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Persistence of aerially applied fenitrothion in water, soil, sediment, and balsam fir foliage

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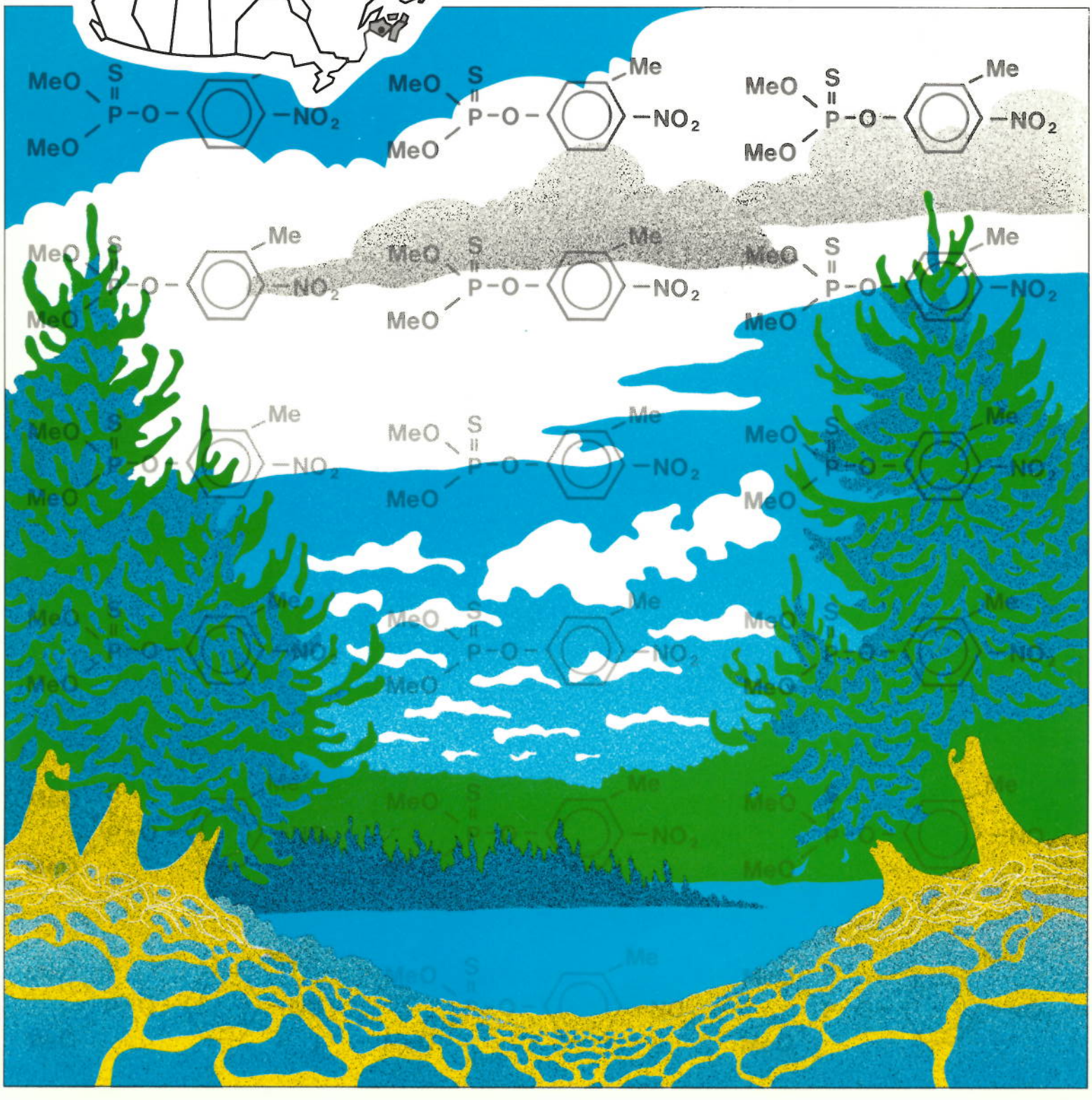

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PERSISTENCE OF AERIALLY APPLIED FENITROTHION IN WATER, SOIL, SEDIMENT, AND BALSAM FIR FOLIAGE

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ABSTRACT

In January 1983, a cooperative study was established to determine whether aerially applied fenitrothion at 2 x 210 g/ha was persisting beyond eight months and accumulating in the New Brunswick environment.

Examined were pond water, pond sediments, mineral soil, and balsam fir, Abies balsamea (L.) Mill., foliage collected in mid winter from sites in New Brunswick sprayed one, two, and three successive years and from unsprayed sites in Nova Scotia. Three recognized laboratories participated in the analysis of samples.

There was reasonable consistency in the residues reported by the different laboratories in water, soil, and sediments, considering that they were near limits of detection. Similar fenitrothion residues were reported in control samples, and it cannot be concluded that residues were present above detection limits in the three substrates from sprayed sites. Fenitrothion residues were positively identified in balsam fir foliage at all treatment sites. Residues in foliage ranged from 0.02 to 0.41 µg/g and tended to persist, and accumulate with each additional year's spray.

