Kinetics of Pesticide Volatilization from the Surface of Water†

R. James Maguire

Rivers Research Branch, National Water Research Institute, Department of Environment,
Canada Centre for Inland Waters, Burlington, Ontario L7R 4A6, Canada

Fenitrothion [O,O-dimethyl O-(p-nitro-m-tolyl) phosphorothionate] and deltamethrin [(S)-α-cyano-3-phenoxybenzyl (1R,3R)-cis-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] in formulations sprayed on the surface of natural water in the laboratory disappeared from water far faster than formulations injected below the surface of the water. Half-lives of disappearance from surface-sprayed water were less than 2.5 h, compared to 5–60 days for disappearance from subsurface-injected water. Analyses of air filters showed that the disappearance from surface-sprayed samples was due in large part to volatilization, which accounted for at least 70% of the pesticide lost from water. The results correlate well with those from earlier field studies of directly sprayed ponds and indicate that volatilization from the surface microlayer is the major dissipation process for these pesticides sprayed on natural waters.

INTRODUCTION

Volatilization from natural waters can be a significant pathway for chemicals that have high vapor pressures and low aqueous solubilities. The rate of volatilization of a chemical depends primarily upon the Henry's law constant, H (the ratio of vapor pressure to solubility), and the liquid-phase and gas-phase resistance (Smith et al., 1980). Examples of chemicals for which volatilization from water is a major dissipation pathway are benzene and 1,1,1-trichloroethane [e.g., Callahan et al. (1979)].

Assessments of the importance of volatilization of chemicals from water are usually based on the assumption that they are uniformly distributed in subsurface water. However, some chemicals such as pesticides may be sprayed on water or drift to water, and volatilization will be faster from the surface of water than from subsurface water. Volatilization from the surface microlayer was thought to be important in studies of the persistence of fenitrothion (Maguire and Hale, 1980) and deltamethrin (Maguire et al., 1989) in small ponds after direct aerial spraying. In these studies, the kinetics of clearance from the surface microlayer were biphasic first order, with half-lives of the fast and slow processes being of the order of minutes and hours, respectively. The fast process appeared to account for >90% of the loss of pesticide from water. It was hypothesized that the fast process was volatilization from the surface microlayer and the slow process represented incorporation into subsurface water and/or chemical or photochemical reaction. Supporting evidence came from laboratory experiments which showed that the pesticides disappeared far faster from surface-sprayed water than from subsurface-injected water. In those experiments it was assumed that the kinetics of most processes would be similar in surface-sprayed water and subsurface-injected water, with the exception of volatilization. However, there were no direct measurements of volatilization. This paper provides direct laboratory evidence of fast volatilization of fenitrothion and deltamethrin from the surface of sprayed water.

MATERIALS AND METHODS

Materials. Technical grade fenitrothion was obtained from Chemagro Ltd. (Mississauga, ON) and purified by elution in benzene from 10% (w/w) water-deactivated Florisil. Aerotex 3470 aromatic solvent and Atlox 3409F emulsifier were obtained from Texaco Canada Ltd. (Mississauga) and Atlas Chemical Co. (Toronto, ON), respectively. A typical fenitrothion formulation for forest spraying at the time of the original experiments contained 11% (w/w) fenitrothion, 1.5% Aerotex 3470, 1.5% Atlox 3409F, and 86% water (Maguire and Hale, 1980).

