# FATE OF FENITROTHION IN SHADED AND UNSHADED PONDS

by

GREGORY PHILIP MALIS

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the University of Manitoba in partial fulfillment of the requirements
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MASTER OF SCIENCE

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## TABLE OF CONTENTS


| | Page |
|---|---|
| LIST OF TABLES | i) |
| LIST OF FIGURES | ii) |
| ABSTRACT | iii) |
| PREFACE | iv) |
| A. Literature Review | 1 |
| 1. Introduction | 1 |
| 2. Chemistry | 1 |
| 3. Mode of Action | 7 |
| 4. Uses and Effects | 9 |
| 5. Environmental Fate | 14 |
| a) field monitoring studies | 14 |
| b) hydrolysis | 16 |
| c) photolysis | 17 |
| d) biodegradation | 19 |
| e) sorption | 19 |
| f) plant uptake | 20 |
| g) fish accumulation | 21 |
| h) volatilization | 23 |
| 6. Environmental Fate of Degradation Products | 24 |
| a) methyl-nitrophenol | 24 |
| b) amino-fenitrothion | 25 |
| c) desmethyl fenitrothion | 27 |
| d) fenitrooxon | 28 |
| e) S-methyl derivatives | 29 |
| f) other products | 29 |
| 7. Field and Laboratory Persistence Studies | 30 |
| 8. Analytical Methodology | 41 |
| a) air | 41 |
| b) water | 45 |
| c) sediment | 48 |
| d) plants and algae | 50 |
| e) fish | 53 |
| f) analysis | 54 |
| i) Radiolabelled techniques | 54 |
| ii) Thin Layer Chromatography (TLC) | 55 |
| iii) High Pressure Liquid Chromatography (HPLC) | 59 |
| iv) Gas-liquid Chromatography (GLC) | 61 |

B. Materials and Methods 64

1. Analytical Standards 64
2. Experimental Design 64
3. Analytical Methods 66
   a) water 66
   b) sediment 68
   c) aquatic plants 69
   d) fish 71
   e) air 71
   f) GLC, TLC, HPLC and LSC Conditions 71
   g) Statistical Analysis 73

C. Results and Discussion 74

1. Water 74
2. Sediment 83
3. Aquatic Plants and Fish 89
4. Air 95
5. Mass Balance 100
6. Environmental Fate Models 102

D. Conclusions 106

References 108
Appendix 115

## TABLES


| Table | Title | Page |
|---|---|---|
| I | Chemical Names and Molecular Structures of Some Compounds of Interest | v. |
| II | UV Parameters of Fenitrothion and Related Compounds | 8 |
| III | Uses of Fenitrothion | 10,11 |
| IV | Photodecomposition Rates of Fenitrothion | 18 |
| V | Influence of Environmental Parameters on Disappearance of Fenitrothion | 37 |
| VI | Standard Pond Specifications | 40 |
| VII | Fixed Solution Model | 42 |
| VIII | Recoveries of Fenitrothion and Some Degradation Products from XAD Resin | 47 |
| IX | Thin Layer Chromatography (TLC) Systems | 56,57,58 |
| X | High Pressure Liquid Chromatography (HPLC) Systems | 58 |
| XI | Gas-liquid Chromatography (GLC) Systems | 62,63 |
| XII | Sunlight Intensities and Water Chemistry | 65 |
| XIII | Sampling Schedule for Field Study | 67 |
| XIV | Half-lines of Fenitrothion and Degradation Products in Pond Water | 77 |
| XV | Total Radioactivity in Water and Extraction Efficienc | 79 |
| XVI | Extraction Efficiency of Sediment | 83 |
| XVII | Sediment Products by HPLC | 85 |
| XVIII | Total Radioactivity in Various Compartments | 87 |
| XIX | Duckweed Extraction Efficiency | 90 |
| XX | Fenitrothion and Degradation Products in Duckweed | 93 |
| XXI | Fenitrothion Fluxes in Air above Ponds | 98 |
| XXII | Mass Balance of $^{14}C$ | 101 |

## FIGURES


| Figure | Title | Page |
|---|---|---|
| I | Mass Spectra and I.R. Spectra of Fenitrothion | 3 |
| II | Mass Spectra and I.R. Spectra of S-methyl Fenitrothion | 5 |
| III | Mass Spectra and I.R. Spectra of Amino-Fenitrothion | 6 |
| IV | Possible Degradation Products of Fenitrothion | 31 |
| V | Schematic of Mixed Pond System (3 compartment) | 35 |
| VI | Schematic of Mixed Pond System (4 compartment) | 39 |
| VII | Dynamic Solution Model | 43 |
| VIII | Soil Extraction Procedure | 51 |
| IX | Fenitrothion and Degradation Products Appearance and Disappearance in Unshaded Ponds | 75 |
| X | Fenitrothion and Degradation Products Appearance and Disappearance in Shaded Ponds | 76 |
| XI | $^{14}C$ Levels in Sediment | 86 |
| XII | GLC Chromatogram of Air Sample | 96 |
| XIII | Environmental Fate Model of Fenitrothion | 104 |

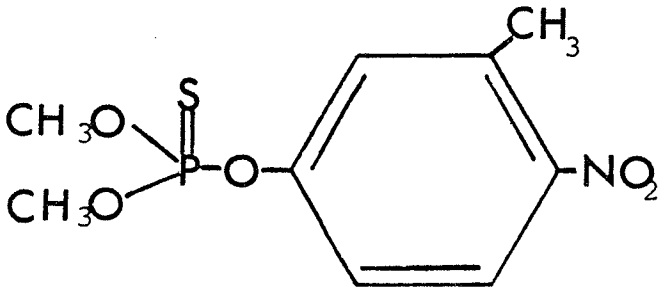
## ABSTRACT

A study of the degradation and dissipation of fenitrothion (O,O-Dimethyl O-(3-methyl-4-nitrophenol) phosphorothioate), in artificial outdoor ponds was conducted in 1979 and 1980. Fenitrothion ($^{14}$C-ring labelled) was applied to two ponds at the rate of 165 g/ha on both years. One pond each year was shaded from direct sunlight with black polyethylene for the first 17 days to simulate forest cover. With initial concentration of about 70 ug/L in the water, half-lives (t1/2's) of fenitrothion were 1.0 and 1.6 days under unshaded and shaded conditions, respectively. The major degradation product, 3-methyl-4-nitrophenol, had similar t1/2's under shaded and unshaded conditions. Other major $^{14}$C containing metabolites were also followed. Fenitrothion concentration 10 cm above the ponds averaged 0.020 and 0.098 ug/m$^3$ over the shaded and unshaded water, respectively, during the first 24 hours after application (Year1). Aquatic macrophytes (Lemna and Typha species) and fish accumulated 3-6% of the added $^{14}$C-fenitrothion by 2 days post treatment. Sediment reached its maximum level of $^{14}$C-fenitrothion at 5 days, being higher in the unshaded pond (27% of added $^{14}$C), than the shaded pond (8.5% of added $^{14}$C) during both years. Greater than 90% of the radioactivity could be accounted for by 2 days post-treatment, however by 21 days overall accountability had dropped to 20%. The data correlated well with two environmental fate models.

## PREFACE

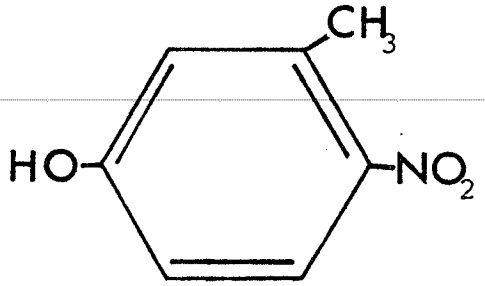
Fenitrothion has been used extensively since 1969 for the spruce budworm (Choristoneura fumiferana) in Canadian forests. A major objective of this study was to follow the dissipation of fenitrothion under conditions resembling a stagnant forest pond at levels indicative of those following aerial spray operations. As of 1978,when this study was initiated, there had been no direct measurement of volatilization or the establishment of the importance of photolysis in the field. At this time, Moody et al. (1978) had indicated a variety of degradation pathways including the first measurement of aquatic plant uptake. This study was designed to examine the previously unmeasured effect of sunlight intensity and volatilization, along with the partitioning of fenitrothion and degradation products into sediment, plants and fish under field conditons. The pool and sampling design was to clarify the importance of the various pathways during the dissipation of fenitrothion and provide a more efficient mass transfer criteria. Although fenitrothion has no registered agricultural use in Canada, there are related organophosphorous compounds, such as parathion (O,O-diethyl O-(4-nitrohenyl) phosphorothioate) that do. Fenitrothion does have numerous such registrations throughout the world, so the experimental design and location also simulated the shallow open agricultural setting of lowlands, natural and constructed potholes, and stagnant irrigation channels.

TABLE I
Chemical Names and Molecular Structures of some Compounds of Interest

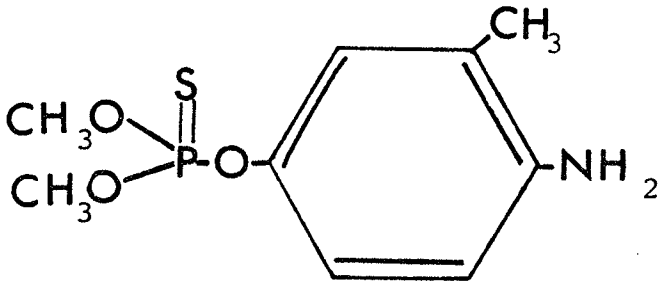


Fenitrothion (F)

O,O-dimethyl-O-(3-methyl-4-nitro-phenyl) phosphorothioate

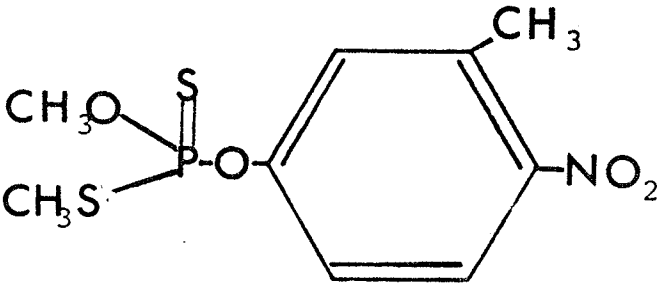


3-methyl-4-nitrophenol (MNP)



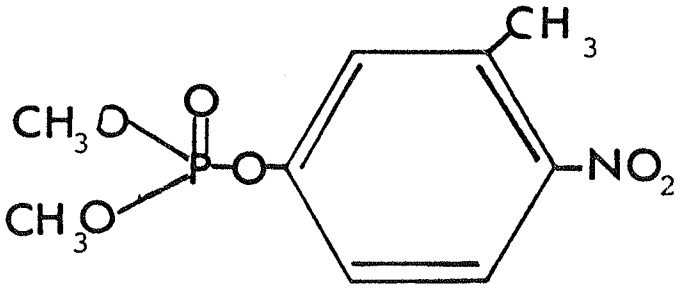
Amino-Fenitrothion (AF)

O,O-dimethyl-O-(3-methyl-4-amino phenyl) phosphorothioate



S-methyl Fenitrothion (SMF)

O,S-dimethyl-O-(3-methyl-4-nitro phenyl) phosphorothioate



Fenitrooxon (FO)

O,O-dimethyl-O-(3-methyl-4-nitro phenyl) phosphorate

# LITERATURE REVIEW

## 1. INTRODUCTION

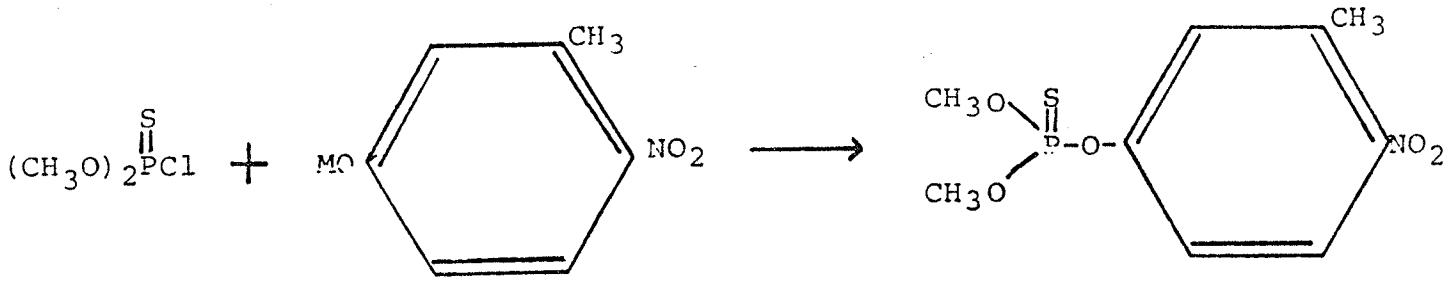
The history and early use of the broad spectrum insecticde, fenitrothion, has been quite thoroughly covered by previous reviews (NRCC 1975, NRCC 1977, Ohno et al. 1976 and Symons 1977).

When Drabek and Pelikan (1956) first reported fenitrothion they indicated that it was less acutely toxic to mammals than many other organophosphorus insecticides (NRCC 1975). It was subsequently introduced in 1959 as an experimental pesticide at both Sumitomo Chemical Company and Farbenfrabriken Bayer-AG (NRCC 1975, Ohno et al. 1976). In Canada, it has been extensively used since 1968 (Symons 1977). This review concentrates on the fate of fenitrothion within aquatic ecosystem compartments and does not attempt to review terrestrial fate or efficacy of fenitrothion and metabolites.

## 2. CHEMISTRY

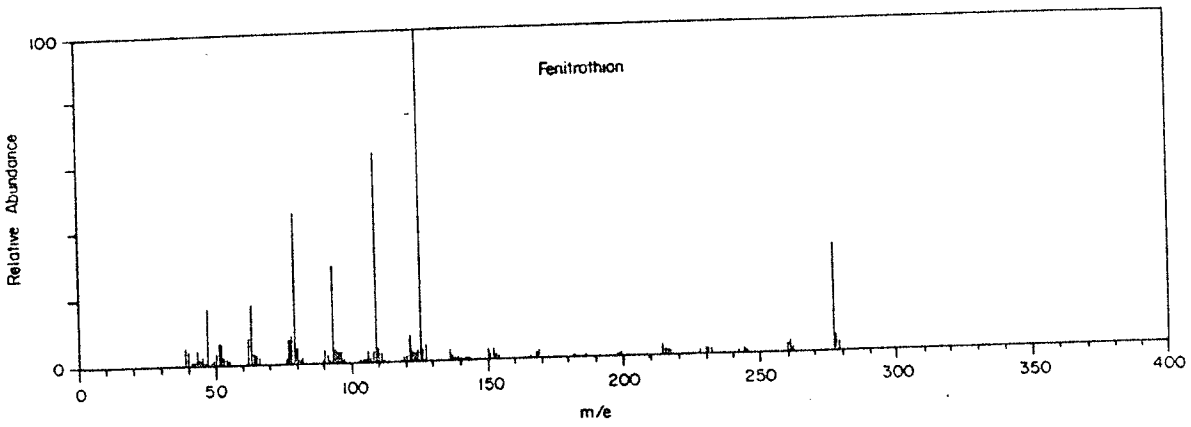
The following chemical properties of fenitrothion are covered by NRCC (1975) and Ohno et al. (1976).

Fenitrothion is prepared in good yield from 3-methyl-4-nitrophenol or its alkaline metal salt and O,O-dimethyl phosphorochloridothiate. Pure fenitrothion is a yellow brown liquid with an unpleasant odor, and



a b.p. of 118°C. The refractive index is ($n_D^{25}$)= 1.5528 and the specific gravity ($d_4^{25}$)= 1.3227. Fenitrothion has a solubility of 20 mg/L in distilled water, being soluble in alcohols,ethers, ketones, esters, aromatic hydrocarbons, and slightly soluble in aliphatic hydrocarbons. Its ultraviolet spectra displays a maximum at 268.5 nm and its infrared spectra, (Fig.I) shows a P-O-C stretching vibration at 1233 $cm^{-1}$ (Zitko and Cunningham 1974), indicating this aromatic linkage is shorter than the similar methyl parathion (1215 $cm^{-1}$). Hydrolysis half-lives in aqueous solutions have been determined as 272 minutes in 0.01 N NaOH (as 40% ethanolic solution) at 30°C. and as 1957 minutes pH 10.99 borate buffer at 25°C. Fenitrothion has an octanol-water partition coefficient (log $K_{ow}$)= 2.33 (MacKay et al. 1985).

The electron impact mass spectrum of fenitrothion, (Fig.I), shows a fragmentation pattern typical of dimethyl phosphorothioates. The base peak ion is m/e=125 with other intense ions at m/e=109 and m/e=79. The parent ion m/e=277, is also quite strong with a weak ion at m/e=260



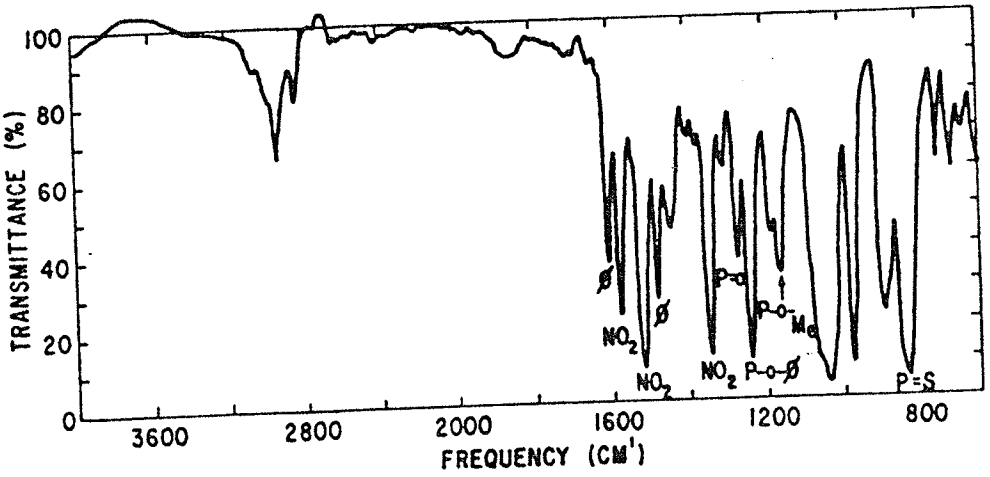
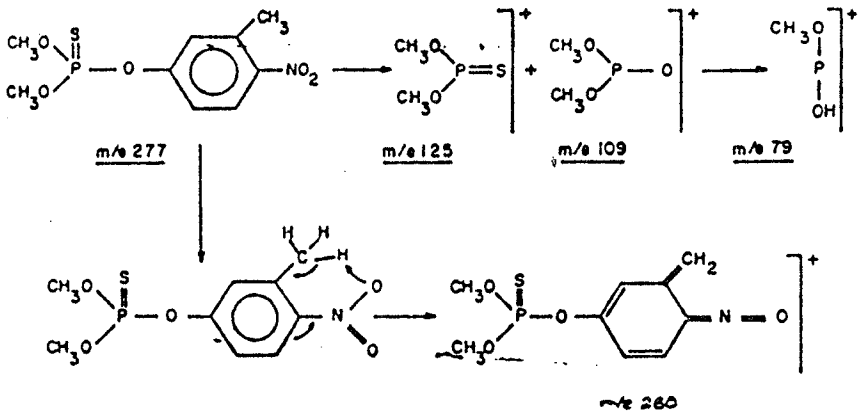



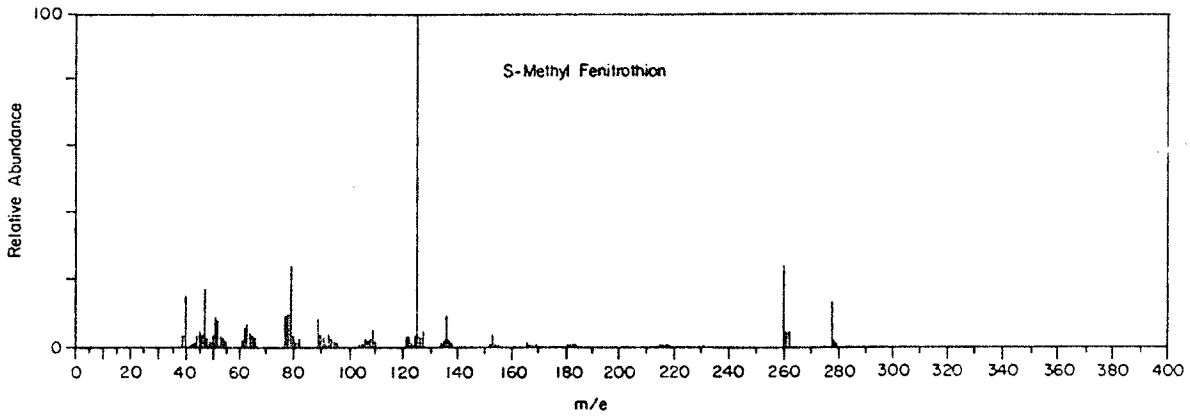

Figure I Mass spectrum and IR spectrum of Fenitrothion - NRCC (1975)

representing a rearrangement and loss of OH (NRCC 1975).




Some isomerization to the SMF occurs during the distillation of fenitrothion (Ohno et al. 1976). This toxic isomer (Rosival et al. 1976, Kovacicova et al. 1971) has been found at levels between 0.16 to 3.7% of the technical material (NRCC 1977, Cochrane et al. 1979 and Miles et al. 1979). Fenitrothion is also converted to SMF under conditions of light, heat, and/or polar solvents (NRCC 1975). Miles et al. (1979) measured an increase in SMF from 0.32% to 0.85% in 6 months stored at 38°C. and to 1.05% in 21 days when stored at 55°C. SMF has an U.V. maximum at 261 nm., (Cochrane et al. 1979) and mass and infrared spectrum similar to that of fenitrothion (Fig. II). The mass spectrum base peak m/e=125 is the same, though there is very little m/e=109. The ion m/e=79 is still present and the ion m/e=260 (loss of OH) is increased possibly due to the greater activation of the P-O bond (NRCC 1975).

Amino fenitrothion, M.W. 247, is one of of the major degradation products of fenitrothion. It has a major U.V. adsorption at 240 nm, with a minor adsorption at 296 nm (Cochrane et al. 1979). Fig. III



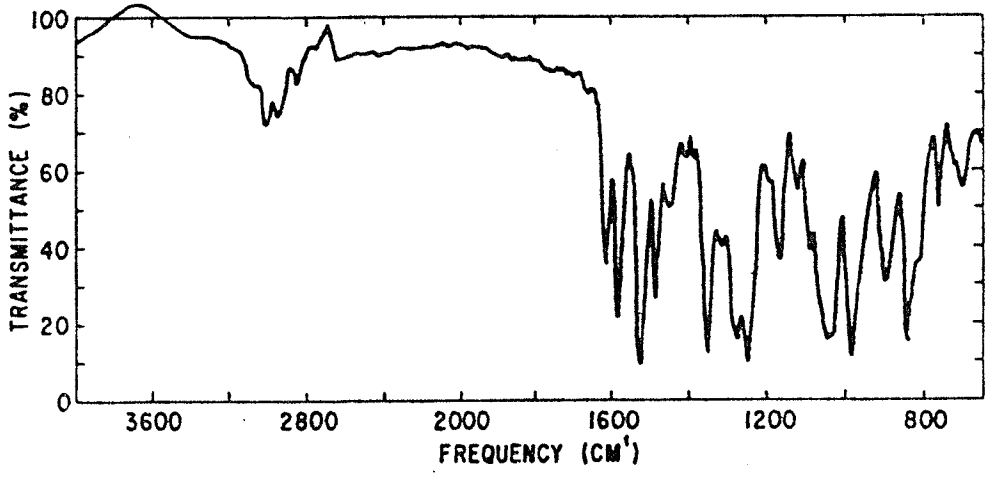
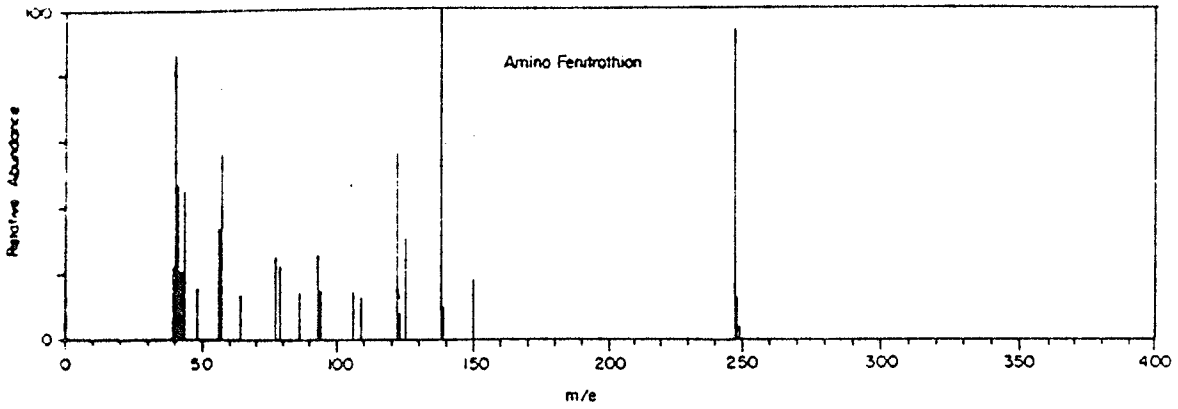




Figure II Mass spectrum and IR spectrum of S-methyl Fenitrothion - NRCC (1975)



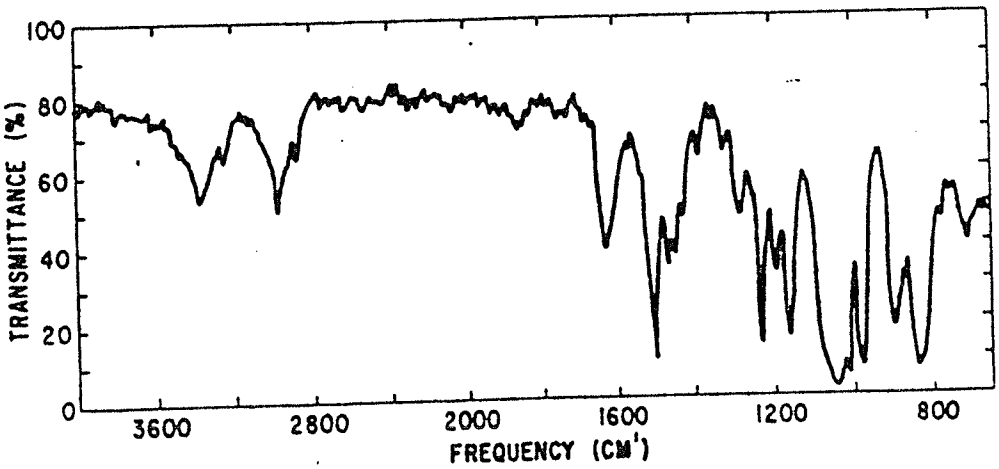




Figure III Mass spectrum and IR spectrum of Amino-Fenitrothion - NRCC (1975)

shows the corresponding I.R. spectrum with the NH asymmetrical and symmetrical stretching vibrations at 3435 and 3290 $cm^{-1}$, respectively. The mass spectrum of AF is comprised of a fairly strong parent ion, no loss of 17, and a base peak of m/e=138 indicating a different fragmentation pattern from the other fenitrothion metabolites (NRCC 1975).

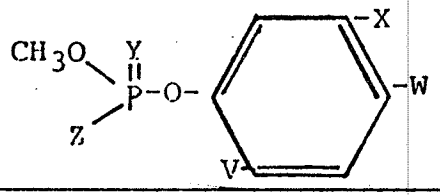
3-Methyl-4-nitro-phenol (M.W.153) is also a major degradation product of fenitrothion. It has a melting of 129°C and is soluble in water, alcohol, ether, benzene, and chloroform (CRC 1979. Its U.V. characteristics (maximum and molar adsorptivity) as determined by Cochrane et al. (1979) are summarized in Table II along with those of fenitrothion and other environmental metabolites. These include fenitrooxon, carboxy fenitrothion and fenitrooxon, desmethyl fenitrothion and fenitrooxon, bis-fenitrothion, and S-methyl-bis-fenitrothion. Figure IV (NRCC 1975) contains these structures along with some other feasible metabolites.

