FENITROTHION RESIDUES IN SELECTED COMPONENTS OF A CONIFER FOREST FOLLOWING AERIAL APPLICATION OF TANK MIXES CONTAINING TRITON® X-100

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Cette publication est aussi disponible en français sous le titre *Concentrations des résidus de fénitrothion dans certaines composantes d'une forêt de conifères après épandage aérien de préparations renfermant l'emulsifiant Triton ® X-100.*

ABSTRACT

Studies on distribution, persistence, and fate of fenitrothion in balsam fir *[Abies balsamea* (L.) Mill.] foliage, forest litter, and soil were conducted in a coniferous forest near Charlo, New Brunswick in 1982, after the aerial application of aqueous and partly oil-based emulsion formulations of the insecticide prepared by mixing with the newly introduced emulsifier Triton® X-100. The formulations were sprayed separately twice each at 210 g AI/ha over two blocks. Analysis of prespray samples indicated the presence of background levels of fenitrothion. Spray distribution and collection efficiency obtained on Kromekote® card-glass plate collection units varied due to physical and environmental factors. With the oil-based cyclosol emulsion, the highest concentrations of fenitrothion that were detected in foliage were 660 and 820 ppb (fresh weight) for the first and second applications respectively. The corresponding values for the aqueous emulsion were 1869 and 1720 ppb. The residue levels initially decreased rapidly, but persisted at low concentrations thereafter. Five days after the second application, the concentrations of fenitrothion in foliage ranged from 230-380 with the oil-based emulsion and 640-710 ppb with the aqueous emulsion. Only low levels of residue were detected in forest litter and soil. The highest postspray concentrations in litter (fresh weight) for both applications ranged from 130 to 290 with both tank mixes. The concentrations in soil were lower with the oil-based emulsion and ranged from 130-140 ppb (fresh weight) whereas with the aqueous emulsion, the residue levels were higher, ranging from 350 to 480 ppb. The concentration levels in all the substrates studied fluctuated, possibly due to contamination by drift from neighbouring operational sprays and consequently the chemical persisted beyond the 5 day postspray sampling period.

RÉSUMÉ

La distribution, la persistance et le devenir du fénitrothion dans le feuillage du sapin baumier *(Abies balsamea* [L.] Mill.), la litière et le sol ont été étudiés dans une forêt de conifères près de Charlo, au Nouveau-Brunswick, en 1982, après épandage aérien de préparations de l'insecticide sous forme d'émulsions aqueuses ou partiellement à base d'huile incorporant un émulsifiant nouvellement commercialisé, le Triton® X-100. Ces préparations ont été pulvérisées séparément à deux reprises à la dose de 210 g/ha d'ingrédient actif sur deux parcelles. L'analyse d'échantillons prélevés avant l'épandage a révélé la présence, dans le milieu, d'une certaine concentration de fénitrothion. L'efficacité de la dispersion et du dépôt, mise en évidence sur des cartes Kromekote®, a varié sous l'action des facteurs physiques et environnementaux. Les plus fortes concentrations de fénitrothion décelées dans le feuillage se chiffrent à 660 et 820 parties par milliard (masse à l'état frais) pour le premier et le second arrosages avec l'émulsion à base d'huile cyclosol. Les valeurs correspondantes pour l'émulsion aqueuse sont de 1869 et 1720 parties par milliard. Les concentrations des résidus ont diminué rapidement au début, puis se sont maintenues à un faible niveau par la suite. Cinq jours après le deuxième arrosage, les concentrations de fénitrothion variaient entre 230 et 380 pour l'émulsion à base d'huile et entre 640 et 710 parties par milliard pour l'émulsion aqueuse. Seulement de faibles concentrations on été mesurées dans la litière et dans le sol. Les plus fortes concentrations (à l'état frais) obtenues dans la litière après les deux arrosages se situaient entre 130 et 290 avec le mélange des deux réservoirs. Les concentrations dans le sol ont été plus faibles avec l'émulsion à base d'huile, variant entre 130 et 140 parties par milliard (masse à l'état frais), qu'avec les émulsions aqueuses où elles se situaient entre 350 et 480 parties par milliard. Des fluctuations des concentrations ont été observées pour tous les substrats étudiés, probablement en raison de la contamination due à la dérive provenant d'arrosages opérationnels réalisés sur des terrains voisins, de sorte que l'insecticide est demeuré présent à des concentrations importantes, au-delà de la période d'échantillonage de cinq jours après l'arrosage.