Analytical standards of all eight possible stereoisomers of deltamethrin (designated 1, 1′, 2, 2′, 3, 3′, 4, and 4′) were provided by Roussel Uclaf (Paris). The parent compound is designated 1-deltamethrin. The purity of the isomers was greater than 95% with the exception of the 2′ isomer, which was contaminated with about 15% of the 1′ isomer. Only 1-deltamethrin and, to a lesser extent, 3-deltamethrin are toxic to insects (Tessier, 1982) and mice (Ruzo et al., 1977). For *Daphnia magna*, isomers 2, 3, and 4 are 2–10-fold less toxic than isomer 1, while isomers 1′, 2′, 3′, and 4′ are inactive (Day and Maguire, 1990). It appears that the only toxicologically significant isomer of 1-deltamethrin produced in aquatic environments is the 3 isomer, and it is produced by sunlight photolysis (Maguire, 1990). Decis 2.5 EC emulsifiable deltamethrin concentrate in xylenes from Hoechst Canada Inc. (Lot DEREHE0101) was bought locally and shown to contain only 1-deltamethrin (Maguire, 1990). Pure cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DBCA) was a gift from Hoechst Canada Inc. Pentafluorobenzyl bromide (PFBBr), p-nitro-m-cresol, acetic anhydride, and sodium azide were obtained from Aldrich Chemical Co. (Milwaukee, WI).

Pesticide grade and HPLC grade organic solvents were obtained from Caledon Laboratories (Georgetown, ON). Polyurethane foam plugs were Soxhlet-extracted with hexane for 24 h (8 cycles/h) before use. The sodium sulfate, silica gel, aluminum foil, and disposable pipets were heated to 500 °C for 24 h before use. All glassware was rinsed with pesticide grade solvents before use.

Volatilization Experiments. Experiments were performed to assess the rate of loss of fenitrothion and deltamethrin from surface-sprayed water samples and from subsurface-injected water samples and the rate of accumulation of the pesticides on air-sampling filters suspended above the solutions. Pesticide formulations were used typical of those sprayed in the field. Analyses of the subsurface-injected water samples included the parent insecticides and hydrolysis products in an effort to determine if hydrolysis was significant over the longer period that these samples were monitored. In addition, experiments were performed to assess the effect of sodium azide on the hydrolysis of the insecticides.

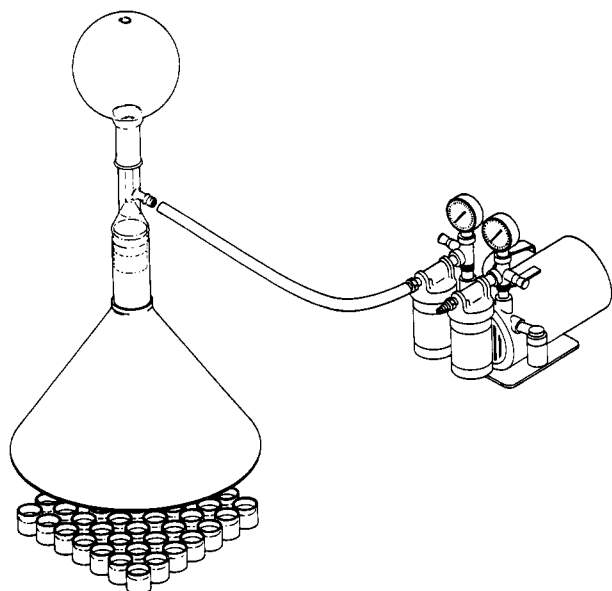(i) *Fenitrothion.* A fenitrothion formulation was sprayed

Pesticide Volatilization from Water

J. Agric. Food Chem., Vol. 39, No. 9, 1991 **1675**

Figure 1. Air-sampling device for measuring pesticide volatilization.

