Bull. Environ. Contam. Toxicol. (1984) 32: 65-74

Bulletin of Environmental Contamination and Toxicology

# Fenitrothion Residue Survey in Relation to the 1981 Spruce Budworm Spray Program in New Brunswick, Canada

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Because of the continuing epidemic of spruce budworm (Choristoneura fumiferana Clemens) in New Brunswick (Canada) 1.93 million hectares of woodland were sprayed with fenitrothion [0,0-dimethyl 0-(3-methyl 4-nitrophenyl)phosphorothioate] in 1981. Thus a chemical residue survey was undertaken to determine the extent of the deposition and persistence of fenitrothion in the environment in general.

Fenitrothion is a very well known insecticide and its use and impact on the environment has been well documented (NRCC No. 14104, 1975; NRCC No. 16073, 1977). In New Brunswick, sporadic environmental surveillance of spray operations has been on-going since the inception of the program to protect the forest which started in 1952. But it was only in 1976 that environmental surveillance was coordinated by the Environmental Monitoring of Forest Insect Control Operations (EMOFICO) Committee which has since published four reports, the latest for the years 1980-81 (Townsed 1982). Environmental monitoring is a multi-faceted surveillance operation that includes many aspects related to the spraying and its impact on the total environment. One of these operations entails the collection and analysis of environmental samples for fenitrothion. Sampling is done before, during and after the spray program. The sites are chosen to represent sprayed and non-sprayed areas but are selected at random such that the data will be representative of the type of chemical contamination expected anywhere in N.B., and not specifically under a spray cloud.

In fact most of the previous studies were to determine the amount of chemical deposition in a sprayed area immediately after spraying and to measure the persistence. In foliage for instance, amounts of 3.5-11.7 ppm of fenitrothion were found immediately after

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spraying but the persistence (95% of original amounts loss) was reported to be 10 days (Sundaram, 1974).

We conducted a first chemical residue survey in relation to the New Brunswick (N.B.) spray program in 1980 (Mallet and Volpé, 1982). That year over 1 million hectares of woodland had been sprayed with fenitrothion. A total of 465 air and water samples from the Nepisiguit River area, the Canaan River area and the City of Moncton area, were analysed for fenitrothion and some of its derivatives.

In water, fenitrothion was detected when spraying occurred in the immediate area of the sites. The maximum level was 20.0 ppb and persistence was usually limited to a few days post-spray except in a still water pond where fenitrothion was detected for 18 consecutive days. Aminofenitrothion, a reductive degradation product of the parent compound was also detected at a maximum level of 8.0 ppb. In air samples fenitrothion was only detected occasionally and the maximum was 1.2 ng/L.

In 1981, the study was repeated for water and air samples from an area that was sampled in 1980, for comparison purposes. But in addition, the study was extended to coniferous foliage, soil litter and river sediment samples, and to the analysis of fenitrothion and some important derivatives, namely hydroxymethylfenitrothion, S-methylfenitrothion, fenitrooxon, aminofenitrothion, formylfenitrothion and nitrocresol. It was thought that the information gathered would supplement that obtained in 1980 such that in the course of successive years a better picture regarding chemical contamination in relation with the spruce budworm spray program would emerge.

## METHODS AND MATERIALS

The apparatus and chemicals used are described in Mallet and Volpé, 1982. In addition a Spectra-Physics (SP 8000B) high pressure liquid chromatograph (hplc) was used for the detection of nitrocresol (Volpé and Mallet, 1981). The chromatograph was equipped with a reversed phase column containing RP-8 (10 um, 4.6 mm I.D. x 25 cm) and a UV detector (254 nm).

Sampling was done in two main areas of New Brunswick. One was the Canaan River area (Fig. 1) where three water sites (A, B and C) were located within range of blocks 78 and 77. The other area was East of Moncton, N.B. (see Fig. 2) near spray blocks 82 and 83. Fives sites (D-H, Fig. 2) were selected for water,

