

Fenitrothion Sprayed on a Pond: Kinetics of Its Distribution and Transformation in Water and Sediment

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Water, suspended solids, and sediment samples were collected from a small pond in a spruce-fir forest in New Brunswick, Canada, before and after the spraying of a fenitrothion [*O,O*-dimethyl *O*-(*p*-nitro-*m*-tolyl) phosphorothionate] formulation for spruce budworm control, and the samples were analyzed for fenitrothion and its degradation and transformation products. Fenitrothion concentrations in water, suspended solids, and sediment fell below detectable levels 2 days after the spray. The only identified products were *p*-nitro-*m*-cresol in water, which persisted less than 2 days, and aminofenitrothion [*O,O*-dimethyl *O*-(*p*-amino-*m*-tolyl) phosphorothionate] in sediment, which persisted less than 4 days. Laboratory experiments indicated that chemical hydrolysis and volatilization of fenitrothion from true solution were both slow processes; however, volatilization of fenitrothion from surface slicks of its formulation sprayed on water was very fast ($t_{1/2} = 18$ min at 20 °C).

Fenitrothion has been used since 1969 in New Brunswick, Canada, for control of the spruce budworm (*Choristoneura fumiferana* [Clemens]) in the province's forests. Millions of hectares have been sprayed annually with 150-300 g of active ingredient per hectare. The routes and rates of environmental transformation and disappearance of fenitrothion are subjects of a great deal of interest (National Research Council of Canada, 1975, 1977).

Kovacicova et al. (1973) determined that the hydrolysis of fenitrothion (i.e., producing *p*-nitro-*m*-cresol and dimethyl phosphorothioate) was a slow process at alkaline pH. Zitko and Cunningham (1974) determined that the hydrolysis of fenitrothion in water at pH 7 was not detectable over a period of 45 days.

Several research groups have reported on the photolysis of fenitrothion (Brewer et al., 1974; Ohkawa et al., 1974; Greenhalgh and Marshall, 1976; Miyamoto, 1977). It appears that fenitrothion dissolved in water and exposed to sunlight decomposes by (1) oxidation of P=S to P=O, (2) oxidation of the *m*-CH₃ group, and (3) cleavage of the P-O-aryl linkage. The main product, initially, is carboxyfenitrothion [*O,O*-dimethyl *O*-(*p*-nitro-*m*-carboxyphenyl) phosphorothionate]. Prolonged irradiation leads to increased amounts of *p*-nitro-*m*-cresol and polymeric humic acids.

Although no thorough studies on the decomposition of fenitrothion in sediments have been reported, Takimoto et al. (1976) showed that the decomposition of fenitrothion in soil is primarily due to microbial activity and is not dependent upon the physical state or chemical nature of the soil. Under aerobic conditions, *p*-nitro-*m*-cresol was the major product, while the major product under anaerobic (flooded) conditions was aminofenitrothion; they also demonstrated aerobic conversion to aminofenitrothion in bacterial cultures.

Fenitrothion appears not to persist in aquatic environments. Sundaram (1974) demonstrated half-lives of 0.25-3.5 days in ponds, but did not identify any degradation products other than traces of fenitrooxon. Lockhart et al. (1977) and Moody et al. (1978) have shown that fenitrothion persists in stagnant and running water for about 4 days and is not persistent in fish; its disappearance could not be accounted for. Small amounts of aminofenitrothion were produced in water, presumably by microbial activity. They also reported the accumulation of

fenitrothion by crayfish and submerged plants.

This work is an attempt to determine the relative importance that volatilization, hydrolysis, and adsorption to sediment have in the disappearance of fenitrothion from aquatic environments. Other pesticides such as parathion and methyl parathion can be transformed by bacteria into soil-bound, "unextractable", residues (Katan et al., 1976; Lichtenstein et al., 1976; Katan and Lichtenstein, 1977; Fuhremann and Lichtenstein, 1978); the possibility that fenitrothion could become strongly bound to sediment was examined. In addition, since fenitrothion is often sprayed on the surface of water bodies in forested areas, we wished to examine the importance of the surface microlayer in the distribution and transformation of fenitrothion. Previous reports have shown that organic matter can be concentrated in surface slicks (Harvey, 1966; Seba and Corcoran, 1969; Parker and Barsom, 1970; Pojasek and Zajicek, 1978).

EXPERIMENTAL SECTION

Materials. Technical grade fenitrothion and fenitrooxon were gifts from Chemagro Ltd. and Sumitomo Chemical Co., respectively. Samples of Aerotex 3470 and Atlox 3409F were gifts from Texaco Canada Ltd. and Atlas Chemical Co., respectively. Fulvic acid was a gift from the Soil Research Institute of the Canadian Department of Agriculture. All organic solvents used in this work were pesticide grade. *p*-Nitro-*m*-cresol and *p*-amino-*m*-cresol were obtained from Aldrich Chemical Co. and purified by sublimation. β -Glucosidase (from almond) was obtained from Sigma Chemical Co. and a β -glucuronidase/aryl sulfatase preparation (from *Helix pomatia*) was obtained from Calbiochem. XAD-2 resin was obtained from BDH Ltd. and cleaned up by Soxhlet extraction with acetone, diethyl ether, and methanol (24 h each). All other chemicals were reagent grade and were used without further purification.