(by use of a sprayer of the type used to develop thin-layer chromatograms) at a nominal 275 g of active ingredient/ha (a typical spray rate in the field) over 125-mL jars filled to the brim with unfiltered natural water from nearby Hamilton Harbour (pH 6.6, dissolved organic matter concentration 4 mg/L, particulate organic matter concentration 3 mg/L, conductivity 530 μmho/cm). An array of 7 × 7 jars packed closely together was covered with a layer of aluminum foil with holes cut out for each jar. Immediately after the spray, the foil was removed and discarded. The purpose of the foil was to prevent the spray from reaching the outside surfaces of the jars or the bench, from which subsequent volatilization would have affected the results. Thus, only the surface of water in the jars was sprayed. Immediately after the removal of the protective foil, an aluminum foil cone was installed 5 cm above the jars. The cone extended 10 cm around the edges of the 7 × 7 array of jars and was connected to a filter funnel containing two 4-cm diameter × 5 cm polyurethane foam plugs in a filter funnel (cf. Figure 1). Air was pumped through the filter at 37 L/min (Gast portable vacuum/pressure pump, Baxter Inc., Toronto). Individual jars were removed at random at intervals over a 3-day period, and the entire contents were extracted and cleaned up as described below. At the same time that water samples were taken, the entire aluminum foil cone–filter apparatus was replaced with a fresh one and extracted as described below. Experiments were performed in triplicate at 20 °C in azide-poisoned water to eliminate bacterial degradation [5 mg/L, incorrectly stated as 0.5 g/100 mL in Maguire et al. (1989)] and in darkened fume hoods to eliminate photolytic transformation. Preliminary experiments indicated that there was no effect of pumping rate on volatilization rate in the range 5–37 L/min. An acknowledged source of error in the experimental design is changing airflow patterns over the jars resulting from the periodic removal of jars of water for analysis.

To assess the rate of volatilization of fenitrothion from its formulation in subsurface water, the formulation was injected 2 cm below the surface of water in jars as described above. The initial fenitrothion concentration was 10 μg/L, a typical concentration observed in subsurface water after aerial spraying in forests for spruce budworm control (Maguire and Hale, 1980). Air filter samples and water samples were taken at intervals over a 128-day period. For such longer air-sampling times a reserve pump was used to allow for periodic maintenance. These experiments were also done in triplicate. In addition, experiments were done in azide-free distilled water.

(ii) *Deltamethrin.* The rate of volatilization of deltamethrin from surface-sprayed and subsurface-injected formulations was determined in the same manner as described above for fenitrothion. For the surface-sprayed experiments, 1-deltamethrin

was sprayed at a nominal 6.2 g of active ingredient/ha (the spray rate in the field). For the subsurface-injected experiments, the initial concentration of 1-deltamethrin was 2 μg/L, and experiments were also done in azide-free distilled water.

Extraction. The air filters were only analyzed for the parent insecticides, as were the surface-sprayed water samples. The subsurface-injected water samples were analyzed for hydrolysis products in addition to the parent insecticides: p-nitro-m-cresol in the case of fenitrothion and DBCA in the case of deltamethrin.

The whole volume of water in jars from the volatilization experiments was acidified to pH 1 and extracted three times with dichloromethane. The inside surface of the jars was rinsed thoroughly with dichloromethane, and the rinsings were combined with the dichloromethane extracts, dried by passage through sodium sulfate, and concentrated to 10 mL. The dichloromethane extracts were solvent-exchanged with hexane and concentrated to 1 mL with nitrogen evaporation. The hexane extracts were cleaned up on activated silica gel columns of 40-cm length and 2.5-cm diameter, with a layer of sodium sulfate for drying. Two hundred milliliters of 60/40 dichloromethane/hexane (v/v) was passed through the column and collected. The eluent was solvent-exchanged into hexane and concentrated to 1 mL for analysis for the parent insecticides; half of this final volume was subsequently analyzed for hydrolysis products as described later.

The aluminum foil cone–filter apparatus shown in Figure 1 was inverted, and 250 mL of dichloromethane was used to rinse the foil and extract the polyurethane filters at the same time, being collected in the round-bottom flask. The extract was treated as described above with the exception that it was not analyzed for hydrolysis products. Preliminary experiments showed that both pesticides broke through one, but not two, polyurethane foam plugs during air sampling.

Analysis. Fenitrothion determinations were made with a Varian 3400 GC-ECD (Georgetown, ON). A 30 m × 0.2 mm i.d. DB-1 column was used under isothermal conditions at 200 °C. Inlet and detector temperatures were 200 and 350 °C, respectively. The injector was operated in splitless mode. The fenitrothion peak eluted at 10 min, and the minimum detectable amount was about 1 pg. p-Nitro-m-cresol was determined by GC-ECD as its acetyl derivative prepared according to standard techniques (Canada Department of Environment, 1981).

