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Off-Target Fallout of Fenitrothion During 1978 Forest Spraying Operations in New Brunswick

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Large-scale forest spray programs have been conducted almost annually in New Brunswick since 1952 in attempts to protect the forest against damage by spruce budworm (Choristoneura fumiferana). Adverse environmental effects resulted in the phasing out of DDT in the late 1960s and its replacement by less-persistent fenitrothion (O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate). In recent years aminocarb (4-dimethylamino-3 methylphenyl methylcarbamate) has assumed an increasingly prominent role in spray operations in that province. Concern over environmental contamination has continued.

The problem of local drift of agricultural chemicals from target areas has been well recognized (AKESSON & YATES 1964). YULE & COLE (1969) reported drift of DDT several miles during forestry operations, and widespread low-level contamination of the atmosphere following forest spraying with fenitrothion in New Brunswick has been measured (YULE et al. 1971). In describing the atmosphere as a sink for applied pesticides, GLOTFELTY (1978) cited surface deposition, washout, and chemical reaction as removal mechanisms. PEARCE et al. (1978) reported residues of DDT in rainwater in New Brunswick and the adjacent Gulf of St. Lawrence in 1967-68 when there was still a substantial regional forest use of that insecticide, but they were unable to identify the source of contamination.

The effectiveness and economy of the use of macroreticular resinous adsorbents for the removal of a variety of organic contaminants from water has been demonstrated. Amberlite XAD-2 resins were employed by RICHARD et al. (1975) for the recovery of atrazine, DDE and dieldrin, and by BERKANE et al. (1977) for the isolation of fenitrothion from water. Chemically-identical XAD-4 resin was applied to the analysis for several organochlorine insecticides and polychlorinated biphenyls (MUSTY & NICKLESS 1974) and hydrolytic products of organophosphorus insecticides (DAUGHTON et al. 1976).

We report here the use of Amberlite XAD-4 resin to recover fenitrothion particularly and also aminocarb from rainwater in 1978 when those insecticides were sprayed from the air in forest protection operations against spruce budworm in New Brunswick.

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MATERIALS AND METHODS

The Amberlite XAD-4 resin column was prepared according to MALLET et al. (1978) as follows. The resin was purified by washing twice with both acetone and methanol. A glass-wool plug was inserted at the lower end of a chromatography glass column (250 x 21 mm i.d.) and a methanol slurry of the resin poured in to a height of 120 mm. Air bubbles were removed by inverting the stoppered column several times. Another glass-wool plug was positioned on top of the resin and the methanol drained. The column was then rinsed twice with 50 mℓ distilled water and allowed to drain to a few mm above the resin, water head being adjusted by attachment of a U-tube to the lower end of the column. The upper end of the column was attached to a glass or Nalgene^{R} funnel, 25-28 cm i.d. Components were connected with sleeves of Tygon^{R} tubing. The funnel was supported in stovepipe which was wrapped in aluminum foil and securely supported in the ground. Having passed through the assembly, the rainwater was allowed to collect in a 4-ℓ amber glass bottle, placed inside the stovepipe, and the volume later measured. The rain collector units were deployed at 11 sites outside forest spray zones and at one site within, as indicated in Figure 1.

At all inland stations except Sevogle and Newcastle, extraction was carried out on site weekly by eluting the resin column with three successive amounts of about 30 mℓ ethyl acetate. The column was regenerated for subsequent use by eluting successively with 50 mℓ acetone, 100 mℓ methanol, and twice with 50 mℓ distilled water. At other locations, columns were replaced by new ones after 4 wk and the same extraction procedures followed in the laboratory. Pending analysis, the eluates were stored for 5-10 wk at 4 C in Sovirel^{R} bottles sealed with aluminum foil. We have found that fenitrothion and aminocarb remain stable for several months under those conditions.

The ethyl acetate eluate was dried by adding 15-20 g sodium sulphate and passing under suction through a glass column packed with 10 g sodium sulphate. It was concentrated on a rotary evaporator at 35 C to 2.0 mℓ, and analysed using a gas chromatograph equipped with a flame photometric detector and a 2 m x 4 mm i.d. glass column packed with 4% OV-101 and 6% OV-210 on 80/100 mesh Chromosorb W(HP). Operating parameters were similar to those described by RIPLEY et al. (1974). The resins used were checked to assure efficiency, average recoveries of fortified samples being essentially 100% for both fenitrothion and aminocarb.