Fenitrothion was purified by elution in benzene from a 10% H₂O-deactivated column of Fluorisil and shown to be pure by gas chromatography with flame ionization (FID), flame photometric (FPD), and electron-capture (ECD) detectors. Fenitrooxon was purified in the same way, except that the eluting solvent was 1:1 (v/v) ethyl acetate-benzene. Aminofenitrothion was prepared by chromous chloride reduction of fenitrothion (Lawrence et al., 1977) and was stable for months in oxygenated toluene or hexane.

Apparatus. Detection and quantitation of fenitrothion and degradation products was done mainly by gas chromatography with ⁶³Ni-ECD, FPD (P mode), or FID as appropriate. A Spectra-Physics 4000 integrator and a

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Hewlett-Packard 3370B integrator were used to calculate peak areas. Generally a 2 m × 2 mm i.d. glass column containing 4% OV-101/6% OV-210 on Chromosorb WHP, 80/100 mesh, was used isothermally at 200 °C. Inlet and outlet temperatures were 220 °C and the following detector temperatures were used: ECD, 350 °C; FPD and FID, 240 °C. The minimum detectable amount of fenitrothion was 5 pg by ECD, 500 pg by FPD (P mode), and 50 ng by FID, and the detectors were calibrated for linearity of response with standards of known concentration. Underivatized *p*-nitro-*m*-cresol was detected and quantitated readily on a Carbowax 20 M column. Confirmations of identity were made by comparing retention times and by cochromatography with authentic samples on OV-101/210, Carbowax 20 M, and OV-225 columns. Confirmations of identity were also made, when amounts permitted, on a Finnigan 1015-C gas chromatograph-mass spectrometer (electron impact, 70 eV) with PDP-8 computer, Cyphernetics spectral library, and reference to other published mass spectra.

Special care was taken for polar compounds such as fenitrooxon which are adsorbed to active sites on columns; the columns needed to be "primed" daily with large amounts of compound to cover all the active sites before reliable peak areas could be obtained. Some environmental samples were injected 30 times into the columns to achieve the same priming effect.

Hydrolysis of Fenitrothion. The kinetics of the production of *p*-nitro-*m*-cresol in buffered and unbuffered aqueous fenitrothion solutions were determined spectrophotometrically at 25 °C over the pH range 11–13.4, and the kinetics at pH 13.4 were determined over the temperature range 5–55 °C. The pK_a (negative logarithm of the acid dissociation constant) of *p*-nitro-*m*-cresol was determined spectrophotometrically to be 7.26 ± 0.03 at 25.0 °C and ionic strength 0.05 M (phosphate). Acidic and basic molar extinction coefficients at 397 nm, the maximum in the visible absorption spectrum, were determined to be $(5.07 \pm 0.16) \times 10^2$ and $(1.68 \pm 0.05) \times 10^4$ L mol⁻¹ cm⁻¹, respectively. Each kinetic determination was performed five times.

Volatilization of Fenitrothion. (A) *From True Solution.* Erlenmeyer flasks of volume 250 mL, each containing 100 mL of fenitrothion in true solution in distilled water (ca. 5 mg L⁻¹), were placed in a cabinet of volume 1 m³ and kept at 20 °C. Periodically, a flask was removed from the cabinet and the whole volume (appropriate volume corrections were made) was extracted with hexane (3 × 25 mL), the flask was rinsed with hexane, the combined extracts were dried with MgSO₄ and concentrated to 1 mL, and aliquots of the hexane extracts were analyzed by gas chromatography. These experiments were also performed for solutions of fenitrothion plus fulvic acid to determine the effect of dissolved organic matter. Five sets of volatilization experiments were performed, and each fenitrothion concentration determined by gas chromatography was the result of three–five injections.

(B) *From Surface Slicks.* A typical fenitrothion formulation as sprayed in New Brunswick (Cochrane and Maybury, 1977), and in particular on the pond described here, was prepared containing 11% (w/w) fenitrothion, 1.5% Aerotex 3470 aromatic solvent, 1.5% Atlox 3409F emulsifier, and 86% water. The mixture was sonicated to produce a stable emulsion and the emulsion was sprayed lightly on the surfaces of water-filled glass bottles (wide mouth, 130 mL), using an atomizer of the type for spraying TLC plates. Periodically, the whole volume of water in one of the bottles was extracted with toluene, the bottle

itself was carefully rinsed with toluene, and the extracts were combined, worked up, and analyzed as described above. These experiments were also performed with fulvic acid solutions in the glass bottles to determine the effect of dissolved organic matter on volatilization from surface slicks. Five sets of volatilization experiments were performed, and each fenitrothion concentration determined was the result of three–five injections.

Field Sampling. Samples of water, suspended solids, and sediment were collected in late May 1977 from a stagnant pond in an uninhabited forested area 8 km due south of the confluence of the Cains and southwest Miramichi rivers in Northumberland County, New Brunswick (lat. 46° 40'; long. 65° 50') before and after a spraying of 1500 g ha⁻¹ emulsion of composition described above. Following is a description of the pond and meteorological conditions at the time of spraying: estimated area, 4.46 × 10² m²; estimated average depth, 0.3 m; water pH 6.7; water temperature, 14 °C; turbidity, 0.9 Jackson units; color, 55 Hazen units; sediment pH 6.0; suspended solids concentration (by continuous flow centrifugation of 600 L), 5 × 10⁻⁴ g L⁻¹; no tree cover, clear and calm, air temperature 17 °C. The weather remained clear and calm for several days after the spraying, with maximum temperatures of 22–25 °C and minimum temperatures of 10–13 °C.