RESUME

En janvier 1983, une étude collective a été mise en place afin de déterminer si le fénitrothion épandu en doubles arrosages aériens à la dose de 210 g/ha chaque fois persistait plus de huit mois et s'accumulait dans l'environnement au Nouveau-Brunswick.

On a échantillonné l'eau et les sédiments d'étangs, le sol minéral et le feuillage du sapin baumier, Abies balsamea (L.) Mill., vers le milieu de l'hiver à des emplacements au Nouveau-Brunswick arrosés une, deux ou trois années de suite et à d'autres en Nouvelle-Ecosse n'ayant pas été arrosés. Trois laboratoires reconnus ont participé à l'analyse des échantillons.

Les résultats obtenus par les différents laboratoires concordaient de façon raisonnable compte tenu du fait que les concentrations des résidus dans l'eau, le sol et les sédiments étaient près des limites de détection. Des concentrations similaires ont été mesurées dans les échantillons témoins, et on n'a pas pu conclure que des résidus étaient présents à des concentrations supérieures aux limites de détection dans les trois substrats aux emplacements arrosés. Des résidus de fénitrothion étaient positivement présents dans le feuillage du sapin baumier à tous les emplacements traités. Les concentrations variaient de 0,02 à 0,41 µg/g et semblaient en général persister et s'accumuler avec chaque année additionnelle de traitement.

INTRODUCTION

A substantial amount of research indicated that fenitrothion does not persist longer than a few hours or days in sediments, soils, or water when applied at rates similar to those used in New Brunswick spray programs (Yule 1972; Eidt and Sundaram 1975; Kingsbury 1978; Maguire and Hale 1980). Recent analyses with lower limits of detection by Mallet and Cassista (1982) and Monenco Ltd. (1982) and others suggest that fenitrothion may persist into the next year, at least in sediments and mineral soils. The work was not conclusive, however, as spray drift from nearby operations may have contaminated the study plots. There is little doubt that fenitrothion persists in foliage for a year or more because it has been demonstrated several times (Yule and Duffy 1972; Yule 1974; Sundaram 1974, 1984; Morin et al. 1983). However, in New Brunswick, there has been some confusion about whether residues might be results of persistence, or of drift from elsewhere in the year of sampling.

The findings reported here are the result of a cooperative effort to address the problem of fenitrothion persistence in water, pond sediments, mineral soils, and conifer foliage. The study was based on two objectives:

(1) To establish whether fenitrothion is persisting in four compartments of the New Brunswick forest ecosystem, eight months after spray for budworm control.

(2) To determine if a correlation exists between residues (if detected) and spray histories of sampled areas.

MATERIALS AND METHODS

Pond water, pond sediment, mineral soil, and balsam fir foliage, Abies balsamea (L.) Mill, were sampled at 12 treated sites in New Brunswick and four control sites in southwestern Nova Scotia in February 1983 (Table 1). All ponds sampled were small and without spray setback zones. Duplicate samples of balsam fir foliage from two of the 12 experimental sites were sent to Quebec for confirmatory analysis. Conifer foliage samples collected at two sites in Quebec by the Ministère de l'Energie et des Ressources were forwarded to New Brunswick for analysis.

Control areas and areas with three different spray histories were sampled.

(1) Sprayed in 1980, 1981, 1982, twice at 210 g/ha
(2) Sprayed in 1980, 1981, twice at 210 g/ha
(3) Sprayed in 1980, twice at 210 g/ha
(4) Control, never sprayed.

The Quebec sites received two applications of fenitrothion at 210 g/ha in 1980 and single applications of fenitrothion at 210 g/ha in 1981 and 1982.

Three laboratories analyzed some samples of all four substrates.

(1) New Brunswick Research and Productivity Council (RPC)
(2) Ontario Research Foundation (ORF)
(3) Université de Moncton (U de M)

A fourth laboratory at the Ministère de l'Environnement du Québec (MEQ) analyzed only balsam fir foliage samples sent from New Brunswick, in exchange for analyses in New Brunswick of samples sent from Quebec.

RPC and U de M received replicate water samples from all sites as well as two spiked and one blank water sample prepared by the Inland Waters Directorate Laboratory at Moncton, New Brunswick. ORF analyzed spiked but not field-collected water samples. Replicate soil and water samples and split sediment samples from each site were analyzed by RPC, U de M, and ORF. ORF analyzed duplicate samples of the three substrates from about one-half the sites.