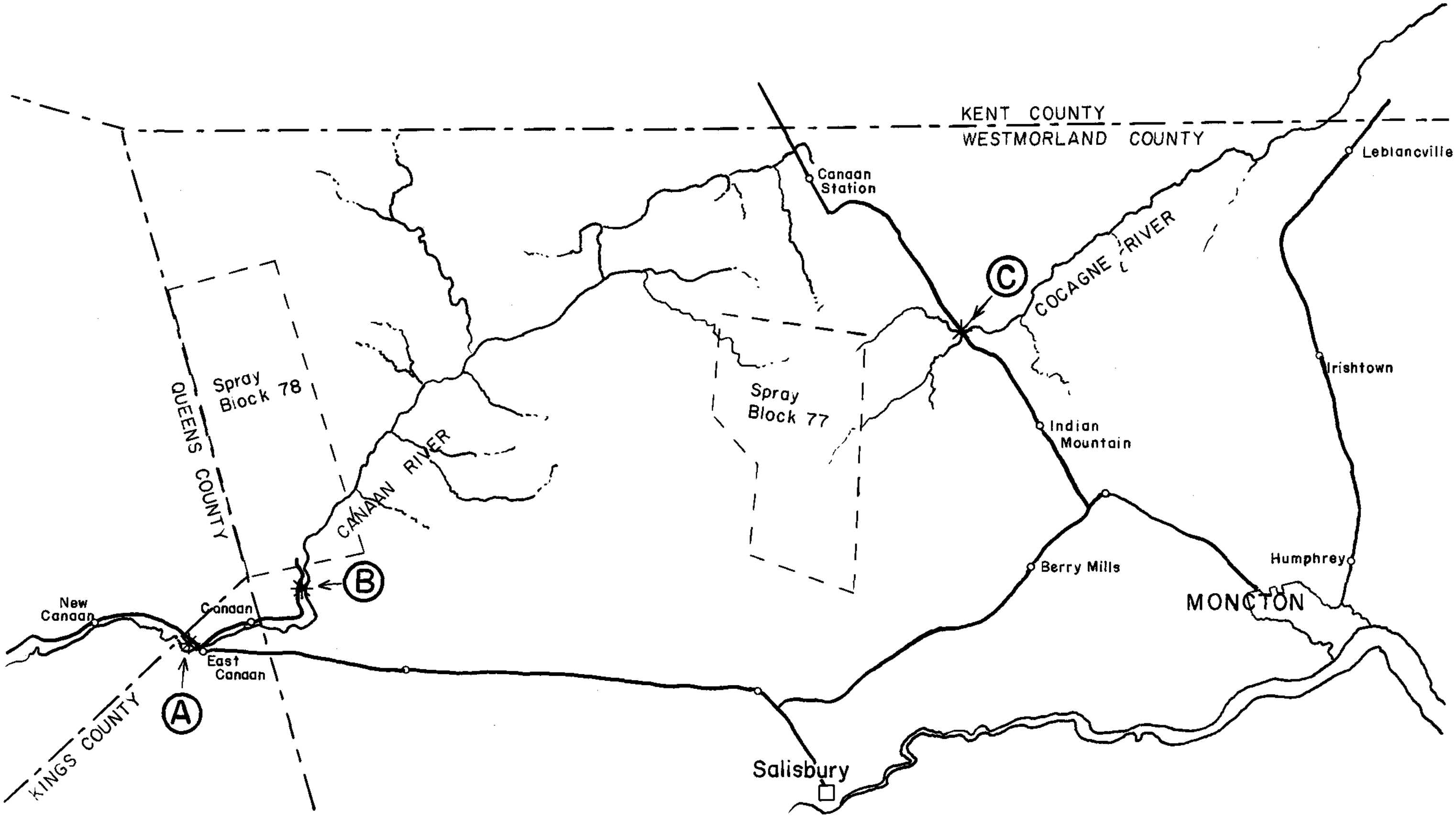

Figure 1: Location of sampling sites A, B, and C.