Samples of water and sediment from three different locations in the pond were collected 4 and 2 days before the spraying to establish base line conditions, intensively the day of the spraying (May 30, 1977, 7:30 a.m.), beginning 40 min after the spraying, and with decreasing frequency over the next few days.

The surface microlayer, which is operationally defined by the type of sampler used, was sampled with a 20 × 20 cm glass plate, fitted with a handle. The plate was gently lowered into the water and then withdrawn vertically over a period of 5 s. The water adhering to both sides of the plate (ca. 5 mL) was scraped into a beaker with a neoprene scraper. This procedure was carried out 20 times for each sample, and the bulk (unfiltered) surface sample was stored covered in the dark and transported to a field laboratory for extraction within 2 h. The thickness of the surface microlayer was estimated to be 60 μm (Harvey and Burzell, 1972; Winchester and Duce, 1977).

Bulk (unfiltered) subsurface water samples were obtained by lowering a stoppered 1-L glass bottle below the surface of the water, filling the bottle and replacing the stopper before removing the bottle from the water; the samples were stored in the dark before transportation to a field laboratory for extraction within 2 h.

The top centimeter or so of sediment was sampled with a metal scoop and the samples (ca. 100 g) were stored in the dark in glass bottles with Al foil lined tops, placed in a freezer within 2 h of collection, and kept frozen until analysis.

Samples of suspended solids were obtained by collecting 600 L of bulk subsurface water in twelve 50-L polyethylene containers with a gasoline-powered pump, transporting the water to the field laboratory where the samples were pooled in a 600-L polyethylene container, and passing the entire volume of water through a continuous flow centrifuge, a process which took 8 h. The resulting slurries (ca. 200 mg of suspended solids in 500 mL) were frozen until analysis. It should be noted that fenitrothion in solution will readily bind to polyethylene (Maguire, 1979); however, experiments with fenitrothion and aminofenitrothion bound to suspended solids in polyethylene containers indicated that very little, if any, of these compounds desorb from the suspended solids and become adsorbed to the

polyethylene, even when the relative surface areas of suspended solids and polyethylene container are the same as those of the field experiments. *p*-Nitro-*m*-cresol binds poorly, if at all, to the suspended solids at the pH of the pond water (6.7), so that the temporary storage of the suspended solids samples in polyethylene containers before centrifugation posed no problems as far as fenitrothion, aminofenitrothion, and *p*-nitro-*m*-cresol were concerned.

Sample Extraction and Analysis. In order to avoid the inconvenience, expense, and possible hazards of bringing large quantities of organic solvents into the field, the surface and subsurface water samples were extracted with XAD-2 resin. The efficiency of this technique has been described for organic contaminants of water in general (Junk et al., 1974; Van Rossum and Webb, 1978) and fenitrothion in particular (Mallet et al., 1978). In the field laboratory, most of the bulk surface and subsurface water samples were acidified to pH 1 and passed through 15 × 1 cm diameter columns containing 15 mL of XAD-2 resin, and the water was discarded. The wet resin was transferred quantitatively to glass jars and refrigerated until elution and analysis.

It was established earlier that fenitrothion, fenitrooxon, and *p*-nitro-*m*-cresol were quantitatively adsorbed on XAD-2 resin from acidified water solutions, and that they could be recovered quantitatively, using organic solvents, from batches of resin which had been refrigerated for as long as 9 months. Fifteen milliliters of XAD-2 resin was found to be adequate to adsorb these compounds from 1 L of water at expected "field concentrations" with no "breakthrough", i.e., no column overloading and loss of pesticide. It was felt that acidification of the water to pH 1 would render polar and acidic derivatives of fenitrothion, such as carboxyfenitrothion, amenable to extraction with XAD-2 resin. For example, and in support of this contention, Takimoto and Miyamoto (1976) were able to extract desmethylfenitrothion [*O*-methyl *O*-hydrogen *O*-(*p*-nitro-*m*-tolyl) phosphorothionate] and desmethylfenitrooxon [*O*-methyl *O*-hydrogen *O*-(*p*-nitro-*m*-tolyl) phosphate] into benzene from aqueous solutions of pH 1, and Daughton et al. (1976) used XAD-4 resin (which differs from XAD-2 only in that its surface area per unit weight is larger) to recover dimethylthiophosphoric and dimethylphosphoric acids from acidified aqueous media. Of course, acidification of water samples would render aminofenitrothion, if present, unextractable; therefore, as a precaution, some water samples were extracted, without pH adjustment, with benzene and the extracts were frozen until analysis. Subsequent extraction of the XAD-2 resin with organic solvents was not designed to yield P-containing moieties such as dimethylthiophosphoric acid.

Fenitrothion and its degradation products were desorbed from columns of XAD-2 resin with 20 mL of toluene during an equilibration period of 15 min, followed by a 5-mL toluene wash. This procedure was found to be adequate for control samples of fenitrothion, fenitrooxon, and *p*-nitro-*m*-cresol adsorbed to the resin. The toluene extracts were dried, concentrated to 1 mL, and analyzed by gas chromatography with three different detectors: ECD, FPD (P mode), and FID with usually three injections per determination with each detector, but occasionally as many as 30 injections to check for polar compounds that adsorbed to column packing material. Aliquots of the toluene solutions were also analyzed by gas chromatography-mass spectrometry when appropriate.

