FENITROTHION RESIDUES IN SOME FORESTRY SAMPLES FROM A PLANTATION FOREST FOLLOWING EXPERIMENTAL SPRAY APPLICATION FOR FIVE CONSECUTIVE YEARS

Information Report FPM-X-66

K.M.S. Sundaram

Forest Pest Management Institute
Canadian Forestry Service
Environment Canada
1984

Catalogue No. Fo46-16/66E

ISSN: 0704-772X

ISBN: 0-662-13244-0

Additional copies of this publication are available from :

Liaison and Information Services
Forest Pest Management Institute
Canadian Forestry Service
Department of the Environment
P.O. Box 490
Sault Ste. Marie, Ontario
Canada, P6A 5M7

Cette publication est aussi disponible en français sous le titre *Résidus de fénitrothion dans quelques échantillons d'une forêt artificielle arrosée expérimentalement cinq années consécutives.*

TABLE OF CONTENTS

ABSTRACT

In May 1976, samples from conifer foliage and bark, maple foliage and bark, forest litter, soil, water, and sediment were collected from various spray plots in a mixed plantation forest near Ottawa, Ontario. The plantation had been sprayed experimentally for five consecutive years (1971-1975) with fenitrothion [0,0-dimethyl 0-(3-methyl-4-nitrophenyl) phosphorothioate] formulations at the dosage of 280 g AI/ha to study the long term effects of its use for spruce budworm control. The samples were analyzed for fenitrothion and its degradation products. Low levels of fenitrothion (to a maximum of 10% of the initial amount deposited) appear to have persisted and accumulated in conifer bark and foliage in proportion to the number of years sprayed, usually in the form of embedded liquid/solid solutions in the cutin layer of conifers which resisted dissipation. The concentration in samples of 1972 bark and foliage, which were subjected to five years of spraying, ranged from (fresh weight) 89 (white pine) to 291 (red pine) ppb and 68 (white pine) to 179 (red pine) ppb respectively. Comparative mean concentrations for 1975 bark and foliage samples (sprayed once) varied from 46 (white pine) to 151 (red pine) ppb and 21 (white pine) to 65 (white spruce) ppb. Conifer foliage acted as a better receptor for fenitrothion, but the bark samples appeared to be better retainers of the chemical. No noticeable systemic activity of the chemical from previous sprayings was observed in the 1976 new growth of buds and shoots. Apart from trace quantities (<10 ppb) of oxon, no other breakdown product was found in conifers. Fenitrothion concentrations in stagnant water and sediment samples were low, and ranged from 0.07 to 0.40 ppb, indicating the absence of any build-up. Foliar leaching and leaf-fall appeared to be the likely sources for the residue levels in water. Simultaneous chemical, bio- and photo-degradations and volatilization prevented the accumulation of the chemical in lentic waters. Fenitrothion concentrations in pond sediments were higher than in water and ranged from 18 to 36 ppb. The distribution coefficients K_d, ranged from 71 to 414 indicating that the chemical was readily translocated from water to sediment. The only identified degradation product in the water/sediment system was aminofenitrothion. Fenitrothion concentrations in litter and soil samples were low due to chemical- and bio-degradations as well as volatilization and surface run off. Consequently, the concentratons in litter ranged from 18 to 63 ppb, and in soil from 13 to 34 ppb on a fresh weight basis. Apart from the sporadic trace levels of p-nitro-m-cresol and aminofenitrothion, no other degradation product was identified in the substrates. Only trace levels of fenitrothion were found in maples. The conifers appear to have acted as reservoirs, or sinks, of sprayed materials and passed them on to the litter/soil strata of the forest floor through foliar leaching and leaf fall. It is likely that the insecticide reached the aquatic environment through similar processes and also by subsurface and surface run-off during rain. The degradation pathway of the chemical appears to be oxidative in conifers and reductive in aquatic and soil/litter environments.

RÉSUMÉ

En mai 1976, des échantillons du feuillage et de l'écorce de conifères et d'érables, ainsi que des échantillons de la litière forestière, du sol, de l'eau et des sédiments ont été prélevés dans diverses parcelles arrosées d'une forêt mixte artificielle, près d'Ottawa (Ontario). Cette plantation avait été arrosée expérimentalement cinq années de suite (1971 à 1975) avec des préparations de fénitrothion (thiophosphate de 0,0-diméthyle et de 0-méthyl-3 nitro-4 phényle) à la dose de 280 g/ha d'ingredient actif pour la répression de la tordeuse des bourgeons de l'épinette. Le fénitrothion et ses produits de dégradation ont été recherchés dans ces échantillons. Le fénitrothion, en faibles concentrations (jusqu'à un maximum de 10% de la quantité reçue), semble avoir persisté et s'être accumulé dans l'écorce et le feuillage des conifères proportionnellement au nombre d'années d'arrosages, ordinairement sous la forme d'inclusions liquides ou solidés dans la cutine. Les concentrations de 1972 dans les échantillons de l'écorce et du feuillage (à l'état frais) varient de 89 x 10^{-9} (pin blanc) à 291 x 10^{-9} (pin rouge) et de 68 x 10^{-9} (pin blanc) à 179 x 10^{-9} (pin rouge) respectivement. Par comparaison, les concentrations moyennes dans les échantillons de l'écorce et du feuillage de 1976 varient de 46 x 10^{-9} (pin blanc) à 151 x 10^{-9} (pin rouge) et de 21 x 10^{-9} (pin blanc) à 65 x 10^{-9} (épinette blanche). Le feuillage des conifères a été un meilleur récepteur du fénitrothion, mais l'écorce a semblé le retenir davantage. Aucune activité systémique notable du produit provenant des arrosages antérieurs n'a été observée dans les nouveaux bourgeons et les nouvelles pousses de 1976. Exception faite de traces ($<10^{-9}$) d'oxon, aucun autre produit de dégradation n'a été trouvé dans les conifères. Dans les eaux stagnantes et les sédiments, les concentrations mesurées de fénitrothion sont faibles, variant de 0,07 à 0,40 x 10^{-9}, ce qui indique l'absence d'accumulation. Le lessivage du produit sur les feuilles et la chute des feuilles seraient probablement à l'origine des résidus dans l'eau. La volatilisation et la dégradation chimique, biologique et photochimique ont empêché l'accumulation dans les eaux stagnantes. Les concentrations de fénitrothion dans les sédiments d'étangs sont plus élevées que dans l'eau; elles varient de 18 à 36 x 10^{-9}. Les coefficients de distribtuion, K_d, sont dans l'intervalle de 71 à 414, indiquant que le produit passe facilement de l'eau aux sédiments. Le seul produit de dégradation identifié dans le système eau-sédiments est l'aminofenitrothion. Dans les échantillons de la litière et du sol, les concentrations de fénitrothion sont faibles en raison des dégradations chimiques et biologiques, ainsi que de la volatilisation et du ruissellement des eaux de surface: elles varient entre 18 et 62 x 10^{-9} dans la litière et entre 13 et 34 x 10^{-9} dans le sol (à l'état frais). Outre des traces sporadiques de p-nitro m-crésol et d'aminofénitrothion, aucun autre produit de dégradation n'a été mis en évidence dans les substrats. Dans les érables, seulement des traces de fénitrothion ont été mesurées. Les conifères ont semblé jouer un rôle de réservoir pour les produits d'arrosage et les avoir transmises à la litière et au sol de la forêt par le lessivage et la chute des feuilles. Le milieu aquatique a probablement été contaminé sous l'action de phénomènes similaires et aussi du ruissellement en surface et souterrain des eaux de pluies. La voie de dégradation du produit semble être par oxydation dans les conifères et par réduction dans l'eau, le sol et la litière.

