The Fate of Fenitrothion in an Aquatic Ecosystem

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Fenitrothion (O, O-dimethyl-0-(3-methyl-4-nitrophenyl)- phosphorothioate) has been used since 1967, in place of DDT for operational control of lepidopterous defoliators in Canadian forests. By 1975, over 52 million acres of forest land had been sprayed at an average rate of 4 oz/acre in an attempt to control the spruce budworm, Choristoneura fumiferana (Clemens) (Roberts, 1975). Direct contamination of aquatic ecosystems has been reported following aerial spray programs, while indirect contamination may occur from surface runoff following rainfall (Eidt and Sundaram, 1975). Post spray fenitrothion levels reached levels as high as 75.5 PPB (75.5 µg/ℓ) in one case (Lockhart et al., 1973), while much lower peak values were reported from other areas (Sundaram, 1974, Eidt and Sundaram, 1975). In all cases, fenitrothion was not detectable 40 days post spray (Roberts, 1975). The rapid dissappearance of fenitrothion from aquatic systems may involve chemical degradation as well as volatilization, adsorption, photolysis, and microbial degradation.

A study was conducted in June 1975, at Pine Creek near Carberry, Manitoba, designed to determine the fate of fenitrothion in stream water. Samples were taken following aerial deposition of an aqueous formulation (10% fenitrothion, 1% Atlox 3409, 1% Aerotex 3470, 88% water (v/v)) at the rate of 4 oz/acre. Intensive water sampling was conducted during the first week post spray; surface and subsurface water samples were taken from both running and stagnant sections of the stream. Aquatic plant samples included surface dwelling Lemna minor (duckweed) and submergent Ceratophyllum demersum (hornwort), both from stagnant water, and submergent Butomus umbellatus (flowering rush) from the running water. This study took advantage of recently developed chromatographic techniques to determine trace levels of fenitrothion and its metabolites (Hallet et al., 1975).

Bulletin of Environmental Contamination & Toxicology,
0007-4861/78/0019-0008 $1.40

MATERIALS AND METHODS

Sample Site - Two adjacent sections of Pine Creek were selected that had relatively little coverage from the forest canopy (consisting mainly of white spruce with some white birch and trembling aspen). One section (Area 1) was stagnant (< 0.02 m/sec.[1] PH7.5) while the other (Area 2) was fast flowing (0.18 m/sec.[1] PH8.2).

Sampling procedure - At eight selected post spray time periods (1-97/hr), water samples were collected in 1ℓ amber, Nalgene^{R} bottles. Surface samples were collected from the stagnant Area 1 where a surface slick had been concentrated by wind action. Subsurface samples were taken at a depth ranging from 0.3-0.5 m. Larger subsurface samples, collected in 23ℓ polyethylene containers, were taken to be tested for trace metabolites. Aquatic plant samples were collected in polyethylene bags from both areas for up to 192 hours post spray. All samples were transported to the laboratory in styrofoam coolers and were kept refrigerated in the dark prior to extraction.

Extraction procedure

a) Water Samples - Initially, water extraction was carried out following the method of Grift and Lockhart, 1974. 0.5ℓ of each of the Nalgene^{R} bottle samples was filtered through Celite 545 and extracted three times with petroleum ether (100, 50, 50 ml) after addition of 2 gm NaCl to prevent emulsification. The combined ether extract was passed through anhydrous sodium sulphate, concentrated to near dryness in a rotary evaporator, and brought up to 5 ml acetone for analysis. All ether extractions were completed within 10 days post spray. Subsequent chloroform extractions of water spiked with fenitrothion, fenitro-oxon, and S-methyl fenitrothion gave greater recoveries.* For this reason, the large water samples were extracted with chloroform. The samples were first filtered under vacuum through Whatman #43 filter paper.

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[1] measured with a Teledyne-Gurley Mode 1622 flow meter

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	Conc'n (ng/µℓ)	pet. ether	chloroform
fenitrothion	1.0	97%	102%
fenitro-oxon	2.5	17%	104%
S-methyl fenitrothion	9.0	53%	97%

3ℓ of water (filtrate) were extracted twice with chloroform (600, 300 ml). This was repeated 4 times until a total of 12ℓ of each sample had been extracted. The chloroform extract was passed through anhydrous sodium sulphate, concentrated to near dryness and brought up to 10 ml acetone for analysis. The remaining extracted water was freeze-dried and brought up in 5 ml methanol and was kept for determination of any polar metabolites not extracted previously by chloroform partitioning. These methanol samples were derivatized by treatment with diazomethane (20 mins. at 26°C) to facilitate detection of polar metabolites (Hallet et al., 1975). The residue obtained from the filtration procedure was extracted twice with 200 ml of ethyl acetate in a polytron sonicator, filtered through pre-rinsed Celite-545, concentrated, and brought up to 10 ml acetone for analysis.