Fenitrothion and its degradation products were extracted from the sediments and suspended solids as follows (Coburn, 1978): a known amount of sediment, whose water

Table I. Hydrolysis of Fenitrothion as a Function of pH and Temperature

pH	$k,^a \text{ h}^{-1}$	$T, ^\circ \text{C}$	$k,^{b,c} \text{ h}^{-1}$
13.34 ^c	3.78 ± 0.54	5.0	1.64 ± 0.16
12.54 ^c	1.37 ± 0.15	15.0	3.85 ± 0.47
11.77 ^c	(1.85 ± 0.23) × 10 ⁻¹	25.0	(1.04 ± 0.02) × 10 ¹
10.76 ^d	(8.64 ± 1.44) × 10 ⁻³	35.0	(2.07 ± 0.10) × 10 ¹
		45.0	(4.14 ± 0.18) × 10 ¹
		55.0	(7.52 ± 0.18) × 10 ¹

^a At 25 °C. ^b At pH 13.4. ^c In unbuffered NaOH.
^d In unbuffered NaOH and carbonate buffer of ionic strength 0.05 M.

content had been determined, was placed in a preextracted cellulose thimble and extracted with 300 mL of 1:1 (v/v) acetone-hexane for 6 h in a Soxhlet extractor (5–10-min cycles). The extracted sediment was retained for further analysis. The extract was dried with MgSO₄ and concentrated to 1 mL. The extract was then adsorbed on a column of 5 × 0.5 cm diameter deactivated silica gel (with a 0.5-cm layer of MgSO₄ on top). This minicolumn was then eluted with 10 mL each of solvents of increasing polarity: (1) toluene, for fenitrothion, (2) 1:1 (v/v) ethyl acetate-toluene, for fenitrooxon and compounds of similar polarity, and (3) acetone, for even more polar compounds. The three extracts were dried and concentrated to 1.0 mL each for gas chromatographic analysis as described for extracts of the water samples.

The sediment samples which had been extracted with acetone-hexane were also subjected to chemical and enzymatic hydrolysis. In one set of experiments, sediment was extracted with 1 N HCl in a Soxhlet apparatus for 24 h. The aqueous solution was then extracted with toluene, the pH of the aqueous solution was adjusted to 12, and the solution was extracted again with toluene. The two toluene extracts were dried and concentrated for analysis. In another set of experiments, sediment samples were stirred for 24 h at pH 5.0 and 20 °C with 100 mg mL⁻¹ solutions of either β-glucosidase or the β-glucuronidase/aryl sulfatase preparation. The solutions were then extracted at pH 1 and 12 with toluene and the various extracts were dried and concentrated for analysis.

Least-squares analyses of the results were done with appropriate programs on a CDC 3370 computer.

RESULTS

Hydrolysis of Fenitrothion. Table I contains data on the production of *p*-nitro-*m*-cresol from fenitrothion as a function of pH at 25.0 °C and as a function of temperature at pH 13.4. The reaction followed first-order kinetics. A plot of log k vs. pH is linear with a slope of unity within experimental error (1.04 ± 0.13); the hydrolysis is subject to specific base catalysis. The data agree well with the $k = 2.12 \times 10^{-2} \text{ h}^{-1}$ at pH 10.99 and 25 °C determined by Kovacicova et al. (1973). A plot of log k vs. $1/T$ (K) yields $E_a = 14.0 \pm 0.3 \text{ kcal mol}^{-1}$. It was also shown that dissolved fulvic acid does not catalyze the hydrolysis of fenitrothion at alkaline pH. No *p*-nitro-*m*-cresol was produced from a solution of fenitrothion at pH 7 over a period of 3 months.

Volatilization of Fenitrothion. The volatilization of fenitrothion from true solutions in distilled water followed first-order kinetics for at least 3 half-lives and the volatilization rate constant under our conditions was $(4.50 \pm 0.32) \times 10^{-4} \text{ h}^{-1}$ at 20 °C, corresponding to $t_{1/2} = 64 \pm 5$ days. The presence of 5 mg L⁻¹ dissolved fulvic acid retarded the volatilization significantly, and an estimate was obtained of $t_{1/2} > 180$ days.

Experiments on the volatilization of fenitrothion sprayed on the surface of distilled water showed that $62 \pm 1.5\%$