## 3. MODE OF ACTION

Fenitrothion, being a pentavalent phosphorus ester, has phosphorylating and alkylating properties. Its toxicity is generally accepted as being due to the phosphorylation of acetylcholinesterase (Eto 1974). Inactivation of the enzyme prevents the breakdown of acetylcholine, a neurohormone, causing impairment of the central nervous system.

Two prerequisites are necessary for phosphorylating activity: 1) decreased pi bond contribution to the P-OAr bond (i.e., decreased double bond character), and 2) increased positive charge on

## Table II Structures and UV parameters of fenitrothion and related compounds




| | Structure | | | | | | UV. nm | | |
|---|---|---|---|---|---|---|---|---|---|
| | Compound | V | W | X | Y | Z | UV Max. | E x $10^3$ (Max.) | E x $10^3$ (269 nm) |
| 1. | Fenitrothion | H | $NO_2$ | $CH_3$ | S | $OCH_2$ | 269 | 6.9 | 6.9 |
| 2. | S-Methyl fenitrothion | H | $NO_2$ | $CH_3$ | O | $SCH_3$ | 261 | 6.0 | 5.5 |
| 3. | Fenitrooxon | H | $NO_2$ | $CH_3$ | O | $OCH_3$ | 268 | 6.8 | 6.8 |
| 4. | Amino fenitrothion | H | $NH_2$ | $CH_3$ | S | $ICH_3$ | 240(296)[a] | 7.1(2.3)[a] | 1.4 |
| 5. | Carboxy fenitrooxon | H | $NO_2$ | COOH | S | $OCH_3$ | 269 | 4.9 | 4.9 |
| 6. | Carboxy fenitrothion | H | $NO_2$ | COOH | O | $OCH_3$ | 269 | 4.5 | 4.5 |
| 7. | Demethyl fenitrothion | H | $NO_2$ | $CH_3$ | S | OH | 300 | 7.6 | 5.0 |
| 8. | Demethyl fenitrooxon | H | $NO_2$ | $CH_3$ | O | OH | 300 | 4.0 | 3.7 |
| 9. | Bis-fenitrothion | H | $NO_2$ | $CH_3$ | S | | 266 | 20.5 | 20.5 |
| 10. | S-Methyl-bis-fenitrothion | | $NO_2$ | | | | 266 | 13.8 | 13.8 |
| 11. | 3-Methyl-4-nitrophenol | | | | | | 305 | 9.04 | 4.0 |

[a] Minor secondary absorption - Cochrane et al. (1979)

the phosphorus atom (Eto 1974). Pi bonding is the result of p electrons from oxygen overlapping with empty d orbitals of phosphorus. This is the configuration of P=O, P=S, P=C, P=N, and P=Se bonds, but a small component is also observed with P=OR bonds (Eto 1974).

Fenitrothion, like any of the other phosphorothioate insecticides must be converted to its oxygen analogue in order to inhibit acetylcholinesterase. This is achieved by mixed function oxidase enzymes (NRCC 1975). This metabolite satisfies the second prerequisite for phosphorylating activity more so than fenitrothion. The greater electronegativity of oxygen compared to sulfur serves to decrease electron density about phosphorous, facilitating nucleophilic attack at its centre.

## 4. USES AND EFFECTS

Fenitrothion is only registered for forestry use in Canada but it constitutes a major insecticide in Canada. In 1971, in New Brunswick alone its use in forestry amounted to 43% of the total of all major insecticides used for agriculture in Canada in that year and a similar high proportion up to at least 1976 (Thomson 1973, Symons 1977). In Canada this is all primarily used for spruce budworm control, but fenitrothion has numerous uses throughout the world. The main use is in plant protection, but it is also used for treatment of stored grains and timber, in public health as well as in veterinary situations. Examples of these uses are given in Table III (Ohno et al. 1976) demonstrating that fenitrothion is a "broad spectrum" insecticide. This broad spectrum activity has prompted concern over the effects on non-target organisms. Terrestrial insects are the most greatly

**Table III: Uses of Fenitrothion**

| INSECT | COUNTRY |
|---|---|
| I.a) Food crops and vegetables | |
| i) Rice | |
| Leaf hoppers | Japan, Korea, India, Sri Lanka, |
| Borers | Japan, China, Spain, Pakistan |
| Fall army worm | Brazil |
| ii) Wheat and Barley | |
| Wheat bug | Iran, Bulgaria, Turkey |
| Wheat stem gall midge | Holland, Sweden |
| iii) Pulses | |
| Thrips | Argentina, Denmark, Sweden |
| Pod borers | Japan, Formosa |
| iv) Vegetables | |
| Aphids | Portugal, Spain, France, Rumania, Poland, Brazil, Japan, Korea, Turkey |
| Colorado potato beetle | Hungary |
| Beet Moth | Chile |
| b) Fruit trees | |
| Mealy bug | Spain, Portugal, Iran, Malaysia, Japan, Sri Lanka, Taiwan, Columbia, U.S.S.R., Turkey, Chile, East Africa, Argentina |
| Gypsy moth | Turkey, U.S.S.R. |
| c) Industrial crops | |
| i) Coffee, cocoa, and tea | |
| Cocoa mirid | West Africa |
| ii) Edible commercial crops | |
| Spinach leafminer | Denmark, Poland |
| iii) Fiber crops | |
| Boll worms | Pakistan, Turkey, Colombia |
| Cotton leaf worm | Brazil, Turkey |
| d) Forage crops | |
| Grass grub | Australia |
| Porima moth | New Zealand |
| e) Horticulture | |
| Thrips | Sweden, Spain, Argentina |
| f) Forest | |
| Hemlock looper | Canada |
| g) Locust | |
| Locust | Ethiopia, Sweden, Australia, Thailand |

| INSECT | COUNTRY |
|---|---|
| II. Stored grains and lumber | |
| i) Stored grains | |
| Not approved by FAO as of 1976 - research only e.g. Pakistan, Australia | |
| ii) lumber | |
| Research studies, in combination with fumigant ethylene dibromide and solvents, perchloroethylene, trichloroethylene) | Japan |
| III. Public health uses | |
| Mosquitoes | Programs in Korea, Kenya and Iran |
| IV. Veterinary uses | |
| Flies, ticks, lice | Japan |

From Ohno et al. (1976)

effected (within the spray program in Canada). After spraying, the kill period lasts about 4 days and there may be considerable "knockdown" of many species of adult insects and spiders. Herbivores are more affected than predators and parasites. Most populations of insects rebound within a year, but there are some long term cases of depressed populations including predators and parasites of the spruce budworm (Symons 1977, NRCC 1975 and NRCC 1977). Other possibly harmful insects have increased in population (Symons 1977). There is also concern about the effect of fenitrothion on pollinators, both for their importance in production of farm crop plants and for fruit and seed production within the forest. Both bumble and solitary bees suffer heavy population depressions after spraying. The fruit and seed set may be reduced by more than one-half the norm (NRCC 1975, NRCC 1977). Aquatic insects are also effected by the spraying program. After spraying, the benthic drift increases in both dead and irritated insects. The ensuing biomass reduction may be light with fairly rapid recuperation, but spraying over consecutive years has in some cases reduced insect abundance in the later years (Symons 1977). This may be important in terms of the food supply of the fish population, especially the commercial species. The water concentrations of fenitrothion typically found in New Brunswick streams are not lethal to fish but with uptake from water and ingestion, significant body burdens can be achieved. These levels can have sublethal effects. Young Atlantic Salmon have been observed to have had difficulties holding and regaining territories. With consecutive years of spraying, fish populations have been reduced to 25% by the third year and underyearlings, unable to migrate from the contaminated area which has a reduction of biomass of insects in the stream, have below

normal growth, although there were no unusual fish mortalities (Symons 1977).

The effects of fenitrothion spraying are greatest on birds living in the upper forest canopy (passerines), with up to 80% reduction in population. The measure of toxicity was calculated from bird song so that the population decrease could be either by mortality or emigration. Mortalities are not generally expected for birds, though some dead or incapacitated birds have been found. These can be explained by patchy spraying and such birds flying through a densely concentrated spray cloud. Acetylcholinesterase activity is depressed by 16-32% in normal behaving Tennessee warblers, bay-breasted warblers, and white throated sparrows, indicating the rather physically undetectable results that may occur from pesticide spraying (Symons 1977,NRCC 1975 and NRCC 1977). There have been no mortalities of mammals (small mammals up to humans) ever reported from fenitrothion spraying including the operators or handlers. Repeated dosages has caused demyelination of the sciatic nerve of rabbits. There has also been an apparent increase of Reye's Syndrome in children in the Maritime provinces of Canada. The spraying may have an effect on the acetylcholinesterrase of the children over the summer months. Fenitrothion is applied as an aqueous emulsion containing water, an aromatic solvent, and a non ionic/anionic detergent. This formulation has enhanced virus lethalty in baby mice which may be significant since Reye's Syndrome is caused by either virus or environmental toxins. The aromatic solvent is of complex composition, containing components such as alkylated naphthalenes which will bioaccumulate in some organisms and may also be cocarcinogens (Symons 1977, NRCC 1977). In later formulations, the standard No. 2 and No. 4 fuel oils which had been used were prohibited (Armstrong 1984).

## 5. ENVIRONMENTAL FATE

### a) Field Monitoring Studies

The actual concentration of deposited fenitrothion depends on many factors, which include the height and speed of the aircraft, type of carrying agent, evaporation rate of carrying agent, droplet size, wind direction and speed, purity of the insecticide, and the local geography (Symons 1977, NRCC 1975 and NRCC 1977). The various field tests of spray deposition revealed that the amount reaching open fields targets varied from 8 to 75%, with the average being between 40 to 50%. A considerable amount of the spray was subject to "drift"; thus the droplets may evaporate and deposit outside the application area. Fields that are 3 and 8 km away from the target site have received detectable amounts (0.02 to 0.15 g/ha) (Symons 1977). More recent surveys (Mallet and Volpe 1982, Mallet and Cassista 1984, Krzymien 1982), detected fenitrothion outside the spray area at levels from 8 ng min/liter at 700 meter downwind to trace amounts at various locations outside the target areas (distances not given). The major pathway of breakdown in the atmosphere is thought to be photodecomposition (NRCC 1975). The exact photodecomposition half-life of fenitrothion in the atmosphere is not known but is assumed to be short. Sundaram (1984) conducted a field experiment comparing application times and two formulations. The formulation which contained moderately volatile petroleum distillate gave higher initial concentration than the polar non volatile emulsifier and the warmer air mass of the evening spraying also yielded a higher concentration compared with the cooler air of the morning spray. Loss was rapid with levels (maximum of 1997 ng/$m^3$), reaching background

levels of 102 ng/$m^3$, (from neighbouring spray drift), by 12 hours in all but one block.

Fenitrothion is generally not persistent in the environment, except in coniferous foliage. The concentration in foliage reaches from 2 to 4 ug/g (NRCC 1975, Symons 1977). There is a 50% reduction within four days and in two weeks the concentration is from 15 to 30% of the original concentration. The degradation or disappearance is due to evaporation, removal by rain, and photolysis. One to ten percent (0.01 to 0.28 ug/g) persists over a year.

The concentration in forest soil reaches about 0.04 ug/g (5% of spray) (NRCC 1975, Symons 1977), with variations due to sporadic spraying and rain washing some off of overhead foliage if this occurs after a recent spraying. Disappearance of fenitrothion in soil to an undetectable level takes 32 to 150 days (half-life of 3 to 6 days) (NRCC 1975, NRCC 1977). Fenitrothion is readily adsorbed by most soils, though not very well to sandy soil where some leaching does take place. After 60 days, up to 30 to 40% of the insecticide is loosely or tightly bond to the soil particles. Disappearance of fenitrothion in soil is mainly by microbial degradation along with photolysis and some volatilization.

The maximum concentration expected in a forest stream 15 cm deep and sprayed at 210 g/ha is about 25 ug/L and again with only 40-50% of applied fenitrothion actually reaching the target, (less if it has to filter through the canopy). Levels seldom exceed 15 ug/L (Symons 1977). More recent studies ( Maguire and Hale 1980 and Morrison and Wells 1981) found levels of 18 ug/L and 10 ug/L (Moody et al. 1978), in subsurface water (surface water had 701 ug/L. Lockhart et al. (1973)

also found high levels (75.5 ug/L) in water. In streams the half-life of fenitrothion is reached in 2 to 8 hours (Symons 1977). In shallow ponds, the half-life is between 0.25 and 3.5 days (Sundaram 1974) and in small lakes (in the first 2 meters) it is about 5 days, after an initial mixing phase of 24 to 48 hours. In all studies cited by the NRCC (1975) report there was no measurable fenitrothion in pond or lake water beyond 40 days after spraying. Maguire and Hale's (1980) results support these conclusions. Their pond study revealed a half-life of 0.6 day, with no detectable fenitrothion after two days. Moody et al. (1978) reported that fenitrothion persists in stagnant and running water for about 4 days. In New Brunswick in 1980 and 1981 (Mallet and Volpe 1982, Mallet and Cassista 1984), stream persistence was limited to a few days, though a small pond had detectable fenitrothion at 18 days. There are numerous possible pathways of disappearance and degradation in an aquatic system. These include: volatilization, hydrolysis, photolysis, adsorption, microbial degradation, and uptake and metabolism by algae, plants, and fish.

**b. Hydrolysis**

Initially, hydrolysis was considered the major pathway of degradation and numerous hydrolysis studies were carried out. The hydrolysis rate increases with increasing pH and temperature. Truchlik et al. (1972) reported half-lives of 5.3 min, 41 min, 192 min, 150 days, and 12.6% hydrolysis at 390 days for solutions in 1M sodium hydroxide, 0.1M sodium hydroxide, buffer pH 12.3, pH 9.2 and pH 7.0 , respectively. The first order rate constant 2.12 X $10^{-2}h^{-1}$ at pH 10.99 and $25^{o}C$ measured by Kovacicova et al. (1971) was in agreement with data of

Maguire and Hale (1980) who measured hydrolysis rates from pH 10.76 to 13.34 and temperatures 5 to 55°C. Greenhalgh et al. (1980) also reported the increase in hydrolysis at more basic pHs and higher temperatures. They also used natural lake water and buffered lake water both at pH 7.5 and 23°C and recorded half-lives of 49.5 and 21.6 days, respectively. Zitko and Cunningham (1974) and Maguire and Hale (1980) both found no hydrolysis at pH 7 at 45 days and 3 months, respectively. In natural aquatic ecosystems with pH 6 to 8, hydrolysis is therefore a minor pathway of degradation.

**c. Photolysis**

Photolysis has become increasingly recognized as an important degradation route. Table IV combines the results of Ohkawa et al. (1974) and Greenhalgh and Marshall (1976) for fenitrothion exposed to ultraviolet irradiation in various solutions purged with air, oxygen, or nitrogen. These short half-lives may indicate a short half-life in the environment. Using the longer wavelength of 313 nm, Brewer et al. (1974), found degradation to be less than 10% in ethanol after 10 hours and less than 5% after 2 hours in an ethanol-water solution. Ohkawa exposed an aqueous solution to sunlight and obtained a half-life of about 11 hours (54.3% remaining). Similarly, Miyamoto (cited in NRCC 1977) exposed aqueous solutions of pH 3, 7, and 9 along with a distilled water solution to sunlight and recorded half-lives of 50, 20, 6, and 10 hours, respectively. In field studies of aquatic microcosms by Weinberger et al. (1982a) there were significant differences between light and darkened systems, which they attributed to photolysis and plant uptake. In a static lake/estuarine model exposed to sunlight, 80% of the fenitrothion was photolysed to degradation products within 6

**Table IV** **Rate of Photodecomposition of Fenitrothion in Various Solutions Irradiated by uv Light.**

| | Half-life of Fenitrothion (min) | | |
|---|---|---|---|
| | Ohkawa et al. (1974) | | Greenhalgh (1976) |
| Solvent | Air | Nitrogen | Oxygen |
| Water | 5 (93%) | 5 (87%) | 7 |
| 50% aqueous MeOH | 20 | 60 | -- |
| Acetone | 50 | 100 | -- |
| MeOH | 100 | 240 (44%) | 120 |
| Benzene | 360 (18%) | 360 (12%) | -- |
| Hexane | -- | -- | 85 |

hours (Weinberger et al. 1982b).

**d. Biodegradation**

Another major degradation pathway is microbial breakdown or metabolism both in the water and sediment. In one study, (NRCC 1975) 65% of the fenitrothion was degraded by Bacillus subtilis in 48 hours. At a pH where hydrolysis would be negligible, Zitko and Cunningham (1974) measured a half-life between 30-40 hours for a non-aerated river water-sediment experiment. In another submerged sediment study, microbial degradation varied, depending on the type of sediment, from 18 to 66% (NRCC 1977). Greenhalgh et al. (1980) attributed up to 16% of disappearance of fenitrothion to microbial degradation in natural lake water. In the two residue surveys in New Brunswick in 1980 and 1981, microbial degradation was often the only measurable route (Mallet and Volpe 1982, Mallet and Cassista 1984).

**e. Sorption**

In a water-sediment system adsorption to the sediment and suspended solids is a final deposition compartment. Zitko and Cunningham (1974) found fine sediment, with a larger surface area, adsorbed more fenitrothion than coarse sediment. The fine sediment showed a pronounced increase in adsorption over four days (33% and 83% adsorption on day 1 and day 4, respectively). Miyamoto (cited in NRCC 1977) found increased adsorption of fenitrothion in the same soil type, in submerged conditions compared to upland aerobic conditions. Moody et al. (1978) noted the strong partitioning of fenitrothion into the sediment. Maguire and Hale (1980) recorded rapid uptake of fenitrothion into the sediment and after four days could not extract either fenitrothion or its main sediment metabolite. Weinberger et al. (1982a) found sediment to be the main sink in a multicompartment field system (plants, algae,

sediment, lake water), the amount being less in a lighted system compared to a darkened system presumably due to a greater rate of fenitrothion degradation in the water compartment exposed to sunlight.

**f. Plant Uptake**

Algae and plants also affect the uptake and degradation of fenitrothion. Moody et al.(1978) found that surface dwelling Lemna minor (duckweed) which received the initial spray deposit had a fairly high level of fenitrothion at 1 hour (1.70 ug/g), but also continued to take up the insecticide rapidly reaching 4.19 ug/g at 10 hours (water at 44 ug/L). Subsequent disappearance of fenitrothion was fairly rapid, possibly by volatilization from the exposed leaf surfaces, and by biochemical and photolytic degradation. Submergent hornwort Ceratophyllum demerson did not achieve as high a level as duckweed but had a significantly higher level at 192 hours of 0.14 ug/g while duckweed had 0.032 ug/g, although fenitrothion was undetectable in water after 97 hours (0.57 ug/L). Lakshminarayana and Bourque (1980) checked for fenitrothion in plankton and benthic algae in a lake and lab test. Fenitrothion in the lake water ranged from 0.06 to 0.09 ug/L although occasional high levels were found in the surface water (0.9 ug/L) and at 3 meter depth (0.4 ug/L), respectively. Phytoplankton had a highest concentration of 0.05 ug/L and zooplankton had a maximum of 0.014 ug/L. The percentage of fenitrothion associated with the algae in this study varied from 0.24 to 5.45%. In a lab study, fenitrothion was added to separate 500 mL unialgae cultures (Chilomonas marina) that represented algal weights from 1.208 g and 1.351 g, but only 5 to 10 % was recovered. Weinberger et al. (1982a) found rapid equilibrium of

fenitrothion in a water/algal system (Chlorella pyrenoidosa) by four hours and rapid desorption when the algae was transferred to fresh water. The bioconcentration factor was estimated as 417 (amount in plant/amount in water). Their water/plant microcosm with Elodea densa reached equilibrium at 2 days in both light and dark systems. However the amount taken up from water in the lightened microcosm was 3 times that in the dark system with the bioconcentration factors being 76 and 24, respectively. In a mixed plant system after five days, the bioaccumulation rate for fenitrothion ranged from 370 to 488. In a field system autotrophic algae (Chlamydomonas and Chlorella) showed rapid uptake of fenitrothion with twice the accumulation in light as in the dark. Elodea absorbed fenitrothion more slowly but again the amount in the light system was 3 fold that of the dark system. This study concluded that accumulation occurred via both passive uptake and a light energized uptake mechanism. Weinberger et al. (1983) also concluded that a portion of uptake was by an active mechanism in their study with both fresh water (Chlorella) and estuarine (Ascophyllum) algae, with two different formulations (Dowanol versus Aerotex). The type of formulation effected both the amount of uptake and also the array of derivatives. Although uptake seemed to increase in lighted microcosms containing algae, degradation can also increase due to photolysis. Zepp and Schlotzhauer (1983) compared photolytic degradation in algae/water to that in distilled water and found methyl parathion and parathion photoreacted 390 times more rapidly in the algae system than in water alone.

**g. Fish Accumulation**

Fish also bioaccumulate fenitrothion rapidly. Miyamoto (cited in

NRCC 1977) studied uptake of fenitrothion by underyearling and yearling rainbow trout (Salmo gairdneri) and southern top mouthed minnows (Pseudorasbora parva) in a constant 20 ug/L environment. The concentration in the fish reached a maximum in 1 to 3 days achieving bioaccumulation factors of 250, 230 and 200 in the underyearling trout, yearling trout, and minnows, respectively. Upon transfer to fresh water the fish lost fenitrothion rapidly with a 1000 fold decrease in 5 days. Miyamoto et al. (1979), in a static tank study using radiolabelled fenitrothion, found one-third and one-half of the radioactivity in the water had been accumulated by the rainbow trout after 6 and 24 hours, respectively. After the 24 hour exposure the fish were transferred to fresh water and the radioactivity in fish tissues was found to have decreased to 20% by 48 hours, most likely due to excretion. Lockhart et al. (1984) exposed rainbow trout to 4.68 ug/L of radiolabelled fenitrothion. The trout at 24 hours reached a bioconcentration factor of 116 and upon transfer to fresh water, depuration was rapid with a half-life of 18 hours. In a lake study, using brook trout (Salvelinus fontinalis) and lake trout (Salvelinus namaycush), peak levels of fenitrothion were reached in 2-4 days after the first application and one day after the second application of fenitrothion (Holmes et al. 1984). These authors found highest levels in the visceral fat of the lake trout (8 days post treatment; 2nd application). High bioaccumulation factors occurred in the fat, for example at four days post treatment (- first application), the ratio was 650 compared with 34 in liver. The ratio for muscle, (225), agreed well with the previous result of Miyamoto (cited in NRCC 1977). The longer persistence of fenitrothion in fish, at least four days after it was undetected in

water, was possibly due to the cold temperature of the lake water (2 to 5°C), slowing metabolism and elimination from tissues. The relative importance of direct uptake via the gills versus ingestion is uncertain. Lockhart et al. (1973) using unfed caged rainbow trout in a slow stream found average concentrations of 0.4 to 0.6 ug/g one day after application and only 3 of 22 fish had detectable levels at 4 days, but dace (Chrosomus eos and C. neogaeas) and brook sticklebacks (Culea inconstans) captured outside the cage in a stagnant pool had full stomachs and levels in their bodies of 4.8 ug/g at 6 hours and 13.7 ug/g the following day. After 8 days levels in all fish captured outside the cage were undetectable.

**h. Volatilization**

Volatilization of fenitrothion across the water-air interface has been difficult to measure and to assess as to its importance in overall disappearance. There are many factors to be considered, including vapour pressure, solubility, Henry's Law constants, aeration rates, wind, water current, and the composition of the surface layer. Marshall and Roberts (cited in NRCC 1977) predicted a volatilization half-life of 93 days for fenitrothion based on the model of Mackay and Leinonen (1975) and disregarded its contribution to disappearance. Metcalfe et al. (1980) measured the volatilization of fenitrothion in a lab study relating it to the reaeration rate into water. Using aeration rates of .01 and .04 mg/L/hr as representative of lakes and rivers, volatilization half-lives of 20.6 and 5.4 days, respectively, were calculated. The half-lives of fenitrothion in a stream and lake study were actually 3 and 5 times less than predicted for volatilization alone

but no actual measurement for volatilization of the insecticide was done. Maguire and Hale (1980) measured a half-life of 64 days for fenitrothion from true solutions in distilled water. This was lengthened to 180 days with the addition of 5 mg/L fulvic acid. Volatilization was rapid from a surface slick with a half-life of 18 minutes with no effect by fulvic acid, suggesting volatilization could be significant in the period shortly after spraying.

## 6. ENVIRONMENTAL FATE OF DEGRADATION PRODUCTS

### a. Methyl-Nitrophenol (MNP)

The most widespread major transformation product of fenitrothion is 3-methyl-4-nitrophenol (MNP). MNP is the major product of hydrolysis, and is also produced by photolytic and enzymic breakdown. MNP is found in water, plants, unsaturated soil, vapour, fish and animals (NRCC 1975, NRCC 1977). In these systems MNP and related compounds are produced by cleavage at the P-O-aryl linkage. It has previously been stated that simple hydrolysis is pH dependant, and that at the pH of natural aquatic systems hydrolysis would be insignificant. MNP becomes the major transformation product through additive production in a variety of ecosystem compartments plus the fact that it is a degradation product of some of the other metabolites of fenitrothion. In an ecosystem study by Miyamoto et al (1979), MNP was the highest degradation product in 5 of 6 compartments, (water, soil, alga, snail, and Daphnid) and second largest in the carp (Cyprinia) (up to 13 products identified). In most compartments MNP was at a significant level even at 21 days, with levels up to 8 times higher than the fenitrothion present. Maguire and Hale (1980) found MNP to be the only degradation product in the surface and

subsurface water in a pond experiment. MNP reached a maximum in both compartments just before 10 hours post treatment and was undetectable in both by 49 hours, though at the previous sampling time (30 hours) it was twice the level of the fenitrothion present in the surface water. In a photodegradation study MNP was the fourth major product within the exposed system but under dark conditions it was the major product in river water, representing 20% of added $^{14}C$-fenitrothion at 32 days (Mikami et al. 1985). Weinberger et al. (1982b) stated MNP was one of two major degradation products in their static lake/bay models. In a water/plant microcosm, MNP was the major derivative in Elodea densa and Sagisttaria sp. and was second in Myriophyllum, reaching maximums of 16.4 ug/g (14 days), 31.4 ug/g (14 days), and 34.4 ug/g (5 days) in each, respectively, following an exposure to 10 mg/L fenitrothion (Weinberger et al. 1982a). In their multi-compartment field study, (plants/algae/
sediment/lake water), MNP was one of a number of derivatives in the light system and again it was the major one in the dark system. Weinberger et al. (1983) in an algae/formulation/water study, found MNP to be the major degradation product but also concluded its level was dependent on the formulation, the ionic content of the water and the algal species.

**b. Amino-Fenitrothion (AF)**

Amino-fenitrothion (AF) is also a major degradation product. Bacteria and fungi actively reduce the nitro group of fenitrothion in both aerobic and anaerobic conditions (NRCC 1975, NRCC 1977). The 1975 review reported 65% of fenitrothion was converted to AF by Bacillus subtilis within 48 hours. The review also reported degradation by other

soil and bacterial species including Escherichia freundii; E. coli, Pseudomonas reptilivora and P. aeruginosa. Miyamoto (cited in NRCC 1977) found levels of AF reaching 55 - 65% in bacterial cultures and levels between 40 - 50% in fungal cultures incubated with fenitrothion. Under submerged conditions (anaerobic) AF was the major decomposition product achieving maximum amounts of 66, 53, 27 and 18% relative to initial fenitrothion in four types of soils. Though levels vary between these soils, tests in bacteria free soils contained fenitrothion suggesting decomposition is almost totally due to microbial action and does not depend on the physical state of the soil. In submerged conditions, the AF tends to disappear slowly. Maguire and Hale (1980) found AF in sediment reached a maximum of about 5 ng/g, (almost the level fenitrothion initially reached), at just over 50 hours followed by a decrease to a non-detectable level at four days. AF was not the major degradation product in the sediment of the 1979 study of Miyamoto et al., but of the seven degradation products found, five were amino compounds. AF was also found in the water and snails but was not detected in alga, Daphnid, and carp. AF has been traced in a number of experiments in natural water. Zitko and Cunningham (1974) detected AF after 5 days in non-aerated river water (half life of fenitrothion approximately 35 hours). In a stagnant section of a creek, Moody et al. (1978) were still detecting AF at the end of their sampling schedule of 97 hours. In lake water, AF comprised between 5 and 16% of the reaction products (Greenhalgh et al. 1980). Weinberger's et al. (1983) study of the effects of alga and co-solvents on degradation revealed very little production of AF in estuarine water and found that levels were affected by the algae present and tank mix used. In a 1980 spray survey in New

Brunswick, AF was detected up to a maximum of 8 ug/L in water and was also detected in air to a maximum 12.0 ng/$m^3$ where the maximum for fenitrothion found was 1.2 ng/$m^3$ (Mallet and Volpe 1982). In the 1981 survey by Mallet and Cassista (1984), which was more extensive and looked for more degradation products than the previous survey, only small amounts of AF were found in the water with no other degradation product detected.

