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PERSISTENCE AND FATE OF DELTAMETHRIN SPRAYED  
ON A POND AND STREAM IN PRINCE EDWARD ISLAND

by

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## EXECUTIVE SUMMARY

Deltamethrin sprayed on a pond and stream in Prince Edward Island disappeared quickly from water, with a half-life of about 1 h. Major routes of degradation or transformation were (i) chemical and photochemical isomerization 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 post-spray. 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 which could be the major route of dissipation of deltamethrin, or any insoluble pesticide, sprayed on a pond.

## MANAGEMENT IMPLICATIONS

The results of this study indicate that deltamethrin is of very low persistence. Because of its extremely high toxicity, however, the 100 m buffer zone between sprayed fields and water bodies should be rigidly enforced.

## RÉSUMÉ POUR LA DIRECTION

Après pulvérisation de deltaméthrine sur un lac et un cours d'eau de l'île-du-Prince-Édouard, le produit est disparu rapidement de l'eau, avec une demi-vie d'environ 1 h. Les principales voies de dégradation ou de transformation étaient les suivantes : 1) isomérisation chimique et photochimique en stéréoisomères inactifs de (2+2')-deltaméthrine; 2) hydrolyse, avec formation ultérieure de produits d'oxydation. Onze jours après la pulvérisation, on n'a retrouvé aucun résidu des stéréoisomères de deltaméthrine, ni des quatre principaux produits de dégradation. Des expériences en laboratoire sur la volatilisation de formulations de deltaméthrine à partir d'eau soumise à une pulvérisation, par opposition à de l'eau traitée par injection sous la surface, ont démontré que la volatilisation à partir de la microcouche superficielle était un processus très rapide, qui pourrait être la principale voie de disparition de la deltaméthrine, ou de tout autre pesticide insoluble, après pulvérisation sur un lac.

## CONSEQUENCES POUR LA GESTION

Les résultats de cette étude montrent que la deltaméthrine présente une persistance très faible. Mais, à cause de sa toxicité extrêmement élevée, la zone tampon de 100 m entre les terrains traités et les aquifères doit être absolument maintenue.

## ABSTRACT

Deltamethrin sprayed on a pond and stream in Prince Edward Island 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 post-spray. 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 which could be the major route of dissipation of deltamethrin sprayed on a pond.

## RÉSUMÉ

Après pulvérisation de deltaméthrine sur un lac et un cours d'eau de l'île-du-Prince-Édouard, le composé avait rapidement disparu de l'eau, sa demi-vie étant d'environ 1 h. Les principales voies de dégradation ou de volatilisation étaient les suivantes : 1) conversion chimique et photochimique en stéréoisomères inactifs de (2+2')-deltaméthrine; 2) hydrolyse, avec formation ultérieure de produits d'oxydation. Onze jours après la pulvérisation, on n'a retrouvé aucun résidu des stéréoisomères de deltaméthrine, ni des quatre principaux produits de dégradation recherchés. Des expériences en laboratoire sur la volatilisation de formulations de deltaméthrine à partir d'eau soumise à une pulvérisation, par opposition à de l'eau traitée par injection sous la surface, ont montré que la volatilisation à partir de la microcouche superficielle était un processus très rapide, qui pourrait représenter la principale voie d'élimination de la deltaméthrine, après pulvérisation sur un lac.

## INTRODUCTION

Deltamethrin [(S)-alpha-cyano-3-phenoxybenzyl (1R,3R)-cis-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] is the most potent insecticide known. Its insecticidal properties were first reported in 1974 (Elliott et al., 1974) and it was developed commercially in France by Roussel Uclaf (Lhoste, 1982). The cis-1R,3R 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, sunflowers, 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 m 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 radiolabelled deltamethrin injected just below the surfaces of two small ponds. Among other things, they demonstrated that (i) deltamethrin rapidly partitioned from water into suspended solids, plants and sediment, with a half-life of 2-4 hr in water, (ii) half-lives for disappearance from sediment were 5-14

d, (iii) some of the injected deltamethrin did volatilize from water, and (iv) major products were IR cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane carboxylic 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 alpha-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 which result 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 its metabolism by mammalian and other enzyme systems (Ruzo et al., 1978, 1979; Shono et al., 1979; Akhtar, 1984; Akhtar et al., 1985; Akhtar et al., 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 (Ruza et al., 1977).

#### METHODS AND MATERIALS

There are 8 possible stereoisomers of deltamethrin. We have used the numbering system given by Ruza et al. (1977) in which the parent deltamethrin is designated as 1 and the only other isomer which is toxic to insects (Tessier, 1982) or mice (Ruza 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 which 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 an 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.

#### Spray Site Location

The study site, Kelvin Grove, is located in a potato growing area of Prince Edward Island 5 km south of Kensington (cf. Figs. 1 and 2). 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 (Alnus sp.) which were ca. 4 m in height. The pond was shallow, 2 m deep at its deepest point. The pond was fed by a stream (ca. 0.25 m<sup>3</sup>/s) but it 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, stream 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 active ingredient per ha. Other spray parameters and the meteorological conditions are given in Tables I and II. Operational requirements dictated that the spraying be done even though the wind speed exceeded the upper limit of 8 km/h specified on the product label. All of the pond was sprayed as well as the stream from a point 50 m downstream to 100 m upstream of the point at which the stream was sampled.

#### Sampling

Sampling was done intensively at one location (A) in the pond and one location (B) in the stream (cf. Fig. 2). The pond site was chosen in order to elucidate the degradation pattern of deltamethrin without the complication of water flow.