Table II. Summary of Kinetic Results

	k, h^{-1}	$t_{1/2}, \text{h}$
A. Surface Microlayer		
fenitrothion disappearance (fast)	2.05 ± 0.19	$(3.38 \pm 0.28) \times 10^{-1}$
fenitrothion disappearance (slow)	$(6.92 \pm 2.14) \times 10^{-2}$	$(1.00 \pm 0.31) \times 10^1$
<i>p</i> -nitro- <i>m</i> -cresol appearance	$(3.27 \pm 0.49) \times 10^{-1}$	2.17 ± 0.32
<i>p</i> -nitro- <i>m</i> -cresol disappearance	$(1.09 \pm 0.16) \times 10^{-1}$	6.36 ± 0.93
B. Subsurface Water		
fenitrothion disappearance	$(7.07 \pm 1.13) \times 10^{-2}$	9.80 ± 1.60
<i>p</i> -nitro- <i>m</i> -cresol appearance	$(2.08 \pm 0.09) \times 10^{-1}$	3.33 ± 0.14
<i>p</i> -nitro- <i>m</i> -cresol disappearance	$(1.91 \pm 0.06) \times 10^{-1}$	3.63 ± 0.11
C. Sediment		
fenitrothion appearance	$(3.89 \pm 0.84) \times 10^{-1}$	1.78 ± 0.38
fenitrothion disappearance	$(4.87 \pm 0.63) \times 10^{-2}$	$(1.42 \pm 0.18) \times 10^1$
aminofenitrothion appearance (k_2 only)	$(3.93 \pm 0.53) \times 10^{-2}$	$(1.76 \pm 0.24) \times 10^1$
D. Suspended Solids		
fenitrothion disappearance	$(2.15 \pm 0.09) \times 10^{-1}$	3.22 ± 0.13
E. Fenitrothion Volatilization		
from true solution	$(4.50 \pm 0.32) \times 10^{-4}$	$(1.54 \pm 0.12) \times 10^3$
from surface slicks	2.33 ± 0.84	$(2.97 \pm 1.07) \times 10^{-1}$

the applied dose volatilized in an exponential fashion with a rate constant of $(2.33 \pm 0.84) \text{ h}^{-1}$ at 20°C , corresponding to $t_{1/2} = 18 \pm 6 \text{ min}$. There was no effect of fulvic acid on this volatilization rate. Presumably 62% and not 100% of the fenitrothion volatilized rapidly because fenitrothion was subject to two processes when it was sprayed on the surface of distilled water: immediate volatilization (perhaps by co-distilling with components of the solvent oil) and incorporation into the subsurface water, from which volatilization is a very slow process, as shown above.

Field Sampling. No traces of fenitrothion or any degradation or transformation products were observed in any water, sediment, or suspended solids sample taken before the spraying.

(A) *Surface Microlayer.* In the surface microlayer the fenitrothion concentration 40 min after the spraying was 1.5 mg L^{-1} ; the concentration decreased to $20 \text{ } \mu\text{g L}^{-1}$ over the next 3 h and to $2 \text{ } \mu\text{g L}^{-1}$ 49 h after the spraying. A plot of the logarithm of fenitrothion concentration vs. time was not linear and suggested that two exponential processes were occurring. The data were treated in a manner analogous to the kinetic treatment of two parallel first-order reactions producing a common product (Frost and Pearson, 1961); Figure 1 shows, for one of the sampling sites of the pond, the appropriate plot in which the concentrations in the fast process were corrected for by contributions from the slow process. Similar behavior was observed for the other two sites, and the averaged results are shown in Table II. The "fast" process is so fast that there was some difficulty in defining it accurately ($t_{1/2} = 0.34 \text{ h}$, and the first samples were not taken until 0.67 h after the spraying). The relative values of the ordinate intercepts of each line in plots such as Figure 1 indicate that, at least after 0.67 h, the fast process accounts for the disappearance of all but 0.2–0.4% of the fenitrothion from the surface microlayer.

p-Nitro-*m*-cresol was the only degradation product of fenitrothion found in surface water. Figure 2 illustrates the variation with time of *p*-nitro-*m*-cresol concentration at one of the sampling sites. The kinetic data were treated as if *p*-nitro-*m*-cresol were B in the reaction scheme



which yields (Frost and Pearson, 1961)

$$[B] = \frac{[A]_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (2)$$

The solid line was calculated by a nonlinear least-squares

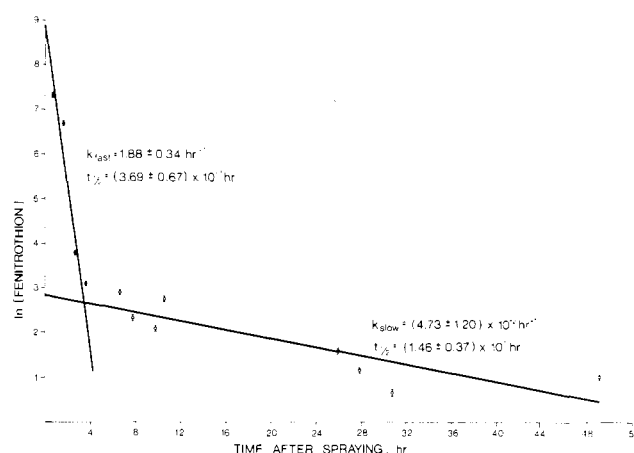


Figure 1. Corrected plot of \ln [fenitrothion] vs. time for the surface microlayer at one of the sampling sites of the pond. Solid circles denote the fast process; open circles, the slow process. Concentrations are in $\mu\text{g L}^{-1}$. Error bars represent standard deviations.