Table 1. Descriptions of sampling sites

Soil, foliage, and sediment sites	Water sites	Parish and county	Coordinates		Name and type	Water body: Depth at sampling point(m)	Water body: Area (ha)
1	1	Douglas, York	N46° 23'	W66° 50'	Middle Brook, beaver pond	0.91	1.0
2	2	Ludlow, Northumberland	N46° 34'	W66° 20'	Priceville, beaver pond	0.45	0.5
3	3	St. George, Charlotte	N45° 27'	W66° 48'	Cranberry Lake	1.22	12.5
4	4	St. George, Charlotte	N45° 26'	W66° 48'	Blind Lake	0.61	3.5
	5				Spike[1]		
6	6	Petersville, Queens	N45° 24'	W66° 23'	Caribou Lake	1.83	25.0
7	7	Petersville, Queens	N45° 22'	W66° 20'	Little Deer Lake	2.44	7.0
	8				Spike[1]		
9	9	Petersville, Queens	N45° 20'	W66° 25'	Little Indian Lake	0.91	12.5
10	10	Petersville, Queens	N45° 21'	W66° 24'	Pond #1 North of Little Indian Lake	0.61	2.5
11	11	Petersville, Queens	N45° 22'	W66° 26'	Pond #2 North of Pond #1	0.61	1.0
12	12	Kent, Carleton	N46° 45'	W67° 00'	Green Lake	0.61	2.5
	13				Blank[2]		
14	14	Westfield, St. John	N45° 15'	W66° 27'	Pond North of Donaldson	0.30	4.0
15	15	Petersville, Queens	N45° 21'	W66° 27'	Spectacle Lake	0.30	14.0
16	16	Queens Co., N.S.	N44° 25'	W64° 55'	Frank Lake	1.52	75.0
17	17	Queens Co., N.S.	N44° 25'	W65° 09'	Minard Lake	0.61	150.0
18	18	Queens Co., N.S.	N44° 23'	W65° 05'	Harmony Lake	0.91	468.0
19	19	Queens Co., N.S.	N44° 22'	W65° 00'	Charlotte Lake	1.22	80.0

[1]Distilled water with a known concentration of fenitrothion added.
[2]Distilled water.

Sampling Procedures

All samples were collected in February and the first week of March 1983. Sample containers and sampling instruments were rinsed with organic solvents: instruments with hexane, and bottles and jars with acetone, twice with ethyl acetate, and with hexane.

Water

An area on the ice of about 4 m^2 was cleared of snow and a suitable hole was drilled with a hand auger and an ice chisel. A hexane-rinsed, air-dried, metal strainer was used to clear the hole of small pieces of ice. The water in the hole was then allowed to sit undisturbed for roughly 5 min before the water sample was taken.

A 4-L brown glass bottle (precleaned and labelled) was immersed quickly to a depth equal to the ice thickness. Replicate samples were collected at each station. The bottles were sealed with hexane-rinsed aluminum foil and capped. The samples were preserved within 4 h with 150 mL pesticide grade hexane. The samples were then delivered to the laboratories.

Sediment

Using the hole cut for water samples, a hexane-rinsed 23 x 23 cm Ekman grab was lowered gently to the bottom of the pond, then closed. The grab was brought to the surface and excess water was allowed to drain off. Using a hexane-rinsed neoprene glove, sediment was mixed and scooped from the grab into three 455-mL Mason jars precleaned with solvents and labelled. Sediment around the mouths of the jars was removed with a hexane-rinsed stainless steel knife; the jars were sealed with hexane-rinsed aluminum foil and capped. Samples froze in the field and were kept frozen until delivered to the laboratories.

Foliage

Three or four balsam fir branches were removed with pole pruners from the exposed crowns of different trees in the vicinity of the pond where sediment and water samples were collected. At about half the sites the trees were beneath a hardwood canopy. Needles of the year 1980 at each site were removed from the branches with a PVC-gloved hand, then thoroughly mixed. At least 30 g were placed in each of three precleaned, 455 mL, Mason jars. The samples were frozen within 6 h and one sample from each site was delivered to each of the analytical laboratories. No foliage was gathered at site 14 because suitable balsam fir trees were unavailable. A separate 30-g subsample from each of sites 2 and 15 was sent to the Ministère de l'Energie et des Ressources du Québec for analysis.

Soil

Soil samples were gathered as close as possible to the vicinity of the foliage collections at each site. Snow and the frozen litter layer were removed with an axe down to the top of the first mineral horizon. Approximately 5 cm including the A, and part of the B horizons were removed, also with an axe, and at least 30 g were placed in each of three precleaned, 455-mL Mason jars. Care was taken to ensure that the vertical distribution of soil was nearly uniform among samples. It was not possible to mix and split samples because the soil was frozen.

Analytical Methodologies

Water

RPC: Three hundred grams of anhydrous sodium sulfate were added to the original 4-L sample container to break down emulsions. The contents including the 150 mL hexane previously added in the field were mixed for 1 h on a magnetic stirrer. The hexane layer was separated and dried by passing it through a column packed with anhydrous sodium sulfate. The mixing and separation were repeated using 50 mL hexane. The combined hexane extracts were subsequently concentrated to a final volume of 1.0 mL, for GC analysis.