Deltamethrin determinations were generally made with an achiral GC-ECD technique (Maguire et al., 1989), with a minimum detectable amount of 5 pg. Confirmation of the identities of stereoisomers in enantiomeric pairs such as (1+1')-deltamethrin was done by high-performance liquid chromatography diode array spectrophotometry (HPLC-DAD) (Waters Associates, Mississauga) with a chiral column [J. T. Baker Bakerbond covalent (R)-N-[3,5-(dinitrobenzoyl)phenyl]glycine, 4.6 mm × 25 cm, 5-μm spherical particle size; Johns Scientific Inc., Toronto]. The DAD was set to 220 nm. Isocratic elution in 0.1% 2-propanol in hexane allowed the separation of the eight deltamethrin stereoisomers (Maguire, 1990). The minimum detectable amount of each deltamethrin isomer was about 75 ng by HPLC-DAD. DBCA was determined as its pentafluorobenzyl bromide derivative (DBCA-PFB) (Maguire et al., 1989).

RESULTS

Fenitrothion. Fenitrothion sprayed on the surface of water disappeared very quickly. The kinetics were first order over 90% of the disappearance, with a half-life of about 0.5 h. Fenitrothion appeared in the air filters with a similar half-life. A summary of the kinetic results of all experiments is given in Table I. In an attempt to determine a mass balance for the air–water system, the amount of fenitrothion in the air filters was compared to the amount in water in all of the jars, the latter being calculated from the kinetics of disappearance from one set of jars extrapolated over all the jars in the system. Figure 2a shows for one experiment that most of the fenitrothion lost from water volatilized and appeared in the air filters. As Table I indicates, an average of 65 ± 18% of the fenitrothion lost from water was accounted for by volatilization.

Table I. Kinetics of Pesticide Disappearance from Sterile Natural Water and Appearance in Air-Sampling Filters[a]

	water		air filters		
	k_{dis}, h⁻¹	$t_{1/2,dis}$, h	k_{app}, h⁻¹	$t_{1/2,app}$, h	% volatilized
fenitrothion					
surface sprayed	1.4 ± 0.3	0.5 ± 0.1	1.3 ± 0.5	0.7 ± 0.3	65 ± 18
subsurface injected	(5.8 ± 2.1) × 10⁻⁴	(1.4 ± 0.5) × 10³	(1.3 ± 0.5) × 10⁻³	(6.2 ± 2.4) × 10²	51 ± 13
(1+2′)-deltamethrin					
surface sprayed	0.4 ± 0.2	2.4 ± 1.2	0.5 ± 0.2	1.7 ± 0.7	71 ± 11
subsurface injected	(6.0 ± 1.9) × 10⁻³	(1.3 ± 0.4) × 10²			
subsurface-injected distilled water, no azide	(4.3 ± 1.4) × 10⁻³	(1.8 ± 0.6) × 10²			

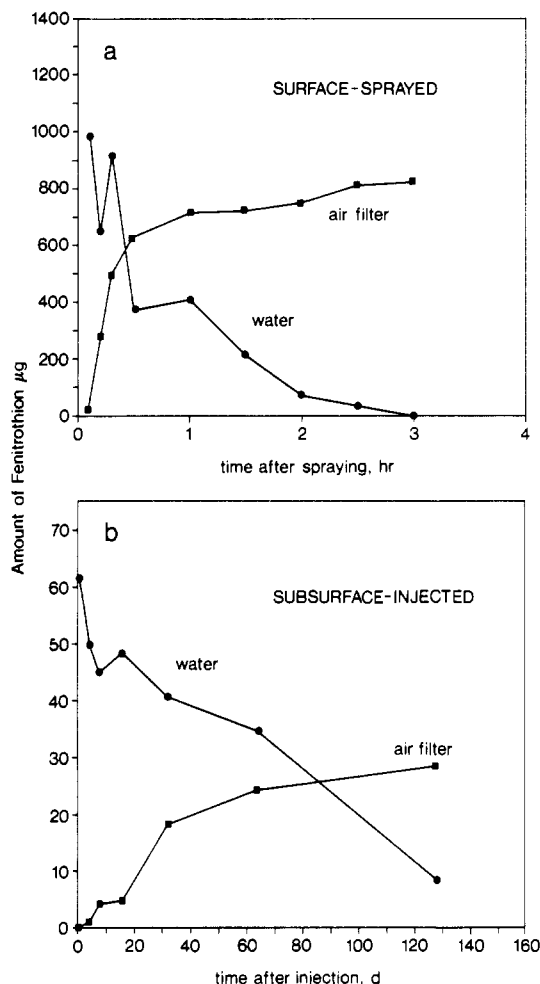[a] Results are averages of three determinations.