ACKNOWLEDGMENTS

The study reported here has been conducted with the excellent cooperation and assistance received from the researchers and staff of the Environmental Impact Project at this Institute. The author owes a considerable debt to C.H. Buckner, P.D. Kingsbury and B.B. McLeod for the help and support given in the protracted field work. Paul Davis, M. O'Connell, P.E. LeCompte, G. Lafrance, Y. Volpe and M. Bryan have contributed greatly to this work by their technical skill, dedication and perseverance.

INTRODUCTION

Fenitrothion [0,0-dimethyl 0-(3-methyl-4-nitrophenyl) phosphorothioate] is an effective substitute for DDT [2,2- *bis* (p-chlorophenyl)-1,1,1-trichloroethane] in the control of spruce budworm, *Choristoneura fumiferana* (Clem.) in eastern Canada. It is usually applied as an aerial spray, at dosages of 0.14 to 0.28 kg A.I./ha, to reduce defoliation by the insect pest with minimum environmental and ecological disturbance (Fettes 1968; Varty 1976; Buckner *et al.* 1977; Symons 1977). Between 1963 and 1980 approximately 9 x 10^6 kg of the material have been sprayed over 30.7 x 10^6 ha of forest (Nigam 1980). This extensive use has attracted a great deal of research interest in relation to its distribution, persistence, transformation and fate in various components of the forest environment (NRCC 1975, 1977).

Studies on the distribution and degradation of fenitrothion in different forest components (Yule and Duffy 1972; Sundaram 1974a) have shown that the bulk of the chemical deposited by aircraft at normal operating dosages is lost rapidly from conifer foliage, forest soil, and natural waters with few breakdown products persisting in these substrates. Unlike some of the persistent organochlorines, the insecticide is usually regarded as environmentally acceptable.

Studies using some of the conifers as indicator species have shown (Yule 1974; Sundaram 1974b; Yule and Varty 1975) that measurable amounts (>0.003 ppm) of fenitrothion have persisted and become concentrated in conifer foliage over a number of years with repeated annual applications. However, the spray histories (dosage, application rate, formulation type, frequency of application, etc.) recorded in the earlier studies varied considerably and the data generated did not encompass a wide enough variety of substrates, such as foliage and bark of soft and hardwood tree species, soil, water, forest litter, sediments, etc., to draw definite conclusions on the accumulation and persistence patterns of this chemical in different forestry components. The work presented here is an intensive study on the persistence and accumulation of fenitrothion in water (pond and stream), sediment, forest soil and litter, different coniferous foliage and bark samples [white spruce, *Picea glauca* (Moench) Voss; red pine, *Pinus resinosa* Ait; white pine, *Pinus strobus* L; balsam fir, *Abies balsamea* L. (Mill)] and red maple, *Acer rubrum* L. (foliage and bark) collected from sprayed plots in Larose Forest following five consecutive years of application beginning in 1971. The spray histories of all the smaller sampling plots during the period are accurately known. The actual insecticide deposits at some of the plots are known, so that some sort of quantitative interpretation between these two is possible. Since fenitrothion continues to be our primary defense against spruce budworm in Canada, the information generated in this study on its persistence and accumulation in different components (*viz.* lithosphere, hydrosphere and biosphere) of the forest environment should be useful, not only in understanding the dynamics of the chemical, but also in evaluating quantitatively some of the biological and ecological consequences of its extensive and prolonged use in forest pest control operations.

MATERIALS AND METHODS

Spray area

Larose Forest, a flat, sandy plantation forest, situated about 50 km east of Ottawa in Clarence Township, Ontario, was selected for this study because of the well documented spray history of the selected sampling plots and of the recorded insecticidal deposit levels at some of the sampling sites. Plot layout in Larose Forest was designed

and prepared by the researchers of the Environmental Impact group at the Institute. Plots, C (control) and T-1 to T-5 were about 8 ha in area and the plot BR was approximately 1000 ha (Fig. 1). The control plot C was about 2.0 km away from most of the experimental plots. Each plot was composed mainly of conifers averaging 10 m in height and up to 20 cm dbh. A scattered undergrowth of maple was common throughout the area with scattered grass; moss patches covered the forest floor.

Application of fenitrothion

The spray plots BR and T-1 to T-5 were sprayed in mid-June with either oil based or aqueous emulsion fenitrothion formulations. The aircraft used was a Cessna 185, fitted with 4 Micronair AU3000 units, flying about 30 m above tree tops. Spray histories of the plots (dosage, application rate, type of formulation used, etc.) for the spray period from 1971 to 1975 are given in Table 1. Plot T-1 received five applications, one in each year, beginning in 1971, at 0.28 kg A.I./ha (0.28 kg A.I. in 1.46 L of formulation) as an aqueous emulsion consisting of 1% (by weight) Arotex® petroleum distillate, 1.4% Atlox 3409® emulsifier, 10% fenitrothion, 0.6% Rhodamine B tracer dye and 87% water. Plot T-2 received four applications, beginning in 1972, at the same dosage of fenitrothion, but with an oil-based formulation (0.28 kg A.I. in 0.44 L of formulation) consisting of (wt %), 53% fenitrothion (tech), 46.7% Arotex solvent and 0.3% Automate B Red dye. Plot T-3, received three applications of aqueous formulation, one in each year from 1973 to 1975. Plot T-4 was sprayed with two applications of the same emulsion, one in 1974 and in 1975, and plot T-5 was treated with one application of oil formulation in 1975. Plot BR had a checkered spray history. It was sprayed intermittently at very high doses (> 280 g A.I./ha) in 1970 by the Ontario Ministry of Natural Resources (Prebble 1975) followed by two experimental treatments of aqueous fenitrothion (0.28 kg A.I./ha), one in 1972 and the other in the following year. In 1974, the plot was treated with aminocarb followed by acephate in 1975.

Sampling of forestry substrates

Forestry samples for the present study were taken from the plots during the early part of May 1976, one year after the completion of five consecutive years of aerial application of the chemical.