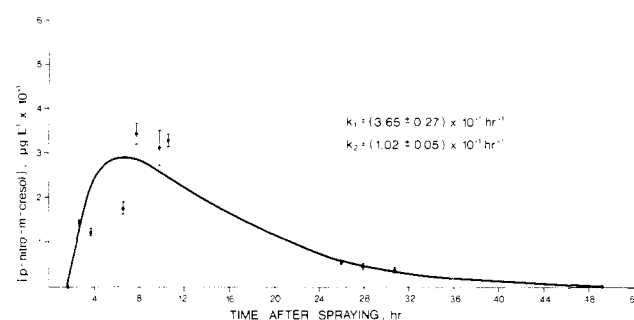


Figure 2. Plot of $[p\text{-nitro-}m\text{-cresol}]$ vs. time in the surface microlayer of one of the sampling sites. Error bars represent standard deviations, and the solid line was calculated by computer.

fit of the data to eq 2, with the "best fit" values of the rate constants as shown in Figure 2. The averaged values of the rate constants from all three sampling sites are shown in Table II.

(B) *Subsurface Water.* Fenitrothion concentrations in subsurface water were about $15 \text{ } \mu\text{g L}^{-1}$ 0.67 h after the spray and declined exponentially to about $0.1 \text{ } \mu\text{g L}^{-1}$ over 49 h. The kinetic data are shown in Table II.

p-Nitro-*m*-cresol was the only degradation product of fenitrothion found in subsurface water. The variation in its concentration was similar to that shown in Figure 2, although in this case the maximum concentration reached

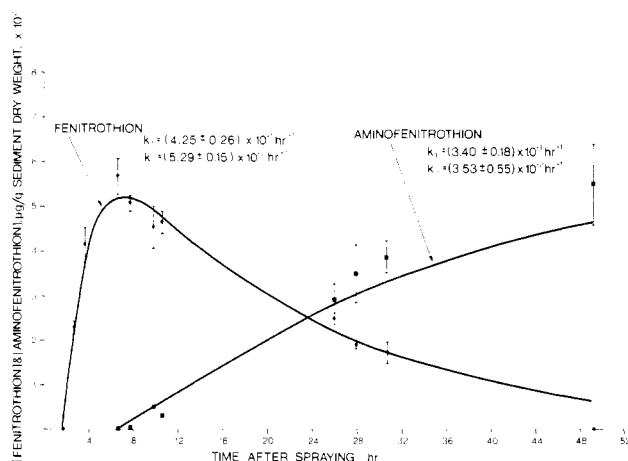


Figure 3. Plot of [fenitrothion] and [aminofenitrothion] in sediment vs. time for one of the sampling sites. Error bars represent standard deviations and the solid lines were calculated by computer.

was about $0.6 \mu\text{g L}^{-1}$. The kinetic data are shown in Table II.

(C) *Sediment.* Figure 3 shows the variation with time of the fenitrothion and aminofenitrothion concentrations in sediment at one of the sampling sites. The data for fenitrothion were treated as if it were B in eq 1. The solid line was calculated by a nonlinear least-squares fit of the data to eq 2, with the "best fit" values of the rate constants as shown, and the averaged values for the rate constants from all three sampling sites are shown in Table II.

No degradation products of fenitrothion were extracted from sediment using organic solvents; however, aminofenitrothion was released by HCl and by both of the enzyme preparations tested. It was established that extraction with 1 N HCl for 24 h in a Soxhlet extractor liberated the maximum amount of aminofenitrothion. The kinetic data for aminofenitrothion were treated as if it were C in eq 1, which yields (Frost and Pearson, 1961)

$$[C] = [A]_0 \left[1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right] \quad (3)$$

The solid line was calculated by a nonlinear least-squares fit of the data to eq 3, with the "best fit" values of the rate constants as shown. The kinetic data are summarized in Table II. Although the kinetics were not monitored in detail, the aminofenitrothion concentration (that extractable from sediments with HCl) declined to zero 4 days after the spraying.

(D) *Suspended Solids.* Fenitrothion was the only compound identified in the suspended solids. Its concentration declined exponentially from $1.9 \mu\text{g}$ (g suspended solids dry weight) $^{-1}$ at 0.25 h after the spraying to $6.5 \times 10^{-3} \mu\text{g}$ (g suspended solids dry weight) $^{-1}$ at 27 h after the spraying. Table II contains the kinetic results.

No trace of fenitrothion or any metabolite was found in water, suspended solids, or sediment 4 days after the spraying.

DISCUSSION

The chemical hydrolysis of fenitrothion, producing *p*-nitro-*m*-cresol and dimethylthiophosphoric acid, appears to be a very slow reaction with little environmental significance as a route of degradation. For example, extrapolation of the data of Table I shows that at pH 7 and 25 °C the half-life for the production of *p*-nitro-*m*-cresol is 54 years. There has been, however, a suggestion that fenitrothion can hydrolyze to desmethylfenitrothion and

methanol at pH 7 (Greenhalgh, 1978); this latter reaction was not examined in this study.

Marshall and Roberts (1977) have used the method of Mackay and Leinonen (1975) to estimate a half-life of 93 days for the volatilization of fenitrothion from a water column 1 m deep. We have demonstrated a half-life of 64 ± 5 days from distilled water at 20 °C; the half-life is considerably longer (>180 days) in the presence of 5 mg L^{-1} fulvic acid, indicating that in natural waters the rate would also be considerably reduced. Thus volatilization from true solution is also a very slow process which appears to have little environmental significance.

