

A PRELIMINARY STUDY ON THE PERSISTENCE  
AND DISTRIBUTION OF MATACIL<sup>®</sup> IN A  
FOREST ENVIRONMENT

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### INTRODUCTION

Several carbamic acid esters have been known for many years to be highly toxic to insects because of their inhibition of the cholinesterase enzyme present in target species (Matsumura 1975). In recent years carbamates are becoming increasingly important in the field of forest pest management programs in Canada primarily due to their effectiveness combined with low mammalian toxicity, high insect toxicity, short residual life in the environment and their relatively harmless decomposition products (Salagbauer and Schlagbauer 1972). Because of these desirable properties, Matacil<sup>®</sup> (4-dimethylamino-*m*-tolyl methylcarbamate), a registered trade mark compound introduced by Bayer in Germany in 1963 (accepted common name "aminocarb") and marketed in N. America by Chemagro Chemical Company, has been used more and more in Canada since 1971 in various experimental and operational forest spray programs against lepidopterous defoliators (Buckner *et al* 1975).

With increasing use of Matacil in insect control programs, it has become necessary to monitor and study its fate in various components of the forest environment in Canada, primarily with respect to possible hazards, and to provide data for registration of the material for forestry use as required by the Canada Department of Agriculture. Consequently, an urgent need arose to develop a rapid and sensitive analytical method to determine the residue levels of the toxicant in soil, water and foliage samples collected from sprayed forest regions. Dr. J.R. Duffy of the University of Prince Edward Island, at the request of Chemical Control Research Institute (CCRI) and with the financial assistance of the Science Subvention Program of the Forestry Service, Environment Canada,

has spent considerable time and effort in researching and developing a suitable analytical residue method for the parent compound in soil, water and coniferous foliage.

During the 1974 spray season, Matacil was sprayed experimentally by aircraft at a dosage of 70 g AI/ha (1.0 oz AI/acre) in Larose Plantation Forest situated about 48 km (30 miles) east of Ottawa, Ontario for control of spruce budworm, *Choristoneura fumiferana* (Clemens). This report describes some of the exploratory and intensive studies made at CCRI on the analytical methodology developed by Dr Duffy using substrates of water, soil and spruce foliage sampled after the spray operation under the following categories:

1. Examination, evaluation, validation and if necessary, refinement and simplification of the analytical method developed by Dr Duffy for forest environmental samples, and to assess the lowest detectable limit of Matacil in the samples.
2. Systematic study of the persistence of Matacil and its half-life in spruce (*Picea* spp.) foliage, forest soil and natural water samples and its distribution in these components.
3. Extension and adaption of the analytical methodology to other samples such as animal tissues, aquatic organisms, etc.

## MATERIALS AND METHODS

### Plan of Operation

The area selected for the aerial application of Matacil was comprised mainly of spruce (*Picea* spp.), pine (*Pinus* spp.) and tamarack (*Larix* spp.). The plot chosen for the insecticide treatment covered an area of 1012 ha (2500 acres) and is designated as Bee Range (BR) 1 and 2 in Fig. 1. The conifer tree component of the plot averaged 10 m (32 ft) in height and up to 23 cm (9 in) d.b.h.

### Matacil Application

Matacil (tech.) was supplied by Chemagro Chemical Company in an oil solution. The spray mixture was prepared by mixing thoroughly the insecticide with automate Red B dye (for colorimetric analysis and droplet measurements) and No. 2 fuel oil in the percent ratio of (V/V) 36 : 1: 63 to give 168 g AI/ℓ (1.4 lb AI/U.S. gal) and applied at the rate of 70 g AI in 0.42 ℓ/ha (1.0 oz AI in 16 fl. oz/acre) 24 m (80 ft) above the forest canopy in one sortie on the evening (1900 hours) of June 6, 1974 using a Pawnee 0235 aircraft fitted with 4 Micronair AU 3000 emission units at an approximate speed of 160 km/hr (100 mph) and a swath width of 61 m (200 ft). The meteorological conditions while spraying were less than ideal with an average wind speed (N - NE) of 7.2 km/hr (4.5 mph), temp. 18.9°C, R.H. 60% and stability ratio of - 0.1.

### Sampling and Extraction

The environmental samples (spruce foliage, soil, stream and pond waters) were taken from the spray plot before spraying (May 16, 1974) and 0.6, 1, 2, 3, 4, 7, 11, 17, 32, 63 and 126 days after the spraying.

1. Foliage

Spruce foliage, selected in this study as an indicator species for the persistence of Matacil, was gathered randomly from 15 to 20 exposed mid-crown branches of trees from the spray area using a pole pruner and transported immediately to the pesticide laboratory at CCRI in plastic bags where *ca* 45 cm of branch tips were defoliated by handcutting of twigs and chopped into small pieces by a Hobart food cutter. The chopped needles were mixed thoroughly, two 10 g aliquots were taken for moisture determination (AOAC 1955) and three 100 g composites of foliage on each sampling day were preserved in mason jars with 200 ml of acetonitrile and stored in darkness at -20°C to prevent possible degradation pending development of a satisfactory methodology by Dr. J.R. Duffy.