Ten dominant spruce trees, with amply developed crowns, were selected randomly in each plot. Pines were scanty and scattered, therefore the best available numbers (not less than 5) from each plot were used in the study. One mid-crown branch from each quadrant of the selected tree was clipped with a pole pruner. The new growth for 1976 was clipped and removed. The branches were pooled by plot, labelled and placed in plastic bags. The bags were sealed and transported immediately to the toxic chemicals section of the Institute in Ottawa where they were held at -20°C until analyzed. New growths from each plot were also treated similarly. Prior to analysis, each twig of the branch was carefully hand clipped with a pair of scissors. The foliage and stems were separated according to discrete yearly growth up to 5 years old. Whenever ill-defined annual growth patterns (especially in pines) caused problems with age classification, the growth of twigs and shoots in each year served as indicators. Each foliage sample collected from a specific species from each plot, was further reduced by hand mixing and quartering to 200 g. The composite subsample thus obtained was machine (Hobart) chopped. Twenty gram aliquots were used for residue analysis and moisture determination. The bark and woody part of the stems of each

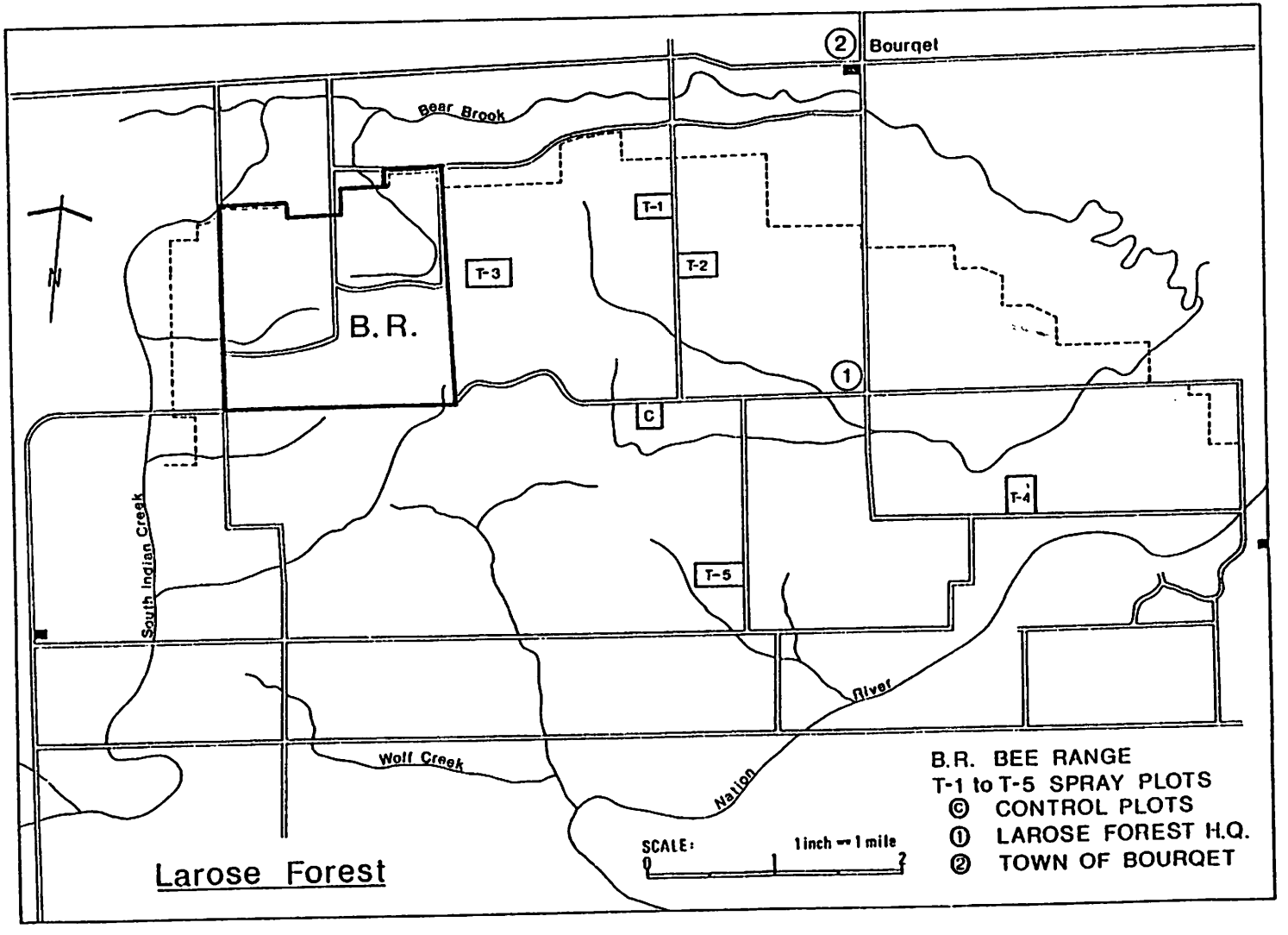
2
Bourqet
Bear Brook
T-1
T-2
T-3
B.R.
1
C
T-4
T-5
South Indian Creek
River
Wolf Creek
Nation
SCALE:
1 inch = 1 mile
Larose Forest
B.R. BEE RANGE
T-1 to T-5 SPRAY PLOTS
© CONTROL PLOTS
① LAROSE FOREST H.Q.
② TOWN OF BOURQET

Figure 1.

Table 1. Spray history of plots

Plots sprayed	Dosage g AI/ha	Application rate (L/ha)	Approx. area of plot (ha)	Formulation sprayed	Years sprayed	No. applications	Total dosage sprayed (g/ha)
T-1[a]	280	1.46	8	A.E.[1]	1971 to 1975	5	1400
T-2	280	0.44	8	O.S.[2]	1972 to 1975	4	1120
T-3[a]	280	0.44	8	A.E.	1973 to 1975	3	840
T-4[b]	280	1.46	8	A.E.	1974 and 1975	2	560
T-5	280	0.44	8	O.S.	1975	1	280
BR*	280	1.46	1000	A.E.	1972 and 1973	2	560
C	0	0	8	-	0	0	0

[1]A.E. aqueous emulsion (density 0.993); (wt %) = Arotex®[3] 1, Atlox® 3409F[4] 1.4, fenitrothion tech.[5] 10, Rhodamine B[6] 0.6 and water 87.

[2]O.S. Oil solution (density 1.122); (wt %) = Arotex® 46.7, Automate Red® B [7] 0.3 and fenitrothion tech. 53.

[3]Texaco Canada Ltd.; Don Mills, Ont., Canada

[4]Atlas Chemical Industries, Brantford, Ont., Canada

[5]Sumitomo Chem. Co., Osaka, Japan

[6]Allied Chemicals, Morristown, New Jersey, U.S.A.