Figure 2. Calculated amounts of fenitrothion in the water and air filter system after (a) surface spraying and (b) subsurface injection.

Fenitrothion injected into subsurface water disappeared far more slowly than that sprayed on the surface. The kinetics were first order over 85% of the disappearance, with a half-life of about 58 days. The results are summarized in Table I. Figure 2b is a typical plot of the variation with time of the amount of fenitrothion in water and air filters, constructed as described above. A substantial fraction of the fenitrothion volatilized, as indicated by its appearance in the air filters with similar kinetics. Table I shows that on average about 51% of the loss of fenitrothion from water was accounted for by volatilization. Only minor amounts of p-nitro-m-cresol were found over the course of the experiments, never amounting to more than 5% of the starting material; therefore, it appeared that hydrolysis was a negligible pathway either in distilled water or in azide-poisoned natural water. The lower recovery of fenitrothion in the air filters in this set of
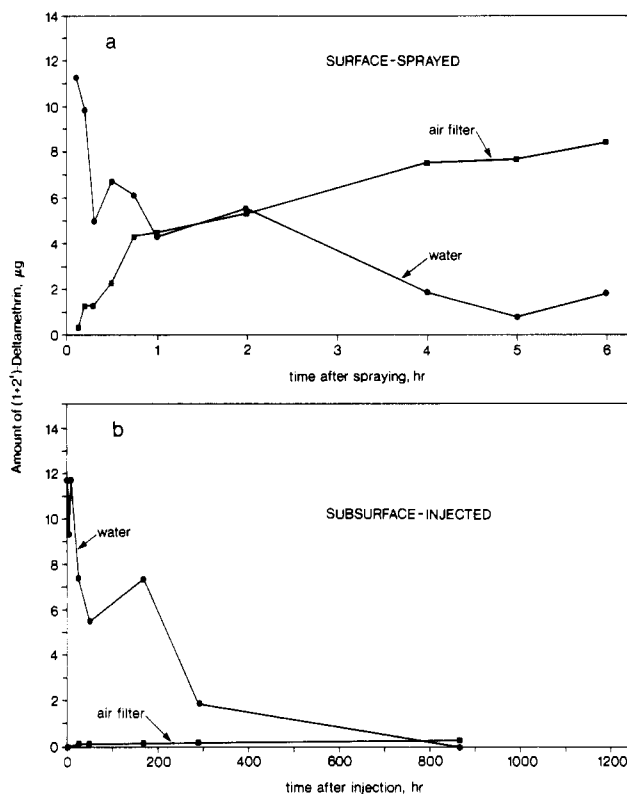

Figure 3. Calculated amounts of (1+2′)-deltamethrin in the water and air filter system after (a) surface spraying and (b) subsurface injection.

experiments may be due to physical losses of fenitrothion or a degradation pathway other than hydrolysis.

Deltamethrin. As noted earlier, 1-deltamethrin in water in the dark isomerizes to 2′-deltamethrin in addition to hydrolyzing (Maguire, 1990). In the experiments reported here, no other isomers were produced. Consequently, deltamethrin in the water and air samples is designated (1+2′)-deltamethrin.