ORF: Two-litre aliquots of the sample were extracted twice with 100 mL hexane and twice with 100 mL methylene chloride by mixing with a magnetic stirrer for 20 min each and separating. The solvent fractions were dried by passing through anhydrous sodium sulfate, pooled, and halved for duplicate analyses. These were concentrated, then made up to 5 mL in benzene for GC analysis.

U de M: Four-litre samples were extracted by adding 100 g anhydrous sodium sulfate to break down emulsions, and by mixing the contents, including 150 mL hexane added in the field, on a magnetic stirrer for 30 min, then separating. The mixing and separations were repeated twice with 100 mL hexane. The extracts were pooled and dried with anhydrous sodium sulfate and concentrated to a final volume of 1.0 mL for GC analysis.

MEQ: Two-litre samples were extracted with 150 mL ethyl acetate and repeated twice using 100 mL of the same solvent. The ethyl acetate extract was then dried by vacuum filtration through 100 g anhydrous sodium sulfate, then concentrated to 20 mL for GC.

Soil and Sediment

RPC: Ten grams of drained sediment or soil was mixed with 100 mL ethyl acetate in a blender. A 10-mL aliquot (equivalent to 1 g of sample) was cleaned by passing through a charcoal column followed by concentration of the eluate to a final volume of 1.0 mL for GC analysis.

ORF: To 20 g of drained sediment or soil, 10 mL (20 mL if dry) 0.5 M sodium sulfate and 150 mL ether were added, and the mixture was shaken for 20 min. The ether was then decanted and dried through anhydrous sodium sulfate. The process was repeated twice with 75 mL ether and the pooled fractions were concentrated and made up to 5 mL in methylene chloride. A Florisil adsorbent column was used for cleanup. A final extract volume of 5 mL in benzene was used for GC analysis.

U de M: Sediments but not soils were filtered to remove excess water. Half of each sample was used for moisture content determination, and half was extracted in a blender using 150 mL ethyl acetate, filtered and rinsed with acetonitrile. The pooled filtrate was then diluted to 2 L with distilled water and passed through an XAD-7 resin column at 130 mL/min followed by 1 L distilled water. The column was then eluted with four 25-mL aliquots of ethyl acetate. The eluate was dried with anhydrous sodium sulfate and evaporated to 10 mL for GC analysis.

Foliage

All foliage samples were split, and the two parts analyzed separately by all laboratories.

RPC: The same procedure as for soil and sediment was used.

ORF: Ten grams was extracted in a Waring Semimicro blender with 100 mL acetone and 60 g anhydrous sodium sulfate for 1 min. The blend was filtered and the filtrate plus 50 mL rinsings were concentrated to dryness; then 5 mL methylene chloride and a small amount of anhydrous sodium sulfate were added. Cleanup on Florisil followed, then analysis by GC.

U de M: Ten grams was homogenized for 5 min with 150 mL acetonitrile in a Polytron homogenizer. After filtering and rinsing the procedure was the same as for soil and sediment.

MEQ: Fifty grams foliage and 150 mL ethyl acetate were mixed for 3 min in a 600-mL glass beaker with a Polytron homogenizer then filtered through glass fibre. The extraction was repeated twice using 100 mL ethyl acetate. The extracts were pooled, dried by passing through a column packed with 100 g sodium sulfate, and concentrated to 20 mL. Ten millilitres of the extract was diluted in 50 mL acetonitrile, placed in a separatory funnel and a partition made with two portions of 25 mL hexane.

The polar phase of acetonitrile was removed and concentrated to about 2 mL, then purified by column chromatography (300 x 20 mm I.D.) containing activated charcoal and Celite (6:4). The eluate benzene: ethyl acetate (4:1) was then concentrated to 5 mL for GC analysis.

Analytical Instrumentation

RPC: A Hewlett-Packard 5840A gas chromatograph (GC) equipped with a nitrogen-phosphorus selective detector (NPD) was used. Packed columns containing 6% OV-101/3% OV-210 for water samples and 1.5% OV-17/1.95% OV-210 for solid substrates were used.

ORF: For analysis of water, a Tracor MT-220 GC with a ^{63}Ni Electron Capture Detector (ECD) was used with a 5% OV-30 column. Foliage samples were analyzed with a Hewlett-Packard 5700 capillary GC equipped with a NPD. The wide-bore DB-5 fused silica column was temperature-programmed after on-column manual injection of the sample. Sediment and soil samples were analyzed on a Hewlett-Packard 5700 GC equipped with an ECD (^{63}Ni) and HP-7671 automatic injector. A 3% SE-30/6% OV-215-packed column was used under isothermal conditions.

U de M: The four sample types were analyzed using a Tracor 560 GC equipped with an NPD. Concentrated extracts were manually injected on a glass column packed with 3% OV-101 and chromatographed under isothermal conditions. For water, a 5-μL aliquot was injected, for foliage, sediment, and soil extracts, 1 μL was injected.