[7]Morton Williams Ltd., Ajax, Ont., Canada.

*Heavily sprayed in 1970 with fenitrothion followed by aminocarb in 1974 and acephate in 1975 (see text for details).

[a]Minor discrepancy regarding the dosage (210 or 280 g A.I./ha) sprayed in 1974.

[b]Similar discrepancy regarding the type of formulation (A.E. or O.S.) sprayed in 1974.

species were carefully removed with a sharp knife. Each type was mixed according to the annual growth as described under foliage, and 100 g composite samples of each were prepared. Twenty gram aliquots were used for residue determination and moisture content. A general cross-section of the samples consisting of branches of each of the conifer species collected from each plot were processed as described above without sorting them according to the annual growth. This served as the mixed age foliage, bark and wood samples.

At the time of sampling, the maple foliage was primarily at the crumpled leaflet stage with few expanded into larger flat leaves. Only the partly opened leaf buds and the adjoining twigs of the current year's growth were clipped, processed as described under conifers for foliage, bark and wood samples, and stored in a freezer for further analysis. A mixed maple foliage sample consisting of leaf buds and bark of 1976 growth was also collected for comparative purpose.

Soil samples were collected with a toothed auger, to a depth of 5 cm, from open areas in each plot where the soil layer was exposed. Ten samples were collected randomly from each plot, pooled and processed according to the techniques described earlier (Sundaram 1974a). Twenty gram aliquots were used each time for residue and moisture analyses. Litter samples were collected from areas where a heavy deposition of organic debris was found and processed as discussed under soil.

Samples of water and sediment were collected from a centrally situated shallow pond (average area 3 m^2; depth 0.2 m) in each plot and from a sandy bottomed, moderate-flowing 0.2-m-deep creek in BR. About a liter of water sampled from the top 1 cm of the surface water was collected from five random locations selected in each pond and in the creek. Clean mason jars with closed lids were lowered to 1 cm below the water's surface. The lids were removed until the jars had filled with water. The caps were then replaced and the jars were removed from the water. The samples were stored in coolers and transported immediately to the laboratory in Ottawa for extraction. The water samples were mildly acidic ranging in pH from 6.2 to 6.6.

Approximately 200 g of the top 1-cm layer of sediment (pH 5.9 to 6.1) from each pond and from the creek bottom were sampled randomly using a flat plastic scoop. The excess water was removed by decantation followed by filtration. The sediment samples were stored in clean glass containers, which were placed in a styrofoam cooler and transported to the laboratory for extraction and analysis.

Analytical procedures

Procedures used for the analysis of conifer foliage, bark, soil, litter, and sediment samples were the same as those used by Yule and Duffy (1972) and Sundaram (1974a). One hundred gram aliquots of the substances were ground for 5 minutes in a Sorvall Omni-Mixer at maximum speed with 2 x 200 mL of ethyl acetate, filtered under section using "S and S Sharkskin " filter paper. The samples were dried by being passed through a column of Na_2SO_4, and concentrated under vacuum to 100 mL. The concentrated extract corresponding to 10 g of substrate was dissolved in 30 mL of CH_3CN and partitioned twice with 20 mL of hexane. The polar phase was flash evaporated to 5 mL and cleaned using an activated charcoal-Celite (Johns Manville Co. Ltd.) column. The column was eluated with a mixture of ethyl acetate and benzene. The ethyl acetate-benzene eluate (200 mL) was gently flash evaporated to dryness, taken up in an aliquot quantity of benzene and analyzed by

gas-liquid chromatography (GLC). The oxon and the cresol metabolites present in the extracts were separated by using a deactivated silica gel column (Bowman and Beroza 1969). The recoveries of fenitrothion and its two metabolites from spiked substrate samples were 86 ± 9 percent. Triplicate determinations were carried out for each substance bracketed by injection of sample standards. Values which differed by 10% from the mean were discarded and, where necessary, analysis was repeated. All residue data recorded in this report have a S.D. of ± 10% of the mean value. No recovery corrections were introduced in the final data recorded. A detailed account of methodology and the GLC parameters used are given in an earlier publication (Sundaram 1974a).

Two dimensional thin layer chromatography (TLC) on silica gel (Takimoto *et al.* 1976) was used to separate and identify the presence of amino (AF), desmethyl and cresol (C) derivatives of fenitrothion in eluates. The pure compounds acted as reference standards and the toluene/ethyl formate/formic acid (5:7:1 v/v) mixture served as the solvent system. The R_f values of authentic compounds obtained in our study were comparable to the data available in literature.

Moisture contents of samples were determined by drying two 20 g duplicates of each sample at 105°C for 16 h in a thermostatic oven (AOAC 1955).

Aliquots of water samples (300 mL) were partitioned twice with 100 mL of pesticide grade benzene. The organic phase was dried through a column of Na_2SO_4 and flash-evaporated to a small volume. Residues were determined by GLC and TLC techniques.

The sensitivity of the FPD (flame photometric detector)-GLC used in the present study was much lower than the currently popular AFID (alkali flame ionization detector) and the N-P (nitrogen-phosphorus specific) detectors. It was also evident during the analyses, that the sensitivity of the FPD-GC fluctuated and was often influenced by peak shape, noise level and the combustion condition in the flame. The minimum detectable limit (MDL) for fenitrothion and its two metabolites (oxon and cresol, the latter analysed by EC-GLC) was found to be 0.01 ppb for water and 10 ppb (fresh wt.) for other substrates. To make sure that the MDL are rigidly maintained, routine recovery checks were made periodically during the study. Similarly, frequent spot checks were made to make sure that the laboratory glassware, syringes, solvents, etc. were free from fenitrothion contamination.

RESULTS AND DISCUSSION

The amounts of fenitrothion found in various substrates collected from the Larose Forest are given in Tables 2 and 3. The results are expressed in terms of "ppb (ng/g) fresh weight" (as sampled) for ecological interpretation, and "ppb oven-dry weight" in parentheses for more standardized comparison of residues between species and sampling times. The concentration based on fresh weight basis is used throughout the following discussion.