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INTRODUCTION

Fenitrothion [0,0-dimethyl 0-(3-methyl-4-nitrophenyl) phosphorothioate] has been a choice insecticide for spruce budworm *[Choristoneura fumiferana* (Clem.)] control in eastern Canada since 1963. The insecticide is usually applied by aircraft at the rate of 2 x 210 g of active ingredient (AI)/ha as either an aqueous emulsion or an oil formulation.

In the spring of 1982 the province of New Brunswick (N.B.), acting on the recommendations contained in the Spitzer task force report (1982), temporarily withdrew the commonly used emulsifier Atlox® 3409F from forestry use. Consequently, a cooperative program known as the "Action Plan" was initiated by the Forest Pest Management Institute (FPMI). This plan required several federal and provincial agencies and pesticide manufacturing companies to develop and field test new formulations of fenitrothion containing acceptable emulsifiers other than Atlox® 3409F. Two candidate tank mixes using the emulsifier Triton® X-100 (octylphenoxynonaethoxyethanol - a nonionic surfactant manufactured by Rohm and Haas) were developed and field tested in N.B. during the summer of 1982. This report summarizes the environmental chemistry studies conducted during that experimental spray program to evaluate the distribution, persistence, and fate of the insecticide in balsam fir *[Abies balsamea* (L.) Mill.] foliage, forest soil, and litter samples.

MATERIALS AND METHODS

Experimental Site

Two 50 ha (1000 m x 500 m) spray blocks, C1 and C3, were selected in a mixed, mature coniferous forest (soft to hardwood ratio ca 75:25 with canopy cover >90%) about 35 km southwest of Charlo, N.B. at 47°50'N and 66°30'W for testing the newly developed experimental formulations of fenitrothion containing Triton® X-100. The residue chemistry plots covered an area of approximately 2000 m^2 with a radius of about 25 m in the centre of each 50 ha spray block. Seven balsam fir, *[Abies balsamea* (L.)] trees about 14.0 m tall with a DBH of 16 cm, and with good foliage were randomly selected in a transect of each plot. In each plot, the selected trees were tagged with plastic ribbon and individually numbered from 1 to 7 with fluorescent paint for identification. Ground vegetation and neighbouring trees were cleared up to a radius of about 5 m to enhance exposure to the spray cloud. A fully exposed soil plot (ca 3 x 5 m) and a litter plot (ca 5 x 5 m) were also established in the same vicinity in each block.

Spray Applications

The test formulations containing Triton® X-100 were sprayed by FPMI with aircraft supplied by Forest Protection Limited (FPL). Each block received 2 applications with an interval between sprays of 5 days. Block C1 received the oil-based fenitrothion emulsion (Formulation #1). Block C3 was sprayed with pure aqueous emulsion (Formulation #3). The composition of each tank mix (vol. %), dosage of AI/ha, application rate, and the formulation each block received are given in Table 1. Aircraft type, spray parameters and meteorological conditions which existed during the spray applications are given in Table 2.

Ground Spray Deposit Assessment

Two glass slides (7.5 cm x 5.0 cm) and a Kromekote® card (10 cm x 10 cm) mounted on a folding aluminum plate (collection unit) (Randall 1980) were used for droplet size and deposit assessments. In each plot, 48 Kromekote® card-glass slide collection units were placed on aluminum stands about 15 cm above the ground level for each spray application. The collection units were positioned in the plot 0.5 h prior to application as shown below:

Table 1. Fenitrothion spray formulations used in 1982 experimental studies near Charlo, N.B.