MEQ: A Hewlett Packard 5730A gas chromatograph equipped with an NPD was used. Packed columns consisting of 4% OV-101 6% OV-210 on Gaschrome Q (80-100 mesh) were used.

Confirmation Procedures

RPC: Gas chromatography-mass spectrometry (GC-MS) was used to confirm the presence of fenitrothion in some sample extracts. The Finnigan 4021 GC-MS system used consisted of a capillary GC with split/splitless injector coupled to a mass spectrometer with EI/CI capability and Incos data system.

The system was run on SIM mode where five ions (m/e 109, 125, 247, 260, 277) were monitored. Standard detectability was > 200 pg. The first two ions were interfered with by a major peak just before fenitrothion which was constituted mainly of the m/e 109 ion. Thus, the last three ions, which were relatively free of interference, were used. Fenitrothion was considered present only if the relative intensities of these ions matched a standard sample.

ORF: Fenitrothion in water was confirmed by GC + NPD using a column of different polarity. Fenitrothion was confirmed by packed column GC using an ECD instead of NPD.

U de M: The presence of fenitrothion was confirmed by three procedures: (1) by spiking sample extracts with fenitrothion to yield an increase of peak height; (2) by analyzing samples using a different detector type such as FPD and a column of different polarity such as 3% OV-101/5% OV-210; and (3) by treating aliquots of extracts with chromous chloride, to reduce any fenitrothion present to aminofenitrothion, analyzing the extracts by GC along with a standard treated the same way, and comparing retention times to confirm presence of fenitrothion.

QME: Fenitrothion in foliage was confirmed by using packed columns of different polarity, i.e., 3% OV-17 on a Gaschrome Q support.

Quality Control

To achieve quality control among laboratories, spiked water samples were prepared, and submitted as blind samples with the field water samples. The spiked samples were prepared at the Inland Waters Directorate analytical laboratory in Moncton, N.B. Water from Turtle Creek near Moncton was used. Analysis by

I.W.D. of three replicate 4-L samples and one 12-L sample of creek water had failed to show any detectable fenitrothion (limits of detection: 0.002 µg/L for 4-L samples, 0.0007 µg/L for 12-L samples).

Three 4-L aliquots were spiked at 0.025 µg/L and another three 4-L aliquots were spiked at 0.20 µg/L. As with field samples, hexane (100 mL) was added for preservative.

The detection limits for each of the three laboratories were

	Water (µg/L)	Soil (µg/g)	Sediment (µg/g)	Foliage (µg/g)
ORF	0.01	0.01 (wet)	0.01	0.01
RPC	0.002	0.02 (dry)	0.05	0.01
U de M	0.003	0.002-0.007* (dry)	0.002-0.07*	0.01

*Varied with sample size.

Sediments were based on drained wet weights; foliage on fresh weights.

RESULTS

The results of analyses for all laboratories are given in Tables 2 to 6 for water, sediment, soil, and foliage. Results of analyses of variance and Duncan's Multiple Range Test for differences among regimes and sites are given in Tables 7 to 9.

DISCUSSION

Water

There was excellent agreement among the three laboratories on the concentration of fenitrothion in spiked and blank water samples (Table 2).

Table 2. Results of analysis of spiked and blank water samples (µg fenitrothion/L). Results not corrected for extraction efficiency

Sample No.	Spiked conc.	RPC	ORF	U de M
5	0.025	0.030	0.03[1]	0.02
8	0.20	0.160	0.20[1]	0.20
13	0.00	ND[2]	-	ND

[1]Means of duplicate analysis: 0.03, 0.02 and 0.19, 0.20, respectively.
[2]Not detectable.

Only RPC and U de M analyzed field samples (Table 3); RPC reported residues in three of the four samples from control sites that were higher than those from treated sites; U de M reported a questionable residue only at one site, because it was at the detection limit of 0.003 µg/L. In samples from treated sites (Table 3), RPC reported fenitrothion in water at very low levels except at site 10 where a significant high concentration of an organic compound, not necessarily fenitrothion, was found. Subsequent attempts by RPC to confirm the presence of fenitrothion with GC/MS were unsuccessful. U de M did not detect fenitrothion in water from 11 of the 12 treated sites; at site 10, they detected an unconfirmed trace which may be ignored. It is difficult to explain why RPC found residues, albeit near the detection limits, in some samples from all treatments. Their data have little meaning because they found residues twice as large in controls located in areas remote from sprayed areas.