Samples were also taken, although less frequently, at two other points in the stream. Site D was ca. 2 km downstream of the spray site. Site C was ca. 0.5 km upstream of the spray site. Analyses of samples collected from the upstream site C before and up to 11 d after the spray showed only the rare occurrence of low concentrations of DBCA and (1+1')-deltamethrin (< 2 ng/L), which may have been due to contamination during sample handling or unrelated spraying of deltamethrin upstream.

#### (i) Subsurface water (sites A and B)

Forty litre samples were collected from a depth of 0.5 m and immediately pressure filtered through 0.45 µm glass fibre filters using compressed N<sub>2</sub> 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. It is recognized that passage through a 0.45  $\mu$ m filter is only an operational definition of the "dissolved" phase and that chemicals such as deltamethrin may still be adsorbed to colloidal material which passes the filter.

(ii) Sediment (site A only)

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 (site A only)

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  $\mu$ m.

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 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.

(iv) Other samples

Two other kinds of samples were taken to provide additional information on the persistence, transport and fate of deltamethrin in aquatic environments.

Larger amounts of suspended solids (up to 3 g) were obtained from the stream at sites B, C and D at various times before and after the spray in order to improve the detection limits for deltamethrin isomers and degradation products in suspended solids. The samples were obtained by pumping 260 L of water through a Westphalia continuous flow centrifuge. The centrifuge retains solids of roughly the size retained by a 0.45  $\mu$ m filter. The suspended solids were preserved in the same way as the sediment.

Potato leaves from the nearby sprayed potato field were collected before and after the spray to compare the products on bean leaves with those on the surface of pond water. The potato leaves (30-45 g) were clipped at intervals after the spray, wrapped in aluminum foil and frozen as soon as possible for transport to the laboratory.

Extraction and Analysis

The methods used for the extraction, clean-up and analysis of the water, sediment, suspended solids and potato leaves 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.

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 g of sediment was extracted and all of any particular suspended solids sample. The extracts were passed through sodium sulfate and concentrated to 10 mL.

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

Potato leaves (30-45 g) were thawed, weighed, cut up and homogenized for 20 min with an ultrasonic probe in 100 mL acetone/pentane (1/1, v/v). Five hundred mL of organic-free water was added to the homogenate and the pentane phase was separated, dried by passage through sodium sulfate, and concentrated to 10 mL.

(ii) Preliminary clean-up of sediment, suspended solids and potato leaf extracts

The 10 mL dichloromethane extracts from above were solvent-changed to 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 pentane. At this point there was usually some precipitation in the test tube, but all material was transferred to the clean-up column in the course of the four-fraction clean-up 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 was used to rinse the test tubes containing the original extract to be cleaned up, and in this way even the precipitated material was transferred to the clean-up column. All four fractions were solvent-changed to 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, suspended solids and potato leaves were analyzed according to the scheme shown in Fig. 3. Essentially the samples were split, 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 acetone solution, adding 30  $\mu$ L 30%  $K_2CO_3$ , 100  $\mu$ L 5% PFBBR solution in acetone, and heating for 3 h at 60  $^{\circ}C$ . 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. Ten mL hexane was passed through the column and discarded. Then 10 mL 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 was performed with a Varian 3400 gas chromatograph and an electron capture detector. A 30 m x 0.2 mm i.d. DB-1 column with 10:1 split was programmed from 220 to 235  $^{\circ}C$  at 0.5  $^{\circ}/min$  followed by a 10 min hold. The inlet temperature was 200  $^{\circ}C$ . 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 represents 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 x 0.2 mm i.d. OV-1 column was used under the following conditions: initial temperature 70  $^{\circ}C$  for 0.5 min., programming rate 1, 30  $^{\circ}/min$  (70-200  $^{\circ}C$ ), rate 2, 5  $^{\circ}/min$  (200-280  $^{\circ}C$ ), 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 x 0.25 mm i.d. SPB-5 column was directly interface to the electron-impact ion source for maximum sensitivity. Electron energy was 70 eV. Operating temperatures were: injection port, 275 °C; interface, 280 °C, column head pressure 4 psi, helium carrier gas. Gas chromatographic conditions were: initial temperature, 70 °C for 0.5 min, programming rate 1, 25 °/min (70-180 °C), rate 2, 2 °/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 is 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 using the modified pressurized beverage containers were not determined, but are 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 article have not been corrected for recovery. The limits of quantitation (Keith *et al.*, 1983) for the compounds of interest in water and sediment, respectively, are: (1+1')-

deltamethrin, 0.1 ng/L and 0.5 ug/kg dry weight; DBCA, 0.2 ng/L and 1 ug/kg; PBald, 0.5 ng/L and 2 ug/kg; PBalc, 0.5 ng/L and 2 ug/kg; PBacid, 0.2 ng/L and 1 ug/kg.

(iv) Laboratory tests of deltamethrin stability and volatilization

Tests were done in the laboratory to determine the stability of (1+1')-deltamethrin in sterilized pond water, and to determine the relative importance of volatilization from water. In one set of experiments, a DECIS formulation was injected 2 cm below the surface of 0.5% (w/v) azide-poisoned pond water in 125 mL jars. The initial deltamethrin concentration was 2 ug/L. Duplicate samples were extracted at intervals over 1 month and the deltamethrin isomers, but not degradation products, were determined. The whole volume of the water sample was extracted, and care was taken to rinse the insides 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 g a.i./ha (the spray rate in the field) over jars of 0.5% (w/v) azide-poisoned pond water in an effort to determine if volatilization from the surface microlayer were significant. Replicate samples were extracted at intervals over 1 month and the deltamethrin isomers, but not degradation products, were determined. Both sets of experiments were carried out at 20 °C in darkened fume hoods to eliminate photolytic degradation and were also carried out in azide-poisoned organic-free water in addition to pond water. Similar results were obtained whether pond water or organic-free water were used.