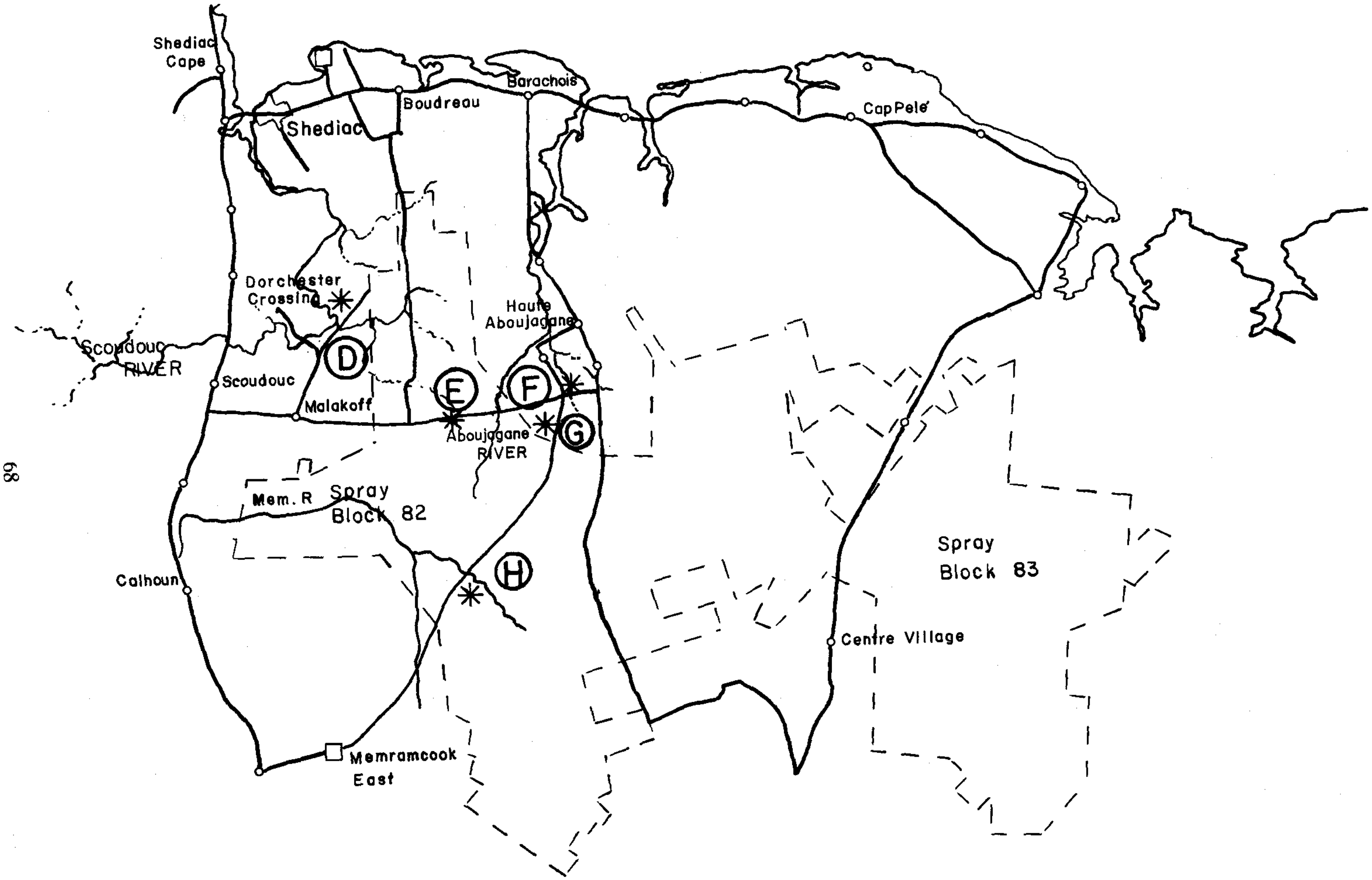

Figure 2. Location of sampling sites D, E, F, G, and H.

air, sediment, soil litter and coniferous foliage sampling.

At the permanent site (F), air was drawn through an XAD-2 column (Mallet and Volpé, 1982) at a rate of 2L per min for 24h for a total of 2880L per sample. At the mobile site (J), air was drawn through a column at a rate of 2L per min for 50 min, for 100L. The mobile site was selected daily always facing the wind and block 82.

Water samples were collected at sites A-F and H. They were drawn from the top 40 cm in the middle of the stream. The samples were collected in amber glass bottles, brought to the laboratory within two hours and extracted immediately thereafter. Most of the samples were passed through an XAD-4 column but some were extracted with ethyl acetate to test for nitrocresol (Volpé and Mallet, 1980). In these cases 50 mL of ethyl acetate were added in the field to act as a preservative. Sediment samples were collected at sites D, E, F and H, in the immediate viccinity of the water sampling sites. Each sample was composed of six sub-samples collected in a plastic freezer bag. Soil litter and coniferous foliage samples were collected at sites E, F, G and H. Each sample was composed of 12 sub-samples collected at equal intervals in a hectare-size lot. All samples except water and air were kept in a freezer at -20°C until further processing.

Each column was eluted with 3 x 30 mL of ethyl acetate. The eluate was concentrated to 1.0 mL and a 5-ul aliquot was injected into a gas chromatograph (Mallet and Volpé, 1980). Standards were also injected for calibration purposes. Each column was regenerated by washing successively with 50 mL of ether, 50 mL of methanol and 100 mL of distilled water for further utilization.