Formulation No.	Block No.	Ingredients (v%)	Application rate (L/ha)	Dosage (g/ha)
1	C1	Fenitrothion[1] (concn.) 11.0, Triton® X-100[2] 2.8, Cyclosol 63[3] 24.0, Water 61.2 and Rhodamine dye[4] 1.0	1.5	210
3	C3	Fenitrothion (concn.) 11.0, Triton® X-100 13.7, Water 74.3 and Rhodamine dye 1.0	1.5	210

[1]Novathion® (tech.) supplied by Cheminova, Lemvig, Denmark, c/o Win Chemicals, Toronto, Ont.
[2]Rohm and Haas Canada Inc., West Hill, Ontario.
[3]Shell Canada Chem. Co. Ltd., Toronto, Ontario.
[4]Allied Chemicals, Morristown, New Jersey, U.S.A.

Table 2. Spray application and meteorological data*

Particulars	C1		C3	
	1st Application	2nd Application	1st Application	2nd Application
Date of application (June, 1983)	12	17	12	17
Spray time (h) (ADT)	2100	0745	0735	0655
Aircraft type	C[1]	C	C	C
Aircraft speed (km/h)	160	160	160	160
Height above canopy (m)	30	30	30	30
Atomiser	MA[2]	MA	MA	MA
Emission rate (L/min)	23.7	23.7	23.7	23.7
Wind speed (km/h) (at 10 m above ground)	3±2	3±1	3±2	3±1
Wind direction+	WSW	NW	WSW	WSW
Temp. (°C) (average of 10 m and 1 m values)	15.5	11.1	13.3	11.7
R.H. (%)	71	75	80	87

*Most of the data were supplied by Mr. Leo Cadogan.
[1]Cessna 188.
[2]Four Micronair (MA) AU 3000 [Micronair (Aerial) Ltd., Sandown, England] with blade angle set at 30°.

Litter plot:	4 collection units (N, S, E and W)
Soil plot:	4 collection units (N, S, E and W)
Sampling tree:	2 collection units per tree (7 trees).
Open space:	26 collection units were placed randomly in the plot.

Care was taken to ensure that ground vegetation did not obscure the surface of the collection units in any way.

The collection units were collected 1 h after the spray application, transported immediately to the field laboratory where the deposits on the glass plates were removed by washing with 3 x 5 mL of pesticide grade ethyl acetate and the eluates were stored in tightly sealed amber coloured bottles away from heat and sunlight until they were transported to the FPMI pesticide laboratory in Sault Ste. Marie, Ont.

In the laboratory, the eluates were first analyzed for the AI by gas-liquid chromatography (GLC). Later they were flash evaporated gently to dryness and the residues were taken in methanol for colorimetric analysis of the Rhodamine dye tracer.

The Kromekote® cards were examined under magnification and the droplet stains were recorded. The resulting counts were grouped according to size and the droplet size spectrum was calculated using the spread factor (S.F.) values. Droplet densities (droplets/cm^2) were then calculated together with NMD, VMD, D_{max}, D_{min} and volume deposit in mL/ha (Table 3).

Sampling of Foliage, Soil and Litter for Residue Analysis

Foliage samples (25-30 cm branch tips) were taken randomly from the midcrown of each sample tree selected. New growths were removed from the cut-up branches of each tree, the needles and associated tender twigs were clipped, placed in labelled plastic bags, sealed, and stored immediately in styrofoam coolers with frozen ice packs. They were then transported to the field laboratory and stored in a freezer at -20°C until analyzed.

The soil in the plot was a sandy loam with a pH of 6.2-6.5. At each sampling, 20 cores (2.5 cm in diameter) were taken randomly from the top 1 cm layer of the soil, wrapped in aluminum foil and subsequently handled as described for foliage.

Forest litter samples were also taken randomly from the litter plot (1 core per sampling period) at the same sample frequency as soil by driving a coring device [(metal frame 15.5 cm x 15.5 cm x 5.0 cm (high)] developed at this laboratory into the ground and removing the contents with a clean trowel. The samples were handled further as described for soil.

Sample Preparation and Analysis

Sample preparation

All samples collected in the field were transported to the FPMI pesticide laboratory in a freezer (-20°C) and left undisturbed at the same temperature until analysis.

(i) Foliage: Prior to analysis, each sample was allowed to thaw, mixed thoroughly in a Hobart bowl chopper and the macerated foliage samples were stored again in sealed plastic bags at -20°C.