(v) 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, even 1.5 y after purchase. As noted above, it is assumed that only the parent enantiomer 1 was present, but since the analytical method can not indicate otherwise, the designation (1+1')-deltamethrin will be used in this paper.

3-Phenoxybenzaldehyde (PBald), 3-phenoxybenzyl alcohol (PBalc), 3-phenoxybenzoic acid (PBacid) and pentafluorobenzyl bromide (PFBBBr) 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 fibre 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.

A mixture of the (1+1'), (2+2'), (3+3') and (4+4') diastereoisomers 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 ug/cm<sup>2</sup>) on glass, was irradiated outdoors with bright summer sunshine for 4 d, and the photoisomers were recovered from the glass with hexane. The electron capture responses of all diastereoisomers were assumed to be identical to that of the (1+1') analytical standard.

## RESULTS

### Subsurface Water - Pond

(1+1')-Deltamethrin disappeared quickly from bulk subsurface water as shown in Fig. 4. 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 d and measurable concentrations were still found 2-3 d after the spray. Table III shows the concentrations of the parent (1+1')-deltamethrin as well as those of the transformation and degradation products detected. The less toxic (2+2')-deltamethrin was the only isomer found. Its concentration never exceeded 14 ng/L but over 2-3 d it became a major contributor to the total deltamethrin concentration. Its concentration was up to 70% 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. However, the total concentration of the deltamethrin isomers and the four products mentioned declined quickly, with only ca. 10% of the original deltamethrin accounted for after 24 h.

Table IV demonstrates that (1+1')-deltamethrin was found in both suspended solids and dissolved phases, but in general exhibited no pronounced preference for either phase. These results agree with those of Muir et al. (1985) on total deltamethrin. The same was true of (2+2')-deltamethrin. By contrast, the four degradation products were only found in the suspended solids phase. Table V shows that the apparent suspended solids-to-water partition coefficients of the (1+1') and (2+2') isomers of deltamethrin were fairly constant with time after the spray. Similar results to those in Tables IV and V were obtained for deltamethrin in stream

water at site B. These observations agree with a prediction made using an octanol-water partition coefficient ( $K_{ow}$ ) of  $2.5 \times 10^6$  (Briggs et al., 1983) and Karickhoff's (1981) regression equation

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

where  $K_{oc}$  is the organic carbon normalized partition coefficient, equal to the suspended solids-to-water partition coefficient ( $K_p$  of Table V) divided by the fractional organic carbon content of suspended solids, usually assumed to be 0.1. This prediction also employed a suspended solids concentration in pond water of 10 mg/L, which is the average of 14 determinations.

(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 5 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 d. (2+2')-Deltamethrin disappeared at a similar rate after 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 d. Degradation products were not looked for in these studies. These results indicate that small quantities of (2+2')-deltamethrin can be produced between the time that an emulsifiable concentrate of deltamethrin

is mixed with water and the time that it is sprayed aerially.

#### Subsurface Water - Stream

The concentration of (1+1')-deltamethrin declined slightly faster in the stream than in the pond. The results are shown in Table VI. A maximal concentration of 220 ng/L was reached 0.7 h after the spray and the concentration declined with a first half-life of about 0.5 h. The concentration declined to about 1 % of its initial maximum after 1 d but low concentrations were found as long as 11 d post-spray, possibly due to the transport of field-derived runoff in small tributaries to the stream and/or unrelated spraying of deltamethrin on fields farther upstream.

As in the case of pond water, (2+2')-deltamethrin, DBCA, PBald and PBalc were detected, but not PBacid. (2+2')-Deltamethrin and DBCA in particular were consistently detected and after the first few hours these chemicals formed a significant part of the total amount of all compounds detected. A mass balance as a function of time was not calculated in Table VI since it would not be informative for a flowing system.

Table VII shows the concentrations of (1+1')-deltamethrin and the only other chemicals detected in bulk subsurface water at site D 2 km downstream of the spray. The water transit time was estimated earlier to be about 2 h. The concentration of (1+1')-deltamethrin reached a maximum of 32 ng/L 6.5 h after the spray and declined to less than 1 ng/L within 3 d. The concentration of the (2+2') isomer was usually less than 1 ng/L and accounted for little of the total concentration of deltamethrin isomers for the first 24 h after the spray. PBacid was observed only twice, and only in the suspended solids phase. No other transformation or degradation products were detected.

### Surface Microlayer - Pond

The initial concentration of (1+1')-deltamethrin of about 50 ug/L in the surface microlayer corresponds to roughly 30% of the deposit estimated using exposed glass fibre filters 30 cm above the surface of the water (Ernst, 1987), which is itself about 30% of the emitted dose of 6.2 g a.i./ha. (1+1')-Deltamethrin disappeared very quickly from the surface microlayer as shown in Table VIII. The half-life was about 5 min, and although less than 1% of the initial deposit remained after 5 h, there was still a significant concentration (42 ng/L) 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. PBald was detected frequently, PBalc only once and no other product was detected.