Table 2 lists fenitrothion residues found in three species (white spruce, white pine and red pine) of conifer (bark and needles) studied following five consecutive years of experimental spray programs. It is apparent from the data that the concentration of fenitrothion in conifers accumulated approximately in proportion to number of years sprayed (Yule 1974; Sundaram 1974b; Yule and Varty 1975). This pattern of progressive accumulation in conifer bark and needles is evident in all plots T-1 to T-5

Table 2. Fenitrothion residues (ppb) in conifers from Larose Forest after experimental spraying of the chemical for five consecutive years from 1971 to 1975

Plot	Growth of year					Mixed-age sample
	1971	1972	1973	1974	1975	
			Spruce bark			
T-1	218(270)	246(311)	249(390)	170(240)	121(210)	169(267)
T-2		199(240)	215(260)	168(340)	119(190)	171(252)
T-3			186(290)	146(270)	168(310)	159(234)
T-4				139(230)	121(250)	128(188)
T-5					116(230)	112(224)
Average	218(270)	223(278)	217(313)	123(270)	129(238)	148(233)
			Spruce foliage			
T-1	146(220)	101(120)	48(90)	42(70)	31(50)	69(106)
T-2		88(170)	89(150)	74(120)	66(100)	73(118)
T-3			72(140)	61(101)	49(103)	55(96)
T-4				154(270)	89(151)	117(192)
T-5					91(180)	94(179)
Average	146(220)	95(145)	70(127)	83(140)	65(117)	82(138)
			White pine bark			
T-1	89(140)	81(170)	91(190)	70(110)	47(90)	56(111)
T-3			76(110)	62(104)	63(130)	62(114)
T-4				39(70)	27(90)	31(88)
Average	89(140)	81(170)	83(150)	57(95)	46(103)	50(104)

Table 2. (concluded) Fenitrothion residues (ppb) in conifers from Larose Forest after experimental spraying of the chemical for five consecutive years from 1971 to 1975.

Plot	Growth of year					Mixed-age sample
	1971	1972	1973	1974	1975	
			White pine foliage			
T-1	68(100)	44(70)	37(80)	31(70)	20(40)	37(76)
T-3			39(71)	29(60)	23(52)	34(64)
T-4				32(70)	21(50)	27(63)
Average	68(100)	44(70)	38(75)	31(67)	21(47)	33(68)
			Red pine bark			
T-1	291(360)	288(432)	299(470)	176(320)	148(240)	236(386)
T-2		194(273)	181(230)	168(360)	102(190)	156(184)
T-4				177(263)	169(250)	170(256)
T-5					186(300)	181(294)
Average	291(360)	241(352)	240(350)	174(314)	151(245)	186(280)
			Red pine foliage			
T-1	179(280)	102(190)	67(93)	60(90)	42(71)	96(147)
T-2		147(220)	89(140)	47(70)	49(90)	80(128)
T-4				113(200)	33(63)	70(133)
T-5					74(110)	71(106)
Average	179(280)	124(205)	78(117)	73(120)	49(83)	79(128)

Woody parts of conifers contained detectable levels (ca 10% of the amount found in needles) of fenitrothion. No attempts were made to quantify them.
Residue values without parentheses = residues in terms of wet weight.
Residue values with parentheses = residues in terms of oven-dry weight.
Samples from control plot contained on average about 15 ppb of fenitrothion.
Some of the shoot samples of 1976 contained trace levels (<10 ppb) of fenitrothion.
Apart from fenitrooxon which was found in traces (< 10 ppb) in some of the 1975/76 red pine bark samples, no other metabolite of fenitrothion was found in the above conifer samples.

Table 3. Fenitrothion residues (ppb) in some forestry substrates collected from Larose Forest in May 1976 following its aerial application for five consecutive years from 1971 to 1975*

Plot / Sample	T-1	T-2	T-3	T-4	T-5	B.R.
Maple[a] bark	13(20)		16(22)	21(32)		12(20)
foliage	26(40)		19(30)	17(30)		19(30)
Spruce bark						22(40)
foliage						14(30)
White pine bark						14(20)
foliage						11(20)
Red pine bark						30(70)
foliage						28(60)
Balsam fir[a] bark						49(90)
foliage						33(61)
Water (stream)						0.03
(pond)**	0.22	0.40	0.31	0.11	0.15	0.07
Soil+	34(50)	15(20)	22(30)	13(20)	21(30)	28(40)
Litter	62(90)	41(60)	63(80)	22(40)	25(40)	18(40)
Sediment (pond)++	18(40)	32(70)	22(50)	31(70)	36(80)	29(60)

*Plot BR was sprayed heavily prior to 1971 with fenitrothion and was resprayed twice during the experimental period in 1971 and in 1973 with aqueous formulation. Samples from control plot contained trace (T) levels of the chemical (T for water 0.01 ppb, for others 10 ppb)

**pH 6.2-6.6

+Sandy loam (pH 5.9-6.3)

++pH 5.9-6.1

[a]Woody parts of maple and conifers contained detectable levels of fenitrothion. No attempts were made to quantify the residue levels.

Residue values without parentheses = residues in terms of wet weight.

Residue values with parentheses = residues in terms of oven-dry wt.

TLC studies indicated the presence of trace quantities of cresol and aminofenitrothion in litter, soil and sediment samples. Apart from these two, no other metabolite was found in the samples studied.

and it is very apparent from the average values recorded for each species in Table 2. Although residue levels increased with time, no precise arithmetic correlation could be established between the amount accumulated and the duration of exposure.

Spruce, white pine and red pine bark samples of 1972 growth contained on average 69, 93 and 93 percent (fresh weight) more fenitrothion than the 1975 year-end residues. Corresponding values for the needles are 125, 224 and 265 percent. All the values are comparatively higher than the mixed-age bark and foliage samples. During the 1972 spray application, 1 h postspray insecticide deposits (as sampled) in spruce bark and foliage samples in plots T-1 and T-2 were found to be 1809 and 2011 ppb and 3500 and 4200 ppb respectively (Sundaram 1974a). The year-end (May 1973) residue data for the corresponding samples from these plots were 246 (85% loss) and 199 ppb (90% loss) and 101 (97% loss) (98% loss) ppb. Some salient points emerge from an examination of the results mentioned above and the data in Table 2. Conifer foliage acted as a better collector for fenitrothion than the barks but the latter appeared to be better retainers of the chemical. Pine, especially red pine foliage and bark, accumulated and retained the chemical more readily than spruce. The difference in deposit levels among the tree species may be attributable to their growth habit, foliar geometry, and especially to the nature and amount of cuticular waxes present in them. The wax pattern on the conifer foliage changes according to tree species, growing conditions, and the age of the foliage (Linskens *et al.* 1965).

The average five-year accumulation level of fenitrothion in conifer foliage (fresh weight) from Larose was nearly eight times less than the one observed by Yule (1974) *(ca* 130 ppb *vs* 1000 ppb) in a New Brunswick forest. Insecticide persistence and its aftermath accumulation are variable and complex properties which are influenced by various environmental (physical and metabolic) factors. Persistence and accumulation depend on the toxicant's properties (hydro- or lipo-philicity, partition coefficient, adsorption/absorption, vapour pressure, volatility, biodegradability etc.) dosage, formulation, mode of application, substrate type and its growth pattern, canopy density, rain, temperature, light, humidity, air movement, and various metabolic (enzymatic and microbial) and physicochemical processes (Westlake and San Antonio 1960; Linskens *et al.* 1965; Gould 1966; Mulla *et al.* 1981). Also, volatilization of the adsorbed chemical to surrounding air could more readily occur within an open plantation forest such as Larose than in a dense natural forest where the wind velocity would be lower and the little chemical that is volatilized could be intercepted and retrapped by surrounding vegetation (Perring and Mellanby 1977). Consequently, a direct comparison of fenitrothion accumulation for dissimilar locations (plantation forest *vs* natural forest) is neither possible or valid.