Table 3. Deposit data for fenitrothion formulations containing Triton® X-100*+

Particulars	C1		C3	
	1st Application	2nd Application	1st Application	2nd Application
Drops/cm^2	12	13	4.4	21
D_{min} (µm)	6	4	6	4
D_{max} (µm)	114	138	114	130
Number mode (µm)	25-40	-	20-30	20-30
Volume mode (µm)	65-90	110-160	-	100-130
NMD (µm)	30	34	21	30
VMD (µm)	58	99	46	44
Vol. (avg.) deposited (spot counting) (mL/ha)	66	100	9	90
Percent (avg.) deposited (spot counting)	4.40	6.67	0.61	6.0
Amt. (avg.) deposited (colorimetry) (g AI/ha)	4.82	10.39	2.80	11.9
Percent (avg.) deposited (colorimetry)	2.30	4.95	1.33	5.67
Amt. (avg.) deposited (GLC) (g AI/ha)	0.67	2.17	5.48	6.88
Percent (avg.) deposited	0.32	1.03	2.61	3.28

*Data supplied by Dr. A. Sundaram.

+Data generated from the collection units placed in the chemistry plot only, therefore the values recorded here are not representative of the entire 50 ha spray block.

(ii) Litter and soil: After thawing, stones, twigs, and other hard materials were carefully removed from each sample then thoroughly mixed either in a Hobart machine or by using a spatula and stored as described under foliage.

Moisture content

Subsamples (2 x 10 g aliquots) of thoroughly mixed foliage, soil and litter were weighed, dried at 105°C for 16 h in a thermostatic oven, cooled and reweighed (AOAC 1955).

Ash content (litter and soil)

The oven dried material was placed in an electric furnace at 500°C for 18 h, cooled and reweighed.

Solvent extraction

(i) Foliage: 40.0 g of chopped sample were homogenized for 5 minutes with 150 mL ethyl acetate (Caledon Chemicals or Fisher Scientific) using a Brinkmann Polytron blender. The blender was rinsed with the solvent and the total mass of homogenate was recorded (~240 g).

(ii) Litter and soil: 40.0 g of thoroughly mixed samples were macerated for 5 minutes with 150 mL ethyl acetate using a Waring blender. The blender was rinsed with solvent and the total mass of macerate recorded (~ 240 g).

Column clean-up

Aliquots of the extracts equivalent to 1 g of sample (5 mL) were taken, concentrated to ca 1 mL, and transferred quantitatively to mini-columns (Pasteur pipettes, Fisher Scientific 13-678-8) containing a layer of glass-wool at the bottom, 0.4 g of a mixture of neutral charcoal and cellulose powder (4:10), and topped with 1 g of anhydrous Na_2SO_4. The mini-columns were attached by Tygon® tubing to glass tubes (55 cm x 8 mm i.d.) to act as reservoirs. The aliquots were allowed to percolate under gravity through the columns and eluted with 35 mL of 25% ethyl acetate in toluene (v/v). The eluates were collected in pre-cleaned containers, concentrated to 5 mL using a Buchii Rotovapor®, quantitatively transferred to a graduated centrifuge tube and concentrated further to 1.0 or 0.5 mL under a stream of dry N_2. The concentrates were sealed and stored at 4°C until analysis.

Gas chromatography

A Hewlett Packard HP 5840A NP-FID gas chromatograph fitted with a 6 ft x 4 mm i.d. glass column and packed with 1.5% OV-17 + 1.95% OV-210 on Chromosorb W HP (80/100 mesh) was used. A carrier gas flow (He) of 40 mL/min and oven temperature of 200°C were maintained.

Spikes and procedural blanks

Spikes and blanks were introduced into each batch of analytical samples after equilibration, especially at the extraction and column cleanup step in order to assess the recovery levels under the experimental

conditions described. The rates of recovery for the three types of substrate (foliage, litter and soil) were 81 ± 7% at 0.1 and 1.0 ppm fortification levels for a 40 g substrate.

Detection limit of the insecticide

The analytical limit of detection for the insecticide was 0.01 µg/mL of the final extract for injection. This in turn was equivalent to 0.01 µg/g of the same on the "as sampled" basis. Due to variations in the moisture contents of different varieties of substrates studied, the calculated minimum detection limit (MDL), on a wet (as sampled) and on oven-dry weight basis are 0.01 µg/g and 0.05 µg/g respectively. Values between 0.01 µg/g (10 ppb) to 0.007 µg/g (wet weight) are reported as traces (T) and values below 0.007 µg/g (7 ppb) are recorded in this report as non-detectable (ND).