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 d if deltamethrin were injected below the surface, as shown in Fig. 6. The half-life of disappearance of (1+1')-deltamethrin from subsurface water in these laboratory experiments (2 d) was much faster than that observed in subsurface water in the pond (1 h), probably because of the absence of photolysis and biological degradation, and the absence of sediment to which to adsorb in the laboratory experiments.

As noted above 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. However, significant concentrations of the (2+2') and (3+3') isomers, and smaller concentrations of the (4+4') isomer, relative to (1+1')-deltamethrin, were detected in potato leaves.

#### Sediment - Pond

Table IX shows that the (1+1') and (2+2') isomers were only 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 d 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 the four degradation products sought, it was clear that the (2+2') isomer and the four degradation products were significant products in the first few hours after the spray, and that (2+2')-deltamethrin formed a significant part of total deltamethrin after that time. Although rapid partitioning of (1+1')-deltamethrin from water to

sediment was expected the sediment analyses yielded no consistent pattern of appearance or disappearance of deltamethrin or degradation products. No trace of any of these compounds was found 24 h post-spray. These results are in contrast to those of Muir et al. (1985), who found half-lives of 5-14 d for total deltamethrin in sediment and even observed deltamethrin residues up to 306 d post-treatment.

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<sup>-1</sup> (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 d. 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. Therefore, we conclude that volatilization of deltamethrin from its formulation sprayed on the surface of water may be an 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 that deltamethrin, or any insoluble pesticides, which settles on it.

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Table I. Spray application parameters.

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Formulation rate	28.06 L/ha
Mixing rate	6 L DECIS 2.5 EC/681 L water
Dosage rate	6.18 g a.i./ha
Nozzles	24 TEE-JET D6-45
Air speed	163 km/h
Boom pressure	310 kPa
Swath width	34 m
Boom height	2.5 m
Droplet size	350 $\mu$ m (average)

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Table II. Meteorological conditions at time of spraying.

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Date	July 10, 1986
Time	07:30
Air temperature	12.2 °C
Relative humidity	79%
Wind speed	3 m/s (10.8 km/h)
Wind direction	282

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Table III. 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 $\times 10^{10}$	% of [Total] at t=0.7 h
0.2	41.1	0.6	9.0				1.13	
0.7	308.0	14.2	3.6	0.6	2.4		6.70	100.0
1.2	120.0	7.3		1.9	7.5	6.2	1.13	17.2
1.7	83.4	8.6		0.8	1.7		1.99	30.0
3.2	45.8	11.7	6.8				1.37	20.0
4.7	20.1	6.4	6.6				0.75	11.0
6.2	11.4	4.9	2.7				0.41	6.0
7.7	11.9	5.9					0.35	5.0
9.2	52.9	2.8				0.9	1.16	17.0
10.7	7.2	2.8		0.6	3.5		0.47	7.0
25.4	3.9	2.7					0.13	2.0
32	3.3	1.2				10.0	0.69	10.0
55	2.0	1.2					0.06	0.9
271								0.0

Table IV. Distribution of (1+1')-deltamethrin in pond water between dissolved phase and suspended solids.

Time after spray, h	% dissolved	% with suspended solids
0.2	71	29
0.7	41	59
1.2	63	37
1.7	47	53
3.2	68	32
4.7	36	64
6.2	25	75
7.7	24	76
9.2	92	8
10.7	97	3
25.4	65	35
32	55	45
55	38	62

Table V. Apparent suspended solids-to-water partition coefficients of deltamethrin isomers as a function of time after spray.

Time, h	$K_p$ apparent (1+1')	$K_p$ apparent (2+2')
0.2	$8.11 \times 10^4$	
0.7	$1.76 \times 10^5$	$2.04 \times 10^5$
1.2	$9.34 \times 10^4$	$1.36 \times 10^5$
1.7	$2.44 \times 10^5$	$2.19 \times 10^5$
3.2	$7.06 \times 10^4$	$4.38 \times 10^4$
4.7	$4.06 \times 10^5$	$3.52 \times 10^5$
6.2	$2.99 \times 10^5$	$2.87 \times 10^5$
7.7	$3.08 \times 10^5$	$3.43 \times 10^5$
25.4	$1.63 \times 10^5$	$3.39 \times 10^5$
average	$(2.05 \pm 1.17) \times 10^5$	$(2.40 \pm 1.11) \times 10^5$

$K_p = (\text{ug/kg in suspended solids}) / (\text{ug/L in dissolved phase})$

Table VI. Concentrations (ng/L) of deltamethrin and transformation products in bulk stream water at site B after the spray.

Time, h	[(1+1')]	[(2+2')]	[DBCA]	[PBald]	[PBalc]
0.2	171.0	2.0	11.2		
0.7	218.0	84.1	9.8		
1.2	95.6	2.8	4.2	0.5	
1.7	43.2	2.4	7.0		
3.2	31.0	2.5	2.5	1.0	2.9
4.7	17.1	3.4	6.0		
6.2	9.5	3.1		0.6	2.0
7.7	4.4	1.2			
10.7	15.7	3.9	12.4		
25.4	1.5	3.3	2.9		
32	3.1	0.6	2.5		
55	0.3		2.6		
94	0.4		3.3		
122	0.5	0.5	3.0		
123	0.4		2.3		
124	0.6		2.7		
125	0.5	0.9	3.2		
126	0.1				
127	0.6				
269	0.9	0.1			

Table VII. Concentrations (ng/L) of deltamethrin isomers and PBacid in bulk stream water 2 km downstream of spray at site D.