No detectable levels of breakdown products were found in conifers except the oxon which was sporadically present in some red pine bark samples at trace levels (< 10 ppb). The multifunction oxidases in the plant tissues probably oxidized the chemical to its oxon. Attempts to isolate the other possible oxidation products including the cresol were not successful although their presence in other plants have been reported (Miyamoto and Sato 1965; Leuck and Bowman 1969).

The 1976 foliage samples, which were in the form of tender shoots and buds at the time of sampling, were analyzed for fenitrothion. Trace levels (< 10 ppb) were occasionally found in some samples, probably due to contamination. This definitely showed

that there was no systemic carry-over of fenitrothion residues from previous sprays, confirming recent observations (Sundaram and Sundaram 1982). Throughout the study, the woody part of the conifer branches contained detectable levels of fenitrothion which varied concurrently with the concentrations found in the corresponding bark samples. No rigorous attempts were made to quantify the levels present in them. The sporadic presence of detectable levels of fenitrothion in some of the samples from the control plot may be due to spray drift and contamination from the experimental spray blocks.

Conifer foliage appeared to be the primary receptor of fenitrothion during spray application. The exact route by which the intercepted chemical dissipates from the foliage is still obscure. The effective mechanism seems to involve physicochemical factors such as volatilization, temperature, weathering action of humidity, rain and wind, photodegradation, hydrolysis, and slough-off rather than metabolic factors (Yule and Duffy 1972; Sundaram 1974a; Sundaram and Sundaram 1982). Most of the sprayed fenitrothion *(ca* 90%) intercepted by conifer needles was lost rapidly and continuously within two weeks through various physical processes. The little that remained *(ca* 10%) being lipophilic, was probably absorbed, transported and stored in cuticular waxes of the foliage thus resisting leaching, volatilization, photo- and bio-degradations. Resinous constituents (long-chain hydrocarbons, carbonyl, hydroxy and carboxy components) of the cuticle (Kolattukudy 1980) probably acted as adhesives causing the fenitrothion molecules to permeate through cuticular pores. The lipoid nature of the cuticle allowed the passage of the polar toxicant molecules to the cutin layer for storage (intracuticular or subcuticular residue). The fenitrothion thus resisted ready dissipation, but was gradually diminished and diluted as the foliage grew. Electron micrograph or preferably scanning electron micrograph studies of unexposed and exposed conifer needles could throw more light on this aspect of residue studies.

Fenitrothion was detected in ppb levels in all the stagnant surface water (pH 6.2-6.6) and sediment (pH 5.9-6.1) samples collected from the ponds in spray plots (Table 3). This phenomenon was reported in previous studies (Montreal Engineering Co. 1978, 1979 and 1981; Pearce *et al.* 1980; Sundaram *et al.* 1983). Foliar leaching of intercepted and adsorbed chemical by rain, leaf fall and its further movement through surface and subsurface drainage waters may have contributed to the disproportionate amounts (0.07 to 0.40 ppb) of the chemical found in pond water. Simultaneous chemical, bio- and photo-degradations coupled with volatilization/codistillation could have prevented the steady accumulation of the chemical (NRCC 1975; Maguire and Hale 1980) in the aquatic system. Among these various processes, chemical hydrolysis could have played a minor role since the waters were mildly acidic. Extremely low levels of fenitrothion found in the stream water in plot BR can be attributed to dilution due to water flow and to restricted use of the chemical in the plot. Attempts to identify the metabolites (cresol, aminofenitrothion, carboxy and desmethyl derivatives) reported in water (NRCC 1975, 1977; Maguire and Hale 1980) have not been successful under the experimental conditions. They were either very labile or existed at extremely low levels.

Fenitrothion concentrations in pond sediments (Table 3) and the corresponding distribution coefficient K_d [K_d = (conc. in sediment)/(conc. in water)] ranged from 18 to 36 ppb and 71 to 414 respectively indicating that pond sediments could act as sinks for fenitrothion if microbial activity is low (Maguire and Hale 1980). Since feni-

trothion is lipophilic [K_{OW} (octanol-water partition coefficient) = 2,380] and only partially soluble in water (20 ppm at 20°C), and since pond sediments contain polar humic substances which accelerate the adsorption and dissolution of the chemical into them (Stevenson 1982), the fenitrothion was readily translocated from water to sediment. Presence of organic and inorganic colloids with large surface areas would also have facilitated the adsorption of the chemical to sediment. Similar observations have been made recently in a number of laboratory and field studies (Sundaram and Szeto 1981; Szeto and Sundaram 1982; Sundaram *et al.* 1983). Decomposition pathways for the chemical in the aquatic system appeared to be reductive in nature (microbial reduction), consequently trace levels of aminofenitrothion (initial stages) and cresol were identified in sediments by TLC. No attempts were made to quantify them.

Table 3 lists the residue levels of fenitrothion found in litter and soil samples. Concentrations in the litter ranged from 18 to 63 ppb and in the soil from 13 to 34 ppb on fresh weight basis. The litter usually contained on average about 70% more fenitrothion than the soil. Although the forest floor acts as a reservoir for sprayed chemicals, due to continuous chemical and biological degradations, rapid volatilization and surface run off, a steady accumulation of the chemical in these two substrates has never been observed before (Yule and Duffy 1972; Sundaram 1974a and b; Sundaram *et al.* 1983). A plausible explanation for the origin of residues in these substrates could be through fall of needles into the litter, and foliar leaching of the intercepted material from the aerial parts of conifers during rain. Larose soil happens to be a sandy loam type with low clay and organic content, consequently the chemical would have been loosely bound to the soil matrix and would have migrated easily to other areas with moving water. The higher amounts found in litter compared to soil is likely due to adsorption and dissolution of the chemical to the lipoidal humus component of litter layer where limited decomposition occurred because of its acidity (pH 5.7) and paucity of microbial content. Fenitrothion found in the soil would be degraded readily by indigenous soil microorganisms catalyzed by surface active soil particles, volatilized, leached through soil profile by rain, and irradiated with sunlight. Takimoto *et al.* (1976) have shown that microbial activity in soil was predominant under field conditions. Apart from sporadic trace levels of aminofenitrothion and the cresol, no other degradation product was identifiable in the substrates. They were either absent or present in trace levels or, because of their strong adsorption to the soil/litter matrices, existed as bound residues and were consequently unextractable through normal analytical procedures.