RESULTS AND DISCUSSION

Spray deposition

In spruce budworm (SBW) control operations, the following 3 factors must be optimized to achieve maximum kill, (a) spray density, (b) droplet size at the target site, and (c) concentration of AI in the spray mix. The first two factors determine the amount of material contacting the insect, either by direct hit or while the insect is crawling and feeding, and the last one determines the lethal effect. Taking the deposit values obtained on the collection units as a function of (a) and (b) [(c) is constant (Table 1)], Formulation 3 (aq. emulsion) (Table 1) gave the same (mean of two applications) droplet density at ground level (12.7 drops/cm^2) compared to the oil-based formulation (12.5 drops/cm^2) (Table 3). However, the aqueous formulation gave a narrower droplet spectrum (NMD and VMD are closer to each other than those of the oil-based one). Number mode and volume mode values are also comparatively lower confirming that the Formulation 3 produced desirable deposit data to enhance targetability.

It is very likely that Formulation 1, because of the presence of volatile cyclosol, would have yielded a large percent of very small droplets above the canopy level. Since small droplets have a large surface/volume ratio, they would have evaporated quickly and a large proportion of them probably drifted away from the spray area. Low average percent deposited on the forest floor in plot C1, as determined by GLC analysis of the glass-slide eluates (1.42 g AI/ha) (Table 3) and comparatively low average level of concentration (1 h postspray) observed in the needles (685 ppb vs 1795 ppb in C3) (Table 4), support this hypothesis. It appears that Triton X-100 emulsifier, because of its good dissolving power for the toxicant and low volatility, would produce a better tank mix and consequently would yield better deposition patterns if an organic phase such as cyclosol is not present in the system.

Results of the spray deposit data for Formulation 3 indicate that the second application was generally more successful and produced a comparatively better droplet density and heavier concentration of fenitrothion on the forest floor than the first application (Table 3). Analysis of the glass plate eluates by GLC showed that the average amounts of fenitrothion reaching the forest floor and the percent deposited in both plots during all four applications were low (3.08 g AI/ha and 1.81% respectively).

Table 4. Fenitrothion residues in balsam fir foliage treated twice with two different formulations at 210 g AI/ha

Time after spraying	Fenitrothion residues (ppb)*	
	Block C1 (oil emulsion)	Block C3 (aq. emulsion)
	1st Application	
Prespray	431 (844)	1057 (2073)
1 h	600 (1220)	1869 (2620)
3 h	550 (1090)	850 (1520)
6 h	560 (1120)	570 (1030)
12 h	660 (1290)	1450 (2620)
1 d	310 (620)	1110 (2090)
2 d	610 (1340)	800 (1490)
5 d	230 (490)+	710 (1470)
	2nd Application	
Prespray	341 (638)	680 (1329)
1 h	770 (1680)	1720 (3520)
3 h	740 (1590)	1570 (2910)
6 h	820 (1580)	1360 (2440)
12 h	540 (1060)	1250 (2280)
1 d	730 (1480)	890 (1600)
2 d	740 (1430)	1160 (2120)
5 d	380 (790)	640 (1310)

*Values without parenthesis represent residue levels in terms of fresh weight (as sampled); values in parenthesis refer to residue concns. in terms of oven-dry weight.

+Values correspond to ca 4.5 d post-spray.

Table 5. Fenitrothion residues in forest litter treated twice with two different formulations at 210 g AI/ha

Time after spraying	Fenitrothion residues (ppb)*	
	Block C1 (oil emulsion)	Block C3 (aq. emulsion)
	1st Application	
Prespray	24 (98)	540 (993)
1 h	170 (540)	130 (230)
3 h	110 (310)	80 (200)
6 h	220 (630)	100 (130)
12 h	100 (270)	100 (170)
1 d	130 (410)	70 (120)
2 d	150 (520)	110 (160)
5 d	70 (270)+	50 (180)
	2nd Application	
Prespray	65 (211)	65 (238)
1 h	220 (860)	140 (430)
3 h	250 (970)	290 (880)
6 h	110 (410)	100 (210)
12 h	220 (790)	200 (460)
1 d	270 (970)	120 (320)
2 d	240 (870)	220 (410)
5 d	160 (690)	70 (270)

*Values without parenthesis represent residue levels in terms of fresh weight (as sampled); values in parenthesis refer to residue concns. in terms of oven-dry weight.
+Values correspond to ca 4.5 d post-spray.