**c. Desmethyl Fenitrothion (DMF)**

Dealkylation is associated with the reaction of "soft" nucleophiles at the methyl carbon atom, followed by cleavage of the C-O P bond (Truchlik and Kovaciova (cited in NRCC 1977)). Dealkylation of fenitrothion to DMF is part of a deactivation process in plants and animals. In these compartments, reaction is attributed to the SH moiety of glutathione alkyl transferase. In the case of an aquatic system, the nucleophile is presumably water (Greenhalgh et al. 1980). In aquatic systems, DMF is found in most compartments including water, soil, algae, snails and fish. In rainbow trout, Miyamoto (cited in NRCC 1977) identified DMF as a minor product after 24 hours accounting for only 0.1% of initial radioactive label, though in water it reached 2.4%. In fish exposed to an initial concentration of 10 ug/L fenitrothion, Miyamoto et al. (1979) found DMF to be the second most abundant metabolite in carp after 3 days (82.3 ng/g). Similarly in snails, DMF was the highest metabolite at 3 days (71 ng/g) and at 21 days was 6.85 ng/g. In water and soils DMF's highest levels were 0.63 ug/L (21 days) and 0.43 ng/g (seven days), respectively. In soil microfloral cultures in four soil types, DMF reached a maximum of 13.9% of total fenitrothion added in one soil (Takimoto et al. 1976). Kikuchi et al. (1984) found fenitrothion actively metabolized to DMF, with levels between 2-7% of

the inital level, by three species of algae. In one species, Chlorella vulgaris, DMF was the only metabolite produced. Greenhalgh et al. (1980) concluded hydrolytic dealkylation was temperature dependent. At pH 5, DMF increased from 28% to 45% of the reaction products over a temperature range from 23°C to 59.5°C. DMF does not seem to be pH dependant. In distilled water (pH 5.9), buffered water at pH 3, 7 and 9, river water (pH 7.4) and sea water (pH 7.8), the levels of DMF under dark conditions at 32 days were 8.6, 16.8, 6.9, 20.6, 13.2 and 19.5% of applied radioactivity, respectively. Under exposure to light DMF was either barely detectable ( 0.4%) or undetectable at 32 days. In the biologically active compartments, fenitrooxon was also produced and also underwent dealkylation. The desmethyl fenitrooxon reached levels of between 2 - 9% of the initial radioactivity in algae (Kikuchi et al. 1984). It also reached maximum levels of 5.03 and 6.14 ng/g, (10 ug/L initial fenitrothion), in snail and carp, respectively. Desmethyl fenitrooxon was continually excreted from the fish into the water and reached levels significantly higher in the water than in the fish (3.0% to 0.3%) (Miyamoto et al. 1979). This can also be the case for all the more water soluble metabolites.

**d. Fenitrooxon (FO)**

The most toxic metabolite of fenitrothion, FO is produced by oxidative desulphuration. As stated earlier, it can be produced in animals, fish, plants and also by photolysis (NRCC 1975, NRCC 1977). FO is not very stable. In biological systems FO is either further broken down or fairly rapidly excreted, not accumulating. In rainbow trout the level in one experiment (Miyamoto et al. 1979) never exceeded 0.2% in the fish though in the water FO did reach 2.8% of the initial

fenitrothion level. In their six compartment study FO was found in only water and carp, reaching a low level in the water (0.05 ug/L) and seen only in the first sampling of the carp (2.46 ng/g at three days). Kikuchi et al. (1984), reported FO within three algal species varied from 0.1 - 4% and was either actively and/or passively transported to the water. Hydrolysis at a neutral pH was slow (Zitko and Cunningham 1974). FO is photolytically produced but FO is also rapidly broken down by photolytic processes. In a photodegradation study in river and sea water, FO levels at two days were 1.2 and 1.7% of total radioactivity, respectively, (7th major breakdown product) and were at the detection limit at 32 days (Mikami et al. 1985). In the majority of natural aquatic ecosystems studied, FO was either not found or only appeared in initial sampling.

**e. S-methyl Derivatives**

S-methyl fenitrothion (SMF) is a better acetylcholinesterase inhibitor than fenitrothion but is generally not found in natural systems; and appears to be a manufacturing by-product (Moody et al. 1978). SMF has been found in plants (NRCC 1975) and in the photodegradation studies of fenitrothion in water both Mikami et al. (1985) and Ohkawa et al. (1974) found SMF produced to levels of 2.4% (2 days) and 3.9% (28 hrs.), respectively.

**f. Other Products**

Carboxy fenitrothion (CF) has been found to be the major photolytic degradation product of fenitrothion in water (Okhawa et al. 1974, Miyamoto (cited in NRCC 1977), and Mikami et al. 1985). Okhawa et al. (1974) found CF represented 17% of fenitrothion products at 28 hours while Miyamoto found 35.9% at 40 hours exposure to sunlight in distilled

water. In river and sea water, Mikami et al. (1985) measured levels of 3.3 and 3.9% of initial fenitrothion added at 2 days, respectively and 4.6 and 3.6% at 32 days, respectively, well above any other photoproduct at this time. Miyamoto et al. (1979) suggested this side chain oxidation may also occur in aquatic organisms, though they did not detect any in their study (except in the water).

The remaining metabolites are produced by either combinations of the previously mentioned degradation routes or are intermediate products. Metabolites such as these found in simulated or natural studies include: 1) 3-methyl-4 aminophenol, 2) desmethylamino fenitrothion, 3) carboxy derivative of amino-fenitrothion and fenitrooxon, and 4) intermediates such as the acetyl and formyl stages before the carboxy derivative of fenitrothion, aminofenitrothion and fenitrooxon. These seldom achieve a significant level, though some have been consistently detected in numerous studies (NRCC 1975, NRCC 1977, Takimoto et al. 1976, Moody et al. 1978, Miyamoto et al. 1979, Weinberger et al. 1982, Weinberger et al. 1983, and Mikami et al. 1985). Figure IV provides structural information on the degradation products. It should be noted that the dimethyl phosphorothioic acid side of fenitrothion, (with its own possible derivatives) though occasionally mentioned, is generally omitted with environmental concern centered on the more organic species.

## 7. FIELD AND LABORATORY PERSISTENCE STUDIES

The majority of the studies done on fenitrothion and its degradation are specialized compartment studies carried out in the laboratory. These studies are important but cannot be considered definitive in actual environmental fate. At the other extreme are

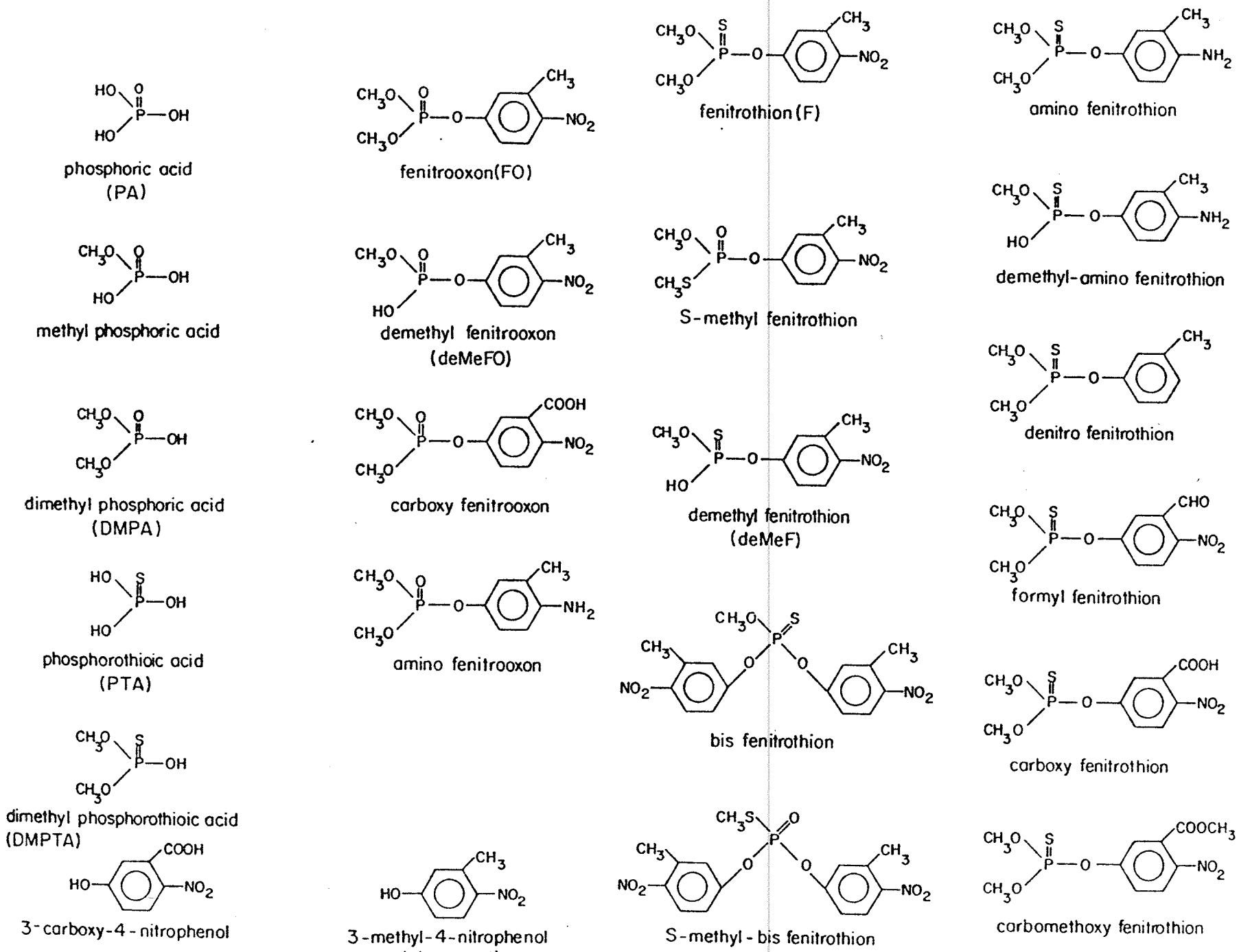



Figure IV Possible Degradation Products of Fenitrothion (NRCC 1975)

surveys during actual spray operations. This may be the ideal situation but the large scope involved and all the natural inherent variations seldomly lead to conclusive results. The concern of this section is with controlled
field studies. These designs allow for the majority of natural interactions while providing the opportunity for detailed study.

Moody et al. (1978) designed a study to determine the fate of fenitrothion in a stream following aerial deposition of an aqueous formulation. Two adjacent areas were chosen that had little overhead coverage. One section was stagnant while the other was fast flowing. At eight sampling times, (1-97 hrs), surface and subsurface (0.3-0.5 m) water samples were collected in 1 liter nalgene bottles from both sites. Additionally, larger subsurface samples were collected in 23 liter polyethylene containers to test for metabolites. Aquatic plants including duckweed, hornwort, and flowering rush were also collected up to 192 hours postspray. Fenitrothion and AF levels were higher in the stagnant area and microbial degradation was cited as a major breakdown pathway. Persistence in aquatic vegetation had not been reported previously and results indicated further investigations should be made to determine any possible ecological ramifications.

Greenhalgh et al. (1980) reported significant difference in degradation rates of fenitrothion between laboratory and natural systems. Their field study included 8 PVC cubes (1 $m^3$), open at the top, that were immersed in a lake. They were filled with lake water, algae, plants and sediments in various combinations. Each system was hand sprayed with an aqueous formulation to simulate an aerial spraying. Temperature and pH were measured during the 14 day study along with levels of fenitrothion in the water. Adsorption by the PVC was

recognized, but not important enough to effect the results that suggested that photolytic or microbial processes were the primary means of fenitrothion's removal from natural systems.

A stagnant pond with no tree cover was used in a 1977 study by Maguire and Hale (1980). This pond had an estimated average depth of 0.3 meter and area of $4.46 \times 10^2$ $m^2$ and was sprayed with an aqueous formulation of fenitrothion on a clear and calm day. The weather conditions remained the same for several days after spraying. Pre-spray samples of water and sediment were collected and intensive sampling began 40 minutes after spraying with decreasing frequency over the next few days. The surface microlayer (60 um approx.) was sampled as well as the subsurface water and sediment. Water (600 L) was passed through a continuous flow centrifuge to obtain 200 mg of suspended solids. "Volumes" of these compartments were calculated to determine relative importance of each. After 2 days, only 9% of the initial fenitrothion could be accounted for, suggesting; a) some error in compartment size calculation, b) the presence of other metabolites that were not detected (only two were found), c) the importance of other compartments not analyzed, and as indicated in later lab studies, d) the possible importance of volatilization especially initially from the surface microlayer.

Weinberger et al. (1982a, 1982b and 1983) designed a number of laboratory experiments using natural components. These included: 1) dynamic stream/estuarine, 2) static lake/estuarine, 3) co-solvent and algae interaction, 4) water, 5) water/sediment, 6) water/flora and 7) water/sediment/flora models. Weinberger et al. (1982a) extended the work done with Greenbalgh's et al. (1980) previously mentioned field study. Algae (three species in dialysis bags) and Elodea were suspended

within the 8 PVC enclosures that were lined with 3-4 cm of sediment. Each system was allowed to equilibrate 5 days before spraying. The study recognized the sediment as the main sink for fenitrothion but also suggested a light energized active uptake mechanism and possibly phytodegradation by plants and algae. The light and dark systems also distinguished different metabolites, (six in light compared to two in the dark, respectively) indicating the importance of the photolytic/oxidative degradation route.

Marshall and Roberts (cited in NRCC 1977) were the first to propose a mathematical model describing the disappearance of fenitrothion in a well mixed pond system. Fig. V is a schematic of their model with the three compartments, (suspended solids, water, and hydrosol) representing the major pools. The first model assumed first order kinetics described all the dissipation and transfer processes. The effective size (V) is described as a measurement of the pollutant holding capacity of a given pool. A materials balance on fenitrothion in the water, hydrosol, and suspended solids yields equations (1), (2), and (3) respectively:

$$V_w \, (dC_w/dt) = k_{hw} \, V_h \, C_h + k_{sw} \, V_s \, C_s - k_{wo} \, V_w C_w - k_{ws} \, V_s \, C_w - k_{wh} \, V_h \, C_w \quad (1)$$

$$V_h \, (dC_h/dt) = k_{wh} V_h C_w - k_{hw} C_h V_h - k_{wo} V_h C_h \quad (2)$$

$$V_s \, (dC_s/dt) = k_{ws} V_s C_w - k_{sw} V_s C_s \quad (3)$$

The removal from water, $k_{wo}$, is the sum of the rate constants for hydrolysis, photolysis, volatilization, bacterial degradation, and removal by fish. Similarly, the rate constant for degradation in hydrosol, $k_{ho}$, includes bacterial degradation and hydrolysis. Both bacterial degradation terms include terms for the numbers of active cells per gram water or gram of sediment. If the insecticide equilibrates rapidly with suspended solids,

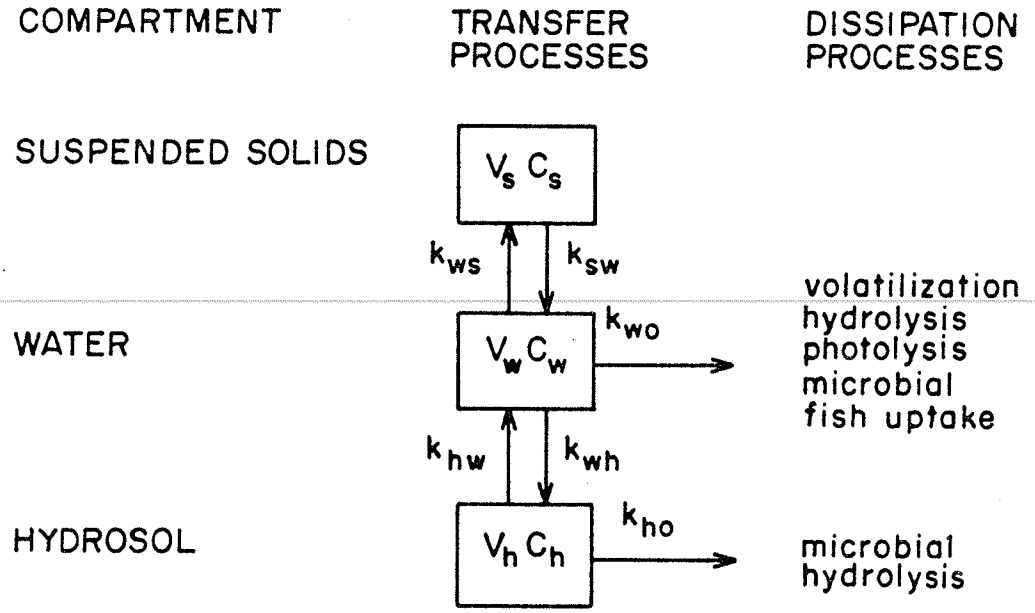



Fig. V Schematic representation of the dynamics of an insecticide in a well-mixed pond system. V denotes the effective size and C the concentration of insecticide in the respective compartments. The sum of all rate constants of the dissipation processes occurring in the water and hydrosol are denoted by $k_{wo}$ and $k_{ho}$ respectively (units $d^{-1}$). The sorption rate constants, $k_{wh}$ and $k_{ws}$, have units of ml/g/d and the desorption rate constants have units of $d^{-1}$.

- NRCC (1977)

($\bar{K}_s = k_{ws}/k_{hw}$), and an equilibrium is established with the hydrosol, ($\bar{K}_h = k_{wh}/k_{hw}$), Marshall and Roberts developed the equation:

$$dC_w/dt = (V_w\, k_{wo} + k_{ho}\, \bar{K}_h\, V_h/V_w + V_s\, \bar{K}_s + V_h\, \bar{K}_n)\, C_w$$

This shows the influence of system specific parameters, $V_w$, $V_s$, $V_h$, and the importance of the chemical nature of suspended solids and hydrosol (for $\bar{K}_s$ and $\bar{K}_h$ partition terms).

The difficult part was calculating parameter estimates from a limited information pool. Parameters that were determined to be insignificant were: 1) volatilization - with a half life of 93 days in a 1 meter water column, 2) hydrolysis - with a half life greater than 100 days unless natural catalysts play a significant role, 3) fish uptake - uptake rate constant of fenitrothion and fish density are too low, and 4) suspended solids - $V_w$ estimated to be much longer than $V_s\bar{k}_s$. Important parameters were: 1) photolysis - though lack of information necessitated estimates using different compounds, and also the importance of quenchers or sensitizers couldn't be determined, 2) microbial degradation - critical parameter is the density of micro-organisms, reported to range from $26 \times 10^1$ to $1.6 \times 10^6$ cells per mL water and $4.3 \times 10^4$ to $9.8 \times 10^7$ cells per gm sediment, and 3) sediment sorption and desorption - depending on sediment chemistry, $\bar{K}_h$ values could range from 1 to 300, with the sorption rate constant between 1 - 50 ml/g/day. Table V shows how dramatically the half-life of fenitrothion in water depends on the specific nature of the particular system treated. The authors concluded the simulations show promise as a tool to predict relative persistence patterns but the failure of studies to include compound and system specific parameters limits discussion on the pesticide dynamics. The modelling could be

Table V Influence of system-specific parameters on disappearance half-lives of fenitrothion in water.

| SYSTEM | Half-life, $\ln 2(1 + \frac{V_h}{V_w}\bar{K}_h)/(k_{wo} + k_{ho}\bar{K}_h\frac{V_h}{V_w})$ days | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $k_{ho}$ ($d^{-1}$) | | | | $k_{ho}$ ($d^{-1}$) | | | | $k_{ho}$ ($d^{-1}$) | | | |
| | 1.0 | 0.1 | 0.01 | 0 | 1.0 | 0.1 | 0.01* | 0 | 1.0 | 0.1 | 0.01 | 0 |
| Depth=1.0 m | $k_{wo}$=2.3 $d^{-1}$ (t 1/2=0.30) | | | | $k_{wo}$=0.17 $d^{-1}$ (t 1/2=4.1 d) | | | | $k_{wo}$=.042 $d^{-1}$ (t 1/2 = 17 d) | | | |
| $\frac{V_h}{V_w}$=.014 $\frac{\bar{K}_h}{30}$ | 0.36 | 0.42 | 0.43 | 0.43 | 1.7 | 4.6 | 5.6 | 5.8 | 2.1 | 12 | 21 | 23 |
| $\frac{V_h}{V_w}$=.014 300 | 0.55 | 1.3 | 1.5 | 1.6 | .82 | 6.1 | 17 | 21 | 0.85 | 7.8 | 43 | 86 |
| Depth=6.0 m | $k_{wo}$=1.67 $d^{-1}$ (t 1/2=0.42 d) | | | | $k_{wo}$=.096 $d^{-1}$ (t 1/2=7.2 d) | | | | $k_{wo}$=.029 $d^{-1}$ (t 1/2=24 d) | | | |
| $\frac{V_h}{V_w}$=.0023 $\frac{\bar{K}_h}{30}$ | 0.43 | 0.44 | 0.44 | 0.44 | 4.5 | 7.2 | 7.7 | 7.7 | 7.5 | 20 | 25 | 26 |
| $\frac{V_h}{V_w}$=.0023 300 | 0.49 | 0.68 | 0.70 | 0.70 | 1.5 | 7.1 | 11.4 | 12.1 | 1.6 | 12 | 33 | 40.4 |

- NRCC (1977)

used to identify one's information requirements, helping to design relevant laboratory and field studies.

Roberts et al. (NRCC 1981) expanded their model in producing a simple computer model as a screen for persistence. The model is described on the schematic in Fig. VI. The computer model deals with both fixed solutions (equilibrated) and dynamic solutions (long equilibration time). The biota in their study included fish, and the catchall compartment could be set up to represent any compartment(suspended sediment in this study). For fenitrothion in a one meter deep pond (Table VI) the following information was calculated: the bioconcentration factor for fish is 225 at steady state. The fractional retention or the fraction of total pollutant in each compartment at steady state in this example has 87% of fenitrothion retained in the sediment exposed to some microbial degradation and 10% in the water exposed to rapid photolytic degradation. Removal rate constants calculated include: 1) $K_p$ (photolysis) = 0.894 day $^{-1}$ 2) $K_v$ (volatilization) = $3.65 \times 10^{-4}$ $day^{-1}$, and 3) $K_h$ (hydrolysis)) = $6.63 \times 10^{-6}$ $day^{-1}$. Fractional degradation depends on pollutant accessibility in the appropriate model. In this example, 82% of removal is via photolysis and 18% via microbial degradation. Equilibration between all compartments, with continuous input of fenitrothion, may take up to 6 months. This time reflects the "slow" compartments, fish and sediment, where water and suspended solids approach equilibrium in less than a week. With a single pulse input, fenitrothion is predicted to clear rapidly from water but concentrations in sediment and fish are relatively high for about one month and indicate the necessity to

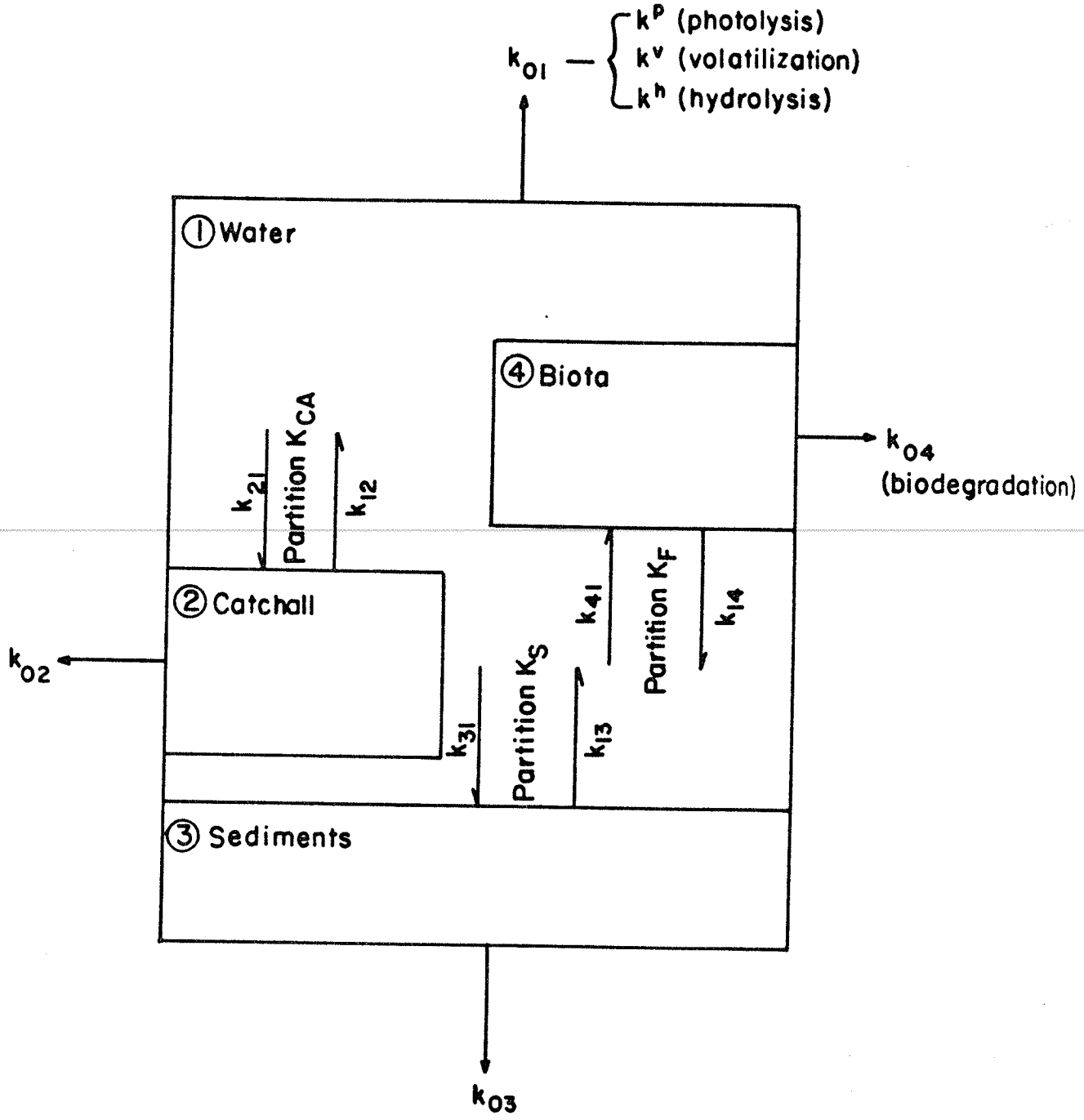



Figure VI Schematic of the four-compartment model. $k_{12}$, $k_{21}$, $k_{13}$, $k_{31}$, $k_{14}$, $k_{41}$ = first-order transfer rate constants. $K_{CA}$, $K_S$, $K_F$ = partition coefficients between each compartment and water. $k_{01}$, $k_{02}$, $k_{03}$, $k_{04}$ = first-order removal rate constants.

- Roberts et al. (1981)

Table VI Definition of the standard aquatic systems.

| | Pond | Lake |
|---|---|---|
| Latitude (°N) | 45 | 45 |
| Temperature (°C) | 20 | 20 |
| Water | | |
| Mean depth (m) | 1.00 | 15 |
| Volume (L) | $3.7 \times 10^6$ | $1.0 \times 10^{10}$ |
| Suspended solids (ppm) | 50 | 5.0 |
| Non-pollutant light attenuation coefficient | high[a] | low[b] |
| Sediment | | |
| Weight (g) | $7.3 \times 10^7$ | $2.9 \times 10^{10}$ |
| Effective depth (cm) | 1 | 1 |
| Organic matter (%) | 10 | 10 |
| Biota | | |
| Number of fish | 185 | $5 \times 10^5$ |
| Average weight of each fish (g) | 100 | 100 |

[a] Light absorption for six polluted water bodies; see Zepp and Cline (1977).