Detectable amounts (> 10 ppb) of fenitrothion were found in maple bark and foliage samples (Table 3). Concentrations (fresh wt.) in bark ranged from 12 to 21 ppb and in foliage from 17 to 26 ppb. Yule and Varty (1975) reported 3 to 4 times more initial deposit of fenitrothion on maple foliage than on conifers. The little that is found in the bark 1 year after the spray could arise from the adsorbed and occluded fraction of the deposited chemical. No satisfactory explanation can be offered for the residues found in the fresh 1976 foliage of the maple tree. Since the maples found in Larose were usually undergrowth of conifers, foliar leaching of the latter during spring rain could have transported and deposited the chemical on to the foliage.

In summary, the residue data obtained from Larose Forest experimental spray program demonstrated that fenitrothion appears to have persisted and accumulated in the

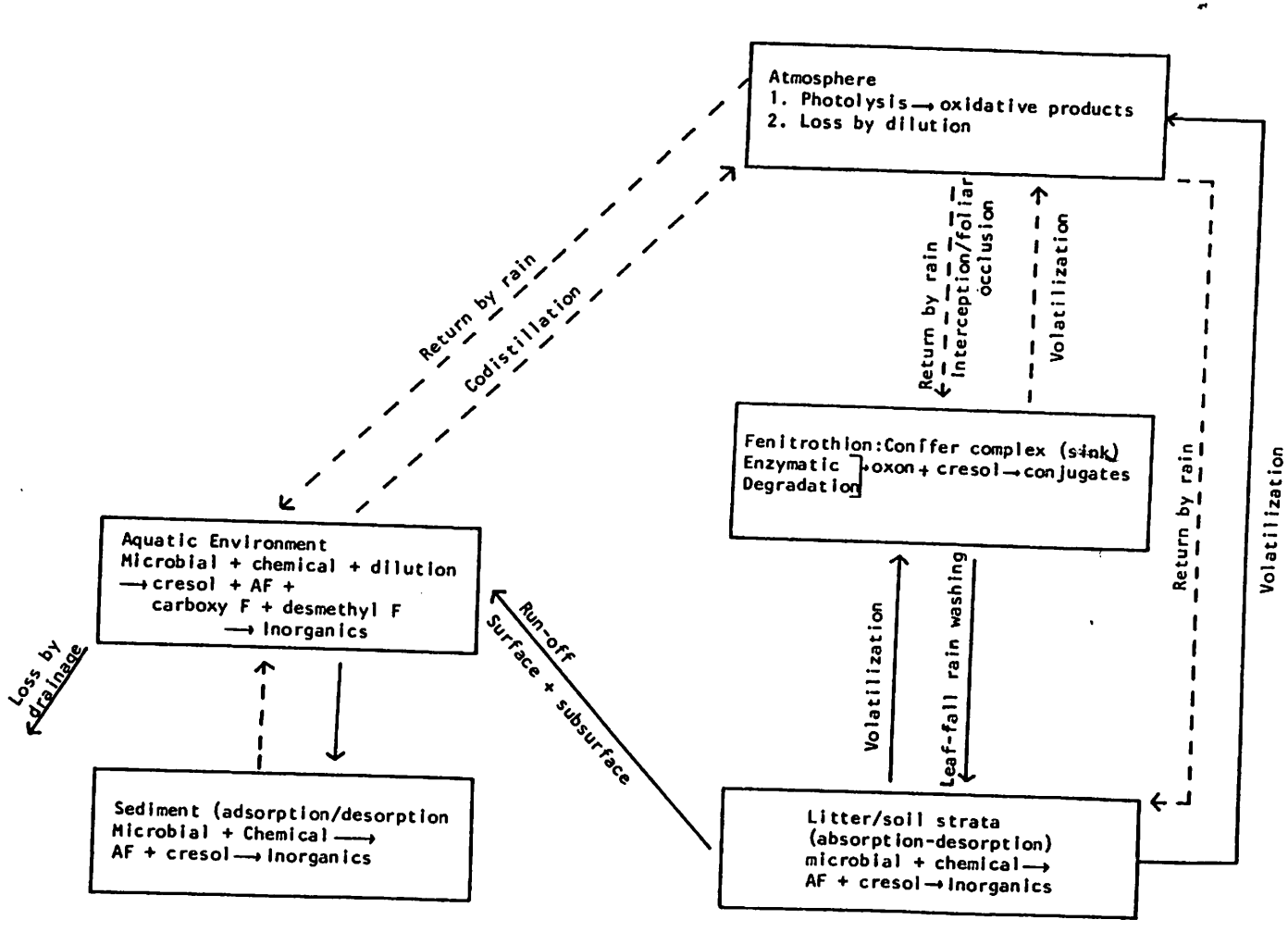

Figure 2. Movement of residual fenitrothion in forestry compartments at Larose Forest.

bark and needles of white spruce, white pine and red pine to measurable amounts over a five year period with repeated annual applications at 280 g AI/ha. The maximum amounts of accumulated residues (fresh weight) found at the end of fifth year period were:

White spruce	- bark 218 ppb, foliage 146 ppb
White pine	- bark 89 ppb, foliage 68 ppb
Red pine	- bark 291 ppb, foliage 179 ppb

The conifers appear to have acted as reservoirs or sinks for sprayed materials and passed them on to the soil stratum of the forest environment. No tangible correlation could be established between the accumulation patterns found and the formulations sprayed. Maple foliage and bark samples (1976 growth) contained on average about 20 ppb and 16 ppb respectively. No significant build-up was found in water, sediment, litter and soil samples. The average residue levels found (as sampled) in them were:

Water (pond)	0.21 ppb
Sediment (pond)	28 ppb
Litter	38 ppb
Soil	22 ppb

It is likely that the insecticide reached them by foliar leaching and run-off during rain and litter fall of needles and twigs. Some of the decomposition products found in the substrates were identified but none were positively quantified. The decomposition pathway appears to be oxidative in conifers and reductive in aquatic and soil/litter environments. Since the interplay of factors (physical, chemical and biological) in a forest environment is complex, controlled ecosystem studies would be useful to gain meaningful insight into the metabolic fate of the chemical in different forestry compartments.

With reference to the observations made in the study and to the above discussions, the scheme given in Fig. 2, although somewhat speculative, summarizes the movement of year-end residues (e.g., those persisting one year after spraying) of fenitrothion in a forest environment.

Extensive and continuing use of fenitrothion would probably warrant a more comprehensive study of its persistence and metabolic fate in various components of the forest environment so that we can correlate and understand fully its possible detrimental effects *vis-a-vis* *subtle* ecological implications and accompanying impact on the ecosystem. In addition we must also strive to elucidate and improve our knowledge on the ecotoxicity of this chemical and its transformation products, especially when they move and persist at near trace levels in various environmental compartments as we have seen in this study. So far no rigorous attempts have been made in this area and the consequences arising from the trace level persistence of the chemical in certain forestry substrate are virtually unknown at present.