Table 6. Fenitrothion residues in forest soil treated twice with two different formulations at 210 g AI/ha

Time after spraying	Fenitrothion residues (ppb)*	
	Block C1 (oil emulsion)	Block C3 (aq. emulsion)
	1st Application	
Prespray	11 (16)	201 (286)
1 h	70 (90)	T -
3 h	90 (110)	480 (600)
6 h	120 (160)	70 (80)
12 h	70 (100)	T -
1 d	140 (190)	T -
2 d	30 (50)	60 (70)
5 d	70 (100)+	190 (280)
	2nd Application	
Prespray	80 (132)	140 (175)
1 h	100 (140)	60 (80)
3 h	80 (120)	170 (240)
6 h	60 (80)	140 (180)
12 h	90 (120)	350 (500)
1 d	130 (190)	70 (100)
2 d	80 (110)	240 (300)
5 d	60 (80)	90 (110)

*Values without parenthesis represent residue levels in terms of fresh weight (as sampled); values in parenthesis refer to residue concns. in terms of oven-dry weight.

+Values correspond to ca 4.5 d post-spray.

T = Traces, <10 ppb but >7 ppb (wet weight).

The GLC technique was the most reliable method used to evaluate the deposit concentrations on the collection units: it is extremely sensitive and measures the AI concentration directly, whereas in the other two, the dye additive acted as a tracer. No correlation existed among the deposit values (Table 3) obtained by all three methods except that the GLC technique gave the lowest mean (average of 4 values) percent deposition (1.81) on the forest floor, compared to colorimetry (3.56%), and spot counting (4.42%).

In conclusion, assessment of deposits on forest floor in random locations over the chemistry plot using the three techniques (GLC, colorimetry and spot counting) indicated that only a fraction of the insecticide released over the canopy descended to the collection units kept on the forest floor.

Fenitrothion persistence

Field studies conducted during the 1982 spray season indicated that most of the prespray samples collected from both the spray blocks contained detectable levels of fenitrothion at ppb range. This may be due to its inherent persistence characteristics* [lipophilicity, low vapor pressure (low evaporation), absorption, adsorption and transport to matrices, slow degradation (chemical, photochemical, biochemical and microbial), etc.] or very likely to its drift from neighbouring spray blocks. The latter hypothesis appears to be correct since operational fenitrothion sprays of areas surrounding the experimental site occurred continuously over a period of three weeks; it is very likely that the chemical was transported to the test blocks via spray drift and contaminated the foliage, soil and litter samples. The high fluctuation in the concentrations of the AI in foliage, litter and soil samples observed during the sampling period (Tables 4-6) could very well be due to this contamination. In addition, our prespray sampling of substrates from N.B. during the spring of 1983 and subsequent analyses strongly support this point of view. This being the case, it would be prudent not to conduct research spray operations close to operational sprays.

Balsam fir foliage

Fenitrothion residues found in balsam fir foliage are recorded in Table 4. The dissipation of the chemical in fir needles appeared to be biphasic. It is apparent from the data that the initial maximum residue levels of fenitrothion obtained in the foliage varied according to the formulations sprayed. Higher 1 h postspray values (as sampled) (1869 and 1720 ppb for 1st and 2nd application) were found with Formulation 3 (fenitrothion + Triton® X-100 + water) (Block C3) compared to Formulation 1 (600 and 770 ppb) (Block C1) which contained in addition to the above, Cyclosol 63 (Table 1). It is very likely that the droplets of Formulation 1, during the fall of 30 m from their release to the canopy level, could have evaporated rapidly because of the presence of the volatile cyclosol component. This resulted in low deposition of the toxicant on the foliage. With Formulation 3, such a rapid evaporation is not possible because of the presence of a higher concentration of Triton® X-100 (13.7% vs 2.8%, Table 1) which is not only nonvolatile but also has the tendency to act as a cosolvent and be linked to the toxicant molecules by strong intermolecular (hydrogen bonding, dipole-dipole and dispersion) forces thereby yielding higher foliar deposits and possibly higher foliar retention.