[b] Light absorption for distilled water.

- Roberts et al. (1981)

sample more than water in field experiments. The fixed solution results are summarized in Table VII and the dynamic solution is pictured in Fig. VII.

## 8. ANALYTICAL METHODOLOGY

The areas of concern are those involved in an aquatic environment and references are directly connected to the compartments of 1) air, 2) water, 3) sediment, 4) plants, and 5) fish. Methods of sampling, extraction and clean-up will be dealt with separately in each compartment. While methods of analysis, (thin layer chromatography (TLC), gas-liquid chromatography (GLC), high pressure liquid chromatography (HPLC), and liquid scintillation counting (LSC)), will also be discussed.

### a. Air

Air sampling has become more important with the advent of better and more portable equipment. These measurements can be used to determine the efficiency of spraying, spray drift to non-target areas and volatilization of the parent compound and metabolites back into the atmosphere. There are a variety of adsorbents used in air sampling, including; 1) impinger liquids such as ethylene glycol and dimethyl formamide (Woodrow and Selber 1978, Sundaram 1984), 2) Amberlite XAD-2, XAD-4, (polystyrene, divinylbenzene copolymer) macro-reticular polymer beads (Woodrow and Selber 1978, Mallet and Volpe 1982, and Hunt and Pangaro 1982), 3) other related resins including Chromosorb 102 and Tenax GC (Raper and Wright 1984, Krzymien 1982) 4) column packings, (GLC and HPLC), GC-Durapak, Carbowax 400/Porasil F, and Porapak $C_{18}$ (Raper and Wright 1984) and 5) Polyurethane foam, polyester urethane-open

Table VII Fixed solution for fenitrothion, at equilibrium, in the standard pond.

AQUATIC/POLLUTANT MODEL FENITROTHION

POND SYSTEM - CONTINUOUS INPUT OF POLLUTANT

| | | |
|---|---|---|
| SYSTEM DESCRIPTION - | JUNE, LATITUDE 45.0 DEG | TEMP 20.0 DEG C |
| | MEAN DEPTH 1.0 METRES | VOLUME 0.370E 07 LITRES |
| | CONC OF SUSP SOLIDS 50.0 PPM | ORGANIC MATTER 10.0% |
| | SEDIMENT WT 0.730E 08 G | REPRESENTATIVE FISH WT 0.100E 03 G |
| | HIGH ATTENUATION | NO. OF FISH 0.185E 03 |
| POLLUTANT DATA - | INPUT VOLUME 0.100E 01 L | CONC OF POLLUTANT 0.102E 06 PPM |
| | VAPOUR PRES 0.540E-04 MM HG | MOLECULAR WT 0.277E 03 |
| | MELTING POINT 0.0 DEG C | SOLUBILITY 0.412E 03 PPM |
| | QUANTUM YIELD 0.230E-01 | LIQUID SOLUBILITY 0.412E 03 PPM |
| | X (PROPORTION: BIODEGRADATION/CLEARANCE FOR FISH) 1.00 | |

| | | | | | |
|---|---|---|---|---|---|
| PARTITION COEFF'S - | KOW = 0.3900E 04 | KW = 0.1000E 01 | | | |
| | KCA = 0.4328E 04 | KS = 0.4328E 03 | KF = 0.2251E 03 | | |
| REMOVAL RATES - | KV = 0.3650E-03 | KP = 0.8944E 00 | KH = 0.6630E-05 | | |
| | K01 = 0.8948E 00 | K02 = 0.4594E 00 | K03 = 0.1164E-01 | K04 = 0.1230E 00 | |
| TRANSFER RATES - | KI = 0.1000E 01 | | | | |
| | K12 = 0.2310E-01 | K13 = 0.2310E-01 | K14 = 0.0000 | | |
| | K21 = 0.1000E 03 | K31 = 0.1000E 02 | K41 = 0.2770E 02 | | |

FIXED SOLUTION FOR CONTINUOUS INPUT SITUATION AT EQUILIBRIUM

SYSTEM COEFFICIENT IS 0.3679E 09 (CORRESPONDING TO A 10.0% DECREASE IN RETENTIVE CAPACITY)

RETENTIVE CAPACITY 8.92 DAYS

FIRST ORDER HALF-LIFE OF SYSTEM AT EQUILIBRIUM 6.18 DAYS

| | | | |
|---|---|---|---|
| FRACTIONAL RETENTION - | FR1 = 0.102485 | FR2 = 0.022180 | |
| | FR3 = 0.875220 | FR4 = 0.000115 | |
| FRACTIONAL DEGRADATION - | FDV = 0.000334 | FDP = 0.817792 | FDH = 0.000006 |
| | FDSS = 0.090909 | FDS = 0.090909 | FDF = 0.000050 |

BIOCONCENTRATION

| | |
|---|---|
| BCF ESTIMATE FOR FISH | 225.1152 |
| BCF ESTIMATE FOR MOLLUSK | 2.6122 |
| BCF ESTIMATE FOR DAPHNIA | 383.9571 |

- Roberts et al. (1981)

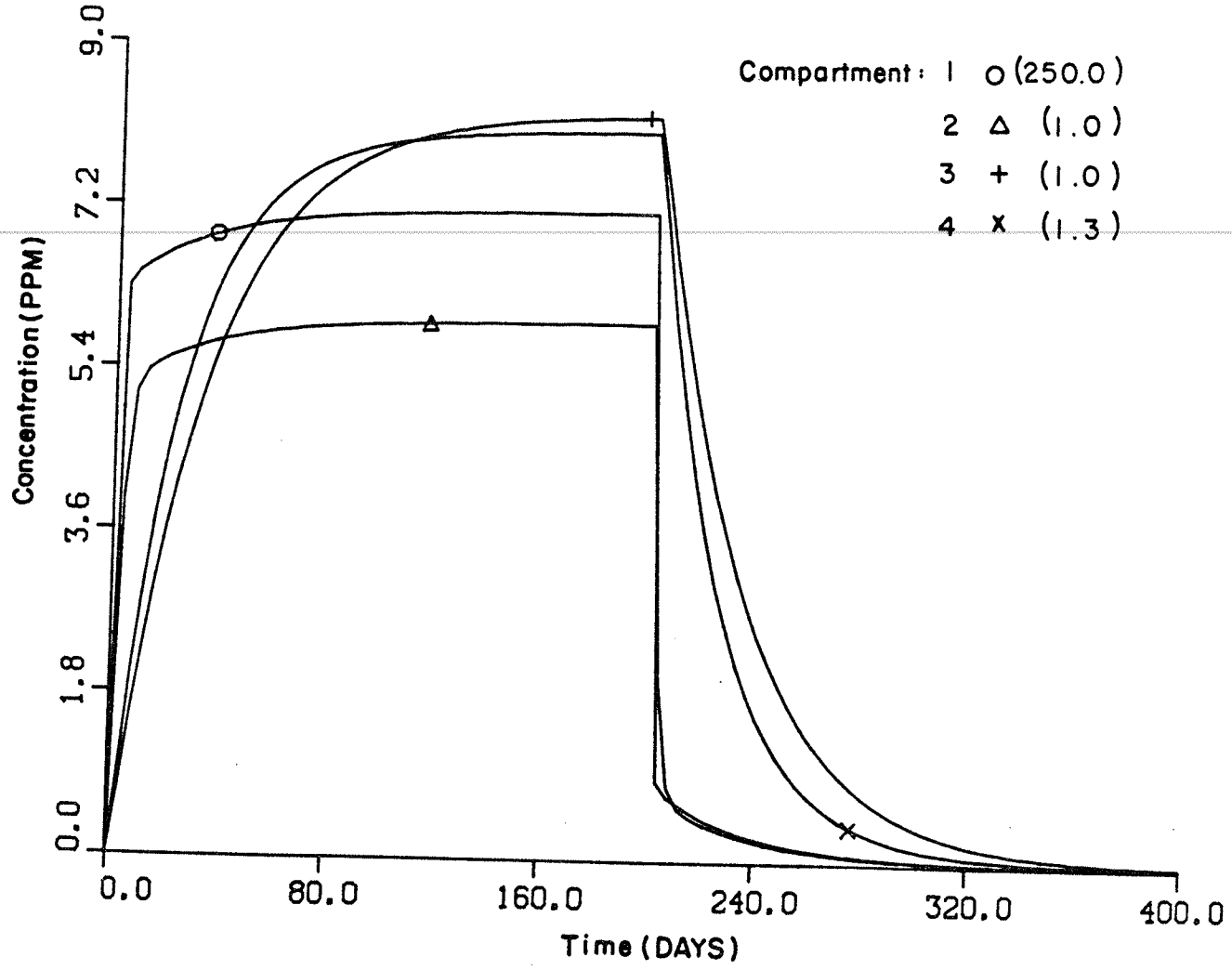



Figure VII Dynamics of continuous input of fenitrothion until equilibrium is attained, followed by cessation of input, in the standard pond. Concentration of fenitrothion in compartments 1, 4 is plotted versus time after addition of fenitrothion to the system.
- Roberts et al. (1981)

cell type (Roper and Wright 1984, Kearney and Kontson 1976 and Grover and Kerr 1981). The sampling system may consist of a particulate filter, adsorbent, flow meter, flow valve, and a stationery or portable battery-operated pump operating with flows from 1 to 50 liters/min. Both impinger examples used 100 mL of their respective scrubbers. The amount of solid adsorbents varied from approximately 25 mg Tenax GC up to 25 grams XAD resin. The adsorbents were packed in either glass, polypropylene or aluminum columns. Polyurethane foam plugs were held within either a polypropylene or glass filter funnel or cylinder. The relative amount of any of these absorbents dictates their "breakthrough" volume or their maximum air volume sampled before pesticide elution. This volume changes from compound to compound, the most important factors being polarity and volatility. Krzymien (1982) found his 25 mg Tenax GC had a breakthrough volume of 780 liters for fenitrothion, well within his sampling schedule.

Preparation of the adsorbents is important to avoid contamination of the sample. Hunt and Pangaro (1982) found uncleaned Amberlite XAD-2 and XAD-4 contained high artifact levels of alkyl derivatives of benzene, styrene, naphthalene, and biphenyl. They used three solvents of varying polarity to clean the resin. Grover and Kerr (1981) Soxhlet extracted polyurethane foams for 80 hours with hexane-acetone (1:1) to remove contaminants.

Grover and Kerr (1981) extracted their sample foams in a Soxhlet apparatus with hexane while Kearney and Kontson (1976) used benzene-acetone (1:1). Woodrow and Selber (1978) extracted XAD-4 resin by shaking it with ethyl acetate. Mallet and Volpe (1982) also eluted

fenitrothion from their XAD columns with ethyl acetate. Dimethyl -formamide used by Sundaram (1984) in an impinger to sample for fenitrothion was evaporated and added was water partitioned with benzene. Fenitrothion can also be desorbed from GLC packings and other adsorbents, like Tenax GC, directly into a GLC (Krzymein 1982).

Krzymien's (1982) sampling grid was located entirely in a spruce-fir forest. The U-shaped grid was oriented for prevailing westerly winds, with the spray line completing the square. The downwind sampling line extended 700 m and the cross-wind sampling line was 750 m long. Samples were positioned every 50 m along the lines, 1.5 m above ground level. The surveys by Mallet and Volpe (1982) and Mallet and Cassista (1984) both used portable and permanent pumps near the spray areas. Sundaram (1984) chose a centrally located sampling site in the middle of each spray block. Six air samplers were randomly placed along the flight path, about 20 m apart from one another.

**b. Water**

The general sampling program for water, in fenitrothion experiments, starts with frequent sampling, tapering off further into the experiment. All experiments include prespray sampling. Extensive sampling programs have been set up by Morrison and Wells (1981), Eidt and Sundaram (1975), Maguire and Hale (1980), Weinberger et al. (1982a), and Holmes et al. (1984). Both surface and subsurface samples of varying depths were collected. The water samples were transported and stored under refrigeration. In both years of the New

Brunswick spray surveys, (Mallet and Volpe 1982, Mallet and Cassista 1984), water samples were either preserved with ethyl acetate added in the field or were extracted through XAD resin columns within two hours.

Volpe and Mallet (1980, 1981) compared Amberlite resins XAD-2, -4, and -7, and liquid-liquid extraction with ethyl acetate or methylene chloride for recovery of fenitrothion and seven derivatives from water. The results are summarized in Table VIII. Water was passed through the XAD column, which was then eluted with either ethyl acetate (used in both spray surveys) or methylene chloride. The lab study concluded that lowering the pH of the water to 3 to facilitate the extraction of MNP and thiocresol reduced the recoveries of some of the derivatives (SMF, FF, HMF, and TC). To maximize recoveries Mallet and Cassista (1984) used the XAD-4 columns for extraction of fenitrothion from natural water and ethyl acetate was used to extract some degradation products from acidified (pH 3) water samples. Maguire and Hale (1980) reversed this procedure, acidifying the water samples to pH 1 passing them through XAD-2 resin columns eluting fenitrothion with toluene. This procedure would extract fenitrothion, FO, MNP and possibly render polar and acidic derivatives such as carboxy fenitrothion extractable. Some water samples were extracted, without pH adjustment, with benzene for AF (Maguire and Hale 1980). Greenhalgh et al. (1980) partitioned lake water with ethyl acetate prior to and after acidification to pH 1 with HCl. The first extract contained fenitrothion and AF and the second, DMF and MNP. Weinberger et al. (1982b) and Kikuchi et al. (1984) also used ethyl acetate to extract water, pH not adjusted. Fisher (1985) used anhydrous ether to extract fenitrothion from water. Grift and Lockhart (1974) and initially Moody et al. (1978) extracted with petroleum ether but subsequent extractions

**Table VIII. Simultaneous recovery* from water of a mixture of fenitrothion and seven derivatives with Amberlite XAD-4**

| Method of recovery | Concentration ppb | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 50 F | 50 AF | 50 FO | 100 SMF | 100 FF | 50 HMF | 50 MNP | 100 TC |
| Amberlite XAD-4 resin | 99 | 91 | 91 | 69 | 21 | 49 | 97 | 30 |
| Amberlite XAD-2 resin | 86 | 92 | 99 | 80 | 20 | 49 | 98 | 57 |
| Amberlite XAD-7 resin | 95 | 91 | 91 | 72 | 22 | 43 | 68 | ND |
| Liquid-liquid extraction with 3 x 40 mL of methylene chloride | 81 | 68 | 88 | 49 | 20 | 27 | 52 | 29 |
| Liquid-liquid extraction with 3 x 40 mL of ethyl acetate** | 101 | 92 | 90 | 92 | 35 | ND | 98 | 27 |
| Environmental water with Amberlite XAD-4 | 96 | 88 | 94 | 73 | 22 | 42 | 94 | 12 |

* Average of three determinations using 3 x 30 mL of methylene chloride as the eluant

** Average of two recoveries

F = fenitrothion, AF = amino-fenitrothion, FO = fenitrooxon, SMF = S-methyl fenitrothion, FF = formyl fenitrothion, HMF = hydroxy methyl fenitrothion, MNP = methyl-nitrophenol, TC = thiocresol

- From Volpe and Mallet (1981)

with chloroform gave greater recoveries of fenitrothion, FO, and SMF. Eidt and Sundaram (1975) and Weinberger et al. (1982a) also used chloroform for extraction while Morrison and Wells (1981) and Holmes et al. (1984) both used hexane extraction. Greve and Goewie (1985) state that less polar solvents like hexane give quantitative extraction of a limited number of organophosphorus insecticides (OPs) though the extracts tend to be cleaner. Alternately, methylene chloride is sufficiently polar to efficiently extract most OPs and its high specific weight is convenient for repeated extractions in a separatory funnel. Extracted water samples have also been freeze dried and the residues dissolved in methanol for determination of polar derivatives (Moody et al. 1978, Weinberger et al. 1982a).

c. **Sediment**

The sampling schedule of sediment is generally not as intensive as the water sampling in the initial post spray time period but as water sampling rate declines the sediment sampling is carried out on the same schedule. Mallet and Cassista (1984) collected sediment from four sites in the immediate vicinity of water sampling sites. Maguire and Hale (1980) collected pond sediment samples four and two days prespray and over the four days post spray. The artificial ponds (PVC-$1m^3$) constructed by Weinberger et al. (1982a) were lined with sediment three to four cm deep, some in 600 mL beakers to facilitate sampling. After five days prespray equilibration, sediment samples were collected up to 28 days post spray. The sediment samples in these studies were frozen until analysis.

Pesticide residues in sediment can be classified into the three categories of free, loosely bound, and tightly bound (Takimoto et al.

1976). The category extracted depends on how rigorous the extraction procedure is. Extraction of the free residues generally entails the use of organic solvents, often water soluble, and some type of mixing process, such as shaking, mechanical mixer-agitator or reflexing-soxhlet type extraction. Grift and Lockhart (1974) used a stainless steel extraction tube, a steel ball bearing, ethyl acetate and a Burrell wrist action shaker. The ethyl acetate was partitioned with acetonitrile and hexane. The ethyl acetate-acetonitrile portion was further cleaned up on an activated Florisil column eluted with 25% benzene in ethyl acetate. Mallet and Cassista (1984), using a Polytron (Brinkman Instruments), homogenized a subsample with acetonitrile. The filtrate was diluted with distilled water and passed through an XAD-7 column. The column was washed with distilled water and fenitrothion eluted with ethyl acetate. Macalady and Wolfe (1985) extracted free organophosphorothioate ester residues by adding acetonitrile to sediment in a centrifuge tube with thorough mixing on a vortex mixer. Further additions of distilled water and isooctane were followed by a period of horizontal agitation on a flat-bed shaker. The sample was finally sonicated and refrigerated for phase separation and analysis of the isooctane layer. Fuhremann and Lichtenstein (1978) extracted methyl ($^{14}C$) parathion from soil using Soxhlet extractions with: acetone-methanol (1:1), ethyl acetate-methanol (1:1), chloroform-methanol (1:1), and isopropanol, after which the soil was combusted to $^{14}CO_2$ to determine bound residue levels (not necessarily methyl parathion). Getzin (1982) extracted free $^{14}C$- parathion by Soxhlet extracting with methanol-chloroform (3:1). The soil was then additionally shaken

in a centrifuge bottle with an aqueous solvent mixture consisting of equal amounts of 0.05 M calcium chloride and acetone. "Bound" residues were extracted by refluxing the previously extracted soil with dimethyl formamide containing 0.4 m oxalic acid (DMF/oxalate). The DMF/oxalate extracts were partitioned with water and hexane, the water portion acidified to pH 2 and extracted with chloroform. Samples of the DMF/oxalate extracted soil were additionally refluxed with 0.5N NaOH. Maguire and Hale (1980) Soxhlet extracted sediment with acetone-hexane (1:1). The extract was then absorbed on a de-activated silica column. The mini column was eluted with solvents of increasing polarity: 1) toluene, for fenitrothion, 2) ethyl acetate-toluene (1:1) for FO and compounds of similar polarity and, 3) acetone for even more polar compounds. The previously extracted sediment was then rigorously Soxhlet extracted with 1N HCl. Weinberger et al. (1982a) followed the method used by Takimoto et al. (1976) for their sediment extraction. Fig. VIII outlines the four extraction procedures of soil, using: 1) shaking with water-methanol (1:3) for free residues, 2) shaking with 1N HCl-methanol (1:3), 3) shaking with 1N-sodium bicarbonate-methanol (1:3), and 4) shaking with 1N NaOH-methanol (1:3), for loosely bound residues. Weinberger et al. (1982a) found the recovery for fenitrothion was greater than 91% and derivatives greater than 84%.

**d. Plants and Algae**

The rapid uptake of fenitrothion and metabolites by algae and plants necessitates a fairly intensive sampling schedule after fenitrothion application as exemplified by Weinberger et al. (1983) (0 hrs to 21 days post treatment). Weinberger et al. (1982a) collected aquatic plants and algae at various time intervals up to 28 days. Moody

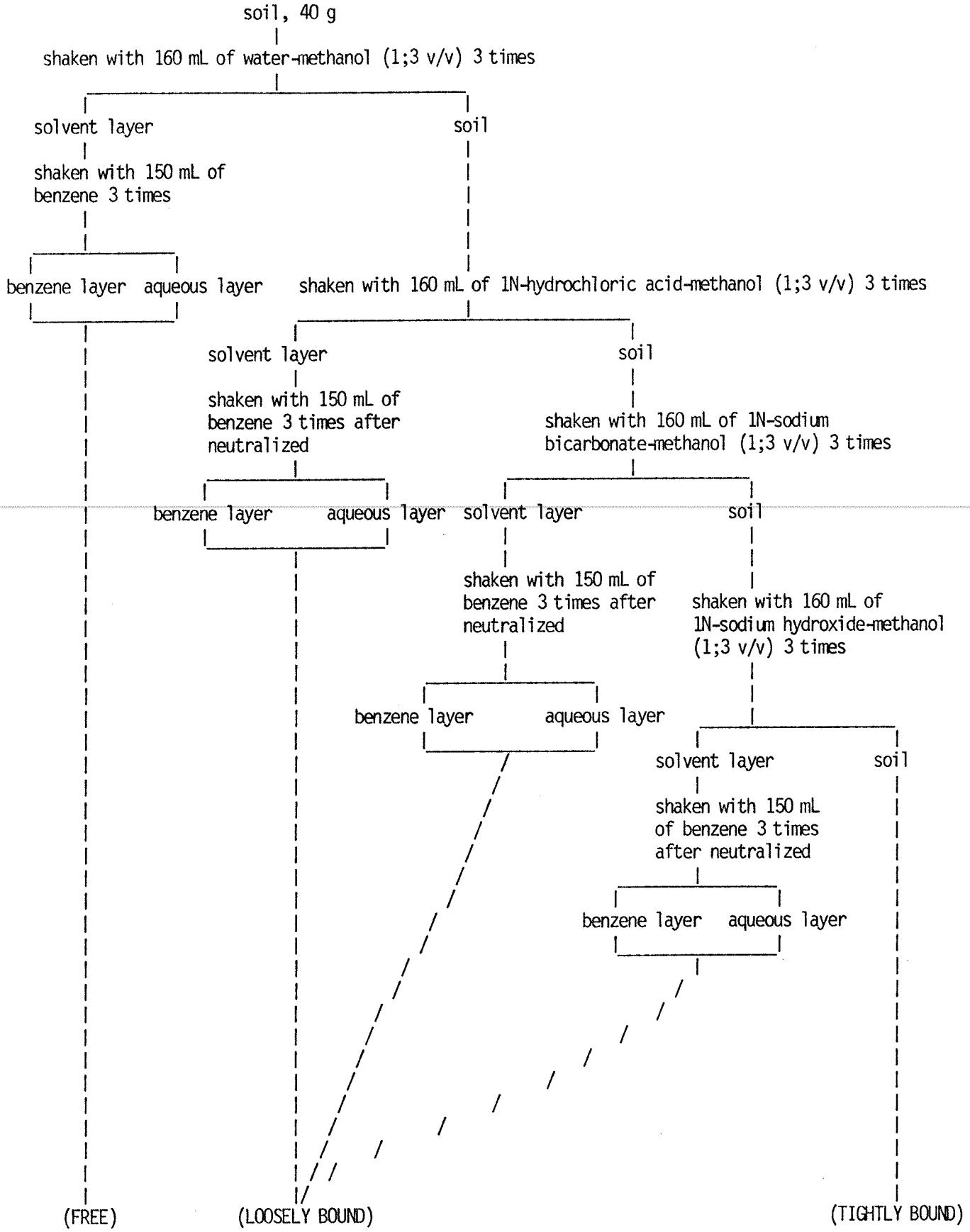



**Figure VIII.** **Separation procedures for decomposition products of Fenitrothion in soil. Takimoto et al. (1976)**

et al. (1978) collected aquatic plants up to 192 hours post spray.

Lakshminarayana and Bourque (1980) removed algae from the water using nets and preserved the samples by adding chloroform. Fisher (1985) removed algae from the water using a wire mesh screen. Algae samples were refrigerated or frozen until analysis.

Plant and algae are often macerated during extraction to expose the maximum amount of tissue to the extracting solvent. Moody et al. (1978) extracted rush and hornwort samples with ethyl acetate in a Waring blender. Clean-up of the extract was achieved on a glass column packed with Celite and charcoal. Compounds of interest were eluted with 25% ethyl acetate in benzene followed by 100% benzene. Weinberger et al. (1982a) also blended their plant and algae samples with ethyl acetate. Fisher (1985) extracted fenitrothion from algae by grinding a sample in a mortar with acetonitrile and a few grains of sand. Homogenates were centrifuged at high speed and the resulting supernatant collected. Weinberger et al. (1983) pelleted the algae cells by centrifuging and extracted them in methanol. The methanol extract was taken up in ethyl acetate-hexane (15:85) for clean-up on a Florisil column. Kikuchi et al. (1984) also pelleted their algae by centrifuging and extracting it with methanol. Lakshminarayana and Bourque (1980) extracted algae with chloroform in an ultrasonic bath. Fenitrothion has been extracted from other non-aquatic plant material using: 1) a Polytron and acetonitrile (Mallet and Cassista 1984) for coniferous foliage, with a clean-up involving diluting the acetonitrile with water, passing it through XAD-7 resin and eluting with ethyl acetate, 2) stirring or shaking ground or whole wheat with methanol, acetone-water (95:5) or hexane (Desmarchelier et al. 1977), 3) blending grain with acetone-water, diluting this with

water and partitioning with dichloromethane (Committee for Analytical Methods for Residues 1985), and 4) shaking wheat with dimethyl formamide and filtering (Perez 1983).

**e. Fish**

Sampling of fish has usually been carried out at a frequency similar to sediment schedules. This was demonstrated by Morrison and Wells (1981) and Holmes et al. (1984). The former study used caged fish while the latter captured trout with gill nets. Fish samples were frozen until analysis.

Extraction of fenitrothion from fish tissue involves some type of maceration- homogenization similar to sediment and plants. Grift and Lockhart (1974) ground their fish samples through a meat grinder and then followed their method already stated for sediment (stainless steel tube, steel ball bearing, and shaking with ethyl acetate). Fisher (1985) also used the same method for fish as previously described for algae (also used for snails, mosquitoes and midges). This included grinding the sample in a mortar with acetonitrile and a few grains of sand then centrifuging and decanting the supernatant for analysis. Morrison and Wells (1981) ground their fish tissue with sodium sulfate and followed with Soxhlet extraction with hexane. Holmes et al. (1984) homogenized fish samples with a food chopper and macerated a portion in a Waring blender with ethyl acetate. Sergeant et al. (1979) placed clam/mussel tissue in a mortar and macerated it with six times its weight of anhydrous sodium sulfate and 5-10 g Ottawa sand until homogeneous and then Soxhlet extracted it with ethyl acetate. The extract was cleaned up by gel permeation chromatography using Bio-Beads SX-3.

**f. Analysis**

i) Radiolabelled techniques

Radiolabelled fenitrothion is useful in both method development and field studies because it allows detection and quantitation of residues with a minimum of extraction steps. This includes rapid analysis of aliquots of water and combustion of sediment, fish and plants for $^{14}CO_2$ determination. With combustion, however, the chemical nature of residues as well as mechanisms and consequences of binding cannot be established (Klein and Scheunert 1982). Chemical nature can be more specifically identified when nuclear techniques are associated with the separation technique of thin layer chromatography (TLC) and high pressure liquid chromatography. Radiolabelled residue spots are located on TLC plates by autoradiography (exposure to X-ray film such as Kodak XR-5 film) (Spillner et al. 1979) or a TLC radioscanner (Aloka model TRM-1B) (Ohkawa et al. 1974).