Previous research indicates that fenitrothion does not persist in either stream or pond water for any length of time (Eidt and Sundaram 1975; Kingsbury 1978; Maguire and Hale 1980). On the other hand, Sundaram (1984) found residues of 0.07 to 0.40 ppb µg/L in shallow ponds (ca. 3 m^2 x 20 cm deep) after one

Table 3. Fenitrothion residues in pond water samples (µg/L). Results not corrected for extraction efficiency

Regime	Site	RPC	U de M
1 Sprayed 1980,1981, 1982	12	ND	ND
	14	ND	ND
	15	0.003	ND
	2	ND	ND
2 Sprayed 1980,1981	1	0.003	ND
	9	0.002	ND
	10	ND	ND
	11	0.002	ND
3 Sprayed 1980	3	0.007	ND
	4	ND	ND
	6	ND	ND
	7	ND	ND
4 Not sprayed	16	0.014	0.003
	17	ND	ND[1]
	18	0.010	ND[1]
	19	0.010	ND[1]

ND - Not detectable.
[1]Duplicate samples also ND.

to five previous consecutive years of spraying. He assumed the fenitrothion was not persistent in the water, but had leached from foliage and from fallen leaves, and was transported in rain and drainage waters.

Sediments

There was little apparent consistency among laboratories for presence and concentration of fenitrothion in sediments (Table 4). ORF found no residues in samples from any of the sites, but RPC detected fenitrothion in samples from five and U de M from five sites. RPC and U de M reported positive results for only two sites in common; the residues were near the detection limits of both laboratories and ranged from <0.005 to 0.17 µg/g. This inconsistency emphasizes the difficulties in detection and measurement of fenitrothion residues near the detection limits and it must be assumed that meaningful residues were not present at any of the sites. Maguire and Hale (1980) observed that fenitrothion in a pond sediment fell below detectable concentrations (assumed to have been 0.01 µg/g) two days following aerial application.

Soils

RPC and ORF did not detect fenitrothion in mineral soils at any of the treated sites (Table 5). U de M detected residues at 8 sites; the reported concentrations were 0.01 µg/g or lower, very close (0.005 µg/g) to their detection limit, which varied with the weight of the sample, but at or below the detection limits of RPC and ORF. Small residues, apparently fenitrothion, were detected by U de M in blanks analyzed with the samples. The results suggest that no meaningful residues were present in the soils at the sites studied. To put this into a biological perspective, Health and Welfare Canada regulations state that 0.1 ppm or less in food is a negligible residue. Our observations are consistent with Miyamoto's (1978) that there is no evidence for accumulation or persistence of fenitrothion in soil. Yule (1974) did not detect fenitrothion concentrations above 0.01 µg/g in the top 15 cm of forest soil. Sundaram (1974) found that concentrations in soil following spray were much lower than in foliage and that by 45 days after spray they had disappeared below his detection limits of 0.005 µg/g. He later reported concentrations of 0.013 to 0.34 µg/g in soil about a year after the last spray (Sundaram 1984). He found no accumulation with repeated annual spraying and postulated various physical and biological reasons for origin and loss.

The organic layer on top of the forest floor was not sampled. Residues were found in litter one year after treatment in Quebec (Morin et al. 1983) and in Ontario (Sundaram 1984) but there was no evidence of accumulation. Sundaram found greater concentrations in

Table 4. Fenitrothion residues in pond sediment samples (µg/g). Results not corrected for extraction efficiency

	Regime	Site	RPC	ORF	U de M
1	Sprayed 1980, 1981, 1982	12	ND (ND)[1]	ND (ND)	ND
		14	ND (ND)	ND (ND)	ND
		15	0.15 (0.06)	ND (ND)	ND
		2	0.17	ND (ND)	0.020 (ND)
2	Sprayed 1980, 1981	1	ND (ND)	ND (ND)	0.07 (0.06)
		9	ND (ND)	ND (ND)	0.020 (0.020)
		10	ND (ND)		ND (ND)
		11	ND (0.05)	ND (ND)	ND
3	Sprayed 1980	3	ND (ND)		ND (0.10)
		4	0.07 (ND)	ND (ND)	0.010 (ND)
		6	ND (ND)		ND
		7	ND (0.07)	ND (ND)	ND
4	Not sprayed	16	ND (ND)		ND
		17	ND (ND)	ND (ND)	ND
		18	ND (ND)		ND
		19	ND (ND)	ND (ND)	ND (ND)

[1]Duplicate samples in parentheses. RPC and U de M results based on dry weights; ORF on wet weights.
ND - not detectable.

litter than in soil and postulated that it was due to adsorption and dissolution of the lipoidal humus component and its persistence due to greater acidity and lower microbial content.

Foliage

The fenitrothion concentrations in foliage from all treated sites (Table 6) were well above the detection limits of all laboratories (>0.01 µg/g). Analysis of variance of the foliage data indicated significant differences among regimes, and sites (Table 7). A more specific statistical analysis using Duncan's Multiple Range Test indicated some significant differences among the four regimes (Table 8). The 1980 foliage from regime 1 (sprayed 1980, 1981, 1982) contained significantly higher residues than that from regime 2 (sprayed 1980, 1981) or that from regime 3 (sprayed 1980); however, regimes 2 and 3 were not significantly different. The failure to demonstrate a significant difference between regimes 2 and 3 could have been due to differences in actual deposition due to drift and differential exposure of sampled foliage.