Time, h	[(1+1')]	[(2+2')]	[PBacid]
1.9	7.6		
2.9	9.5	0.3	
3.9	11.5	0.5	
4.9	26.3	0.5	
6.4	32.0	0.6	
7.9	12.9	0.2	
9.4	9.2		
10.9	7.4	1.2	
25.9	4.8	0.2	
31	4.2	0.7	2.6
54	0.9	0.2	2.3

Table VIII. Concentrations (ng/L) of deltamethrin and transformation products in bulk surface microlayer of the pond at site A after the spray.

Time, h	[(1+1')]	[(2+2')]	[(PBald)]	[(PBalc)]	[Total], mol/L x 10 <sup>7</sup>	% of [Total] at t = 0.1 h
0.1	49400	6110	61.9	67.2	1.11	100.0
0.3	19300	804	50.7		0.40	36.0
0.4	2970	91.8	19.1		0.06	5.0
0.6	1690	89.0	7.7		0.04	3.0
0.7	862	95.8	6.6		0.02	2.0
0.9	720	80.0			0.02	2.0
1.7	368	40.9	10.3		0.01	1.0
3.3	680	75.5			0.02	2.0
4.2	595	73.6			0.01	1.0
4.8	229	57.2	7.2		0.01	1.0
6.4	80.8	20.2				
7.8	99.2	24.8				
9.3	203	41.5				
10.7	69.3	20.7				
26	14.6	9.4	10.7			
32						
55	42.3	8.7				

Table IX. Concentrations (ug/kg dry weight) of deltamethrin and transformation products in pond sediment (top 2 cm only) at site A after the spray.\*

Time, h	[(1+1')]	[(2+2')]	[DBCA]	[PBald]	[PBalc]
0.2					
0.7			56.6	3.8	
1.2	11.2	1.8		9.7	20.3
1.7				2.5	
3.2			429.2		
4.7			240.6		
6.2			158.4		
7.7			315.8		
9.2			132.8		
10.7	7.3	1.7			
25.4	8.1	0.9			
32					
55					

\*top 2 cm only

## FIGURE CAPTIONS

Figure 1. Location of Kelvin Grove site on Prince Edward Island.

Figure 2. Diagram of Kelvin Grove site.

Figure 3. Analytical scheme for deltamethrin isomers and some degradation products in extracts of water, sediment, suspended solids and potato leaves.

Figure 4. Concentration of (1+1')-deltamethrin in bulk subsurface pond water at site A after the spray.

Figure 5. Percentage of deltamethrin isomers in sterile pond water in the dark after injection.

Figure 6. 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.