Deltamethrin sprayed on the surface of water also disappeared very quickly. The kinetics of disappearance of (1+2′)-deltamethrin were first order over 85% of the disappearance, with a half-life of about 2 h. Deltamethrin appeared in the air filters with a similar half-life, as shown in Table I. Figure 3a, constructed as described above for fenitrothion, shows for one experiment that most of the (1+2′)-deltamethrin lost from water volatilized and appeared in the air filters. As Table I indicates, an average of 71 ± 11% of the (1+2′)-deltamethrin lost from water was accounted for by volatilization.

Deltamethrin injected into subsurface water disappeared far more slowly than that sprayed on the surface. The kinetics were first order over 90% of the disappearance, with a half-life of about 5 days. The kinetic results are given in Table I. (1+2′)-Deltamethrin was only found
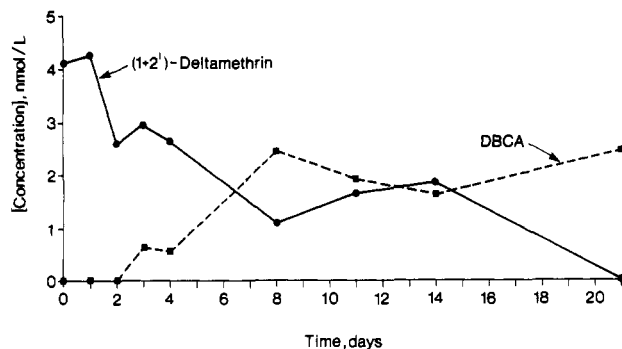
Figure 4. Hydrolysis of deltamethrin in natural water containing 5 mg/L sodium azide.

sporadically in the air filters and in small amounts as shown by Figure 3b, which was constructed as described for fenitrothion. In no case did the amount of (1+2')-deltamethrin found in the air filters exceed 3% of that initially present in the water. The disappearance of (1+2')-deltamethrin from subsurface water was likely due to hydrolysis. Figure 4 shows that DBCA production accounted for 60% of the loss of deltamethrin in one incubation experiment. Furthermore, it appeared that hydrolysis was faster in 5 mg/L azide-poisoned natural water than in distilled water, with half-lives of 130 and 180 h, respectively (cf. Table I).

DISCUSSION

This work has confirmed that volatilization is the major pathway of dissipation for fenitrothion and deltamethrin formulations *sprayed on the surface of water* in laboratory experiments. In each case, about 70% of the pesticide lost from water was found on the air-sampling filters, and the half-lives of volatilization were 0.7–1.7 h, as shown by rates of appearance in air filters. These findings agree well with observations of the disappearance of each pesticide sprayed on ponds. Those field observations indicated that the faster of the two processes in the biphasic dissipation from the surface microlayer accounted for over 90% of the pesticide lost, and the half-life of the faster process was 0.3 h for fenitrothion (Maguire and Hale, 1980) and 0.1 h for deltamethrin (Maguire et al., 1989). The similarity of the results observed in the field and in the laboratory indicates that it is likely that volatilization is the single most important pathway of dissipation from water when these pesticides are sprayed on the surface of water in the field. The minor discrepancies between field and laboratory results for fenitrothion or deltamethrin may be ascribed to other dissipation processes in the field and to difficulties in the laboratory work in air sampling compared to sampling the whole volume of water in the jars. A biphasic clearance of pesticide from water was not observed in the laboratory experiments, probably because the whole volume of water in the jars was sampled, not the surface microlayer. Such sampling conditions are analogous to sampling subsurface water in the field, in which case only monophasic exponential dissipation was observed.

In contrast to volatilization from its sprayed formulation, the volatilization of fenitrothion from water after subsurface injection was a very slow process. This was expected since its Henry's law constant of 0.75 Torr L mol^{-1} (National Research Council of Canada, 1975) indicates a compound of low volatility from water (Smith et al., 1980). Its half-life of volatilization was about 25 days as shown by its rate of appearance in the air filters. This was about 900 times slower than volatilization from

sprayed solutions. That the recovery of fenitrothion in air filters was as high as it was (51%) over 128 days indicates the relative stability of fenitrothion in solutions in which photolysis and bacterial degradation were prevented.