b) Plant samples - Each sample of hornwort or rush (ca. 100 gm) was thawed at 37°C and the excess surface water was discarded. The sample was extracted three times (300,200, 100 ml) with ethyl acetate in a Waring blender. The combined extracts were passed through anhydrous sodium sulphate, filtered through Celite-545 and concentrated to about 25 ml. The concentrate was placed in a glass column (i.d. 22 mm) that had been dry packed successively with 3 cm Celite-545, 7.0 gm of a charcoal (Nuchar C-190N) and Celite mixture, and 3 cm of anhydrous sodium sulphate (Moody et al., 1975). The extract was eluted successively with 100 ml of 25% ethyl acetate in benzene and 100 ml benzene. The eluant was concentrated to near dryness and brought up to 10 ml acetone for analysis.

The procedure for duckweed extraction differed in that the homogenized sample was first separated into solid and aqueous components by centrifugation (10 mins. at 2°C and 5,900 RCF). The residue was extracted and passed through charcoal as detailed above for the other species. The aqueous supernatant was decanted and extracted three times (100, 50, 50 ml) with chloroform and passed through anhydrous sodium sulphate. This extract was concentrated and brought up to 10 ml acetone for analysis. All solvents used were nanograde and glass distilled.

Analysis - Samples were analysed with a Pye (model 104) gas chromatograph (GC) equipped with an alkali flame ionization detector. The glass column (1.8 m x 4 mm (i.d.)) contained 4% SE-30/6% QF-1 Chromosorb W. Column temperature was 210°C, nitrogen flow 40 ml/min., air flow 500 ml/min., and hydrogen flow 35 ml/min. A second column packed with 3% SE-30 Ultraphase on Chromosorb W was used for crosschecking. Peak areas

of duplicate sample injections were compared with intermittent duplicate standard injections to calculate the PPB (ng/gm) of fenitrothion in the sample.

RESULTS AND DISCUSSION

Table 1 gives levels of fenitrothion detected in water samples at different time intervals. These levels were initially much greater in the surface than in the subsurface water of Area 1 probably due to slow mixing in stagnant water. Rainfall at 21, 38, 65, and 84 hours post spray could account for the fluctuating levels recorded for Area 2. The relatively high level in the surface slick could be due to the affinity of fenitrothion for the oily components present.

TABLE 1

1) SMALL (0.5 L) WATER EXTRACTS:

	PPB FENITROTHION (F) & AMINOFENITROTHION (AF)							
	AREA 1 (STAGNANT)				AREA 2 (RUNNING)			
TIME	SURFACE		SUBSURFACE		SURFACE		SUBSURFACE	
(HR)	F	AF	F	AF	F	AF	F	AF
1	701	NA	9.46	0.05	1.32	TR	1.11	TR
10	44.1	0.35	9.03	0.08	0.57	TR	0.52	ND
23	14.1	0.11	7.45	0.08	0.28	ND	0.22	ND
50.5	3.57	0.08	2.73	0.09	0.14	ND	0.42	ND
70	1.77	0.07	1.15	0.08	0.24	ND	0.35	ND
75	1.89#	0.17#						
84.3	0.84	0.04	0.61	0.03	0.23	ND	0.21	ND
97	0.67	0.02	0.57	0.02	0.23	ND	ND	ND

NA - not analyzed
ND - not detectable <0.01 PPB
TR - trace
\# - suface slick sample

2) LARGE (12ℓ) WATER EXTRACTS:

TIME	WATER	SEDIMENT	
(HR)	PPB (F)	WET WEIGHT (GM)	PPM (F)
26	4.75	0.58	0.89
72	0.36	0.66	0.37

The metabolite referred to in Table 1 had the same GC characteristics as aminofenitrothion, with a relative retention time of 0.74 under the conditions specified earlier with a 3% SE-30 column. Since this metabolite was not detected in the original spray formulation it must have been formed in situ, possibly by microbial degradation. This is consistent with a report by Yasuno et al., (1965) that bacteria isolated from polluted water were capable of inactivating fenitrothion by reduction of the nitro group to give the amino metabolite. Zitko and Cunningham (1974) reported that fenitrothion was degraded to aminofenitrothion and demethylaminofenitrothion (0-methyl-0-(3-methyl-4-aminophenyl)-phosphorothioate) in laboratory held river water. Possible traces of the demethylamino metabolite were detected in the freeze-dried water samples from Area 1. The rapid disappearance of fenitrothion in aquatic systems could thus be partially explained by the pathway depicted in Figure 1.