Those water samples to which 50 mL of ethyl acetate were added in the field were brought to the laboratory and usually processed the same day. They were extracted with an additional 3 x 40 mL of ethyl acetate at pH 3.0 (HCl), the extract was dried with anhydrous sodium sulfate and evaporated almost to dryness, then diluted to 1.0 mL with methanol for quantitative analysis by hplc.

For sediment, soil litter and coniferous foliage samples a 1.0 Kg sample was obtained from the original gross sample by quartering. The sample was macerated using a Polytron (Brinkmann Inst.). A 10g sub-sample was homogenized with 150 mL of acetonitrile. The filtrate was diluted to 2L with distilled water and passed through an XAD-7 column at 130 mL/min. The column was washed with 1L of distilled water and eluted with 4 x 25 mL of ethyl acetate at the same flow rate. The eluate was dried with anhydrous sodium sulfate and concentrated to 1.0 mL for quantitative purposes (Haché et al., 1981).

The spray regime consisted of two successive applications of fenitrothion (active ingredient) at 210 g/ha. The formulation contained by weight 14.5% technical fenitrothion, 1.4% Dowanol, 1.5% Atlox 3409F, and 82.6% water.

## RESULTS AND DISCUSSION

The results of the 1980 study (Mallet and Volpé, 1982) showed that the amount of fenitrothion in air and water samples was low and not persistent. The data also showed that only one water sample per day per site was sufficient to evaluate the level of fenitrothion present. It was with this information in mind that the 1981 survey was undertaken.

The results from the Canaan River area are presented in Table 1. The samples collected on May 25 were

Table 1. Fenitrothion (ppb) in Water from Canaan River Area (1981)

| Sampling Date | Canaan River at East Canaan (Site A) | Canaan River (Site B) | Head of Cocagne River (Site C) |
|---|---|---|---|
| May 25 | 1.00 | 1.30 | 0.70 |
| 26 | 0.22 | 0.22 | 0.91 |
| 27 | 0.09 | 0.05 | 0.37 |
| 28 | 0.16 | 0.09 (A.F.) | 0.30 (A.F.) |
| 29 | Traces (A.F.) | 0.04 (A.F.) | 0.14 (A.F.) |
| 30 | Traces | N.D. | 0.07 |
| 31 | Traces (A.F.) | Traces (A.F.) | 0.04 (A.F.) |
| June 1 | Traces (A.F.) | Traces (A.F.) | Traces (A.F.) |
| 2 | Traces (A.F.) | Traces (A.F.) | Traces (A.F.) |
| 3 | 0.08 | 0.80 | 0.66 |
| 5 | 0.09 | 0.08 | 0.32 |
| 15 (post-spray) | N.D. | N.D. | N.D. |

LEGEND: N.D. means below detection limit of 0.01 ppb; Traces means less than 0.04 ppb; A.F.: indicates the presence of small amounts (less than 0.1 ppb) of aminofenitrothion.

supposed to be pre-spray. But other areas of New Brunswick had been sprayed earlier in the week and contamination via air drift could have occurred. Fenitrothion was detected at all three sites in agreement with the two successive spray applications May 26 and June 3. In general, the amounts detected were low (maximum 1.30 ppb) and post-spray samples did not contain detectable amounts (less than 0.01 ppb) of fenitrothion. Small amounts of aminofenitrothion (< 0.1 ppb) were detected in some samples. In general, the results agreed very well with those obtained in 1980 for the same area.

The majority of samples in 1981 were collected East of Moncton, at sites A-F and H (Fig. 2). Some of the sites (D, F and G), were outside the spray block. However, in all cases the head waters of the brooks tested originated from somewhere in a sprayed area.

The results for the water samples are given in Table 2. Small amounts of fenitrothion were present in pre-spray samples. It was presumed that the source of of fenitrothion was the 1980 Spray Program i.e., from small amounts that remained in the soil or foliage over the year and that were leached in the water following heavy rainfalls in the area in May. However, there is always the possibility that it came via air drifts, from other areas of N.B. that were sprayed before May 26. Nonetheless, samples obtained imme-

Table 2. Fenitrothion (ppb) in Water from Aboujagane Area (1981)

| Sampling Date | Site D | Site E | Site F | Site H |
|---|---|---|---|---|
| May 29 (pre-spray) | Traces | 0.11 | N.D. | 0.11 |
| June 11 | N.D. | 0.16 | N.D. | 0.50 |
| 12 | 0.09 | 1.10 | 0.28 | 0.26 |
| 13 | 0.39 | 0.07 | 0.15 | 0.11 |
| 14 | N.D. | 0.95 | N.D. | N.D. |
| 15 | Traces | N.D. | N.D. | N.D. |
| 16 | N.D. | N.D. | N.D. | N.D. |
| 17 | N.D. | N.D. | 0.12 | 0.22 |
| 18 | N.D.[1] | 0.05[1] | 0.05[1] | 0.55[1] |
| 19 | 0.06 | N.D. | N.D. | 0.05 |
| 24 | 0.88 | 0.94 | 0.75 | 0.88 |
| July 1 | N.D.[1] | Traces[1] | N.D. | N.D.[1] |