Volatilization of deltamethrin from water after subsurface injection was a negligible process. This was also expected since its Henry's law constant of 95 Torr L mol^{-1} (Muir et al., 1985) indicates a compound of low to medium volatility from water (Smith et al., 1980) and since hydrolysis was a competing process.

In the experiments reported in this paper fenitrothion volatilized from surface-sprayed water faster than deltamethrin. This result was not expected on the basis of their Henry's law constants. However, in the case of surface microlayers the Henry's law constant will probably not be a good predictor since it is the ratio of vapor pressure to aqueous solubility, and a surface microlayer with pesticide adjuvants is a significantly different environment from subsurface water. The volatilization kinetics (cf. half-lives of appearance in air filters of 0.7 h for fenitrothion and 1.7 h for deltamethrin in Table I) may be more appropriately correlated with vapor pressures, which are 5.4×10^{-5} Torr for fenitrothion (National Research Council of Canada, 1975) and 3.8×10^{-7} Torr for deltamethrin (Muir et al., 1985).

Surface microlayers of natural waters have long been of interest in environmental chemistry because they are often enriched in metals, lipophilic contaminants, nutrients, and dissolved and particulate organic matter [e.g., Liss (1975)]. In particular, contamination of the surface microlayer by high concentrations of toxic substances relative to subsurface water may pose hazards to organisms that spend part or all of their lives at the air–water interface (Von Westernhagen et al., 1987). The hazard may be acute in areas sprayed directly or areas close to aerial pesticide spray operations. The results of this work however, indicate that the hazard from extremely high concentrations of pesticides in surface microlayers is likely to be short-lived.

ACKNOWLEDGMENT

LITERATURE CITED

Callahan, M. A.; Slimak, M. W.; Gabel, N. W.; May, I. P.; Fowler, C. F.; Freed, J. R.; Jennings, P.; Durfee, R. L.; Whitmore, F. C.; Maestri, B.; Mabey, W. R.; Holt, B. R.; Gould, C. "Water-Related Environmental Fate of 129 Priority Pollutants. Vol. II: Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines and Miscellaneous Compounds". U.S. Environmental Protection Agency Report EPA-440/4-79-029b; EPA Office of Water and Waste Management: Washington, DC, 1979.

Canada Department of Environment. *Water Quality Branch Analytical Methods Manual*; Canada Department of Environment: Ottawa, ON, 1981.

Day, K. E.; Maguire, R. J. Acute Toxicity of Isomers of the Pyrethroid Insecticide Deltamethrin and Its Major Degradation Products to *Daphnia magna*. *Environ. Toxicol. Chem.* **1990**, *9*, 1297–1300.

Liss, P. S. Chemistry of the Sea Surface Microlayer. In *Chemical Oceanography*; Riley, J. P., Skirrow, G., Eds.; Academic Press: New York, 1975; Chapter 10, pp 193–243.

Maguire, R. J. Chemical and Photochemical Isomerization of Deltamethrin. *J. Agric. Food Chem.* **1990**, *38*, 1613–1617.

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.

Maguire, R. J.; Carey, J. H.; Hart, J. H.; Tkacz, R. J.; Lee, H.-B. Persistence and Fate of Deltamethrin Sprayed on a Pond. *J. Agric. Food Chem.* **1989**, *37*, 1153–1159.

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.

National Research Council of Canada. *Fenitrothion: The Effects of Its Use on Environmental Quality and Its Chemistry*; NRCC Publication 14104; National Research Council of Canada: Ottawa, ON, 1975; 162 pp.

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

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, 1982; Chapter 2, pp 37–66.

Von Westernhagen, H.; Landolt, M.; Kocan, R.; Furstenberg, G.; Janssen, D.; Kremling, K. Toxicity of Sea-Surface Microlayer: Effects on Herring and Turbot Embryos. *Mar. Environ. Res.* **1987**, *23*, 273–290.