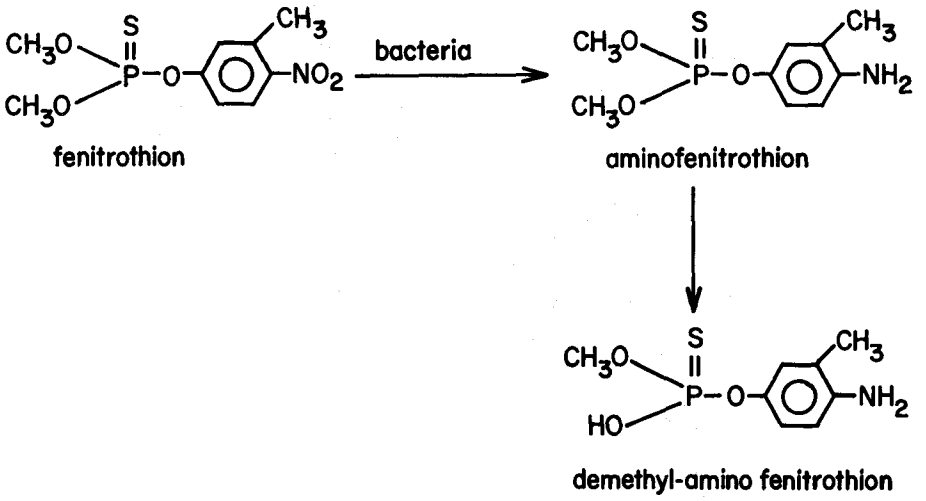

Figure 1. Possible degradation route of fenitrothion.

Traces of S-methyl fenitrothion (0,S-dimethyl-0-(3methyl-4-nitrophenyl)-phosphorothioate) were detected in the surface water of Area 1 at 1 hour (4.4 PPB) and 10 hours (trace) post spray but were not detectable in any of the other samples. Analysis of the original spray formulations demonstrated the presence of 2.47% S-methyl fenitrothion, a value consistent with those reported for some technical formulations (Marshall et al., 1974). Although

this would imply that S-methyl fenitrothion was not being formed *in situ*, its short term presence may still be significant since its *in vitro* anticholinesterase activity is 2 to 3 orders greater than that of fenitrothion (Kovacicova *et al.*, 1973).

Table 2 presents the data obtained from the aquatic plant analyses. The levels of fenitrothion present in the surrounding water are given for comparison and demonstrate the accumulation of the pesticide in the plants from Area 1. The surface dwelling duckweed would have received the initial fenitrothion deposit directly; however, the data also shows rapid uptake of the pesticide during the initial 10 hours post spray. The subsequent rapid disappearance of fenitrothion may be the result of volatilization from the exposed leaf surface as reported previously for conifer tissue (Moody *et al.*, 1975) or to biochemical and photolytic degradation.* Residues persisted at relatively high levels for at least 192 hours in the submergent hornwort.

TABLE 2

FENITROTHION RESIDUES IN AQUATIC PLANTS

			SAMPLE MATERIAL			
SAMPLE SITE	SPECIES	TIME (HR.)	PPM RESIDUE	PPM SUPERNTANT	NET PPM	WATER PPB
Stagnant	L. *minor* (duckweed)	1	1.44	0.26	1.70	701
		10	4.00	0.19	4.19	44
		23	0.10	0.03	0.13	14
		192	0.03	0.002	0.032	(0.67: 97 hr)
Stagnant	C. *demersum* (hornwort)	23			0.12	7.45
		70			0.15	1.15
		192			0.14	(0.57: 97 hr)
Flowing	B. *umbellatus* (rush)	23			ND	0.22
		70			ND	0.35
		192			ND	ND

* Two unidentified metabolites were detected in the duckweed extracts.

Persistence of fenitrothion in aquatic vegetation has not been reported previously and future investigations should be made to determine the possible ecological ramifications. Table 1 also showed strong partitioning of fenitrothion in the water sediment. This may be due to adsorption to the particulate matter, or it may be indicative of active uptake of fenitrothion by microphytes, such as the unicellular algae. These organisms comprise the basis of the aquatic food chain, and it is recommended that they be considered in future investigations of this nature.

ACKNOWLEDGEMENTS

The authors wish to thank D. Metner and R. Vickery for sampling assistance, and M. Wilson and B. Gibb for technical advice. We also wish to thank the Chemical Control Research Institute, Environment Canada, for partial support of this project.

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