. W. A Practical Sampling and Extraction System for the Quantitative Analysis of Sub-ng/L Organochlorine Contaminants in Filtered Water and Suspended Solids. In *Methods for Analysis of Organic Compounds in the Great Lakes*; Sonzogni, W. C., Dube, D. J., Eds.; University of Wisconsin Sea Grant Institute: Madison, WI, 1986; Vol. II, pp 27–34.

Harvey, G. W. Microlayer Collection from the Sea Surface: A New Method and Initial Results. *Limnol. Oceanogr.* **1966**, *11*, 608–613.

Hill, B. D. Persistence of Deltamethrin in a Lethbridge Sandy Clay Loam. *J. Environ. Sci. Health* **1983**, *B18*, 691–703.

Hill, B. D.; Schaalje, G. B. A Two-Compartment Model for the Dissipation of Deltamethrin on Soil. *J. Agric. Food Chem.* **1985**, *33*, 1001–1006.

Hill, B. D.; Inaba, D. J. An Impingement Plate Method to Detect Deposits of Pyrethroid Insecticides. *J. Environ. Sci. Health* **1987a**, *B22*, 643–662.

Hill, B. D.; Johnson, D. L. Persistence of Deltamethrin and Its Isomers on Pasture Forage and Litter. *J. Agric. Food. Chem.* **1987b**, *35*, 373–378.

Karickhoff, S. W. Semi-Empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils. *Chemosphere* **1981**, *10*, 833–846.

Keith, L. H.; Crummett, W.; Deegan, J., Jr.; Libby, R. A.; Taylor, J. K.; Wentler, G. Principles of Environmental Analysis. *Anal. Chem.* **1983**, *55*, 2210–2218.

Khan, S. U.; Zhang, L.-Z.; Akhtar, M. H. Bound Residues of Deltamethrin in Bean Plants. *J. Agric. Food Chem.* **1984**, *32*, 1141–1144.

Khan, S. U.; Behki, R. M.; Tapping, R. I.; Akhtar, M. H. Deltamethrin Residues in an Organic Soil under Laboratory Conditions and Its Degradation by a Bacterial Strain. *J. Agric. Food Chem.* **1988**, *36*, 636–638.

Lhoste, J., Ed. *Deltamethrin Monograph*; Roussel-Uclaf: Paris, France, 1982; 412 pp.

Maguire, R. J.; Hale, E. J. Fenitrothion Sprayed on a Pond: Kinetics of Its Distribution and Transformation in Water and Sediment. *J. Agric. Food Chem.* **1980**, *28*, 372–378.

Muir, D. C. G.; Rawn, G. P.; Grift, N. P. Fate of the Pyrethroid Insecticide Deltamethrin in Small Ponds: A Mass Balance Study. *J. Agric. Food Chem.* **1985**, *33*, 603–609.

Mulla, M. S.; Navvab-Gojrati, H. A.; Darwazeh, H. A. Toxicity of Mosquito Larvicidal Pyrethroids to Four Species of Freshwater Fishes. *Environ. Entomol.* **1978**, *7*, 728–430.

Ruzo, L. O.; Casida, J. E. Degradation of Decamethrin on Cotton Plants. *J. Agric. Food Chem.* **1979**, *27*, 572–575.

Ruzo, L. O.; Holmstead, R. L.; Casida, J. E. Pyrethroid Photochemistry: Decamethrin. *J. Agric. Food Chem.* **1977**, *25*, 1385–1394.

Ruzo, L. O.; Unai, T.; Casida, J. E. Decamethrin Metabolism in Rats. *J. Agric. Food Chem.* **1978**, *26*, 918–925.

Ruzo, L. O.; Engel, J. L.; Casida, J. E. Decamethrin Metabolites from Oxidative, Hydrolytic and Conjugative Reactions in Mice. *J. Agric. Food Chem.* **1979**, *27*, 725–731.

Shono, T.; Ohsawa, K.; Casida, J. E. Metabolism of trans- and cis-Permethrin, trans- and cis-Cypermethrin and Decamethrin by Microsomal Enzymes. *J. Agric. Food Chem.* **1979**, *27*, 316–325.

Smith, J. H.; Bomberger, D. C., Jr.; Haynes, D. L. Prediction of the Volatilization Rates of High-Volatility Chemicals from Natural Water Bodies. *Environ. Sci. Technol.* **1980**, *14*, 1332–1337.

Tessier, J. Structure, Synthesis and Physical-Chemical Properties of Deltamethrin. In *Deltamethrin Monograph*; Lhoste, J., Ed.; Roussel Uclaf: Paris, France, 1982, Chapter 2, pp 37–66.

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; 25 pp.

Zitko, V.; McLeese, D. W.; Metcalfe, C. D.; Carson, W. G. Toxicity of Permethrin, Decamethrin and Related Pyrethroids to Salmon and Lobster. *Bull. Environ. Contam. Toxicol.* **1979**, *21*, 338–343.