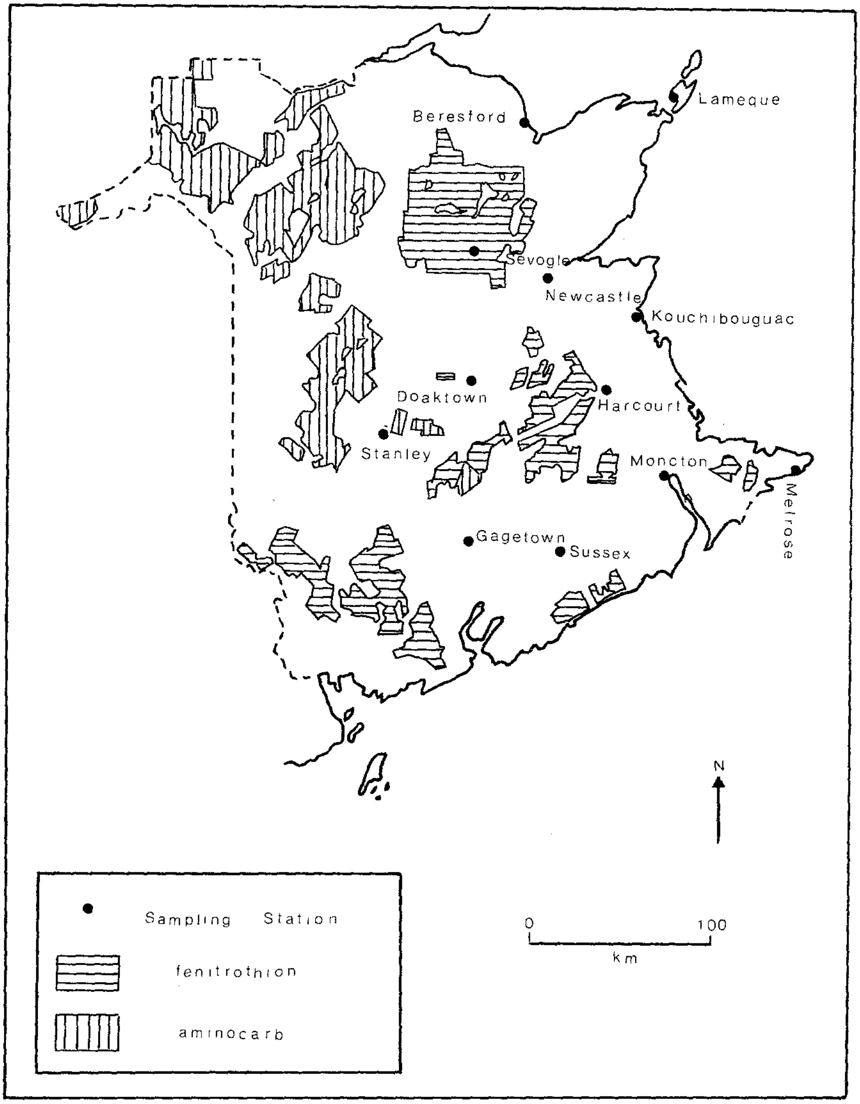

Figure 1. Outline map of New Brunswick showing forest areas sprayed in 1978 and location of rain collection units.

RESULTS AND DISCUSSION

Concentrations in rainwater of fenitrothion recovered from resin columns deployed at the 12 sites are given in Table 1. Outside the forest spray zone, fenitrothion was found in one-half of the samples and ranged up to 1.1 µg/ℓ. It occurred at 0.16 µg/ℓ at one site (Lamèque) 85 km from the nearest place of application. In contrast, a concentration of 77 µg/ℓ was recovered from rainwater collected

TABLE 1

Fenitrothion concentrations in rainwater samples collected in New Brunswick in 1978. (Concentrations are expressed as µg/ℓ).