By contrast, the volatilization of fenitrothion which has been sprayed on the surface of water appears to be a very fast process, in the laboratory at least; it may also have been important in the pond under investigation, but we have no direct evidence of this since the significance of the surface volatilization experiments was not realized until after the field work was done. More intensive sampling at short time intervals after spraying should clarify this matter; in this case, sampling was not begun until 0.67 h after the spray (cf. $t_{1/2} = 0.3 \text{ h}$ for volatilization from the surface of water). It is instructive to consider the maximum amount of fenitrothion which could be deposited on the surface of the pond after the spraying of, nominally, 210 g ha^{-1} active ingredient. Thus 9.37 g would fall on the pond. If this amount were instantaneously and evenly distributed throughout the mean depth of 0.3 m, the concentration at time zero would be $9.37 \times 10^6 \mu\text{g}/1.36 \times 10^5 \text{ L} = 6.89 \times 10^1 \mu\text{g L}^{-1}$. By comparison, the concentration observed in subsurface water at $t = 0.67 \text{ h}$ is $1.8 \times 10^1 \mu\text{g L}^{-1}$, about 26% of that theoretically present initially. This calculation suggests that about 74% of the fenitrothion initially present is gone after about 0.67 h, but of course it should be regarded with some caution since the nominal amount of fenitrothion may not have reached the pond because of such factors as spray drift and spray droplet evaporation.

Before the field work is discussed, note should be made of three points. First, it is possible that the extraction methods used (XAD-2 resin extraction of acidified water samples and benzene extraction of neutral water samples) may have failed to extract some particularly polar degradation product. Second, this study has not considered aquatic plants as significant environmental "compartments" because of the relatively large (estimated) sediment: plant weight ratio of the pond; Moody et al. (1978) have shown, however, that some submerged plants are capable of accumulating fenitrothion. Third, there is no a priori reason why the disappearance of a particular compound in the environment should exhibit relatively uncomplicated kinetic behavior. Within experimental error, however, the kinetics reported in this study are simply first order or of the first-order consecutive or concurrent types, and the appropriate rate constants are so derived; a first-order rate constant for, e.g., the disappearance of fenitrothion from water may be the sum of first-order rate constants for several processes.

The field work revealed only two degradation or transformation products of fenitrothion, *p*-nitro-*m*-cresol in surface and subsurface water, and aminofenitrothion in sediment. *p*-Nitro-*m*-cresol is produced at about the same rate in surface and subsurface water and disappears at about the same rate, as shown in Table II. *p*-Nitro-*m*-cresol is a product of the photolysis of fenitrothion (Miyamoto, 1977), and it is presumed that its presence in pond water is a result of photolysis, rather than hydrolysis which has been shown to be extremely slow at natural pH. It may

Table III. Amounts (μg) of Fenitrothion, *p*-Nitro-*m*-Cresol, and Aminofenitrothion in Various Compartments of the Pond

time after spraying, h	surface		subsurface		sediment		suspended solids, F^a	total
	F^a	NC^b	F^a	NC^b	F^a	AF^c		
0.67	4.17×10^4	0	2.50×10^6	0	0	0	8.50×10^1	2.54×10^6
1.67	2.25×10^4	0	2.61×10^6	0	0	0		2.63×10^6
2.67	1.26×10^3	4.06×10^2	2.09×10^6	0	6.71×10^4	0		2.15×10^6
3.67	6.24×10^2	3.42×10^2	1.09×10^6	1.02×10^4	1.28×10^5	0		1.23×10^6
6.58	5.10×10^2	4.90×10^2	1.11×10^6	3.14×10^4	1.67×10^5	0	2.40×10^1	1.30×10^6
7.75	2.88×10^2	9.58×10^2	8.49×10^5	5.93×10^4	1.49×10^5	2.93×10^3		1.06×10^6
9.75	2.24×10^2	1.15×10^3	8.73×10^5	7.76×10^4	1.33×10^5	1.47×10^4		1.10×10^6
10.58	4.42×10^2	9.16×10^2	7.26×10^5	5.95×10^4	1.37×10^5	8.55×10^3	1.30	9.32×10^5
26.0	1.36×10^2	1.49×10^2	2.86×10^5	6.62×10^3	7.37×10^4	1.22×10^5		4.88×10^5
27.92	8.70×10^1	1.31×10^2	2.35×10^5	2.43×10^3	5.66×10^4	1.48×10^5	2.90×10^{-1}	4.42×10^5
30.67	5.30×10^1	1.07×10^2	2.65×10^5	2.86×10^3	5.07×10^4	1.43×10^5		4.61×10^5
49.25	7.70×10^1	0	6.94×10^4	0	0	1.61×10^5		2.30×10^5

^a Fenitrothion. ^b *p*-Nitro-*m*-cresol. ^c Aminofenitrothion.

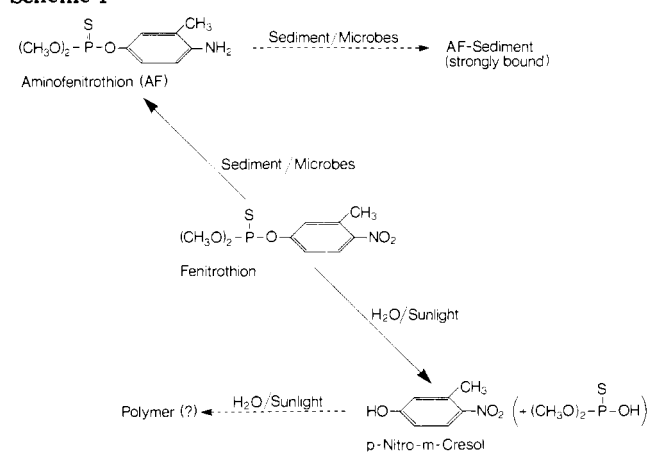
disappear through photolytically mediated polymerization to substances resembling fulvic or humic acids (Miyamoto, 1977) which may then bind to the sediment or suspended solids, or merely remain in solution.