The scintillation cocktail is important for efficient counting while minimizing quenching. Aqueous samples use fluors such as: dioxane/naphthalene/PPO and commercial products Aquasol-2 or Instagel (Fisher 1985, Mikami et al. 1985, and Spillner et al. 1979). Weinberger et al. (1983) added macerated algae tissue to Scintiverse cocktail and Fisher (1985) used NCS tissue solubilizer along with the fluor used for water samples. Other cocktails used for organic solvent extracts and TLC scrapings are toluene based and dioxane cocktails (Mikami et al. 1985, Takimoto et al. 1976). Samples were combusted in instruments such as the Packard Tricarb Sample Oxidizer and $^{14}CO_2$ trapped in specific cocktails like Carbo-Sorb or Permafluor V (Spillner 1979).

ii) Thin Layer Chromatography (TLC)

The majority of TLC analysis of fenitrothion and metabolites has been achieved using silica gel coated plates (0.25 mm gel thickness) with or without fluorescent indicator. There have also been a variety of developing solvents used to separate the various compounds. Table IX summarizes the systems used and the respective Rf values for fenitrothion and the major metabolites detected. Two dimensional silica plate development with a second direction solvent system has also been used to improve separation (Zitko and Cunningham 1974, Mikami et al. 1985 and Takimoto et al. 1976). Alumina plates were used by Zitko and Cunningham (1974) to separate dansyl chloride (fluorogenic) labelled amino derivatives. Hallet et al. (1974) used cellulose plates to separate the acidic desmethyl fenitrothion (DMF).

The dansyl chloride labelling is one of a number of ways to enhance detection. A large proportion of experimenters have used silica gel precoated with fluorescence indicator in which compounds are detected by the quenching of gel fluorescence when viewed under short and long wave length UV light. The other detection alternative is chemical treatment of the plate to achieve visual spots. Ohkawa et al. (1974) treated the plates with; 1) 20 % (w/v) potassium hydroxide in methanol spray followed by heating, then over-spraying with 1.0% diazotized sulfanilic acid (w/v, aqueous), 2) 1% palladium chloride in 1N hydrochloric acid spray followed by heating or 3) exposing to iodine vapour. Mikami et al. (1985) also used a 2% palladium chloride in 2N hydrochloric acid spray which is specific for P=S compounds. Both Greenhalgh and Marshall (1976) and Hallet et al. (1974) used a spray of 2,6-diazobromoquinoamine

## Table IX: Thin Layer Chromatography (TLC) Systems

RF

| Amino-<br>Developing Solvents | Fenitrothion | Amino Fenitrothion | S-Methyl Fenitrothion | Fenitrooxon | 3-Methyl-4-Nitrophenol | Desmethyl Fenitrothion | Others |
|---|---|---|---|---|---|---|---|
| 1. Toluene/ethyl Formate formic acid (5/7/1) | | | | | | | Demethyl Fenitrooxon |
| - Kikuchi et al. (1984) | 0.73 | 0.37 | -- | 0.46 | .056 | 0.27 | 0.12 |
| - Takimoto et al. (1976) | 0.73 | 0.37 | -- | 0.46 | 0.56 | 0.27 | Carboxy Fenitrothion 0.40 |
| - Mikami et al. (1985) | | | | | | | |
| 2. Toluene/ethyl acetate/ acetic acid (5/7/1) | | | | | | | Carboxy Fenitrothion |
| - Ohkawa et al. (1974) | 0.92 | -- | 0.75 | 0.67 | 0.80 | -- | 0.15 |
| - Greenhalgh & Marshall (1976) | 0.51 | -- | 0.38 | 0.32 | 0.52 | (Formyl Fenitrothion) | 0.55 |
| - Weinberger et al. (1983) | | | | | | (0.58) | |
| 3. Hexane/ethyl acetate/ acetic (500/250/1) | | | | | | | |
| - Fisher (1985) | 0.46 | -- | 0.17 | 0.09 | 0.29 | -- | |
| 4. Ethyl acetate/cyclohexane (1/3) | | | | | | | |
| | | | | | | (Formyl Fenitrothion) | Carboxy Fenitrothion |
| - Greenhalgh & Marshall (1976) | 0.76 | -- | 0.1 | 0.06 | 0.20 | (0.26) | 0.15 |
| - Yule and Duffy (1972) | 0.58 | 0.214 | 0.149 | 0.09 | 0.38 | 0.713 | |
| - Weinberger et. al (1983) | | | | | | | |
| 5. Ethyl acetate/hexane (1/3) | | | | | | | |
| - Zikko & Cunningham (1974) | 0.45 | -- | 0.11 | 0.08 | 0.25 | -- | |
| - Sergeant et. al (1979) | | | | | | | |

## Table IX

### RF

| Developing Solvents | Fenitrothion | Amino-Fenitrothion | S-Methyl Fenitrothion | Fenitrooxon | 3-Methyl-4-Nitrophenol | Desmethyl Fenitrothion | Others |
|---|---|---|---|---|---|---|---|
| 6. Benzene/ethyl acetate (4/1) | | | | | | | |
| - Takimoto et. al (1976) | 0.74 | 0.35 | | 0.25 | 0.42 | 0.0 | |
| - Kikuchi et. al (1984) | 0.74 | 0.37 | | 0.25 | 0.42 | 0.0 | |
| - Ohkawa et. al (1974) | -- | -- | 0.50 | .024 | -- | -- | |
| 7. Toluene/ethyl acetate/ propanol/acetic acid (8/12/5/3) | | | | | | | Carboxy Fenitrothion |
| - Takimoto et. al (1976) | 0.70 | 0.46 | -- | 0.55 | 0.60 | 0.40 | 0.52 |
| - Kikuchi et. al (1984) | 0.70 | 0.46 | -- | 0.55 | 0.60 | 0.40 | |
| 8. Ethyl acetate/hexane (3/2) | | | | | | | Formyl Fenitrothion |
| - Greenhalgh and Marshall (1976) | 0.47 | -- | 0.30 | 0.22 | 0.42 | -- | 0.47 |
| 9. Toluene/acetic acid (7/1) | | | | | | | |
| - Ohkawa et. al (1974) | 0.75 | -- | 0.47 | 0.40 | 0.35 | -- | Carboxy Fenitrothion |
| - Mikami et. al (1985) | | | | | | | 0.22 |
| 10. Dichloromethane/ether/ ethyl formate/formic acid (2/4/2/1) | | | | | | | Carboxy Fenitrothion |
| - Takimoto et al. (1976) | 0.87 | 0.62 | -- | 0.56 | 0.80 | 0.49 | 0.50 |
| - Kikuchi et al. (1984) | | | | | | | |
| 11. Benzene/hexane/ ethanol (20/5/1) | 0.59 | 0.30 | -- | 0.18 | 0.18 | 0.0 | |
| - Takimoto et al. (1976) | | | | | | | |

Table IX

| Developing Solvents | Fenitrothion | Amino-Fenitrothion | S-Methyl Fenitrothion | Fenitrooxon | 3-Methyl-4-Nitrophenol | Desmethyl Fenitrothion | Others |
|---|---|---|---|---|---|---|---|
| | RF | | | | | | |
| 12. Hexane/acetone (4/1) | -- | -- | 0.24 | 0.18 | 0.26 | -- | |
| 13. Butanol/acetic acid/ water (4/1/2) | -- | -- | 0.81 | -- | 0.84 | -- | Carboxy Fenitrothion 0.71 |
| 14. Butanol/acetone/ water (4/5/1) Ohkawa et al. (1974) | -- | -- | -- | -- | -- | -- | Carboxy Fenitrothion 0.80 |
| 15. Isooctane/dioxane (2/1) | 0.63 | 0.42 | -- | 0.39 | 0.46 | -- | |
| 16. Toluene/diethyl ether (9/2) | 0.89 | 0.63 | -- | 0.38 | 0.79 | -- | |
| 17. Chloroform/ethanol (10/1) | 0.97 | 0.90 | -- | 0.93 | 0.74 | -- | |
| 18. Hexane/diethyl ether Spillner et al. (1979) | 0.50 | -- | -- | -- | -- | -- | |

in glacial acetic acid (also specific for P-S bonds) or an enzyme inhibition technique using extract of steer liver homogenate as the spray reagent as modified by Mendoza (1972) which was sensitive to fenitrothion, FO, and SMF.

(iii) High Pressure Liquid Chromatography (HPLC)

The majority of HPLC analysis for fenitrothion and metabolites has been achieved on reverse-phase (RP) column coupled to a UV detector with either fixed wavelength or variable wavelength capability. The column packing consists of hydrocarbon chains, usually $C_8$ or $C_{18}$, bound to support material. The most variable parameter, depending on application, is the mobile carrier solvent composition which for reverse phase chromatography usually involves water in combination with a water miscible organic solvent.

Perez (1982) separated fenitrothion from other pesticides using an RP-8 column with the solvent combination of acetonitrile-water (7:3). In another study, Perez (1983) used methanol-water (6:4) containing pentane sulphonic acid to separate fenitrothion from two pesticides. Grieve and Goewrie (1985) separated fenitrothion from ten pesticides with an Ultrasphere ODS (RP) column utilizing acetonitrile-water (1:1). Table X summarizes the results for fenitrothion and metabolites of Volpe and Mallet (1981) and Cochrane et al. (1979), both using a RP-8 column. Weinberger et al. (1982) used an RP-18 column with an eluting solvent of acetonitrile-water (60:40) to establish retention times for fenitrothion, SMF and carboxy methyl fenitrothion. Greve and Goewie (1985) report the use of other specific detectors for organophosphates, including: 1) alkali-flame ionization, 2) fluorescence labelling and 3) mass spectrometry interfacing.

## Table X: High Pressure Liquid Chromatography (HPLC) Systems

Rentention Times (min.)

| | Reference | (Detector) Solvent | Fenitrothion | Fenitrooxon | Amino-Fenitrothion | S-Methyl Fenitrothion | 3-Methyl-4 Nitrophenol | Others | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Hydroxy methyl Fenitrothion | Formyl Fenitrothion |
| 1. | Volpe and Mallet (1981) | Acetonitrile/water (1:1) (254 nm) | 11.0 | 3.8 | 4.6 | 5.0 | 3.4 | 5.4 | 5.6 |
| | | | | | | | | Desmethyl Fenitrothion | Carboxy Fenitrothion |
| 2. | Cochrane et. al (1979) | 20% Acetonitrile-Water-PICA (269 nm) | | | | | 10.3 | 6.7 | 5.7 |
| | | 30% Acetonitrile-water pH 2.35 | 51 | 12.6 | | 19.7 | 9.0 | | 17.4 |
| | | 30% Acetonitrile-water | | 12.4 | | 19.7 | 9.0 | | |
| | | 55% Acetonitrile-water | 7.1 | | | | | | |

(iv) Gas Liquid Chromatography (GLC)

Gas liquid chromatography (GLC) analysis is the most extensively used analytical technique for fenitrothion. Analytical methods use a non-polar liquid phase (OV-1, OV-101, SE-30, Dexsil 200) or slightly more polar phases (Ov-17, Dexsil 300, OV-210) or a combination phase (4% OV-101, 6% OV-210). Underivatized polar compounds such as methyl-nitrophenols have been chromatographed on polar phases such as Carbowax 20M. Table XI summarizes the columns used and compounds analyzed with their respective retention times. With the wide variety of carrier gas flow rates, percent liquid phase loadings, column lengths and diameters, and column oven temperatures these retention times are difficult to extrapolate from one reference to another.

Polar metabolites can be derivatized, alkylating their hydroxyl or carboxylic acid groups to make them more amenable to GLC. Greenhalgh and Marshall (1976) used diazomethane to methylate carbomethoxy fenitrothion and a carboxymethoxy fenitrooxon. Weinberger et al. (1982a) alkylated the polar fraction with ethereal diazoethane and Hallet et al. (1974) butylated DMF.

The detector of choice is the alkali flame ionization detector (AFID) which is nitrogen-phosphorous selective and also has good sensitivity. The electron capture detector has good sensitivity (5 pg fenitrothion) but is less selective. The flame photometric detector is phosphorous or sulphur selective but has poorer sensitivity (500 pg fenitrothion) and the flame ionization detector (FID) is the poorest in both categories of selectivity and sensitivity (50 ng fenitrothion) (Maguire and Hale 1980). Sensitivity and compound identification can also be improved for organophosphorous pesticides with the use of capillary columns (Greve and Goewie 1985).

Table XI: Gas-Liquid Chromatography Systems

| References | Column | Detector | Compounds (retention time) |
|---|---|---|---|
| Eidt 75 | 5% OV1 | FPD | F |
| Greenhalgh 76 | 3% SE 30 | AFID | F (3.7 min. = 1), FF (1.4), SMF (1.58), FO (0.84), FFO (1.22), MNP (0.31), HMF (2.48) |
| | 4% SE 30/6% QF-1 | AFID | F (3.5 min. = 1), FF (1.41), SMF (1.67), FO (1.12), FFO (1.82), MNP (0.29), HMF (2.06), |
| Greenhalgh 80 | 6% SE 30/4% QF-1 | AFID | F (5.6 min.), AF (4.1 min.) SMF (9.4 min.) |
| Grift 74 | 5% DC-200 | FPD | F (3.18 min. = 1) AF (0.91) |
| | 5% SE 30 | FPD | F (2.42 min.) |
| Hallet 74 | 4% SE 30/6% QF-1 | AFID | F (5.375 min. = 1), FO (1.186), MNP (0.244), SMF (1.860), AF (0.767) |
| Holmes 84 | 4% OV101/6% OV210 /3% OV17 | AFID | F |
| Krzymien 82 | Ultra-Bond 20M | AFID | F (3.5 min.) |
| Maguire 80 | 4% OV101/6% OV210 | ECD, FID, FPD | F, AF, FO |
| | Carbowax 20M | ECD, FID | MNP |
| Mallet 82 | 3.6% OV101/5% OVHO | FPD | F, AF |
| Metcalfe 80 | 3% OV 101 | ECD | F |
| Mount 85 | 3% PPE-6R | FID | F (16 min.) |
| | 7.5% OV 210 | FID | F |

| References | Column | Detector | Compounds (retention time) |
|---|---|---|---|
| Moody 78 | 4% SE 30/6% QF-1 | AFID | F, AF |
| | 3% SE 30 | AFID | F, AF |
| Morrison 83 | 3% Dexsil 300 | AFID | F |
| Ohkawa 74 | 10% SE 30 | FID | F |
| | 20% QF-1/10% DC-200 | FID | FO |
| Sergeant 79 | 3% OV 101 | FPD | F (8.1 min.) |
| | 11% OV 17/QF-1 | FPD | F (6.9 min.) |
| Spillner 79 | 10% OV 17 | FID | F (2.08 min.), MNP (3.40 min.) |
| Sundaram 74 | 5% OV1 | FPD | F (8.0 min.), FO (6.1 min.) |
| | 3.8% SE 30 | FPD | F FO |
| | 20% OV 101 | ECD | MNP (6.8 min.) |
| Sundaram 84 | 3% OV 17 | AFID | F (5.62 min.) |
| Weinberger 82a | 4% SE 30/6% QF-1 | AFID | F (5.85 min. = 1), AF (0.74), FO (1.1), SMF (1.72) |
| Weinberger 83 | 4% SE 30/6% QF-1 | AFID | F, AF, FF, MNP |
| Volpe 80 | 3.6% OV101/5% OV210 | FPD | F (8.1 min.), AF (4.4 min.), FO (8.4 min.), FF (14.4 min.), SMF (15 min.), HMF (21.3 min.) |
| Zitko 74 | 4% SE 30 | FPD | F, FO, AF |

F = fenitrothion, AF = amino-fenitrothion, FO = fenitrooxon,
SMF = S-methyl fenitrothion, FF = formyl fenitrothion,
FFO = Formyl Fenitrooxon, HMF = hydroxy methyl fenitrothion
MNP = 3-methyl-4-nitrophenol
FPD = Flame photometric detector, FID = flame ionization detector
AFID = alkali flame ionization detector, ECD = electron capture detector

## MATERIALS AND METHODS

### 1. ANALYTICAL STANDARDS

Fenitrothion ($^{14}$C-ring labelled, specific activity 73.7 uCi/mg) was provided by Sumitomo Chemical Company Limited. Fenitrothion, fenitrooxon (FO), S-methyl fenitrothion (SMF), and amino-fenitrothion (AF) were obtained from R. Greenhalgh (Agriculture Canada, Ottawa). The hydrolysis product 3-methyl-4-nitrophenol (MNP) was obtained from Aldrich Chemicals, St. Louis. Standards were prepared in ethyl acetate or methanol (all solvents were glass distilled (Caledon)).

### 2. EXPERIMENTAL DESIGN

Three small ponds (4.078 m x 2.6 m x 0.48 m depth) at Glenlea, Manitoba were used in the study. One pond was maintained as a control and one was shaded from direct sunlight with a shelter (5.3 m x 4 m x 1.5 m height) of black polyethylene (four mm thickness) erected two days prior to the start of the experiment. The shelter was open at the north end which allowed entry of reflected light and slits in the plastic allowed circulation of air. Sunlight intensities in the two ponds, (400-700 nm measured in micro Einsteins per meter squared second ($uE/m^2sec$)), and some chemical characteristics of the pond water are given in Table XII. The ponds were constructed one year prior to the experiment by covering a ten mL polyethylene liner with sand, (6 cm), silty clay sediment and clay based sod (10 cm). Sides of the ponds were formed with layers of sod over the plastic liner. Sediment at the time of the experiment had pH 7.6 and organic matter content of 4.9 and 5.2% in the shaded and unshaded ponds, respectively. The pond volumes of approximately 3550 and 3600 liters for the shaded and unshaded ponds,

Table XII Water chemistry parameters and light intensity in outdoor ponds following fenitrothion treatment - Year 2.

| Pond | Time (days) | pH | TSS[a] (mg/L) | Chloro (ug/L) | Susp. C (mg/L) | Light Intensity ($uE/m^2 sec$)[b] + 4 cm | - 15 cm |
|---|---|---|---|---|---|---|---|
| Shaded | 1 | n.s | 8 | 32.0 | 3.5 | 45 | 20 |
| Unshaded | | 8.06 | 10 | 97.0 | 8.0 | 1450 | 775 |
| Control | | 7.52 | 28 | 208.0 | 17.1 | -- | -- |
| Shaded | 14 | -- | -- | -- | -- | 30 | 14 |
| Unshaded | | -- | -- | -- | -- | 1700 | 800 |
| Shaded | 35 | 8.02 | 8 | 15.1 | 1.4 | 1300 | 750 |
| Unshaded | | 8.80 | 16 | 11.2 | 3.4 | 1550 | 800 |
| Control | | 7.94 | 9 | 37.8 | 4.89 | -- | -- |

a - TSS = Total suspended solids; Chloro = chlorophyll a; Susp. C = suspended carbon.

respectively, were maintained with spring melt and rain water from a large polyethylene lined dug-out. The ponds were eutrophic with abundant macrophytes (duckweed (Lemna minor), cattails (Typha sp.)). A bloom of filamentous green algae (Spirogyra sp.) occurred in the unshaded pond during Year 2. Fathead minnows (Pimephales promelas) were added to the ponds one week prior to the study each year.

The shaded and unshaded ponds were each treated on two consecutive years, (mid-day July 17, 1979 and again on June 24, 1980), with fenitrothion at a rate of approximately 165 g/ha, similar to commonly used rates of application (Symons 1977). The formulation consisted of fenitrothion (175 mg Year 1 and 163.4 mg Year 2; technical grade), $^{14}$C-fenitrothion (100 uCi, 1.36 mg, Year 1; 90 uCi, 1.22 mg, Year 2), and 33 mg Aerotex 3470, an aromatic hydrocarbon solvent, (Texaco Canada Ltd.) and 34 mg Atlox, a nonionic/anionic detergent, (Atlas Chemical Co.) in 500 ml of water. The formulation was stirred into the upper ten cm of the water column with a metal rod. Water (0-30 cm depth), sediment (0-3 cm depth cores), fish, duckweed, algae, cattail shoots (portion of the plant above sediment) and air were collected, once pre-treatment and at the various time intervals listed in Table XIII up to 77 days post-treatment. All samples except water were stored at -50°C in sealed containers until analysis.

## 3. ANALYTICAL METHODS

### a. Water

Depth integrated water samples (800-900 mL, duplicates) were collected by attaching a screw-cap, with inlet (6 mm i.d. glass) and outlet nozzles (6 mm i.d. U-tube), to a one liter amber glass sample bottle which was clamped to a metal rod and lowered slowly through the water column (0-30 cm depth). Methylene chloride ($CH_2Cl_2$) (10 mL) was

## Table XIII Sampling Schedule

x = Sample Taken

| Time | Water | | (Sediment - duckweed - cattails) | Air |
|---|---|---|---|---|
| | 1979 | 1980 | | |
| Pretreatment | x | x | x | x |
| 0.5 (hour) | x | | | |
| 1 | x | x | | |
| 2 | x | | | |
| 3 | | x | | |
| 4 | x | | | |
| 6 | | x | | |
| 8 | x | | | |
| 12 | x | x | | |
| 18 | x | | | |
| 24 | x | x | x | x |
| 36 | x | x | | |
| 48 | x | x | x | x |
| 3 (days) | x | x | x | x |
| 5 | x | x | x | x |
| 7 | x | x | x | x |
| 10 | x | x | x | x |
| 13 | x | x | x | x |
| 17 | x | x | x | x |
| 18 | | x | | x (1980) |
| 20 | | x | | x (1980) |
| 21 | x | x | x | x |
| 28 | x | x | x | |
| 35 | x | x | x | |
| 49 (1979) | x | | x | |
| 50 (1980) | | x | x | |
| 77 | x | x | x | |

added to the sample immediately after collection. The samples were transported to the laboratory in coolers and stored at 4°C until analyzed. The volume of each sample was measured and in 1980, two 1 mL samples were taken for LSC. Water samples were acidified with HCl to pH 2.0 and partitioned with $CH_2Cl_2$ (150, 75, 75 mL). The $CH_2CL_2$ extracts were dried by passage through a ten gram anhydrous sodium sulfate column (rinsed with $CH_2Cl_2$). The combined extracts were evaporated to a small volume on a rotary evaporator, transferred to a graduated centrifuge tube and evaporated under a nitrogen stream and taken up to an appropriate volume in ethyl acetate. Portions of the extract were analyzed by LSC and by GLC. The remaining extract was evaporated to a small volume, half applied to one TLC system, half to the other, and radioactivity detected by auto radiography.

**b. Sediment**

Samples were randomly taken (3 cm depth; 12-14 cores per pond) with a coring device and stored in two wide mouth glass jars (6-7 cores/jar) with aluminum foil lined caps. A portion of each sediment sample (0.5 g duplicates in 1979, triplicates in 1980) was combusted on a Packard 306 oxidizer (Packard Instruments, Chicago) and the $^{14}CO_2$ was collected in $CO_2$-M-Met (Amersham Corp., Oakville, Ontario) and analyzed by LSC. Samples (20 g wet weight) were refluxed with 150 mL acetonitrile-water (9:1) for 17 hours. The reflux mixture was then filtered under suction, rinsing the flask and filter cake four times with 25 mL acetonitrile. This was quantitatively transferred to a 500 mL round bottom flask, evaporated to approximately ten mL and transferred to a separatory funnel with glass distilled water, adjusting the volume to 50 mL (1 mL analyzed by LSC).

This was partitioned three times with 40 mL $CH_2Cl_2$, each extract passed through a ten gram anhydrous sodium sulfate column and the combined extracts concentrated to a small volume. Aliquots were assayed by LSC to determine total extractable radioactivity. Some extract duplicates were combined and evaporated under a $N_2$ stream to dryness. One mL MeOH-$H_2O$ (9:1) was added to the residue, sonicated, and loaded onto a pre-rinsed reverse phase ($C_{18}$) Sep Pak (Waters Associates, Mississauga, Ont.). Any residue left in the test tube was sonicated with 0.5-1 mL MeOH-$H_2O$ (9:1) and loaded onto the Sep-Pak. MeOH-$H_2O$ (9:1) was forced through the Sep-Pak with the first 3.5 mL collected and analyzed by HPLC. Unextractable radioactivity in sediment was determined by combustion of a small portion of the extracted sediment filter cake. In 1980, selected samples of combined duplicate filter cakes were also re-extracted by refluxing 17 hours with 150 mL 1N HCl. These were filtered, rinsed twice with 30 mL 1N HCl and once with 30 mL $H_2O$. The filtrate was transferred to a separatory funnel and partitioned with $CH_2Cl_2$ (100, 50 and 50 mL). The combined extracts (dried by passage through a sodium sulfate column) were evaporated to an appropriate volume and portions analyzed by LSC. The aqueous phase was further adjusted with NaOH to pH 10 and extracted once with 75 mL $CH_2Cl_2$. An evaporated aliquot was analyzed by LSC.

**c. Aquatic Plants**

Duckweed was sampled from the pond surface using a sieve (1 mm openings) and stored in glass jars. Cattail stalks were cut off at the base (sediment) and at the water surface. These were further cut into small pieces and stored in glass jars. Before analysis, the entire sample was homogenized in a small Waring blender. Portions

(0.5 g wet weight) of each sample (duckweed and cattails) were combusted (duplicate 1979, triplicate 1980) and $^{14}CO_2$ activity obtained by LSC. Dry weight of plants was determined by air drying (three days) to a constant weight.

Twenty grams wet weight, of duckweed was extracted with either 160 or 200 mL MeOH at low speed for ten minutes in a Waring blender. The macerate was filtered under suction, washed three times (40 mL MeOH), evaporated to five to ten mL and transferred with water to a separatory funnel. The volume was adjusted to 50 mL and extracted with $CH_2Cl_2$ as described for sediment. Aliquots of the extracts were either directly analyzed by LSC or combusted and the $^{14}CO_2$ activity analyzed. Selected aqueous phases were acidified to pH 2 and partitioned twice with 35 and 25 mL $CH_2Cl_2$, dried and evaporated to a small volume for analysis. Plant extracts were cleaned up using $C_{18}$ Sep Paks (MeOH-$H_2O$, (9:1)) as described for sediments. Aliquots of the fractions collected were analyzed by LSC. In 1980 some of these fractions were analyzed by TLC. The MeOH - $H_2O$ (in a graduated centrifuge tube) was evaporated to water (approximately 0.3 mL), adjusted to 1 mL $H_2O$ and extracted four times with ethyl acetate (3, 3, 2, and 1 mL) using a vortex test tube mixer. The extracts were dried on a mini sodium sulfate (1 g) column, combined, and evaporated to a small volume and applied to TLC plates, developed by solvent System I and analyzed by autoradiography.

The same procedure used for duckweed was used for cattails except that five mL of water was added at the blending stage due to the cattails lower water content. The filamentous algal bloom that occurred in the unshaded pond in 1980 was sampled (day 13 to day 35) with the sieve and stored in glass jars. Portions (0.5 g wet weight) in

triplicate were combusted and $^{14}CO_2$ activity counted.

**d. Fish**

Three minnows were collected from each pond at each sample time with a minnow trap baited with dog biscuits (various flavours), and stored in plastic (Whirlpak) bags. Whole fish (average weight three grams) were rinsed with water and homogenized by either chopping and mixing with a large knife (1979) or with a K-tel Salad Chef (a zig zag stainless steel blade within a round plastic housing that is depressed by a spring loaded shaft which automatically rotates the blade about 5° when released - 1980). Subsamples (0.5 g) in triplicate were combusted and $^{14}CO_2$ activity analyzed by LSC.

**e. Air**

Polyurethane foam plugs (open cell - 55 x 45 mm diameter) were prepared for use by Soxhlet extraction with hexane-acetone (1:1) for 84 hours. The foam plugs were placed in glass tubes located above the center of each pond. The tubes were located ten cm above each pond (Year 1) or at two, five and ten cm heights (Year 2). Air flows were maintained at ten L/min (measured at the tube entrance). Sampled foams were placed in wide-mouth glass jars with Teflon lined screw caps and ten mL hexane was immediately added. Extraction was carried out as soon as possible. This involved a two hour Soxhlet extraction with 250 mL hexane-acetone (95:5). These extracts were evaporated to appropriate volumes and assayed by LSC and GLC.

**f. GLC, TLC, HPLC and LSC Conditions**

GLC was carried out with a Tracor 560 or Perkin Elmer gas chromatograph, both equipped with nitrogen-phosphorus detectors. Columns (2 mm i.d. x 1.8 m) containing 3% OV-17 on Chromosorb W-HP

(80/100 mesh) were operated at a 30 mL/min. carrier gas flow. The operating temperatures were: 1) injection port, 200°C, 2) oven, 200°C and, 3) detector, 250°C, for analysis of fenitrothion and AF. MNP was chromatographed on a column of 1% SP-1240 DA on Supelcoport 100/120 mesh at an oven temperature of 190°C. Chromatograms (1979) were displayed on a strip chart recorder while 1980 results were displayed on an SP-4100 integrator-recorder (Spectra Physics). Quantitation used an external standard and peak heights for the strip chart results and integrated areas on the SP-4100.