*Some degree of persistence is necessary for any effective forestry pesticide as long as it is related to the insect control that is to be achieved.

Five days posttreatment, the losses of fenitrothion observed were rapid, showing values of 62 and 50% in Block C1 and 62 and 63% in Block C3. This observed rapid dissipation suggests that the fenitrothion residues found in foliage may not have been molecularly incorporated initially to the needles and were therefore readily available for dissipation through various physical processes. Similar work carried out earlier (Sundaram and Sundaram 1981, 1982) confirmed initial rapid loss of the chemical from conifer needles.

Eventually the chemical could have approached a state of molecular dispersion in the conifer foliage and become somewhat isolated from the forces that caused its loss and breakdown resulting in a curvilinear decrease with time thereby showing a tendency to persist in the needles. We are not yet sure if Triton® X-100 enhances this phenomenon or not. The difference in rates of disappearance suggests that the initial one is primarily due to physical factors (volatilization, leaching, photolysis and weathering action of humidity, rain and wind). The latter one, which is slow, could be due to the dissolution of the polar insecticide molecules into the lipophilic substances such as terpenoids and waxes (polymeric alcohols, carbonyl compounds, esters, etc.) contained in the fir foliage leading to the formation of solid solutions which then get embedded into the cuticular waxes resisting rapid physical and possible biodegradations with time (Yule and Duffy 1972; Sundaram 1974).

Table 7 shows the half-lives ($T_{\frac{1}{2}}$) (calculated from concn. vs time plot) of fenitrothion present in fir needles, forest litter and soil. The $T_{\frac{1}{2}}$ of the chemical in foliage is well within the range found by others (Yule and Duffy 1972; Sundaram 1974).

Residues in forest litter

Residues of fenitrothion found in forest litter are given in Table 5. The maximum initial concentrations of fenitrothion in Blocks C1 and C3 were low and ranged from 220 to 270 ppb and 130 to 290 ppb, respectively. The sudden increase or decrease in concentrations of litter-bound fenitrothion was difficult to explain. These variations could have been caused by increased humidity, rainfall, run-off or rapid metabolic activity due to sunlight, or contamination by drift. Also the residue levels did not decrease rapidly although the half-lives ($T_{\frac{1}{2}}$) (as sampled) ranged from 2.1 (Block C3) to 2.8 days (Block C1) (Table 7).

Forest litter, an organic layer overlapping the soil, is formed by surface additions of fallen needles, twigs, stems, flowers, cones and bark which are gradually compressed and degraded by soil microorganisms. This organic matter consists of carbohydrates [cellulose, hemicellulose (polyglucuronic and xylan units)], humin, humic acid, fulvic acid, phenolic and carboxylic compounds, lignins, nitrogeneous compounds (proteins, amino acids, etc.) and lipids. Forest litter is not only acidic (pH of aqueous suspension 5.4) but also provides a strong adsorptive surface for various molecules. It is very likely that fenitrothion molecules are adsorbed strongly onto litter particulates, thus persisting for some time in detectable levels. Adsorption to litter particulates is enhanced by the lipophilic component cyclosol present in Formulation 1 (Block C1); therefore the persistence of fenitrothion in litter samples (as sampled), although not significant, was higher in Block C1 than in Block C3 [$T_{\frac{1}{2}}$ (mean for both applications) 2.8 vs 2.3 days] (Table 7).

Table 7. Half-lives (days) of fenitrothion in fir foliage, forest litter and soil

Formulation	(Fen. + cyclosol + Triton® X-100 + water)				(Fen. + Triton® X-100 + water)			
	1st application		2nd application		1st application		2nd application	
Substrate	A.S.	O.D.	A.S.	O.D.	A.S.	O.D.	A.S.	O.D
Foliage	2.8	3.0	3.0	3.4	2.6	2.5	2.7	2.1
Litter	2.8	2.9	2.8	3.0	2.4	2.2	2.1	2.0
Soil	2.7	3.0	2.9	2.9	2.2	2.5	2.1	2.3

A.S., as sampled; O.D., oven-dry (105°C for 16 h, AOAC 1955).