Figure 1

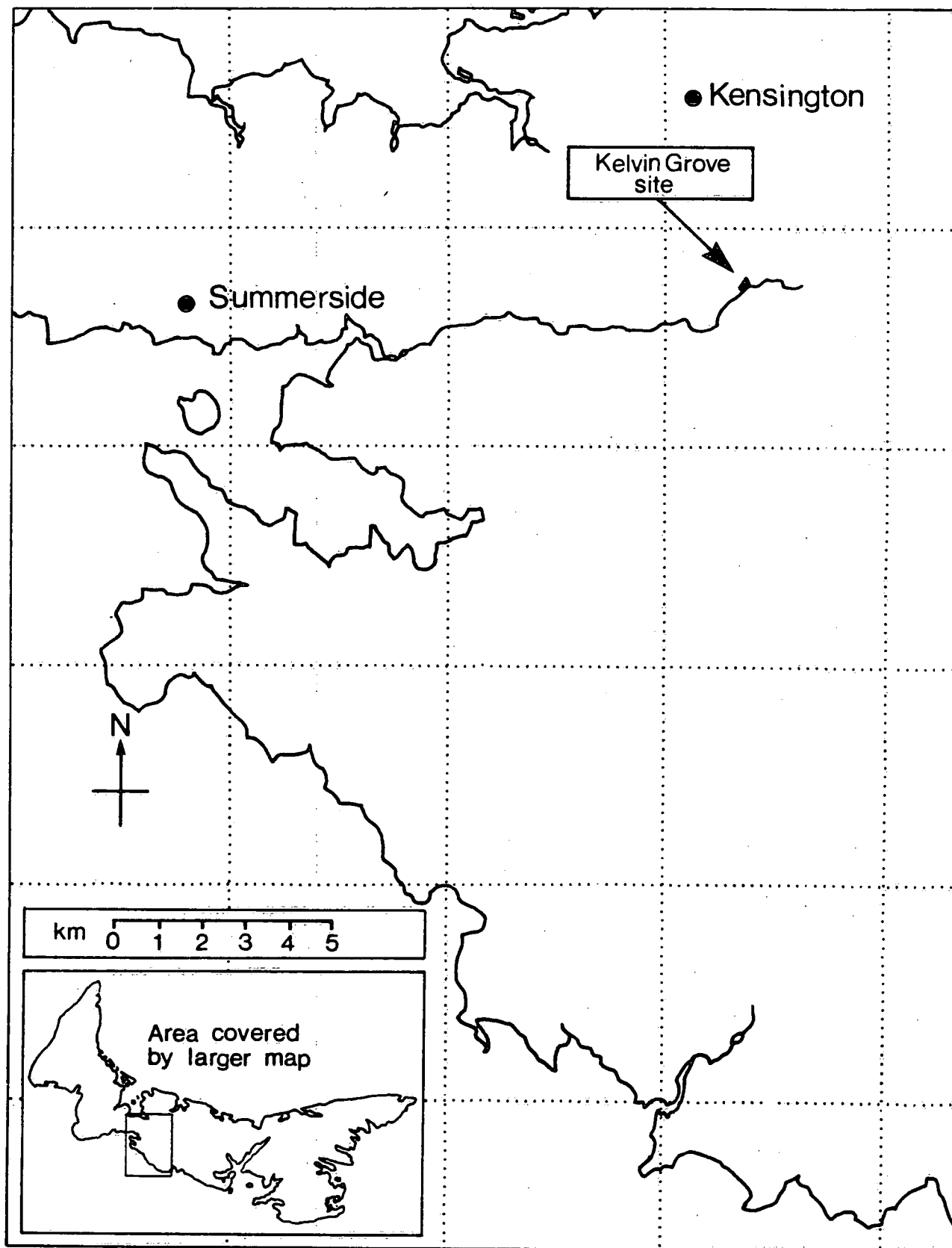


Figure 2

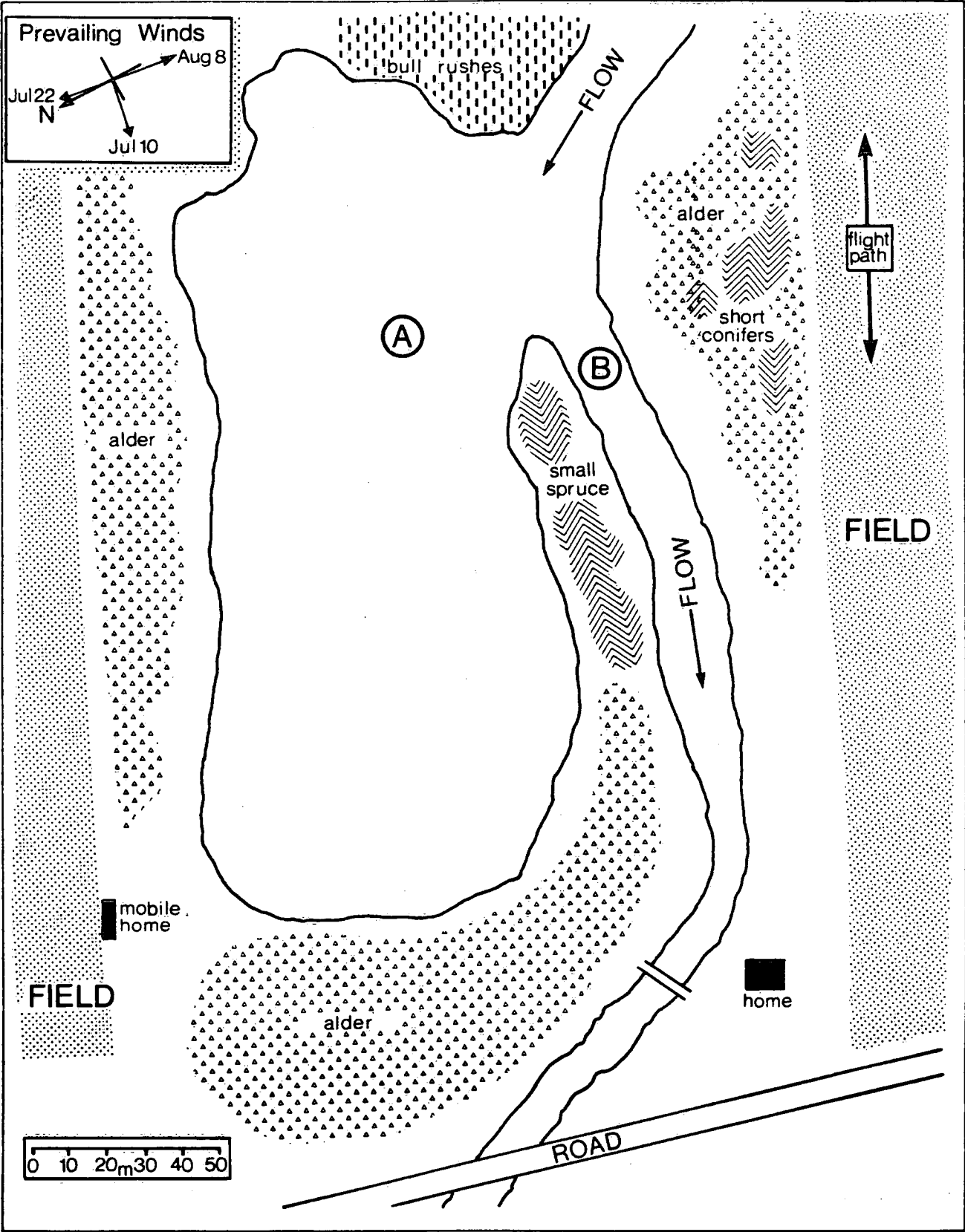