HPLC separations were carried out with a reverse phase 25 cm x 4.5 mm i.d. column (uBondapak-$C_{18}$) using methanol-water (45:55) at 1.8 mL/min. for 13.5 min. followed by methanol-water (60:40) for 20 minutes. A Waters 6000A pump, Model 440 fixed wavelength UV detector (254 nm) and a fraction collector (LKB Multirac) were used. Fractions eluting from the column were collected and assayed by LSC. Retention times of Fenitrothion, AF and MNP under these conditions were 27.0, 11.0, and 7.5 minutes, respectively.

TLC separations were performed on silica gel plates, 20 x 20 cm, 0.25 mm layer, (Camag-1979, Merck 60-1980) using two solvent systems (out of 16 tested - Appendix 1). System I was toluene-ethyl formate-formic acid (5:7:1) (Takimoto et al. 1976) and System II was carbon tetrachloride-methylene chloride-methanol (5:7:1). Autoradiography was carried out by exposing TLC plates to X-ray film (Kodak NS-2T) for up to one month. Radioactive spots were scraped and extracted with methanol to establish the quanitity of each degradation product by LSC. Rf's (fenitrothion = 1) of AF, MNP, FO and SMF were 0.22, 0.76, 0.53 and 0.73 on System I and 0.83, 0.66, 0.77 and 0.60 on

System II.

All LSC samples were counted on a Beckman 7500 scintillation counter for ten or twenty minutes. Blanks of all materials were used to determine background counts. Three scintillation cocktails (12 to 14 mL) were used with glass scintillation vials. Organic extracts used PCS (Amersham) - Xylene (2:1), aqueous samples were mixed with Aquasol and, as previously stated, combusted $^{14}CO_2$ was collected in $CO_2$-M-Met.

**g. Statistical Analysis**

All half-lives are calculated from first-order decay curves (ln concentration vs time (days)). Appendix 2a follows an example calculation of the linear regression fit of fenitrothion disappearance in unshaded conditions (1980). The concentration value is multiplied by 100 before the natural log is taken to avoid negative values from low concentrations. The half-life is calculated from the equation;

t 1/2 = 0.693/Slope.

The significant differences between first order rate constants (0.05 level of significance) in shaded and unshaded ponds were assessed using using the t-test. The student's t is calculated using the equation;

$$t = \frac{\text{difference in slopes (rates)}}{\text{standard error of difference}}$$

The factors needed are obtained from the respective linear regression equations. For example, in fenitrothion decay between unshaded and shaded conditions, student's t = 15.97, the critical value, (76 degrees of freedom), for significance, P = 0.05, is 2.00. The same student's t calculation was used to determine significance differences (P = 0.05) between rate constants observed each year within treatments (shaded or

unshaded).

## RESULTS AND DISCUSSION

### 1. WATER

Fenitrothion disappeared rapidly from unshaded ponds decreasing to 0.01 ug/L from an initial level of 70 ug/L (Year 1) or 60 ug/L (Year 2) within ten to thirteen days each year (Fig. IX and Appendix 2). In shaded water, fenitrothion levels decreased more slowly, reaching 0.01 to 0.02 ug/L by about 17 days each year (Fig. X). Half-lives of fenitrothion calculated from first-order decay curves (ln concentration versus time (days)) were significantly greater in shaded treatments each year (Table XIV). The half-lives observed were within the range found elsewhere in field studies in ponds and small lakes (Symons 1977).

The data for Table XIV and the Fig. IX and X was obtained from the combination and averaging of the two TLC systems used (Appendix 2.a.). The group of "other products" include all unidentified metabolites so there is no discrimination in the different Rfs or number of spots per system. Appendix 2.c. gives examples of the two TLC systems, relating fenitrothion and each metabolite as a percentage of the total radioactivity available. The GLC results reported in Appendix 2.b. agree well with the fenitrothion results of Table XIV and reveals the same information through the half lives of 1.36 days (Year 1) and 1.67 days (Year 2) in the shaded ponds and 0.87 days (Year 1) and 1.09 days (Year 2) in the unshaded ponds.

The cover over the shaded pond was removed at 17 days

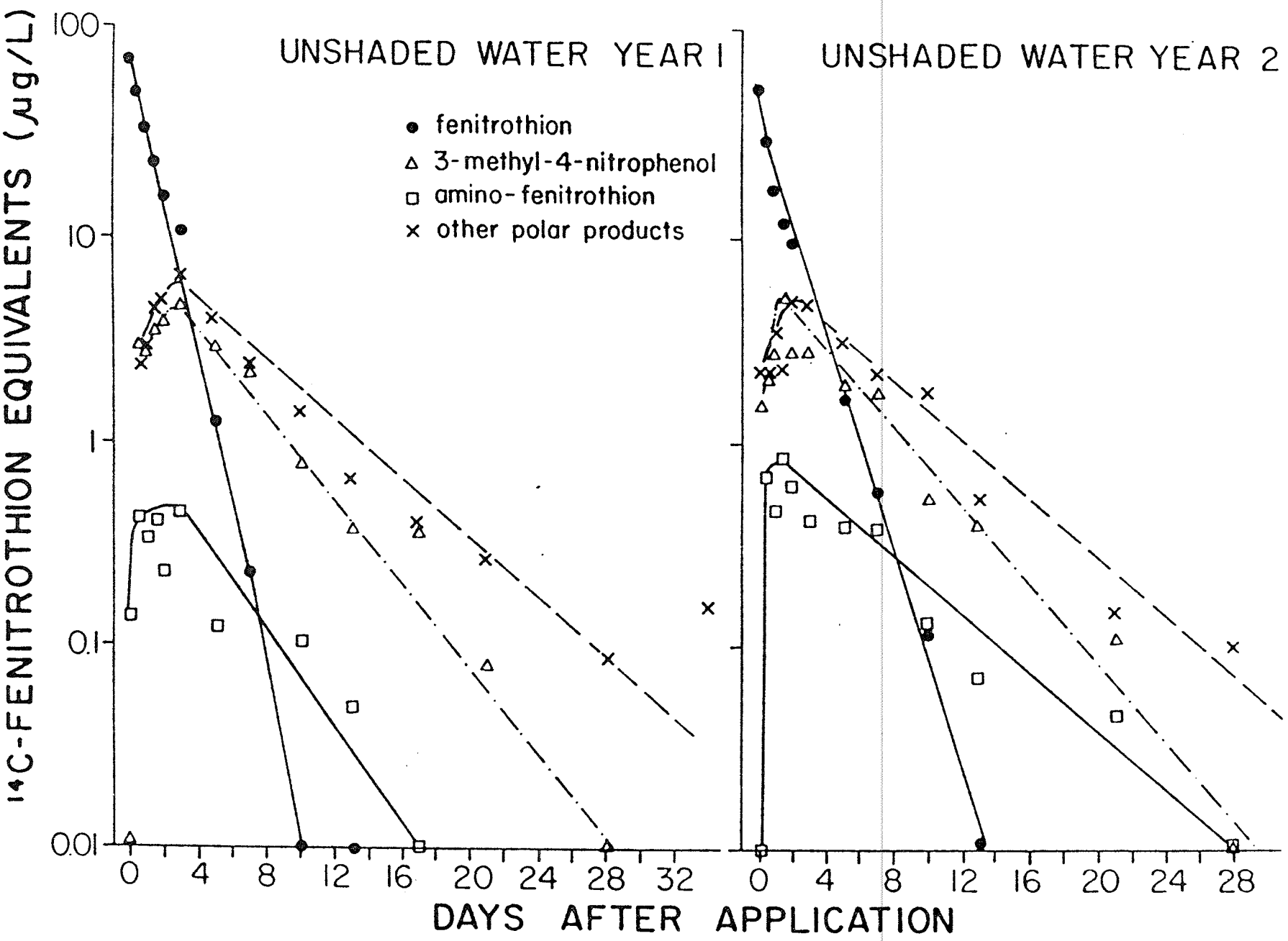



Figure IX Disappearance of fenitrothion and degration products in unshaded pond water following addition of the insecticide each year

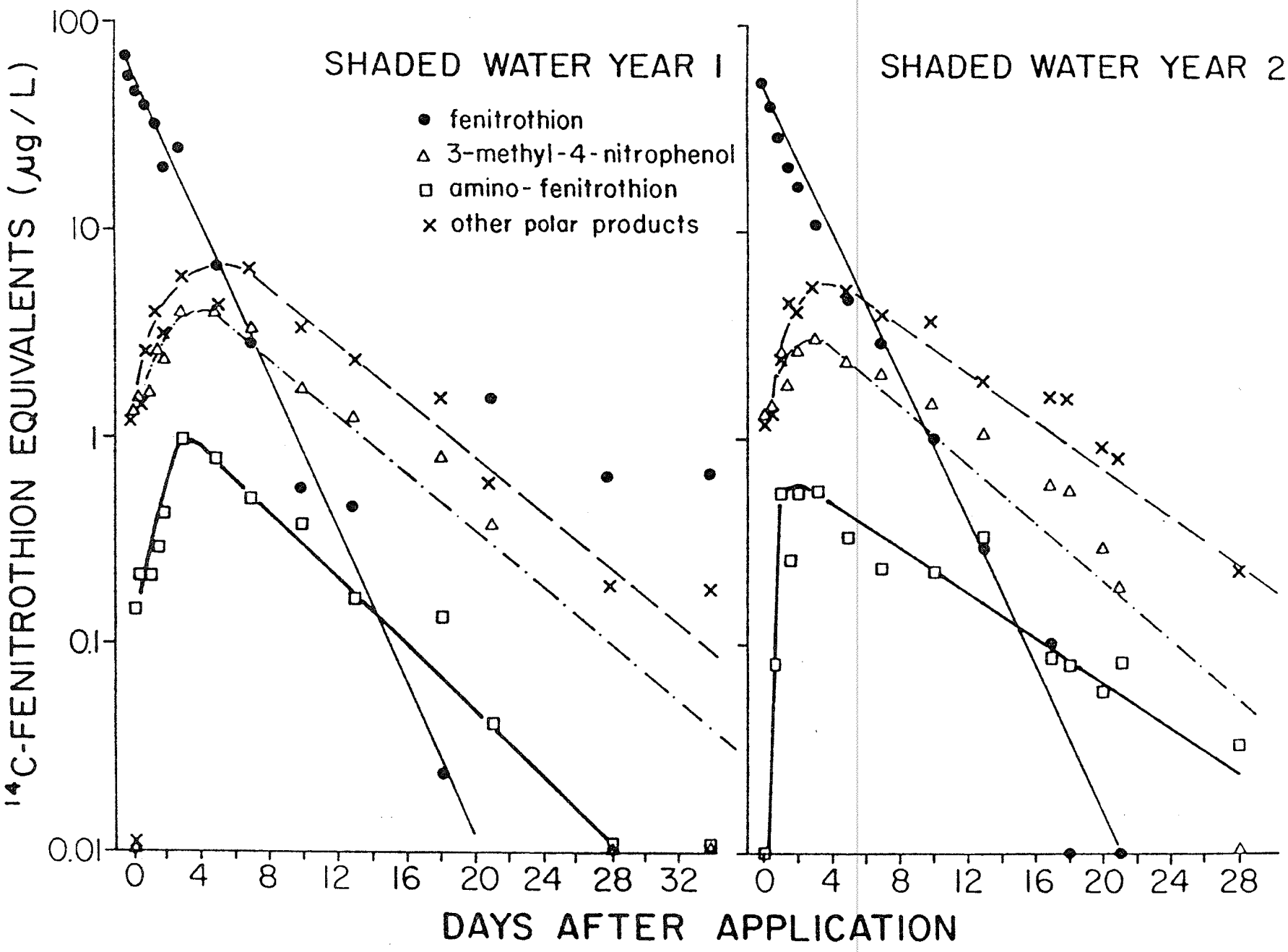



Figure X Disappearance of fenitrothion and degradation products in shaded pond water following addition of the insecticide each year.

**Table XIV** Half-lives (t 1/2) of fenitrothion and degradation products in pond water - Year 1 and 2.

| Compound | Condition | Time interval (days) Year 1 | Time interval (days) Year 2 | t 1/2 (days) + CL Year 1 | t 1/2 (days) + CL Year 2 |
|---|---|---|---|---|---|
| Fenitro-thion | S | 0-17 | 0-18 | 1.56 ± 0.12 | 1.70 ± 0.14 |
| | U | 0-10 | 0-17 | 0.79 ± 0.05* | 1.22 ± 0.08*@ |
| MNP | S | 3-28 | 3-28 | 2.93 ± 0.75 | 3.51 ± 0.54@ |
| | U | 3-28 | 1.5-21 | 2.94 ± 0.24 | 3.69 ± 0.32@ |
| AF | S | 3-28 | 3-28 | 3.80 ± 0.25 | 6.54 ± 0.91@ |
| | U | 3-17 | 1.5-28 | 3.62 ± 2.68 | 4.42 ± 0.49* |
| Other products | S | 3-28 | 3-35 | 4.97 ± 0.59 | 5.42 ± 0.38@ |
| | U | 3-28 | 2-35 | 4.13 ± 0.32* | 4.98 ± 0.66*@ |
| Total $^{14}C$ | S | 0-28 | 0-35 | 4.44 ± 0.48 | 4.03 ± 0.15@ |
| | U | 0-28 | 0-35 | 2.97 ± 0.26* | 3.64 ± 0.37*@ |

* indicates significant differences between first order rate constants (0.05 level of significance) in shaded and unshaded ponds using the t-test.
@ indicates significant differences (p = 0.05) between rate constants observed each year within treatments (shaded or unshaded) using the t-test.
"other products" refers to all unidentified spots on TLC plates.

post-treatment in the first year because of damage from a rainstorm. Removal coincided with an unexplained increase in fenitrothion concentrations (Fig. X). This increase was not observed in Year 2 when the shade was removed at the same time (Fig. X). It is possible that disturbance of the water and the sides of the pond by the storm may have released sediment and plant-associated fenitrothion back into the water column. Our initial speculation after Year 1 was that there may be a sunlight-induced release mechanism from the plants. The levels of the degradation products did not increase proportionately though at the level of approximately one ug/L fenitrothion, metabolite detection would be close to its limit.

Fenitrothion was extracted efficiently with $CH_2CL_2$. In the initial time period immediately following pesticide application (one hour), extraction efficiency of radioactivity was 93.8%. This extract is greater than 99% fenitrothion according to TLC results.

3-Methyl-4-nitrophenol (MNP) was the major degradation product identified in water extracts in the unshaded ponds reaching a maximum of 4.38 ug/L ($^{14}C$-fenitrothion equivalents) on day three (Year 1). By day 7 MNP represented 64.4% of the extractable $^{14}C$ and at day 21 still represented 47% of the extractable $^{14}C$. These were the highest levels achieved by any single degradation product (both years) In Year 2, MNP reached a maximum concentration of 2.73 ug equivalents /L at 36 hours and represented 44% of extractable $^{14}C$ on day 13. MNP was not detected at 28 days in either year in the unshaded ponds. MNP was also a major product under shaded conditions during the first 13 days each year but declined to less than 20% of extractable $^{14}C$ by 21 days

Table XV Total Radioactivity in Water as $^{14}C$-Fenitrothion Equivalents (ug/L)

| Time | covered 1979 Extract | covered 1980 Prior to Extraction | covered 1980 Extract | covered % Extracted | uncovered 1979 Extract | uncovered 1980 Prior to Extraction | uncovered 1980 Extract | uncovered % Extracted |
|---|---|---|---|---|---|---|---|---|
| .5 hr. | 82.52 | | | | 69.75 | | | |
| 1 hr. | 70.29 | 58.37 | 54.40 | 93.2 | 72.04 | 60.34 | 56.89 | 94.3 |
| 2 hr. | 68.78 | | | | 71.39 | | | |
| 3 hr. | | 53.47 | 50.27 | 94.0 | | 54.78 | 47.48 | 86.7 |
| 4 hr. | 64.69 | | | | 58.94 | | | |
| 6 hr. | | 50.77 | 48.14 | 94.8 | | 49.87 | 40.87 | 81.9 |
| 8 hr. | 59.04 | | | | 50.54 | | | |
| 12 hr. | 54.3 | 48.07 | 42.45 | 88.3 | 44.36 | 41.04 | 34.77 | 84.7 |
| 18 hr. | 54.16 | | | | 43.70 | | | |
| 24 hr. | 46.72 | 37.03 | 33.67 | 90.9 | 40.54 | 36.54 | 23.96 | 65.6 |
| 36 hr. | 40.38 | 36.87 | 28.22 | 76.5 | 30.94 | 33.03 | 20.26 | 61.3 |
| 48 hr. | 35.90 | 32.29 | 24.10 | 74.6 | 24.69 | 30.41 | 18.12 | 59.6 |
| 3 days | 36.90 | 34.66 | 19.63 | 56.6 | 22.74 | 28.20 | 12.05 | 42.7 |
| 5d. | 16.00 | 22.73 | 12.22 | 53.8 | 7.36 | 19.05 | 7.14 | 37.5 |
| 7d. | 11.95 | 16.19 | 9.12 | 56.6 | 4.79 | 17.74 | 5.17 | 29.1 |
| 10d. | 6.01 | 15.6 | 6.43 | 41.2 | 2.28 | 9.4 | 2.7 | 28.7 |
| 13d. | 4.09 | 12.75 | 3.58 | 28.1 | 1.09 | 7.11 | 1.03 | 14.5 |
| 17d. | 2.52 | 7.03 | 2.35 | 33.4 | 0.727 | 5.80 | 0.58 | 10.0 |
| 17+21 hr. | | 7.44 | 2.24 | 30.1 | | | | |
| 20d. | | 3.11 | 1.27 | 40.8 | | | | |
| 21 | 2.62 | 3.68 | 1.05 | 28.5 | 0.359 | 5.15 | 0.310 | 6.0 |
| 28 | 0.85 | .08 | .25 | | 0.086 | 1.80 | 0.11 | |
| 35 | 1.72 | 0. | .10 | | 0.160 | 0. | 0.08 | |
| 49(50) | .108 | | .22 | | 0.464 | | 0. | |
| 77 | .007 | | .10 | | 0. | | | |

(Fig.X). The maximum levels of MNP (2.81 and 2.03 ug equivalents/L, Year 1 and Year 2) were reached both years at 36 hours. Under shaded conditions MNP was not detected at 28 days. Amino-fenitrothion (AF) was also detected with maximum levels at about one ug equivalent/L (shaded and unshaded). AF generally represented less than 10% of the extractable $^{14}C$ in all systems though in shaded conditions (Year 2) it was 28% after 28 days . This was also the only time it was detected at 28 days post treatment. AF is more efficiently extracted at higher pHs (Maguire and Hale 1980) than at pH 2, therefore the levels achieved by AF in water may actually be underestimated. With the extraction system used, AF probably represents a portion of the unextractable $^{14}C$ left in water (Table XV).

Up to seven other unknown degradation products (Year 2 - including immobile material at Rf=0) were observed (TLC). Two major unknown products having Rfs of 0.48 and 0.44 were found in water under both shaded and unshaded conditions. An additional product which had an Rf of 0.40 (TLC System I) was found under shaded conditions. Maximum levels (ug equivalents/L) for shaded and unshaded conditions were; 1.64 (36 hours) and 1.28 (9 hours), respectively, for the compound at Rf 0.48, 1.40 (five days) and 0.85 (three days), respectively, for the compound at Rf 0.44. The maximum level of the product at Rf 0.40 was 0.52 ug/L. The product at RF = 0.48 was not detected after 17 days in shaded conditions and after ten days in unshaded conditions. The metabolite at Rf 0.44 was detected for up to 28 days (shaded) and represented a maximum of 39.3% of extractable $^{14}C$ at 17 days (shaded). It was not detected after 17 days in unshaded conditions. The product at Rf 0.40 was detected a few times in unshaded conditions during the first three days post-treatment, while in shaded conditions it was detected up to 28 days and at maximum represented

45% of the extractable $^{14}C$ at 21 days. In TLC System II, one major unidentified product (Rf = 0.37) was observed along with significant material at the origin (RF=0). Levels (ug equivalents/L) for the product at Rf 0.37 reached 1.19 (seven days) and 0.65 (two days) under shaded and unshaded conditions, respectively, while the material at the origin reached 1.19 (three days) and 1.29 (two days). Both products were present at 28 days in shaded conditions but were both undetectable after 17 days under unshaded conditions. The product at Rf 0.37 reached a maximum of 48% (shaded) of extractable $^{14}C$ on day 18. The material at maximum Rf 0 represented 45.6% at day 17 in unshaded conditions. The relatively low concentrations of the unknowns prevented further identification. These compounds did not have the Rfs of FO or SMF; however, their TLC mobility in System I was similar to carboxy fenitrothion and DMF (Takimoto et al. 1976). Both of these compounds have been previously identified in natural waters (Weinberger et al. 1982a). The radioactivity which is immobile in System II may have consisted of DMF, which is immobile in non-acidic TLC solvent systems (Takimoto et al. 1976), as well as other polar products such as desmethyl amino fenitrothion. The concentrations of all the unidentified products were summed and plotted in Fig. IX and X as "other products". These products represent about 75% of the extractable radioactivity in extracts at 21 days in the covered pond and about 53% at 21 days in the uncovered pond.

Amino-fenitrothion (AF) and "other products" disappeared more rapidly in unshaded than in shaded water in both Years 1 and 2 (Table XIV) while MNP showed no significant differences although it decreased overall more rapidly in the first year of the study. Maximum concentrations of MNP and "other products" were observed at two to three

days post-treatment each year and were higher in unshaded water. However, degradation of MNP and "other products" was slower in shaded ponds so that by 17 days higher levels of these products were present in shaded water than unshaded water.

Much of the radioactivity in the water samples (Table XV) was unextractable with methylene chloride (pH 2) within 48 hours after treatment (25% shaded; 41% unshaded). Unextractable radioactivity increased to 71.5% (shaded) and 94% (unshaded) by 21 days. The identity of this unextractable material was not investigated because of the low levels. Weinberger et al. (1982a) have reported similar high proportions of unextractable $^{14}C$ (about 70% at 20 days) in lake water and identified carboxy amino-fenitrothion in the "polar" fraction. DMF and desmethyl amino-fenitrothion are also possible components of the aqueous phase since like other phosphate diesters they are not efficiently extracted into organic solvents at acid pH (Greenhalgh 1981).

The longer half-lives of fenitrothion and degradation products under shaded conditions indicates the importance of photolysis in the disappearance of the insecticide from shallow water bodies (Symons 1977). However, the differences in half-lives were less than 2-fold compared to about 30-fold greater light intensity (in the visible range) with unshaded conditions (2 cm depth, Table XII). According to Zepp and Cline (1977) photolysis rate (dP/dt) is directly related to sunlight intensity at each wavelength $I_y$ (290 to 400 nm)
$dP/dt=\Phi(P)\ E\ I_y\ e_y$ where $\Phi$= quantum yield, (P)= concentration of pollutant and $e_y$= molar absorptivity. However our sunlight intensities were obtained over 400 nm. Intensity in the uv range may not have been 30 fold higher because of the higher proportion of uv in reflected light.

## 2. SEDIMENT

The extraction procedure for sediment was tested with pre-treatment samples (Year 1) from both ponds. The first spiked samples (4.8 ug/kg fenitrothion) were allowed to stand for 15-30 minutes, then refluxed with acetonitrile for two hours. This produced recoveries of 112% and 105% for the shaded and unshaded ponds. An additional study of this method allowed the spiked samples to stand for one and three days before extraction, producing recoveries of 98% and 64% for the shaded pond and 97% and 87% for the unshaded pond sediment. In actual Year 1 sediment samples, recovery of total $^{14}C$ declined even more rapidly than the previous lab study indicated. The recoveries for day one samples were 88% and 68% for the shaded and unshaded ponds, falling rapidly by day five to about 35% and 40%, respectively. Later samples (days 28, 49 and 77) had the additional 17 hour reflux with acetonitrile-water (Table XVI).

**Table XVI Extraction Efficiency of $^{14}C$ from Sediment (Year 1)**

| Time (days) | 2 Hour Reflux (% extracted) | 17 Hour Reflux (% more extracted) | [a]Total % Extracted |
|---|---|---|---|
| | Shaded Pond | | |
| 28 | 42.0 | 57.8 | 66.8 |
| 49 | 39.6 | 20.8 | 47.8 |
| 77 | 32.5 | 50.0 | 48.7 |
| | Unshaded Pond | | |
| 28 | 31.4 | 23.3 | 38.7 |
| 49 | 37.3 | 34.1 | 50.0 |
| 77 | 14.7 | 43.2 | 21.0 |

[a]determined by combustion of filter cakes after second reflux.

With the significant improvement in recoveries from the second 17 hour reflux, Year 2 samples omitted the two hour reflux, all undergoing the 17 hour acetonitrile-water reflux with similar extraction efficiencies (Table XVII) as Year 1 samples (Table XVI). For an additional increase in recoveries of bound residues, a 17 hour acid reflux (1 N HCl) was performed on selected Year 2 samples (Tables XVII). The increase in recoveries in the pre-treatment sediments is quite significant with 82% and 77% more $^{14}C$ extracted. The other sediment samples had an average increase in extraction of about 20%.

The Sep Pak clean-up before HPLC was not 100% efficient largely because of restrictions in the volume of methanol-water that could be collected because of the break-through of interfering compounds. The average recovery of $^{14}C$ for the 0-3.5 mL fraction was 87% (low 57.1%, high 94.9%). The initial tar residue of three samples could not be totally dissolved and transferred in the two steps provided in the method. Solvent volumes used in the transfer could not be increased because of band broadening of compounds throughout the Sep Pak. These samples had reduced efficiencies of 49%, 63%, and 69% (day 13 and 5-shaded, day 13-unshaded, respectively).

In Year 1, $^{14}C$ fenitrothion reached maximum concentrations in sediment within five days post-treatment (Table XVIII; Fig. XI). The levels achieved represented 19% (unshaded) and 10% (shaded) of the $^{14}C$ initially applied to the ponds (Fig. XI). These levels were calculated from a three cm depth-volume of $3.83 \times 10^5$ $cm^3$ and a 1.38 $g/cm^3$ bulk density (shaded) and $4.04 \times 10^5$ $cm^3$ and a 1.27 $g/cm^3$ bulk density (unshaded). After 77 days, levels had declined to about 60% and 30% of the maximum in unshaded and shaded ponds, respectively. The

**Table XVII Concentration of fenitrothion and major degradation products in sediment extracts - Year 2 determined by HPLC analysis.**

| Time (days) | Extractable[a] (%) | ug/kg (dry wt) as fenitrothion equivalents | | | |
|---|---|---|---|---|---|
| | | Fenitro | AF | MNP | polar pdts[b] |
| Shaded | | | | | |
| Pre- | 47.7 (86.8) | -- | -- | -- | -- |
| 1 | 65.4 (74.0) | 8.0 | 82.0 | 7.4 | 28.0 |
| 2 | 76.9 | 7.6 | 49.6 | 3.8 | 13.0 |
| 3 | 61.1 (75.0) | -- | -- | -- | -- |
| 5 | 70.1 | 4.2 | 59.0 | 6.4 | 22.2 |
| 10 | 54.7 (65.7) | 4.2 | 28.4 | 4.8 | 54.0 |
| 13 | 64.2 | 9.0 | 26.8 | 4.2 | 40.2 |
| 21 | 58.4 (69.0) | 0.5 | 32.0 | 4.4 | 29.6 |
| 50 | 56.8 (72.7) | 0.5 | 36.8 | 0.5 | 13.4 |
| Unshaded | | | | | |
| Pre- | 23.2 (41.0) | -- | -- | -- | -- |
| 1 | 68.9 (74.0) | 32.4 | 100.8 | 28.0 | 60.0 |
| 3 | 59.6 (76.3) | -- | -- | -- | -- |
| 5 | 54.8 | 9.4 | 118.2 | 17.0 | 37.2 |
| 10 | 47.0 (54.3) | 0.5 | 49.2 | 8.0 | 67.0 |
| 13 | 37.6 | 13.2 | 38.6 | 14.6 | 63.0 |
| 21 | 23.5 (29.4) | 1.6 | 25.2 | 0.5 | 33.4 |
| 50 | 30.1 (38.2) | -- | -- | -- | -- |

a - extractable with a single 17 hour acetonitrile-water reflux. Results in parentheses indicate % extractable from the sediment residuum after additional extraction with 1N HCl.

b - other polar products which eluted (as radioactive peaks) in the solvent front under the conditions used in HPLC analysis.