LEGEND: 1. For these samples liquid-liquid extraction was used to test for the presence of nitrocresol by hplc (Mallet et Volpé, 1981).

diately after the spray contained small amounts of fenitrothion corresponding with the two successive spray applications. In the post-spray samples fenitrothion was not detectable except at site E, where traces were found. Degradation products could not be detected in any of the sample. Thus the results from these water samples confirm those obtained from the Canaan River area and also those from the 1980 survey (Mallet and Volpé, 1982) that is, the contamination was light and not persistent.

Air sampling sites were also established East of Moncton (sites F and J). At the permanent site ("F" in Fig. 2) a total of 2880L of air were passed through an XAD column for each 24h sample. The other site (J) was variable, in the sense that sampling was done at different places each day, always facing the wind around block 82. For practical purposes, each sample was limited to 100L. The results in Table 3 indicate that fenitrothion was only detected twice at the permanent site at levels of 0.08 and 0.04 ng/L. Fenitrothion was never detected at the variable site. These results confirm the 1980 data which suggested that the level of fenitrothion in air was practically negligible.

Table 3. Fenitrothion (ng/L) in Air from Aboujagane Area

| Sampling Date | Site F | Site J (VARIABLE) | |
|---|---|---|---|
| June 12, 1981 | 0.08 | Drisdelle: | N.D. |
| 13 | traces | Drisdelle: | N.D. |
| 14 | N.D. | Shediac: | N.D. |
| 15 | N.D. | Malakoff Rd: | N.D. |
| 16 | N.D. | Malakoff Rd: | N.D. |
| 17 | 0.04 | Drisdelle: | N.D. |
| 18 | N.D. | Drisdelle: | N.D. |
| 19 | N.D. | Malakoff Rd: | N.D. |

LEGEND: At Site F, sampling was done 24h for 2880L of air and the detection limit was set at 0.04 ng/L.

Site J was variable depending on wind direction. Only 50 min sampling each day for 100L was done and the detection limit was set at 0.05 ng/L.

In order to better document the distribution of fenitrothion in the environment, a limited number of sediment, soil litter and coniferous foliage samples were analysed. The results in Table 4 indicate that some pre-spray samples contained small amounts of fenitrothion. This would tend to support the earlier

Table 4. Fenitrothion (ug/g) in Other Substrates from Aboujagane Area

| | SITE | May 26 (pre-spray) | June 17 | July 1 (post-spray) |
|---|---|---|---|---|
| Sediment | D | - | - | - |
| | E | N.D. | N.D. | N.D. |
| | F | Traces | N.D. | N.D. |
| | H | Traces | N.D. | N.D. |
| | G | N.D. | Traces | N.D. |
| Coniferous foliage | D | N.D. | 0.23 | 0.05 |
| | E | - | - | - |
| | F | 0.03 | 0.22 | 0.09 |
| | H | 0.02 | 0.28 | 0.21 |
| | G | 0.09 | 0.53 | 0.43 |
| Soil litter | D | N.D. | 0.14 | 0.04 |
| | E | - | - | - |
| | F | N.D. | 0.09 | 0.10 |
| | H | 0.02 | 0.06 | 0.19 |
| | G | Traces | 0.13 | 0.05 |

LEGEND: (-) means no sample was taken; Traces means less than 0.01 ppm.

assumption that traces of fenitrothion in water samples may have originated from the surrounding areas. The samples of foliage and soil litter collected after the second spray application, June 17, contained higher levels of fenitrothion and the post-spray samples collected two weeks later contained similar levels of fenitrothion indicating persistence.

The only derivative detected was aminofenitrothion in water samples. Other degradation products such as fenitrooxon, aminofenitrothion, S-methylfenitrothion, hydroxymethylfenitrothion and formylfenitrothion were not present anywhere in water at levels comparable with fenitrothion. Another degradation product, nitrocresol, was analysed by hplc but was never detected.

A. The project was supported by Environment N.B. Thanks are given to S. Laviolette, C. Pitl and F. Cyr who were responsible for processing the samples.

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Received July 13, 1983; Accepted August 18, 1983