Within experimental error the rate constant for the appearance of aminofenitrothion in sediment is equal to the rate constant for the disappearance of fenitrothion from sediment; these two processes may be directly linked, perhaps through microbial reduction with subsequent covalent bond formation between the amino group of aminofenitrothion and some organic component of the sediment, as suggested by Katan et al. (1976) for the binding of aminoparathion to soil. No attempt was made to fractionate the sediment into humin, fulvic acid, and humic acid in order to determine to which fraction the aminofenitrothion was bound; the use of this fractionation technique with radioactive fenitrothion would be helpful in determining the fate of fenitrothion in sediments. We speculate that this binding process may represent a major "sink" for fenitrothion in aquatic environments, although the question of the mobilization of bound fenitrothion [or aminofenitrothion, which is significantly less toxic (Miyamoto, 1977)] residues by sediment-dwelling biota has not been addressed. In this connection, Fuhremann and Lichtenstein (1978) have shown that earthworms can mobilize unextractable, soil-bound residues of methyl parathion. No aminofenitrothion could be extracted from the sediments sampled 4 days after the pond was sprayed, and it is not clear whether this was because the aminofenitrothion had degraded, or whether it had become even more tightly bound, hence unextractable.

With reference to the preceding discussion, Scheme I summarizes the observed and proposed degradative pathways for fenitrothion in the pond.

It is desirable to determine to what extent the distribution and fate of fenitrothion in the surface microlayer, subsurface water, suspended solids, and sediment can be quantitatively accounted for; the definition of effective sizes of the various compartments (e.g., Marshall and Roberts, 1977) is useful in this regard, since comparisons can then be made of absolute amounts of fenitrothion, *p*-nitro-*m*-cresol, and aminofenitrothion in the various compartments. The effective sizes of the surface microlayer and subsurface water are defined as their volumes. The volume of the surface microlayer is taken to be 28 L ($4.46 \times 10^2 \text{ m}^2 \times 60 \mu\text{m}$) and the volume of the subsurface water is taken to be $1.36 \times 10^5 \text{ L}$ ($4.46 \times 10^2 \text{ m}^2 \times 0.3 \text{ m}$). The effective size of the sediment is defined for convenience since there is a good deal of interstitial water in the sediment, in volume terms, i.e., as the volume of a 1-cm thick section of sediment over the area of the pond. Thus

Scheme I



the "volume" of the sediment is $4.46 \times 10^3 \text{ L}$. This definition of the effective size of the sediment necessitates the expression of the concentrations of fenitrothion and aminofenitrothion in units of $\mu\text{g}/\text{L}$ of sediment" and the conversion is made according to the following formula:

$$[\mu\text{g}/(\text{g sediment dry wt})] \times [0.47(\text{g sediment dry wt})/(\text{g sediment wet wt})] \times [1.4(\text{g sediment wet wt})/(\text{"mL of sediment"})] \times [10^3(\text{"mL of sediment"})/(\text{"L of sediment"})] \quad (4)$$

The figure 0.47 is the average of measurements of the water content of 80 sediment samples taken from the pond; the density factor 1.4 for sediments has been suggested by Neely and Blau (1977) and Marshall and Roberts (1977). The effective size of the suspended solids is defined as the total weight of suspended solids in the pond. The average recovery from the centrifugation experiments was ca. 200 mg/600 L; thus in the whole volume of the pond the effective size is 45 g. Table III shows, for one of the sampling sites of the pond, the amounts (obtained by multiplying the effective size by the concentration) of fenitrothion, *p*-nitro-*m*-cresol, and aminofenitrothion in the various compartments as a function of time and the total amount of parent insecticide plus degradation products. Inspection of the data reveals that (1) the suspended solids pool is not a significant compartment, nor is the surface microlayer in terms of capacity (although it is in terms of transport through the air-water interface); (2) the amount of *p*-nitro-*m*-cresol rapidly increases in the subsurface water until it reaches almost one-tenth the amount of fenitrothion at $t = 9.75 \text{ h}$, but it also decreases rapidly; (3) the amount of aminofenitrothion in the sediment increases

so that $t = 49.25$ h it is the major component of the total amount of fenitrothion plus identified degradation products in the water-sediment system. However, a comparison of the total amount at 49.25 h with the total amount at 0.67 h reveals that only 9% of the fenitrothion initially present in the pond can be accounted for after 2 days. One reason for this lack of accountability is of course that *p*-nitro-*m*-cresol in the subsurface water is degraded or transformed quickly to a compound whose identity and concentration are unknown. The lack of accountability may also be due to (1) errors in assumptions concerning the effective sizes of the compartments, (2) the possibility that other degradation products were not detected, and/or (3) volatilization from the water-sediment system.

In summary, we speculate that a large fraction of fenitrothion reaching the surface of the pond volatilizes rapidly, while the fraction which remains in the water disappears or degrades within a few days, largely through mechanisms of photolysis and microbial reduction.

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