Figure 3

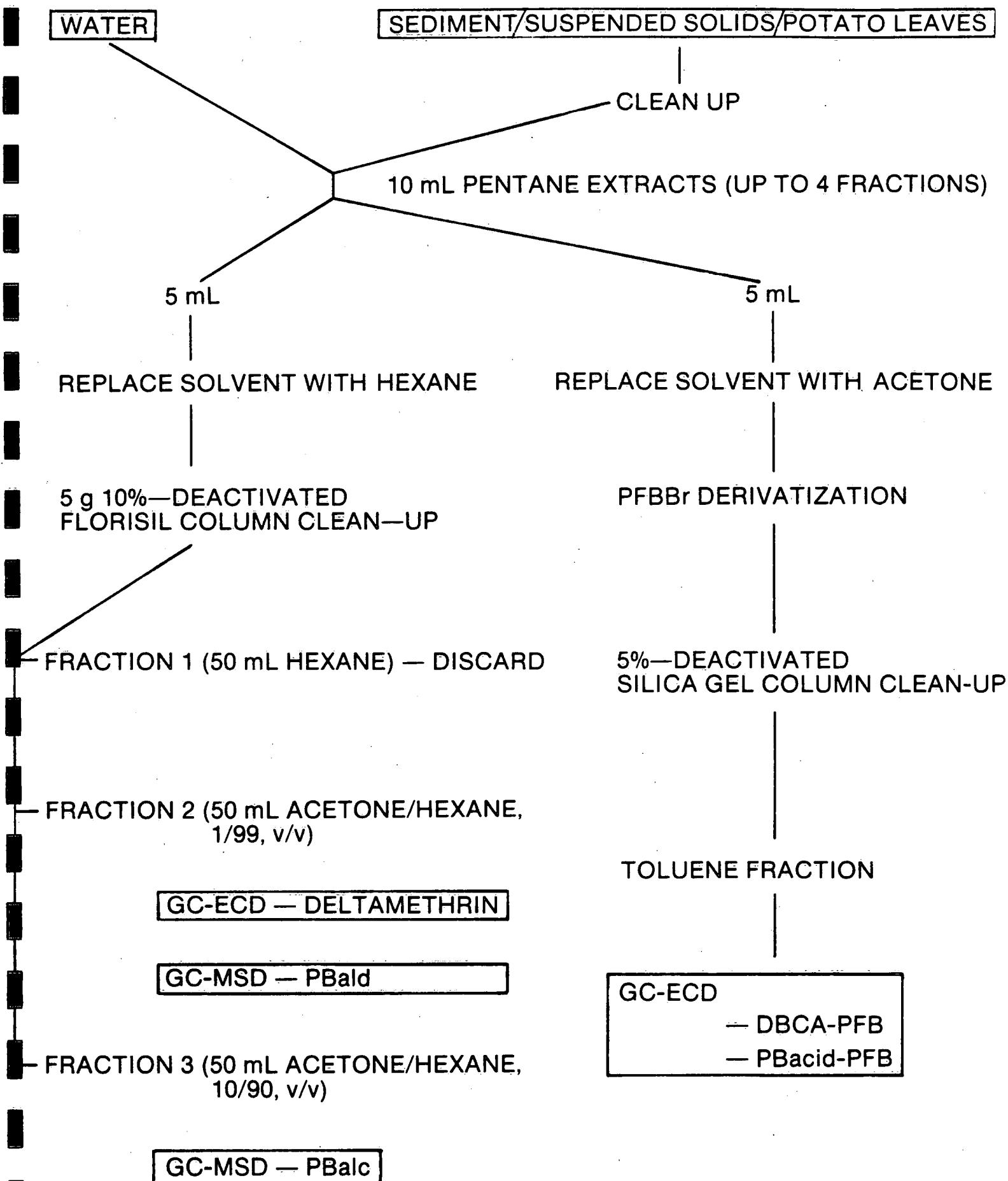


Figure 4