The sites could have received drift from adjacent or nearby spray areas. In Quebec, Morin et al. (1983) measured fenitrothion residues in balsam fir foliage 14.5 km from a spray zone; concentrations decreased with distance from the spray block. Significant residues in water have been recorded as far as 30 km from sprayed areas (Monenco 1978).

Another factor of importance could be the location of the trees sampled within the forest and the position of the branches sampled. Although more than one tree was sampled at each site, sometimes all of the trees available at a site were under a hardwood canopy. Also, at

Table 5. Fenitrothion residues in inorganic soils samples(µg/g). Results not corrected for extraction efficiency

	Regime	Site	RPC		ORF		U de M[2]	
1	Sprayed 1980, 1981, 1982	12	ND	(ND)[1]	ND	(ND)	0.004	
		14	ND	(ND)	ND	(ND)	0.008	(0.006)
		15	ND	(ND)	ND	(ND)	ND	
		2	ND	(ND)	ND	(ND)	0.005	
2	Sprayed 1980, 1981	1	ND	(ND)			0.007[3]	
		9	ND	(ND)	ND	(ND)	ND	
		10	ND	(ND)			ND	
		11	ND	(ND)	ND	(ND)	ND	
3	Sprayed 1980	3	ND	(ND)			0.009	(0.006)
		4	ND	(ND)	ND	(ND)	0.007	
		6	ND	(ND)			0.005	
		7	ND	(ND)	ND	(ND)	0.01	(0.007)
4	Not sprayed	16	ND	(ND)			ND	
		17	ND	(ND)			ND	
		18	ND	(ND)			ND	
		19	ND	(ND)	ND	(ND)	ND	

ND - not detectable.
RPC and U de M results based on dry weights; ORF results on wet weights.
[1]Duplicate samples in parentheses.
[2]Reported values reflect low detection limits.
[3]Confirmed with another instrument.

some sites, foliage could not be collected from the top half of the trees and was collected from the lower half. Translocation of fenitrothion does not occur (Prasad and Moody 1976), thus higher concentrations could accumulate at the tops of trees not in an understorey. This could help explain residue differences from site to site. Actual deposition on the canopy is highly variable and chance alone could produce the lack of difference between regimes 2 and 3.

There is mixed evidence in literature of fenitrothion accumulation in foliage. Yule (1974) stated that fenitrothion residues appeared to have persisted and accumulated in balsam fir foliage over a number of years with repeated annual applications. Morin et al. (1983) were unable to demonstrate accumulation of fenitrothion residues in foliage with increasing numbers of years of treatment.

Residues in foliage can be of ecological significance. McNeil et al. (1979) found that fenitrothion residues in jack pine needles were increasingly toxic to the larvae of Swaine jack pine sawfly, Neodiprion swainei (Midd.), with each year's accumulated residues.

Residues recorded by U de M were generally lower than those reported by ORF or RPC. The different methods used by the laboratories may have affected the results; there is no other explanation for the differences among laboratories.

A wide range of residues occurred among sites within the same regime, with

Table 6. Fenitrothion residues in balsam fir foliage (µg/g fresh weight). Results not corrected for extraction efficiency

	Regime	Site	RPC 1	RPC 2	RPC $\bar{x}$	ORF 1	ORF 2	ORF $\bar{x}$	U de M 1	U de M 2	U de M $\bar{x}$
1	Sprayed 1980, 1981, 1982	12	0.12	0.13	0.12	0.18	0.26	0.22	0.06	0.07	0.07
		15	0.26	0.26	0.26	0.18	0.19	0.18	0.13	0.10	0.12
		2	0.41	0.40	0.40	0.31	0.35	0.33	0.29	0.37	0.33
2	Sprayed 1980, 1981	1	0.22	0.26	0.24				0.03	0.18	0.10
		9	0.07	0.09	0.08	0.07	0.08	0.08	0.07	0.07	0.07
		10	0.10	0.14	0.12				0.07	0.09	0.08
		11	0.05	0.07	0.07	0.06	0.07	0.06	0.04	0.04	0.04
3	Sprayed 1980	3	0.06	0.08	0.07				0.04	0.05	0.04
		4	0.09	0.14	0.11	0.09	0.10	0.10	0.04	0.06	0.05
		6	0.02	0.02	0.02				0.02	0.02	0.02
		7	0.28	0.32	0.30	0.16	0.15	0.16	0.20	0.19	0.20
4	Not sprayed	16	ND	0.03					ND	ND	
		17	ND	0.02		ND	ND		ND		
		18	ND	0.02					ND	ND	
		19	ND	0.01		ND	ND		ND		

$\bar{x}$ mean of two parts of divided sample.
ND - not detectable.