Site	Collection period			
	24 May-3 June	3-9 June	9-16 June	16-29 June
Gagetown(35)[a]	N.D.[b] (0.42)[c]	N.D. (1.44)	N.D. (1.29)	N.D. (1.01)
Sussex(45)	N.D. (0.31)	0.09 (1.66)	N.D. (1.50)	N.D. (0.45)
Moncton(25)	N.D. (1.20)	0.02 (1.56)	trace (0.27)	N.D. (0.18)
	25 May-2 June	2-8 June	8-15 June	15-26 June
Stanley(35)	0.34 (0.55)	0.11 (2.20)	N.D. (1.04)	N.D. (1.20)
Doaktown(10)	0.42 (2.55)	0.23 (1.25)	N.D. (0.83)	0.20 (1.09)
Harcourt(5)	0.86 (1.85)	1.1 (2.50)	N.D. (1.02)	N.D. (0.50)
	15 May-13 June	13 June-6 July		
Beresford(25)	0.44 (2.54)	0.61 (4.87)		
Lamèque(85)	0.16 (2.85)	N.D. (3.25)		
	16 May-14 June	14 June-6 July		
Kouchibouguac(35)	0.32 (3.78)	0.10 (1.86)		
Melrose(20)	0.26 (3.73)	N.D. (1.69)		
	19 May-28 June			
Newcastle(20)	0.25 (5.05)			
Sevogle(0)	77 (8.21)			

[a] Approximate distance(km) from nearest point of fenitrothion application given in parentheses.

[b] N.D. = not detected. Detection limit was 0.01 µg in 1 ℓ rainwater.

[c] Volume(ℓ) of collected rainwater given in parentheses.

in the area sprayed with that insecticide. Fenitrothion was confirmed in selected samples by GC/MS. No residues of fenitrooxon, amino fenitrothion, and S-methyl fenitrothion were recovered, limits of detection being 0.05, 0.01, and 0.05 µg/ℓ, respectively. Rainwater which had passed through the columns at the four coastal sites and at Newcastle and Sevogle, as well as chloroform rinsings of the glass funnels, taken at those sites at the end of the study, were also analysed for fenitrothion and the aforementioned degradation products. Fenitrothion occurred, at low levels, only in the sample from Sevogle, and in one sample from both Harcourt and Stanley. Using a method adapted and developed in our laboratory for routine residue monitoring, eluates of the resin columns at those six locations were analysed for aminocarb by high performance liquid chromatography, with UV-absorbance and fluorescence detection. If present, that insecticide was below the limit of sensitivity (0.05 µg/ℓ) of the technique.

About 1,540,000 ha of New Brunswick forest were sprayed between 26 May and 22 June in 1978, most of that area being treated twice. Nearly 295,000 kg of technical fenitrothion and 94,000 kg of technical aminocarb were formulated and emitted by spray aircraft. Since the only regional use of fenitrothion was against spruce budworm, we conclude that residues of that insecticide which were recovered from the resin columns originated in the forest spray operations. After examining local meteorological records and spraying schedules, however, we were unable to relate the contamination to specific spray sorties. That was probably partly because the periods during which precipitation samples were collected were out of phase with those during which spray aircraft were active, since no spraying took place when it was raining. In their study of atmospheric contamination by fenitrothion during a large-scale forest spray operation in New Brunswick, YULE et al. (1971) concluded that cause-and-effect relationships were not amenable to precise analysis under maritime weather conditions. Prevailing winds in the region at the time of our study were from the southwest and fenitrothion residue levels were generally lowest at downwind sites farthest removed from the scene of spraying. Fenitrothion spraying over the forests of the Gaspé Peninsula of Québec, about 75 km to the north and northwest of Beresford and Lamèque, could have contributed to contamination at those sites. Our failure to detect aminocarb might be due to the possibly more ephemeral nature of that insecticide, to the more distant scene of spray application, or to the less sensitive analytical technique.

The study indicates that atmospheric transport and subsequent surface deposition or the scavenging effect of falling rain, or both, are mechanisms in the redistribution of the forest spray cloud beyond the target area. They may at least partly account for the recently-reported (VARTY 1978) presence of fenitrothion in shellfish in the littoral zone of New Brunswick remote from the place of insecticide application.

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