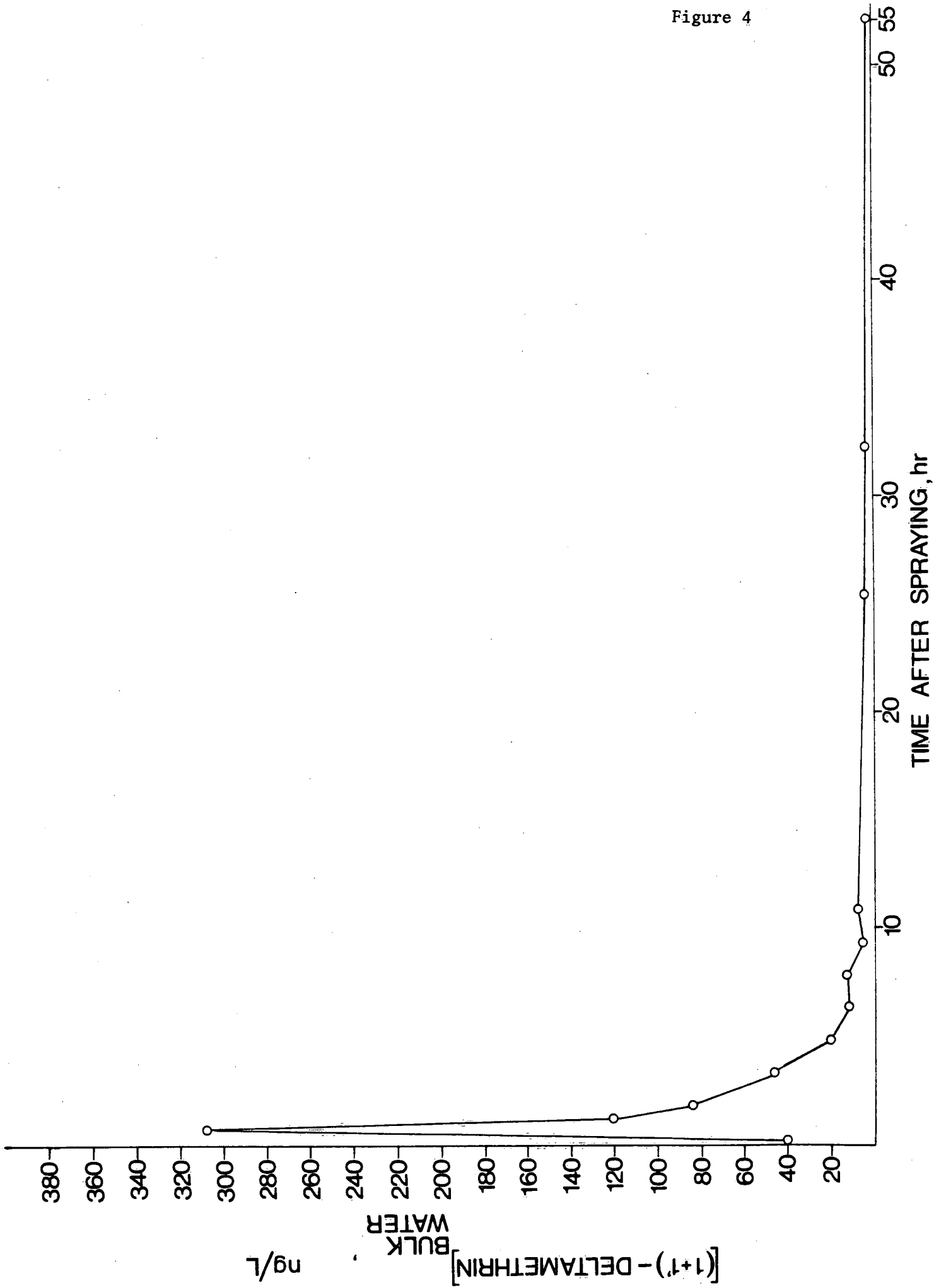


Figure 5

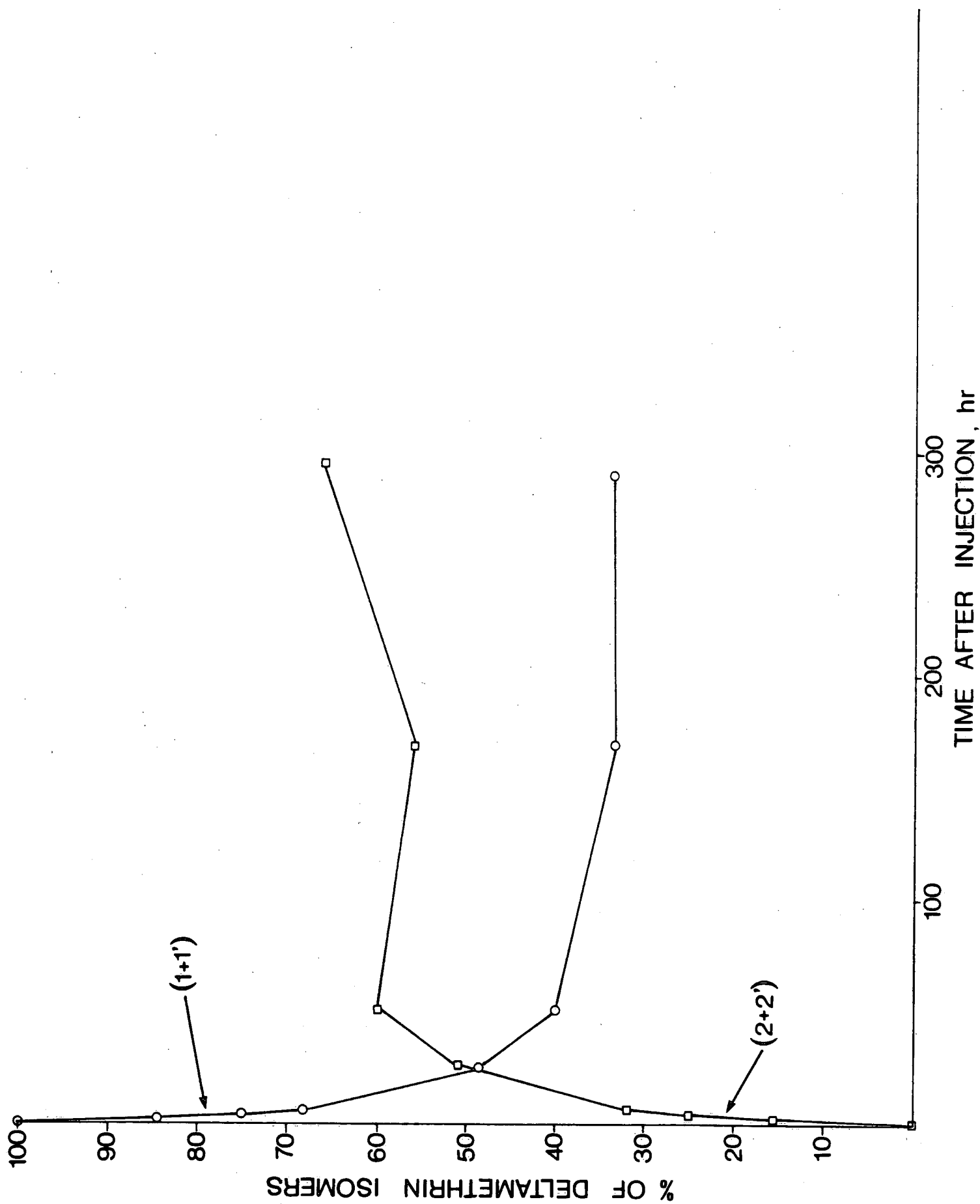


Figure 6