Table 7. Analysis of variance of fenitrothion residues in balsam fir foliage

Source	DF	SS	F	Probability of greater value of F
Regimes	3	0.430	92.23	0.0001
Sites	11	0.312	18.23	0.0001

Table 8. Results of Duncan's Multiple Range Test for fenitrothion residues in foliage by spray regimes

Regime	Mean*	N
1 (3 sprays)	0.225a	18
2 (2 sprays)	0.093b	20
3 (1 spray)	0.104b	20
4 (control)	0.005c	16

*Means followed by same letter not significantly different, $\underline{P} = 0.05$.
df = 57 MS = 0.002

one site usually quite different than the others (Table 9). Although the sites within a regime differed, the scatter within sites was not great, indicating reasonably good agreement among laboratories. The differences among laboratories were greatest at four of five sites with higher concentrations (sites 1, 7, 12, and 15, but not 2). The differences in residues reported in foliage could result from either differences in quantitation techniques or extraction efficiences. Since the results from all three laboratories that analyzed spiked and blank water samples were close to actual concentrations and the procedure was the same for all media, the calibration curves were probably similar. It is nonetheless probable that the differences among laboratories in residues found in foliage were due to differences in procedure.

Results for New Brunswick foliage samples analysed in Quebec were similar to those reported by U de M and RPC (Table 10). The same was also true of samples forwarded from Quebec to Environment New Brunswick and analyzed by RPC, U de M, and ORF. Quebec samples were not comparable with New Brunswick samples, all from regime 1 (sites 2 and 15). The Quebec stations received double applications of 210 g/ha in 1980 but only single applications in 1981 and 1982. Also, site 2 in Quebec received an extra, unmeasured amount of fenitrothion in 1982 from a jettisoned spray load.

Table 9. Results of Duncan's Multiple Range Test for the differences in fenitrothion residues in foliage by site

Regime	Site	N	Mean*
1 (3 sprays)	2	6	0.354a
3 (1 spray)	7	6	0.216b
1	15	6	0.185b
2 (2 sprays)	1	4	0.173bc
1	12	6	0.135cd
2	10	4	0.099de
3	4	6	0.086e
2	9	6	0.073e
2	11	6	0.055e
3	3	4	0.055ef
3	6	4	0.018f
4 (no spray)	16	4	0.007f
4	17	4	0.006f
4	18	4	0.006f
4	19	4	0.003f

*Means followed by the same letter not significantly different at 95% level of confidence.

CONCLUSIONS

1. Although fenitrothion residues near detection limits were reported in pond water, pond sediments, and mineral soils by one or more participating laboratories, the inconsistency and small concentrations reported preclude any conclusions about the presence of fenitrothion residues. The question can only be answered by further more rigorous study, but it is hardly worth the effort because accumulation and biological significance have not been demonstrated. The concentrations reported were generally less than 0.1 ppm, which is considered negligible in human food.

2. Fenitrothion residues were persistent, and in general, accumulated in balsam fir foliage over three successive years of spraying. Foliage sprayed twice did not contain statistically different residues from those in foliage sprayed once, but residues were significantly greater in foliage sprayed three times.

Table 10. Results of analyses of balsam fir foliage samples exchanged with Ministère de l'environnement du Québec

Stations (Quebec) and site (N.B.)	Province	Lab	Fenitrothion (µg/g wet weight) 1	2	$\bar{x}$
1	Quebec	MEQ	0.20	0.19	0.20
		U de M	0.12	0.15	0.14
		RPC	0.23	0.34	0.29
2	Quebec	MEQ	3.39	3.28	3.34
		U de M	2.13	2.40	2.26
		RPC	2.00	2.40	2.20
2 (3 sprays)	New Brunswick	MEQ	0.40	-	0.40
		RPC	0.41	0.40	0.40
		U de M	0.29	0.37	0.33
		ORF	0.31	0.35	0.33
15 (3 sprays)	New Brunswick	MEQ	0.20	-	0.20
		RPC	0.26	0.26	0.26
		U de M	0.13	0.10	0.12
		ORF	0.18	0.19	0.19

3. Differences among laboratories in reported residues in foliage were probably due to differences in analytical procedure.

RECOMMENDATIONS

To increase confidence in future residue analyses, at concentrations near detection limits, it is important that a second laboratory analyze some duplicate samples. Laboratories should receive samples without knowledge of duplicates, replicates, or sites. It is advisable that laboratories should participate in independent tests with known samples. Even with these precautions, conclusions based on results near detection limits must be interpreted with extreme caution.

To reduce differences in results, different methods, using the substrates to be studied, should be calibrated. A certified reference material would allow determination of extraction efficiencies among laboratories.

Because sample size and instrument sensitivity affect detection limits, both should be established in advance, and detection limits should be agreed to by the parties involved.

Residues should also be reported as dry or wet (fresh) weights. When dry weights are given, moisture contents and the method of determination should be specified.

Persistence and accumulation of fenitrothion in compartments other than water, sediment, soil, and balsam fir foliage should be studied. For example, the fate of residues in animals that consume balsam fir foliage would seem as

important as the fate of animals that consume contaminated foliage. The persistence, accumulation if any, and fate of fenitrothion in litter should be investigated.

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