Figure XI $^{14}C$ levels in Sediment

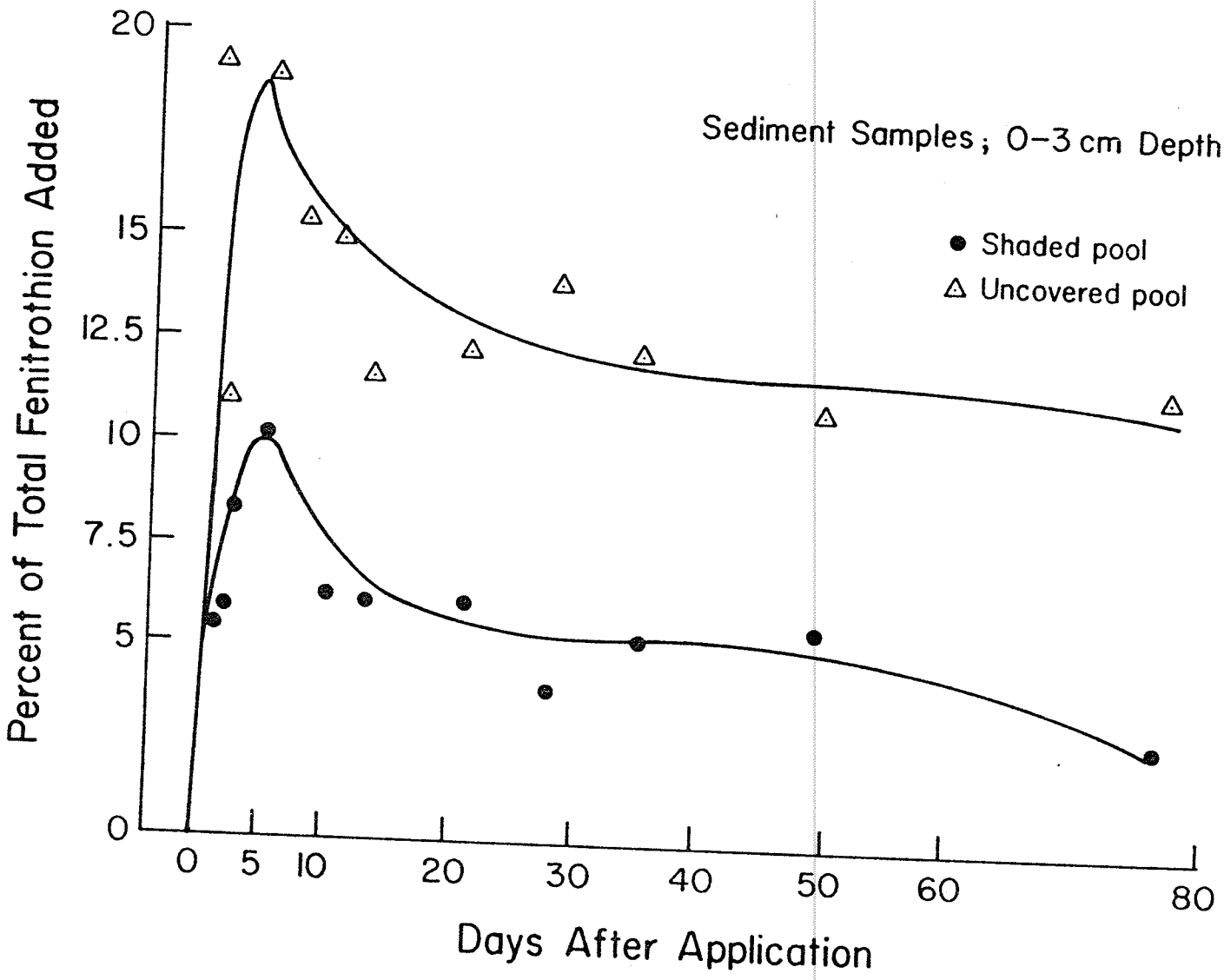


**Table XVIII** **Total radioactivity[a] expressed as fenitrothion equivalents (ug/kg) in various compartments of each pond during a two year study.**

| Time/year | Pond | Total fenitrothion concentrations (ug/kg)[b] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | water | sediment | duckweed | cattails | fish | algae | air[c] |
| Year 1 | | | | | | | | |
| Pre-treat | S | <0.01 | <0.5 | <100 | <10 | <10 | -- | <0.001 |
| | U | <0.01 | <0.5 | <100 | <10 | <10 | -- | <0.001 |
| 1 hour | S | 70.3 | -- | | | | | |
| | U | 72.0 | -- | | | | | |
| 12 hours | S | 54.3 | -- | | | | | |
| | U | 44.4 | -- | | | | | |
| 24 hours | S | 46.7 | 34.0 | 17471 | 578 | 3320 | -- | 0.098 |
| | U | 40.5 | 131.6 | 12343 | 355 | 4919 | -- | 0.020 |
| 2 days | S | 35.9 | 37.6 | 17171 | 360 | 3113 | -- | 0.028 |
| | U | 24.7 | 74.1 | 19886 | 820 | 2166 | -- | 0.004 |
| 5 days | S | 16.5 | 66.2 | 17800 | 454 | 1517 | -- | 0.010 |
| | U | 7.36 | 128.6 | 23486 | 498 | 690 | -- | 0.009 |
| 10 days | S | 6.01 | 40.0 | n.s. | 1783 | 491 | -- | 0.002 |
| | U | 2.28 | 98.8 | 17200 | 2188 | 340 | -- | 0.001 |
| 21 days | S | 2.62 | 39.4 | 13829 | 773 | 176 | -- | <0.001 |
| | U | 0.36 | 82.0 | 8657 | 804 | 363 | -- | <0.001 |
| 35 days | S | 1.72 | 33.0 | 2971 | 208 | 178 | -- | -- |
| | U | 0.16 | 83.4 | 5000 | 1104 | 264 | -- | -- |
| 77 days | S | 0.01 | 19.6 | 2429 | 96 | 224 | -- | -- |
| | U | <0.01 | 80.0 | 1900 | 77 | 263 | -- | -- |
| Year 2 | | | | | | | | |
| Pre-treat | S | <0.01 | 81.8 | <100 | 213 | <10 | <10 | <0.001 |
| | U | <0.01 | 146.4 | <100 | 213 | <10 | <10 | <0.001 |
| 1 hour | S | 58.4 | -- | -- | -- | | | |
| | U | 60.3 | -- | | | | | |
| 12 hours | S | 48.1 | -- | -- | -- | 1827 | | |
| | U | 41.0 | -- | -- | -- | 3053 | | |
| 24 hours | S | 37.0 | 192.4 | 14243 | 2334 | 1198 | -- | 0.048 |
| | U | 36.5 | 321.8 | 5757 | 1417 | 931 | -- | 0.049 |
| 2 days | S | 32.3 | 96.2 | 11600 | 3367 | 1536 | -- | 0.028 |
| | U | 30.4 | 271.2 | 9229 | 320 | 1176 | -- | 0.014 |
| 5 days | S | 22.7 | 131.4 | 17129 | 511 | 796 | -- | 0.004 |
| | U | 19.1 | 347.2 | 13143 | 658 | 569 | -- | 0.009 |
| 10 days | S | 15.6 | 166.6 | 21529 | 2122 | 692 | -- | 0.001 |
| | U | 9.40 | 263.6 | 12686 | 833 | 336 | -- | <0.001 |
| 21 days | S | 3.68 | 113.0 | 6600 | 692 | 366 | -- | 0.001 |
| | U | 0.36 | 255.4 | 7114 | 272 | 432 | 8236 | 0.001 |
| 35 days | S | 0.10 | 85.4 | 1900 | 1202 | 148 | -- | -- |
| | U | 0.08 | 141.6 | 2657 | 77 | 482 | 4427 | -- |
| 77 days | S | <0.01 | 87.4 | 686 | 24 | 229 | -- | -- |
| | U | <0.01 | 143.2 | n.s. | 85 | 240 | -- | -- |

a - Determined by combustion of sediment, duckweed, cattail, fish and algae sub-samples and by direct assay of water samples using LSC. Average of duplicates (water or triplicate analyses (all others except air).

b - All results are expressed on a dry weight basis except fish (fresh wt whole fish). Water content: Sediment (50%), duckweed (93%), Cattails (75-90%).

c - Air results as ug/$m^3$ averages at 10 cm height over time interval.

maximum levels achieved in Year 2 were 31% (day five) and 13% (day ten) in unshaded and shaded conditions (pre-treatment subtracted). These levels, though higher than in Year 1, declined more rapidly and after 35 days levels were similar to those observed in pre-treatment samples (Table XVIII). Levels of radioactivity were consistently higher in the sediment of unshaded ponds. The greater productivity under unshaded conditions which was evident from larger duckweed biomass, higher concentrations of suspended solids, chlorophyll and suspended carbon (Table XII), may have resulted in the deposition of more $^{14}C$ fenitrothion on the bottom of the unshaded pond in falling detritus during the first 17 days. Higher levels of radioactivity were observed at 350 days post-treatment (pre-treatment Year 2, Table XVIII) in both ponds than at 77 days due to deposition of duckweed and other plants from the previous summer. Sedimentation has been demonstrated to be an important mode of loss of hydrophobic compounds from the water column in aquatic systems (Hamelink and Waybrant 1976). However, in the present study the exact quantity of deposition was not measured.

Amino-fenitrothion was the major degradation product in sediment representing 64% and 62% of extractable radioactivity in shaded and unshaded ponds, respectively, after five days (Table XVII). After 13 days, unidentified polar products (eluting in the solvent front on HPLC analysis) represented a large portion of the extractable radioactivity. More radioactivity was unextractable from sediment in unshaded ponds, especially in the 10-50 day post-treatment period. Fenitrothion yielded about 24% unextractable residue when incubated with silt loam soils under submerged conditions for 30-60 days (Takimoto et al. 1976). A similar portion of the radioactivity was unextractable in the shaded

pond sediment. The greater proportion of unextractable residues in the unshaded system may reflect formation of degradation products in the water column which are subsequently irreversibly bound to sediments or sedimented detritus. Phosphate diesters, in particular, are difficult to extract from sediments and water (Muir and Grift 1983) and may account for much of this unextractable residue.

The predominance of AF in sediments may account in part for the levels of AF in the water columns during the first 21 days post-treatment. It is more polar than fenitrothion and would be expected to partition more readily back into the water column. AF has frequently been reported as a major degradation product of fenitrothion in stagnant pools (Maguire and Hale 1980, Moody et al. 1978) and in flooded soils (Takimoto et al. 1976).

### 3. AQUATIC PLANTS AND FISH

In previous experiments by Weinberger et al. (1983) and Kikuchi et al. (1984) recoveries of fenitrothion from algae using methanol extraction averaged 99 and 96%, respectively, in laboratory experiments. These high recoveries were obtained with algae placed into steady state concentrations for short equilibration times (0.5 hr, Weinberger et al. 1983). In our study $^{14}C$ was rapidly accumulated from the water column by duckweed with maximum concentrations observed after five to ten days post-treatment in both years (Table XVIII). This time to reach maximum concentrations was much greater than for sediments. recovery of $^{14}c$ from duckweed was poor (Table XIX) suggesting $^{14}c$ was present as polar products which were conjugated, irreversibly bound to plant tissue or incorporated into natural components. Weinberger et al. (1983) also

had decreased recoveries by day three (92%). The extraction efficiency in the earliest sample extracted in our study (day 2, shaded, Year 1) was 44.8%. The extaction efficiency of $^{14}C$ from ducweed in shaded conditions was down to 22.9% by day seven. The extraction efficiency for $^{14}C$ from duckweed in the unshaded pond in Year 1 was 15.5% on day three and 11.3% on day ten. In Year 2, the extraction of $^{14}C$ from duckweed in the shaded pond on day three had an efficiency of 45.2%, decreasing to 25.8% on day 13. The extraction of $^{14}C$ from duckweed in the unshaded pond had an extraction efficiency of 40.9% on day five decreasing to 17.8% on day 13. The very low extraction figures for the samples from the unshaded pond, Year 1, may have suggested a difference in photolytic metabolism but this was not substantiated in Year 2.

Initial duckweed extractions in Year 1 involved partitioning of the neutral aqueous extract (after MeOH extraction and evaporation) with methylene chloride ($CH_2Cl_2$). This produced even poorer recoveries. Improved recoveries were obtained by acidifying the aqueous phase (pH 2)

**Table XIX Duckweed Extraction Efficiency (Year 1)**

**$^{14}C$-Fenitrothion equivalents (ug/kg)**

| | shaded | | | unshaded | | |
|---|---|---|---|---|---|---|
| Time (day) | neutral extraction | acid extraction | aqueous unextractable | neutral $H_2O$ | acid extraction | aqueous unextractable |
| 2 | 346 | 193 | - | - | - | - |
| 3 | 286 | 111 | 20 | 154 | 68 | 17 |
| 5 A | - | - | - | 196 | 67 | 63 |
| B | - | - | - | - | 231 | 49 |
| 7 A | 404 | 26 | 136 | - | - | - |
| B | - | 516 | 94 | - | - | - |
| 10 A | - | - | - | 74 | 36 | 58 |
| B | - | - | - | - | 138 | 40 |

- - indicates not examined for $^{14}C$ recovery.

(Table XIX). All samples in Year 2 were acidified (pH 2) in order to extract the aqueous phase (Table XX). The acid extraction resulted in improved recoveries of $^{14}C$ of 15% to 70%. Levels of unextractable $^{14}C$ in duckweed tended to increase over time in a similar manner as observed in water. The cattail extraction followed a similar pattern to the duckweed. Samples from the shaded pond (Year 2) had extraction efficiencies of 88%, 24.2% and 12.4% on days 3, 7 and 13 post-treatment, respectively.

Sep Pak clean-up of duckweed samples had resulted in similar problems as noted for the sediment extracts. The tarry residue could not all be dissolved in the one mL of MeOH:$H_2O$ (9:1) used to transfer it to the Sep Pak. This led to the implementation of a second Sep Pak clean-up of the remaining residue. The combination of the two clean-ups had an average collection efficiency of 83.6% of the initially available radioactivity. This efficiency level, as in sediment, was due to the limited volume of eluting solvent collected (3 mL) before substantial interference breakthrough (3 - 4.5 mL).

The levels observed in duckweed at five days represented concentration factors (BCFs) of 754 and 688 in shaded and unshaded exposures, respectively (Year 2), based on total radioactivity in water and duckweed. Concentrations in duckweed decreased to approximately 10% of the maximum by 35 days in each year (Table XVIII). Levels of radioactivity in the plants were not noticeably different in shaded and unshaded conditions. This differs from results of Weinberger et al. (1982a) who observed three-fold greater concentrations of $^{14}C$-fenitrothion in Elodea densa in field microcosms under lighted compared to darkened conditions.

Duckweed did not grow well under shaded condtions and by 17 days the density of the plant population was about 10% of that in the unshaded pond.

Fenitrothion, AF and MNP, were identified in duckweed extracts (Table XX). The proportion of each compound was similar to that observed in water at the same sampling time suggesting that the MNP and AF may have accumulated from water rather than formed in the plant. BCFs calculated with actual water and duckweed concentrations of fenitrothion were 108 and 140 in shaded and unshaded ponds, respectively, at three days post-treatment (Table XX). These BCFs are similar to results obtained in laboratory studies with fenitrothion (Lockhart et al. 1984) where equilibrium BCFs of 280 were observed during five day exposures, and are higher than BCFs observed in field monitoring following aerial spraying (Moody et al. 1978).

Cattails contained 10 to 20-fold lower levels of $^{14}$C-fenitrothion than duckweed throughout the study (Table XVIII). This difference probably reflects the greater surface area to volume ratio of duckweed. No differences between shaded and unshaded plants could be discerned. The large variability in the results for cattails as compared to duckweed may be attributable to the difficulty in obtaining representative samples from the large plants. Radioactivity was detected in cattails in pre-treatment samples (350 days post-treatment, Year 1), although levels of radioactivity in water and duckweed were below detection limits. The plants appeared to be accumulating radioactivity from sediments, the major sink for radioactivity at 350 days or the previous year's root-rhizome system, and translocating it to the emergent portion of the plant. The low extraction efficiency of the radioactivity in sediment at 350 days and the rapid degradation of

**Table XX Concentrations of fenitrothion or degradation products in duckweed extracts - Year 2.**

| Time | Extractable | ug/kg (dry wt) fenitrothion equivalents[a] | | | | | |
|---|---|---|---|---|---|---|---|
| (days) | (%) | Fenitro | phenol | AF | polar | pdts[b] | BCF[c] |
| Shaded | | | | | | | |
| 3 | 45.2 | 1086 | 871 | 129 | 3285 | | 108 |
| 7 | 20.3 | 571 | 1300 | 43 | 2472 | | 204 |
| 13 | 25.8 | 243 | 2486 | 671 | 714 | | 810 |
| Unshaded | | | | | | | |
| 3 | 40.9 | 629 | 1986 | 57 | 2699 | | 140 |
| 7 | 35.7 | 186 | 1143 | 129 | 3071 | | 310 |
| 13 | 17.8 | 243 | 1029 | 14 | 1214 | | 24300 |

a - determined by assay of radioactive spots on TLC plates (System I) and confirmed by HPLC.
b - polar products refers to unidentifed radioactive spots on TLC plates having short Rf values on System I and radioactivity not partitioned into dichloromethane.
c - BCF calculated with actual concentrations of fenitrothion in water (Fig. IX and X) and duckweed.

fenitrothion (Table XVII) suggests that cattails were accumulating polar degradation products from sediment.

Filamentous green algae absorbed relatively high levels of radioactivity from water with a BCF of 846 (based on total $^{14}C$ in water) at 13 days post-treatment. The algal bloom occurred only in the unshaded pond in Year 2 between 10 and 35 days post-treatment. The maximum concentration was at 17 days (9388 ug/kg, dry wt.). The size of this compartment could not be estimated due to its changing nature. Algal blooms are commonly observed following insecticide addition to ponds, due to reduction in grazing crustaceans by the insecticide (Hurlbert 1975). Similar concentration factors for fenitrothion in two species of autotrophic algae were observed by Weinberger et al. (1982a) (BCF=417 Chlorella).

Maximum concentrations of $^{14}C$-fenitrothion in fathead minnows were observed in the initial sampling time each year (Table XVIII). Levels in fish were similar in unshaded and shaded ponds, reflecting the fact that during the first 24 hours post-treatment intact fenitrothion was the major source of radioactivity in water in both ponds. Fenitrothion is more likely to accumulate from water than its more polar degradation products. Concentration factors of 42 and 54 (calculated with actual fenitrothion concentrations in water) were observed in minnows at 24 hours post-treatment in shaded and unshaded ponds (Year 2). These BCFs were about three-fold lower than equilibrium BCFs calculated from laboratory studies with rainbow trout but are within the range predicted for fenitrothion (12 to 293) based on its octanol-water partition coefficient or water solubility (Lockhart et al. 1984). Radioactivity in fish decreased to less than 50% of the initial concentrations by ten days post-treatment but low levels persisted in fish during the

remaining sampling period. The persistence of radioactivity may be due to ingestion of contaminated detritus by the minnows, as well as to utilization of some of the $^{14}C$ ring label by the fish in natural products.

**4. AIR**

Concentration of fenitrothion in air sampled 10 cm above treated ponds was highest in the first 24 hours post-treatment (Table XVIII). GLC analysis of the extracts from polyurethane foam traps indicated that only fenitrothion was present (Figure XII). The levels of fenitrothion were generally higher above the shaded ponds. This was expected because the polyethylene shelter reduced wind movement over the water surface which would have diluted the observed concentrations. Radioactivity was still detected in samples at 21 days though concentrations were near the detection limit (0.001 ug/$m^3$). Mallet and Volpe (1982) reported the detection of ng/L levels of AF as well as fenitrothion in air samples collected near treated areas in New Brunswick; however, the source of AF was not clear from their study.

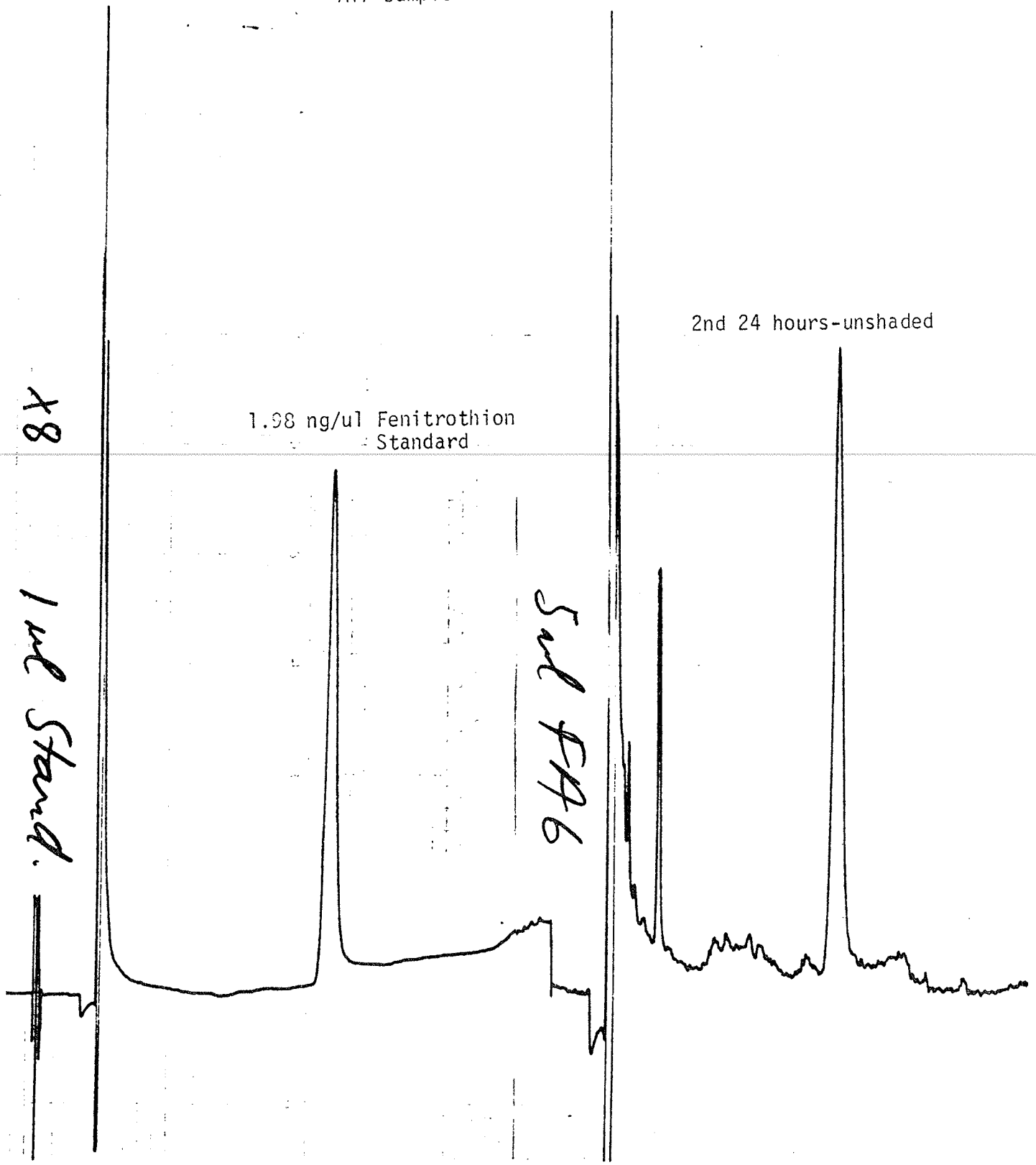
During Year 2, a concentration gradient was observed in samples taken two, five and ten cm above the water surface (Table XXI). The concentration gradient (ug/$m^3$) was converted to a flux (ug/$m^2$ hr.) by use of the aerodynamic equation (Parmele et al. 1972) which incorporated windspeed and temperature gradient obtained at a nearby site.

$$\text{Flux} = \frac{k^2 (C_2-C_1) (U_2-U_1)}{\phi^2 [\ln (z_2-d/z_1-d)]^2}$$

$C_2-C_1$ = concentration gradient (ug/$m^3$), k = von Karmen constant (0.4)

$U_2-U_1$ = wind gradient ($m^3$/sec.)

Figure XII Gas-Liquid Chromatography (GLC)
Air sample



$\phi$ = stability correction term

$\phi = (1 + 16\ RI)^{.33}$

RI = gradient Richardson number

$$= \frac{g(T_2-T_1)(z_2-z_1)}{°K\ (U_2-U_1)^2}$$

g = acceleration of gravity, $T_2-T_1$ = temperature gradient, $z_2-z_1$ = height difference, K° = temperature (average)

$[\ln (z_2-d/z_1-d)]^2 = 4.83$ $z_2 = 0.1$ m $z_1 = 0.02$ m

d = displacement parameter (0.01 m)

Only daily averages of wind speed and temperature could be used since air samples were changed on a 24 hour basis during the first three days post-treatment. Therefore, calculations can only roughly approximate the actual volatilization of the compound from the unshaded pond. Actual wind speeds over the shaded pond were not measured. In order to estimate a flux, the wind gradient was assumed to be 10% of that in unsheltered conditions.

Flux of fenitrothion from the pond surface was also estimated by use of the Fick's law relationship:

$$\text{Flux} = (K_{01})\ (Ci) \qquad (ug/m^2\ hr)$$

where $K_{01}$ is the overall volatilization rate constant (m/hr) calculated using the procedure of Smith et al. (1981) and Ci is the concentration gradient between the water and air (approximately equal to the water concentration) over the time interval. To obtain a $K_{01}$ value, mass transfer coefficients for oxygen from water of 1.8 cm/hr ($k_w$) and the gas mass transfer coefficient of water of 2100 cm/hr ($k_g$) were used. These values are typical of ponds and lakes 100 to 1000-fold larger in

**Table XXI** Calculated[a] and predicted[b] flux of fenitrothion from treated ponds.

| Time interval (days) | Temp.[c] T2-T1 (deg K) | Wind[c] U2-U1 (m/sec) | Concentration ($ug/m^3$) C2-C1 S | U | Flux ($ug/m^2$ hr) S | U | predicted |
|---|---|---|---|---|---|---|---|
| 0 - 1 | 0.75 | 0.45 | 0.151 | 0.113 | 0.127 | 5.52 | 14.4 |
| 1 - 2 | 1.75 | 0.60 | 0.084 | 0.060 | 0.079 | 3.80 | 5.6 |
| 2 - 3 | 0.25 | 0.10 | 0.020 | 0.004 | 0.011 | 0.03 | 3.0 |
| 5 - 7 | 1.75 | 0.10 | 0.004 | 0.0017 | 0.001 | 0.005 | 0.5 |

a - calculated by use of the aerodynamic method

b - predicted by use of the equation: Flux = $K_{01}$ (Ci) $K_{01}$ = volatilization rate in a 0.5 m depth system, Ci = average concentration of fenitrothion in water over the time interval. $K_{01} = [1/Kw + RT/HKg]^{-1}$ for 1 m depth. H = Henry's constant (atm $m^3$/mol) and Kw and Kg are liquid and gas phase mass transfer coefficients for fenitrothion in ponds calculated from kw and kg values for oxygen and water respectively as described by Smith et al. (1981)

c - temperature gradients (T2 at 10 cm and T1 at 2 cm) are average values for the time interval. Wind speed gradients were estimated for a graph of ln height vs average speed (m/sec) (U2 = 10 cm, U1 = 2 cm) for the unshaded pond. Wind speeds in the shaded pond were estimated to be 10% of those in the unshaded treatment.

surface area than those in the present study, so they may overestimate actual volatilization rates. These values are adjusted for fenitrothion using a correction factor based on molecular weight (Liss and Slater 1974). $K_w$ (fenitrothion) $= k_w\sqrt{\frac{32}{277}} = 6.118 \times 10^{-3}$ m/hr

$K_g$ (fenitrothion) $= k_g\sqrt{\frac{18}{277}} = 5.35$ m/hr

These values are used in the equation:

$$K_{01} = \left(\frac{1}{K_w} + \frac{RT}{K_g H}\right)^{-1}$$ for a one meter depth

R = gas constant = $8.2 \times 10^{-5}$ $m^3$ atm/mol K

T = 295°K H = Henry's constant

$$H = \frac{\text{vapour pressure}}{\text{water solubility}} = \frac{7.36 \times 10^{-8} \text{ atm}}{.0722 \text{ moles/m}^3} = 1.02 \times 10^{-6}$$

The value of $K_{01}$ obtained was $2.18 \times 10^{-4}$ m/hr which suggest a half-life of fenitrothion of 66 days for a 0.5 m depth (Mackay and Leinonen 1975). Similar half-lives were observed in the laboratory study by Maguire and Hale (1980) (64 $\pm$ 5 days). The flux of fenitrothion predicted from the Fick's law relationship was two to three-fold greater than that calculated by use of the aerodynamic equation (Table XXI). Although the concentrations of fenitrothion were high enough to be readily detected up to 10 cm above the water in windy conditions (ng/$m^3$), the loss of fenitrothion is small since mg/$m^3$ quantities were present in the water column. A higher predicted than calculated flux is consistent with observations that fulvic acids in water reduce the volatilization rate of fenitrothion (half-life greater than 180 days) (Maguire and Hale 1980).