REFERENCES

A.O.A.C. 1955. Official methods of analysis (8th ed.). Assoc. Official Anal. Chem., Washington, D.C. 1008 pp.

Bowman, M.C.; Beroza, M. 1969. Determination of Accothion, its oxygen analog and its cresol in corn, grass and milk by gas chromatography. J. Agric. Food Chem. 17:271.

Buckner, C.H.; Sarrazin, R.; McLeod, B.B. 1977. The effects of the fenitrothion spray program on small mammals. pp. 377-390 in Proc. Symp. "Fenitrothion: the long-term effects of its use in forest ecosystems." NRCC Publ. No. 16073.

Fettes, J.J. 1968. Chemical control of forest insects by aircraft. Pulp and Paper Mag. of Canada. 69(18): 90.

Gould, R.F. 1966. Organic pesticides in the environment. Adv. Chem. Series No. 60, Am. Chem. Soc., Washington, D.C.

Kolattukudy, P.E. 1980. Biopolyester membranes of plants: Cutin and Suberin. Science 208: 990-1000.

Leuck, D.B.; Bowman, M.C. 1969. Persistence of O,O-dimethyl O-4-nitro-*m*-*tolyl* phosphorothioate, its oxygen analog and its cresol in corn and grass forage. J. Econ. Entomol. 62: 1282.

Linskens, H.F.; Heinen, W.; Stoffers, A.L. 1965. Cuticula of leaves and the residue problem. Residue Reviews 8: 136-176.

Maguire, R.J.; Hale, E.J.. 1980. Fenitrothion sprayed on a pond: Kinetics of its distribution and transformation in water and sediment. J. Agric. Food Chem. 28(2): 372-378.

Miyamoto, J.; Sato, Y. 1965. Determination of insecticide residues in animal and plant tissues. II. Metabolic fate of Sumithion in rice plant applied at the preheading stage and its residue in harvest grains. Botyu-Kagaku 30: 45.

Montreal Engineering Co. Ltd. 1978. Assessment of the effects of the 1977 New Brunswick spruce budworm control program on fish food organisms and fish growth. Prepared for the New Brunswick Department of Natural Resources.

Montreal Engineering Co. Ltd. 1979. Effects on fish of the 1979 New Brunswick spruce budworm control program. Prepared for the New Brunswick Department of Natural Resources.

Montreal Engineering Co. Ltd. 1981. Fenitrothion accumulation by plants and invertebrates in two experimentally sprayed streams in New Brunswick. Prepared for the New Brunswick Department of the Environment.

Mulla, M.S.; Mian, L.S.; Kawecki, J.A. 1981. Distribution, transport and fate of the insecticides malathion and parathion in the environment. Residue Reviews 81: 1-172.

Nigam, P.C. 1980. Use of chemical insecticides against the spruce budworm in Eastern Canada. CANUSA Newsletter, 11:1-3.

NRCC. 1975. Fenitrothion: The effects of its use on environmental quality and its chemistry. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, NRCC No. 14104, Ottawa, Ont., Canada, 162 pp.

NRCC. 1977. Fenitrothion: The Long-Term Effects of Its Use in Forest Ecosystems. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, NRCC No. 16073, Ottawa, Ont., Canada, 628 pp.

Pearce, P.A.; Brun, G.L.; Witteman, J. 1980. Off-target fallout of fenitrothion in rain. in I.W. Varty, Environmental Surveillance in New Brunswick, 1978-79: Effects of Spray Operations for Forest Protection Against Spruce Budworm. EMOFICO Report.

Perring, F.H.; Mellanby, K. 1977. Ecological effects of pesticides", Academic Press, London, England, 193 pp.

Prebble, M.L. 1975. "Aerial control of forest insects in Canada". Environment Canada, Ottawa, Ontario, 328 pp.

Stevenson, F.J. 1982. Humus Chemistry, John Wiley and Sons, New York, N.Y. 443 pp.

Sundaram, K.M.S. 1974a. Distribution and persistence of fenitrothion residues in foliage, soil and water in Larose Forest. Env. Can. For. Serv. Chem. Cont. Res. Inst. Inf. Rept CC-X-64, 43 p.

Sundaram, K.M.S. 1974b. Persistence studies of insecticides: III Accumulation of fenitrothion and its oxygen analog in foliage, soil and water in Larose Forest. Env. Can. For. Serv. Chem. Cont. Res. Inst. Inf. Rept. CC-X-65, 21 p.

Sundaram, K.M.S.; Sundaram, A. 1982. Influence of formulation on droplet size, deposit concentration and persistence of fenitrothion in conifers following a simulated aerial application. Env. Can., Can. For. Serv. Res. Notes 2(1):2-5.

Sundaram, K.M.S.; Feng, J.; Nott, R.; Feng, C. 1983. Distribution, dynamics, persistence and fate of aminocarb and fenitrothion formulations containing Triton X-100 in a New Brunswick forest environment. Env. Canada For. Serv. For. Pest Manage. Inst. File Rept. 44, 83 p.

Sundaram, K.M.S.; Szeto, S. 1981. The dissipation of nonylphenol in stream and pond waters under simulated field conditions. J. Environ. Sci. Health B16(6): 767-776.

Symons, P.E.K. 1977. Dispersal and toxicology of the insecticide fenitrothion: predicting hazards of forest-spraying. Residue Reviews 38: 1-36.

Szeto, S. and K.M.S. Sundaram. 1982. Behaviour and degradation of chlorpyrifos-methyl in two aquatic models. J. Agric. Food Chem. 30(6): 1032-35.

Takimota, Y., Hirota, M.; Inui, H. and Miyamoto, J. 1976. Decomposition and leaching of radioactive Sumithion in 4 different soils under laboratory conditions. J. Pesticide Sci. 1:131-143.

Varty, I.W. 1976. Environmental effects of the spruce budworm spray program in New Brunswick - 1976. Env. Canada Can. For. Serv., Maritimes For. Res. Centre, Inf. Rept. M-X-67, 21 p.

Westlake, W.E. and J.P. San Antonio. 1960. Symp. on Nature and Fate of Chemicals Applied to Soils, Plants and Animals, 105-115.

Yule, W.N. 1974. The Persistence and fate of fenitrothion insecticide in a forest environment. II. Accumulation of residues in balsam fir foliage. Bull. Environ. Contam. Toxicol. 12(2):249-252.

Yule, W.N.; Duffy, J.R. 1972. The persistence and fate of fenitrothion insecticide in a forest environment. Bull. Environ. Contam. Toxicol. 8:10-17.

Yule, W.N.; Varty, I.W. 1975. The persistence and fate of fenitrothion insecticide in a forest environment. III. deposit and residue studies with black spruce and red maple. Bull. Environ. Contam. Toxicol. 13(6):678-680.