Residues in Forest Soil

The forest floor is usually considered a major receptor of aerially applied spray materials. As observed under forest litter, only low levels of fenitrothion reached the soil surface. The maximum fenitrothion content (Table 6) found in the soil samples ranged from 140 to 130 ppb (Block C1) and 480 and 350 ppb (Block C3). The half-lives in soils (as sampled) ranged from 2.1 to 2.7 days (Table 7). Fenitrothion concentrations did not decrease rapidly, probably due to contamination by off-target drift and also partly due to the influence of additives (retention and penetration into soil matrices) present in the formulations. Variability, which is inherent in sampling and analyzing forest soil samples, also should be taken into account. After the 2nd application, 5 day postspray soil (as sampled) samples contained 60 ppb (Block C1) and 90 ppb (Block C3) with considerable fluctuation in concentrations, thus indicating that although the rate of loss is high, a tendency for the chemical to persist in soils in measurable levels existed beyond 5 days. This suggests that the residue may have been bound to particulate matter and hence unavailable for degradation. No definite correlation was found between the insecticide content in soil and its organic content; qualitatively from our preliminary studies we can say that higher soil organic content enhanced persistence. Further work is necessary to confirm this observation.

Mechanisms for the disappearance of fenitrothion from the forest floor include volatilization, leaching through the soil profile by water, degradation by various physicochemical processes including sunlight, and biological means. Among these, a combination of chemical and bacterial degradations and volatilization from the soil surface probably played vital roles.

SUMMARY AND CONCLUSIONS

Two new formulations of fenitrothion with Triton® X-100 emulsifier have been developed at this Institute and field tested for their efficacies against spruce budworm, the associated environmental impacts and environmental chemistry. The spray mixes were aerially applied at operational dosages over two 50 ha spray blocks near Charlo, N.B. During the study, different forestry substrates (conifer foliage, litter and soil) were sampled and analyzed to examine the fate of the insecticide.

The additives (water, cyclosol and Triton® X-100) in the new tank mixes played significant roles in producing characteristic droplet spectra and deposition patterns on the Kromekote® card-glass plate collection units. The droplet densities, NMDs and VMDs obtained varied among the two formulations and even within the 1st and 2nd applications of the same formulation.

All prespray foliage, litter, and soil samples contained detectable levels of fenitrothion as a contaminant either due to inherent persistent characteristics (lipophilicity, low vapour pressure and biodegradability) of the chemical or due to drift from surrounding operational spray blocks.

Residue levels of fenitrothion in the samples varied according to the type of formulation sprayed. The fenitrothion concentrations found in soil and litter samples were low and persisted beyond the sampling period probably due to the lipophilic nature of the chemical as well as the litter/soil matrix. In addition, soil/litter type, organic content, moisture, pH, etc., had considerable influence on insecticide persistence. Relatively high concentrations of fenitrothion were intercepted and retained by fir needles, showing a tendency by them to accumulate the sprayed material. The rate of loss was uneven although the half-lives were low. Fenitrothion appeared to be more stable in the environment; whether it is due to its ubiquity or its input into the spray blocks through indirect sources (drift) is not clear.

The additives in the formulation played a significant role in enhancing foliar deposition and persistence of fenitrothion. Presence of a volatile and low viscous adjuvant like cyclosol 63 (24%) along with Triton® X-100 (3%) in Formulation 1 gave rise to a lower foliar deposition and persistence in Block C1 compared to Formulation 3 used in Block C3 which contained fenitrothion, water and a higher percentage of Triton® X-100 (10.7%). It is likely that Triton® X-100 being partly hydrophilic and partly lipophilic acted especially at high concentrations, not only as an emulsifier but also as a solvent and sticker for fenitrothion. In addition, the low volatility and surface tension coupled with high viscosity and boiling point of Triton® X-100 assisted greater penetration of the active material through lipoidal leaf cuticles of balsam fir needles, causing the chemical to persist longer.

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