## 5. MASS BALANCE

Greater than 90% of the radioactivity added to the ponds could be accounted for during the first two days post-treatment in Year 2 (Table XXII). These results are calculated by multiplying the concentrations of total $^{14}C$ observed in each compartment by the weight of each compartment. The weights used for the water and sediment (0 to 3 cm depth) compartments were thought to be within 10% since the dimensions of the ponds were known. Weights of aquatic plants were estimated by multiplying their area by plant density and are therefore subject to considerable error. Water was the major compartment for $^{14}C$-fenitrothion for the 1 to 5 day period but by 21 days most of the remaining radioactivity was in sediment, especially in the unshaded pond (13% and 18.5%, Year 1 and 2). The higher accountability of radioactivity in unshaded ponds was not expected. Greater photodegradation in the unshaded water was expected to give increased amounts of degradation products. The higher levels of $^{14}c$ in sediments indicate the polar products initially produced were adsorbed to the larger biomass and suspended sediments of the unshaded pond and deposited in the sediment. Aquatic plants, fish and air were minor compartments of radioactivity throughout the study. The accountability of $^{14}C$-fenitrothion was considerably reduced by 21 days. In Year 1, estimates of total fenitrothion in water were obtained by use of extractable radioactivity (Table XV) which was low by day 5, (53.8% and 37.5% extracted - Year 2 - shaded and unshaded), resulting in low estimates of total fenitrothion in water. Another source of error could be greater deposition of fenitrothion on sediments on the sides of the ponds, which is not taken into account by only sampling the pond bottom.

Table XXII Percent[a] of added $^{14}C$-fenitrothion in each compartment.

| Time | Water | | Sediment | | plants | | fish | | air | | total | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (days) | S | U | S | U | S | U | S | U | S | U | S | U |
| Year 1 | | | | | | | | | | | | |
| 0.5 | 109.2 | 90.60 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 1 | 93.9 | 82.6 | 5.1 | 20.8 | 2.8 | 3.7 | 1.1 | 1.7 | -- | -- | 102.9 | 108.8 |
| 2 | 72.2 | 50.4 | 5.4 | 11.7 | 2.6 | 6.1 | 1.1 | 0.7 | -- | -- | 81.5 | 68.9 |
| 5 | 32.2 | 15.0 | 9.9 | 20.3 | 0.8 | 7.0 | 0.5 | 0.2 | -- | -- | 43.4 | 42.5 |
| 21 | 5.2 | 0.7 | 5.9 | 13.0 | 0.4 | 2.5 | 0.3 | 0.3 | -- | -- | 11.8 | 16.5 |
| Year 2 | | | | | | | | | | | | |
| 0.5 | 103.7 | 89.6 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 1 | 79.8 | 79.8 | 17.8 | 29.7 | 3.2 | 2.3 | 0.7 | 0.7 | 0.1 | 0.6 | 101.5 | 113.1 |
| 2 | 69.6 | 66.4 | 17.0 | 21.2 | 3.4 | 2.7 | 1.1 | 0.1 | 0.1 | 1.0 | 91.1 | 91.4 |
| 5 | 48.9 | 41.7 | 8.0 | 34.0 | 0.7 | 4.1 | 0.2 | 0.2 | 0.1 | 1.0 | 57.8 | 81.0 |
| 21 | 7.9 | 0.8 | 5.0 | 18.5 | 0.2 | 0.2 | 0.3 | 0.1 | 0.1 | 1.0 | 13.4 | 22.6 |

a - estimated using the following compartment sizes: water = 3.55 $m^3$ shaded, 3.6 $m^3$ unshaded; sediment = 264.4 kg dry wt shaded, 279.2 kg dry wt unshaded; duckweed, 0.5 kg dry wt (unshaded), 0.05 kg shaded at 5 and 21 days; cattails 1 kg dry wt; fish 0.6 kg. Air losses by use of the aerodynamic equation results.

This has been observed with pyrethroid insecticides in similar outdoor ponds and appears to be due to initial stratification of the formulation in the warm upper 10 cm of water layer which is observed in the ponds during the day (Muir et al. 1985). Movement of water soluble products below three cm in sediment may also have occurred. Breakdown of degradation products in the water column and sediment via microbial activity to yield $^{14}CO_2$ or other volatile carbon fragments is another pathway of loss. Mikami et al. (1985) observed 31% of the applied $^{14}C$ as $^{14}CO_2$ at 26 weeks in submerged soils.

Volatilization of AF and MNP is unlikely, however, since they have smaller $K_{01}$ values than fenitrothion.

## 6. Environmental Fate Models

The experimental data and results compared well with two environmental fate models. Roberts et al. (1981) used Year 1 fenitrothion results from the unshaded pond (from Fate of Fenitrothion in the Aquatic Environment, Malis and Muir, 15th Annual Workshop for Pesticide Residue Analysis (in Western Canada), April 30, 1980). This system, as described in the literature review, was found to be compatible with our microcosm design.

Comparative results by Roberts et al. (1981) are as follows:

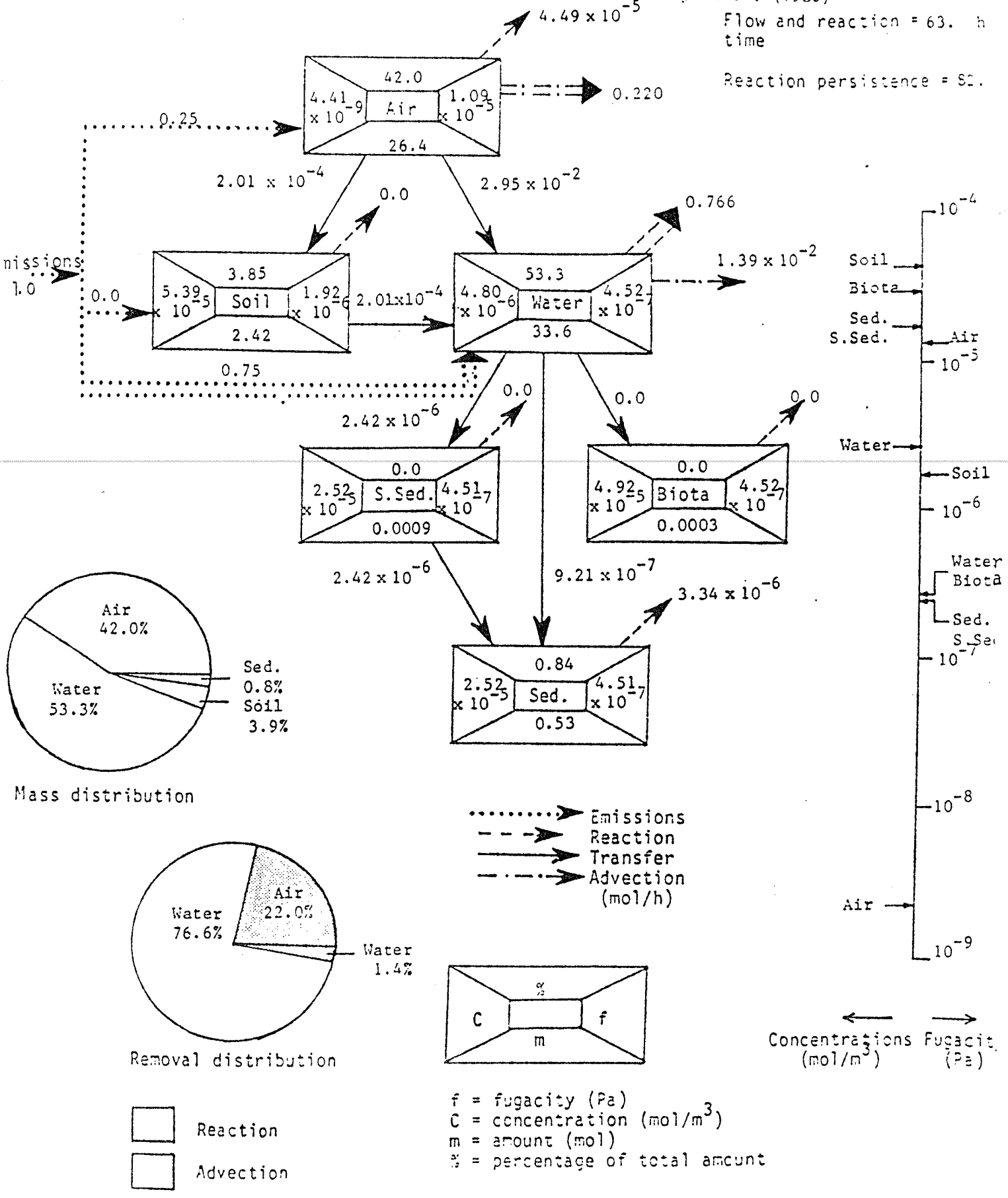
| Fenitrothion (Year 1) | Model |
|---|---|
| t 1/2 = 0.79 days<br>Fractional Retention: sediment (0.54), water (0.27), plants (0.17), fish (0.06)- data after five days | t 1/2 = 0.45<br>Sediment (0.85), water (0.06), plants (0.05) (0.04 - system at equilibrium) |

| | |
|---|---|
| BCF fish = 55-80 | BCF fish = 225 |
| **Fenitrothion (Year 1)** | **Model** |
| Degradation: Mainly by photolysis and bacteria. No hydrolysis at pH = 7.8. Fraction volatilized approx. $9 \times 10^{-6}$ | Photolysis (0.82) microbial (0.18), Fraction volatilized approx. $3 \times 10^{-6}$ |

This points out the short half-life of fenitrothion, sediment as the main sink, the relative unimportance of volatilization and the major breakdown by photolysis and microbial action. The model overestimates the capacity of the sediment and fish and underestimates that of water and plants compared to the experimental results.

Mackay et al. (1985) set up a six compartment model including: air, soil, water, fish, suspended solids and sediment (Fig. XIII). It took into account partitioning, reaction, advection and intercompartmental transfer at a steady state to evaluate environmental behavior. This breaks down to: a) partitioning (capacity), b) reactions of hydrolysis, oxidation, photolysis, biolysis (first order rates) and sediment burial, c) advective flows in air and water and d) diffusive and material transfer. Each compartment in Fig. XIII contains the data on the amount, concentration, and percent of the total amount of chemical and fugacity. The broader arrows in the figure represent the more important processes. Chemical - specific data used for fenitrothion are: molecular mass (277), solubility (2.7 $g/m^3$), vapour pressure ($9.19 \times 10^{-3}$ Pa), octanol-water partition coefficient (2.33) and reaction rate constants for biodegradation in water ($2.28 \times 10^{-2}$/hr) and sediment ($1.70 \times 10^{-6}$). Other parameter constants were generally taken from systems larger than this study. The model estimates that

Figure XIII Fenitrothion - Mackay et al. (1985)



fenitrothion is not persistent, remaining in the environment for two to four days. Mackay et al. (1985) satisfactorily compares their results with results from this study's persistence of ten days (unshaded) under conditions of negligible advection. Their shorter persistence is mainly caused by a large initial loss to air (25%) because they assume fenitrothion was introduced by aerial contamination. They recognized the importance of the reactions in water but underestimate the capacity of sediment.

## CONCLUSIONS

The effect of shading an outdoor pond for the first 17 days after addition of fenitrothion was to increase the half-life of the insecticide by about 50% despite a 30-fold reduction in light intensity. The decline in insecticide residues in water was rapid, dropping from 70 ug/L to about 0.01 ug/L by 17 days. Shaded conditions decreased the quantities of "other products" and MNP, (but not AF because of its microbial origins), that were formed. No major products unique to shaded or unshaded conditions were identified.

A large portion of radioactivity in water, sediment and plants was unextractable with conventional techniques, especially in samples taken after ten days post-treatment. Fenitrothion and MNP were not major components in these compartments in shaded or unshaded conditions after this time. It appears that most of the radioactivity was in the form of products difficult to partition from water to organic solvents, such as those with amphoteric characteristics (aminocresols) or phosphoric acid esters. Weinberger et al. (1982a) observed a similar proportion of unextractable material in their field studies. Further studies on the fate of fenitrothion may need to overcome analytical difficulties posed by these products. Results at 350 days post-treatment were interesting from the viewpoint of long-term persistence of the $^{14}C$-ring label. Most of the radioactivity in the ponds was present in sediment (likely from sedimentation of plant material from the previous year) and 77% was unextractable with acetonitrile, indicating that it was not in the form of fenitrothion. Cattails appear to be accumulating this radioactivity from sediment and translocating it to the growing portion of the plant.

Predicted and calculated flux values of fenitrothion were arrived

at independently, both suggesting that volatilization from water is slow compared to other paths of degradation of the insecticide. This helps confirm predictions of the two-film theory of volatilization (Smith et al. 1981, Mackay and Leinonen 1975). Maguire and Hale (1980) have shown losses of fenitrothion from surface films to be very rapid (t 1/2 = 18 $\pm$ 6 minutes for 62% of applied dose). A surface film was not formed in the present work because the insecticide formulation was mixed into the upper 10 cm of the water column.

The radioactivity added to the ponds was only accounted for successfully during the first five days post-treatment, despite knowledge of the size of the major compartments and the use of direct assays such as combustion to $^{14}CO_2$. Loss of radioactivity due to penetration to lower depths in sediment and degradation of the ring label to volatile carbon fragments and $^{14}CO_2$ in the water column and sediment may have occurred, but are unlikely to total all the 70 to 80% unaccounted for.

Two environmental fate models of organic chemicals used the experimental data and results to validate each model's design. The similarities between the field experiment and the mathematical models help to support their use as a diagnostic tool but incorrect simplifications and assumptions can lead to significantly wrong estimates in real compartments.

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## APPENDIX

1. TLC Systems Investigated

2.a) Example of TLC and Calculation of ln Concentration versus Time

b) GLC Results for Fenitrothion

c) Example of Percent of Fenitrothion and Metabolites versus Time in the Two TLC Systems

## Appendix 1: $R_F$ Values of Solvent Systems Tested for TLC

| Solvent System | AF | SMF | F | FzO | MNP |
|---|---|---|---|---|---|
| 2-propanol-$H_2O$-$NH_4OH$ (90:10:1) | 0.53 | 0.46 | 0.61 | 0.50 | 0.47 |
| 2-propanol-$H_2O$-$NH_4OH$ (95:5:1) | 0.58 | 0.50 | 0.65 | 0.55 | 0.50 |
| ethylacetate-hexane (2:1) | 0.47 | 0.46 | 0.70 | 0.45(T) | 0.52 |
| (1:1) | 0.23 | 0.30(t) | 0.55 | 0.26(T) | 0.37 |
| 2-propanol-$H_2O$-$NH_4OH$ (75:24:1) | 0.77 | 0.81 | 0.85 | 0.82 | 0.67 |
| Toluene-diethyl ether (19:1) | 0.17 | 0.16 | 0.54 | 0.25(T) | 0.23 |
| (10:1) | 0.17 | 0.18 | 0.54 | 0.22(T) | 0.22(t) |
| $CH_2Cl_2$-ethyl ether (10:1) | 0.35 | 0.34 | 0.67 | 0.35(T) | 0.43 |
| Hexane-2 propanol-$NH_4OH$ (50:50:1) | 0.57 | 0.50 | 0.82 | 0.54 | 0.49 |
| Toluene-ethyl acetate-acetonitrile (5:7:1) | 0.46 | 0.44 | 0.57 | 0.41 | 0.41 |
| Hexane-ethyl acetate-formic acid (80:40:5) | 0.03 | 0.28, 0.13 | 0.39 | 0.24, 0.11 | 0.27 |
| Hexane-acetone-formic acid (70:30:2) | 0.67 | 0.64 | 0.69 | 0.53(t) | 0.64 |
| Hexane-acetone (4:1) | 0.087 | 0.09 | 0.25 | | 0.13 |
| Butanol-acetone-$H_2O$ (4:5:1) | 0.89 | 0.977 | 0.99 | 0.90(t) | 0.87 |
| Solvent Systems used in Experiment | | | | | |
| Toluene-Ethyl formate-formic acid | 0.15 | 0.5 | 0.68 | 0.36 | 0.52 |
| (5:7:1) (System I) | 0.22 | 0.73 | 1.0 | 0.53 | 0.76 |
| $CCl_4$-$CH_2Cl_2$-methanol | 0.5 | 0.39 | 0.65 | 0.50 | 0.43 |
| (5:7:1) System II | 0.83 | 0.66 | 1.0 | 0.77 | 0.66 |

T = severe tailing, t = slight tailing

Most close values cannot be used because of either a large spot diameter and/or uneven solvent front which would cause overlap in a sample.

## Appendix 2.a. Calculation of Linear Regression Fit and t 1/2

### ln Concentration vs. Time

Fenitrothion

1980 (uncovered)

| Time (days) | SI (ppb) | SII (ppb) | ln [avg. conc. x 100] |
|---|---|---|---|
| 0.083 | 43.31 | 29.3 | 8.152 |
| 0.375 | 25.91 | 24.2 | 7.823 |
| 1.0 | 13.54 | 13.04 | 7.190 |
| 1.5 | 8.75 | 7.86 | 6.718 |
| 2.0 | 5.49 | 6.09 | 6.359 |
| 3.0 | 3.24 | 2.82 | 5.709 |
| 5.0 | 1.13 | 0.91 | 4.618 |
| 7.0 | 0.39 | 0.32 | 3.563 |
| 10.0 | 0.05 | 0.07 | 1.777 |

slope = - .620

$r^2$ = -.994

$t\ 1/2 = \frac{.693}{.620} = 1.12$ days

## Appendix 2b Fenitrothion by GLC (ug/L)

(Water)

| | Shaded | | Unshaded | |
|---|---|---|---|---|
| Time (days) | 1979 | 1980 | 1979 | 1980 |
| 0.021 | 61.09 | | 61.60 | |
| 0.041 | 51.55 | 65.09 | 50.86 | 63.88 |
| 0.083 | 36.51 | | 38.18 | |
| 0.125 | | 52.63 | | 51.46 |
| 0.167 | 36.22 | | 32.75 | |
| 0.25 | | 49.44 | | 43.27 |
| 0.33 | 30.08 | | 26.90 | |
| 0.50 | 27.12 | 42.42 | 21.84 | 30.18 |
| 0.75 | 25.71 | | 25.33 | |
| 1.0 | 31.28 | 33.65 | 26.10 | 21.56 |
| 1.5 | 19.56 | 24.64 | 12.03 | 12.14 |
| 2.0 | 11.46 | 17.98 | 9.25 | 9.06 |
| 3.0 | 7.43 | 12.72 | 4.67 | 3.95 |
| 5.0 | 2.96 | 5.71 | 0.65 | 1.75 |
| 7.0 | 1.42 | 2.42 | 0.19 | 0.52 |
| 10.0 | | 0.80 | | 0.09 |
| 13.0 | | 0.28 | | |
| ln concentration versus time: | | | | |
| $t_{1/2}$ (days) | 1.36 | 1.67 | 0.87 | 1.09 |
| $r^2$ | .985 | .997 | .989 | .992 |

Results are calculated from the equation:

$$\text{Concentration (ppb)} = \frac{C \text{ (ng.std)}}{M \text{ (inj. vol.)}} \cdot \frac{\text{(sample extract volume)}}{\text{(sample } H_2O \text{ vol.)}}$$

C = Peak height (1979) area (1980) of sample
M = Peak height (1979) area (1980) of Standard

Results are the average of duplicate analysis

Appendix 2.c. An Example of the Percent Fenitrothion and Metabolites of Total Radioactivity versus Time

TLC System I - 1980 (covered)

| | Compounds or RFs | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OPM/L Time (day) | Fenitrothion | Phenol | Amino-F | .486 | .438 | .402 | .299 | .159 | 0 | Other (.097) | Total (dpm/L) |
| .083 | 95.25 | 2.46 | 0. | 1.62 | 0 | .31 | 0 | 0 | .21 | .16 | 47759 |
| .375 | 92.78 | 3.88 | 0. | 2.31 | 0. | .67 | 0. | 0. | .36 | 0. | 40077 |
| 1 | 83.34 | 8.54 | 0. | 5.05 | 0. | 1.99 | 0. | 0. | 1.08 | 0. | 32063 |
| 1.5 | 75.88 | 9.37 | .93 | 8.94 | 2.83 | 0. | 1.23 | 0. | 1.02 | 0. (.097) | 25229 |
| 2 | 69.64 | 11.33 | 1.25 | 6.35 | 6.02 | 0. | 1.71 | .88 | 2.06 | .75 (.097) | 21518 |
| 3 | 53.39 | 16.78 | 1.87 | 10.78 | 8.30 | 2.35 | 2.05 | 1.11 | 2.24 | 1.11 (.097) | 17377 |
| 5 | 39.14 | 19.98 | 2.75 | 9.35 | 16.50 | 3.32 | 2.33 | 1.58 | 3.37 | 1.67 | 10384 |
| 7 | 29.92 | 25.07 | 2.84 | 9.29 | 21.52 | 3.26 | 2.18 | 1.90 | 4.02 | 0. | 7671 |
| 10 | 15.07 | 25.87 | 4.86 | 9.38 | 28.77 | 6.13 | 3.23 | 2.02 | 4.64 | 0. | 5044 |
| 13 | 7.84 | 29.26 | 4.80 | 9.38 | 38.71 | 4.43 | 0. | 2.40 | 3.19 | 0. | 2666 |
| 17 | 3.06 | 25.56 | 7.62 | 12.64 | 39.30 | 6.12 | 0. | 0. | 5.71 | 0. | 1733 |
| 17.875 | 0. | 25.95 | 6.85 | 0. | 16.94 | 43.90 | 0. | 0. | 6.37 | 0. | 1665 |
| 20 | 0. | 23.89 | 9.73 | 0. | 14.59 | 44.43 | 0. | 0. | 7.35 | 0. | 925 |
| 21 | 0. | 18.39 | 15.76 | 0. | 14.12 | 45.16 | 0. | 0. | 6.57 | 0. | 609 |
| 28 | 0. | 0. | 28.16 | 0. | 7.28 | 29.13 | 0. | 0. | 35.44 | 0. | 206 |

Appendix 2.c. (cont'd) TLC System II - 1980 (covered)

| Time | Fenitrothion | Phenol | Amino-F | .433 | .368 | .201 | .160 | .065 | 0 | .123 | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .083 | 95.42 | 2.21 | 1.24 | 0. | .21 | 0. | 0. | 0. | .91 | 0. | 49004 |
| .375 | 93.36 | 2.81 | 1.67 | .38 | .24 | .15 | .21 | 0. | 1.18 | 0. | 39662 |
| 1 | 82.58 | 7.75 | 3.23 | 1.07 | 1.12 | .24 | .52 | 0. | 3.49 | 0. | 30727 |
| 1.5 | 75.66 | 9.84 | 4.96 | 1.89 | 1.74 | .56 | .69 | .81 | 3.85 | 0. | 25447 |
| 2 | 69.89 | 9.62 | 3.34 | 3.48 | 3.45 | .91 | .85 | 1.06 | 6.59 | .80 | 21306 |
| 3 | 54.85 | 13.71 | 3.94 | 6.07 | 6.58 | 1.35 | 1.77 | 1.76 | 8.58 | 1.39 | 16902 |
| 5 | 39.71 | 18.17 | 2.37 | 7.18 | 13.22 | 1.30 | 2.39 | 2.13 | 11.81 | 1.72 | 9797 |
| 7 | 31.51 | 21.90 | 2.19 | 7.33 | 19.62 | 1.46 | 2.93 | 2.11 | 10.95 | 0. | 7397 |
| 10 | 15.21 | 21.48 | 1.98 | 9.35 | 25.23 | 2.29 | 4.23 | 2.65 | 15.58 | 2.00 | 4898 |
| 13 | 8.84 | 27.81 | 0. | 0. | 45.33 | 4.45 | 0. | 0. | 13.57 | 0. | 2226 |
| 17 | 5.64 | 24.66 | 0. | 0. | 41.80 | 7.52 | 0. | 0. | 20.38 | 0. | 1330 |
| 17.875 | 0. | 23.71 | 0. | 0. | 47.82 | 9.51 | 0. | 0. | 18.96 | 0. | 1514 |
| 20 | 0. | 23.08 | 0. | 0. | 46.39 | 12.78 | 0. | 0. | 17.75 | 0. | 845 |
| 21 | 0. | 16.05 | 0. | 0. | 42.54 | 11.07 | 0. | 0. | 30.34 | 0. | 623 |
| 28 | 0. | 0. | 0. | 0. | 39.19 | 31.08 | 0. | 0. | 29.73 | 0. | 74 |

APPENDIX 2.c. (cont'd)

TLC SYSTEM II - 1980 (covered)

| Time | Fenitrothion | Phenol | Amino-F | .433 | .368 | .201 | .160 | .065 | 0 | .123 | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .083 | 95.42 | 2.21 | 1.24 | 0. | .21 | 0. | 0. | 0. | .91 | 0. | 49004 |
| .375 | 93.36 | 2.81 | 1.67 | .38 | .24 | .15 | .21 | 0. | 1.18 | 0. | 39662 |
| 1 | 82.58 | 7.75 | 3.23 | 1.07 | 1.12 | .24 | .52 | 0. | 3.49 | 0. | 30727 |
| 1.5 | 75.66 | 9.84 | 4.96 | 1.89 | 1.74 | .56 | .69 | .81 | 3.85 | 0. | 25447 |
| 2 | 69.89 | 9.62 | 3.34 | 3.48 | 3.45 | .91 | .85 | 1.06 | 6.59 | .80 | 21306 |
| 3 | 54.85 | 13.71 | 3.94 | 6.07 | 6.58 | 1.35 | 1.77 | 1.76 | 8.58 | 1.39 | 16902 |
| 5 | 39.71 | 18.17 | 2.37 | 7.18 | 13.22 | 1.30 | 2.39 | 2.13 | 11.81 | 1.72 | 9797 |
| 7 | 31.51 | 21.90 | 2.19 | 7.33 | 19.62 | 1.46 | 2.93 | 2.11 | 10.95 | 0. | 7397 |
| 10 | 15.21 | 21.48 | 1.98 | 9.35 | 25.23 | 2.29 | 4.23 | 2.65 | 15.58 | 2.00 | 4898 |
| 13 | 8.84 | 27.81 | 0. | 0. | 45.33 | 4.45 | 0. | 0. | 13.57 | 0. | 2226 |
| 17 | 5.64 | 24.66 | 0. | 0. | 41.80 | 7.52 | 0. | 0. | 20.38 | 0. | 1330 |
| 17.875 | 0. | 23.71 | 0. | 0. | 47.82 | 9.51 | 0. | 0. | 18.96 | 0. | 1514 |
| 20 | 0. | 23.08 | 0. | 0. | 46.39 | 12.78 | 0. | 0. | 17.75 | 0. | 845 |
| 21 | 0. | 16.05 | 0. | 0. | 42.54 | 11.07 | 0. | 0. | 30.34 | 0. | 623 |
| 28 | 0. | 0. | 0. | 0. | 39.19 | 31.08 | 0. | 0. | 29.73 | 0. | 74 |