2. Soil

Eight to ten cores of soil samples were taken randomly on each sampling day to a depth of 10 cm (4") using a 10 cm diameter toothed auger in the vicinity of the foliage sample collections. Samples were mixed well and transported at once to CCRI in plastic bags. In the laboratory, each soil sample was passed through a 1.25 cm mesh screen to remove large stones and debris and weighed. The pile of sieved, moist soil was mixed thoroughly by hand. A composite sample of approximately 600 g was sieved (No. 8 mesh, 2.4 mm opening) and three 100 g aliquots were stored in 100 ml of acetonitrile, as for foliage. Two 10 g quantities of the soil were used for moisture (AOAC 1955) and pH (Atkinson *et al* 1958) determinations.

3. Water

Approximately 2 litre samples of surface water (1.0 to 2.5 cm from the water surface) were collected on each sampling day (Tables I and II) from the centre of the pond (BR-1) and the stream (BR-2) in the spray plot (Fig. 1) in separate Mason jars fitted with screw caps and aluminum foil covers. The jars of water were transported immediately to the pesticide laboratory at CCRI for extraction and storage. Temperature and pH were recorded for each water sample at the site of collection.

In the laboratory, the pH of the water sample (1.5 l from each sampling site) was adjusted to 7.5 by the addition of a few drops of saturated sodium bicarbonate. The sample was then extracted twice with 100 ml of toluene. Afterwards the toluene extract was dried by passing it through a column of anhydrous sodium sulphate (50 g). The final volume was adjusted to 300 ml and was split into three 100 ml portions equivalent to 500 ml of the original water sample. Each 100 ml portion of toluene was stored at  $-10^{\circ}\text{C}$  in amber colored air-tight bottles, sealed with screw caps lined with teflon.

One set of each sample (water, foliage and soil) collected on different sampling periods was shipped to Dr J.R. Duffy in Charlottetown, P.E.I. and one set to Dr. T. B. Waggoner of Chemagro in Kansas City for method development and residue studies respectively.

The selection of acetonitrile for storing the coniferous foliage and forest soil samples and toluene for extracting the Matacil residues from natural waters had been chosen as a result of a literature survey (Holden 1973) and some preliminary tests conducted at the pesticide laboratory in CCRI.

### Analytical Methodology

As mentioned earlier under "Introduction" the analytical methodology for Matacil present in coniferous foliage (spruce), forest soil and natural waters, was developed by Dr J.R. Duffy (pers. comm.). His method is described here with minor modifications introduced by the first author at CCRI to serve as a ready source of information for the benefit of practicing pesticide scientists, chemists and laboratory staff here and elsewhere.

#### 1. Foliage

Each of the 100 g spruce foliage samples kept in frozen storage was homogenized twice with 200 ml of acetonitrile in a Sorvall-Omni-Mixer for 2 min at speed 6. The slurries were filtered under suction, rinsed with the solvent (30 ml), combined and an aliquot equivalent to 10 g of foliage was taken and the acetonitrile flashed down under low pressure to 5 ml. The concentrate was transferred quantitatively to a 500 ml separatory funnel, 200 ml of 0.5N sulphuric acid was added and the sample shaken. The acid layer was extracted three times with 50 ml of ethyl ether saturated with water followed by one extraction with 50 ml of chloroform once, and both the extracts discarded. The pH of the aqueous fraction was adjusted to 7.5 by addition of saturated  $\text{NaHCO}_3$  solution while stirring with a magnetic stirrer. The resulting aqueous solution was then extracted four times with 50 ml of benzene. The benzene extracts were pooled, washed thrice with distilled water containing  $\text{NaCl}$  and dried employing a benzene-azeotripe procedure for about 90 min using a Dean-Stark condenser.

The colourless dried extract was solvent stripped to *ca* 2 ml



and transferred quantitatively with the aid of anhydrous benzene to a 15 ml screw-capped, calibrated centrifuge tube and 0.5 ml of *fresh* heptafluoro butyric anhydride (HFBA)\* was added. The tube containing *ca* 10 ml of the reaction mixture was sealed with a cap containing a teflon lining and heated in a temperature controlled oil-bath at 120°C\*\* for two hours. Afterwards the tube was removed, cooled, flash-evaporated gently to dryness and the residue<sup>+</sup> was taken up in dry benzene for EC-GLC analysis.

A schematic representation of the extraction procedure for Matacil residues in spruce foliage is given in Fig. 2 listing the sixteen different steps involved in the analytical procedure.

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- \* The reagent is unstable and is decomposed rapidly in presence of moisture, storing the material in a desiccator did not help much. For better results, a fresh ampoule should be opened for each set of experiments.
- \*\* Temperature control is important to avoid the decomposition of the reagent and the derivative.
- + The HFBA derivative is also unstable. GLC analysis of the material should be carried out immediately.

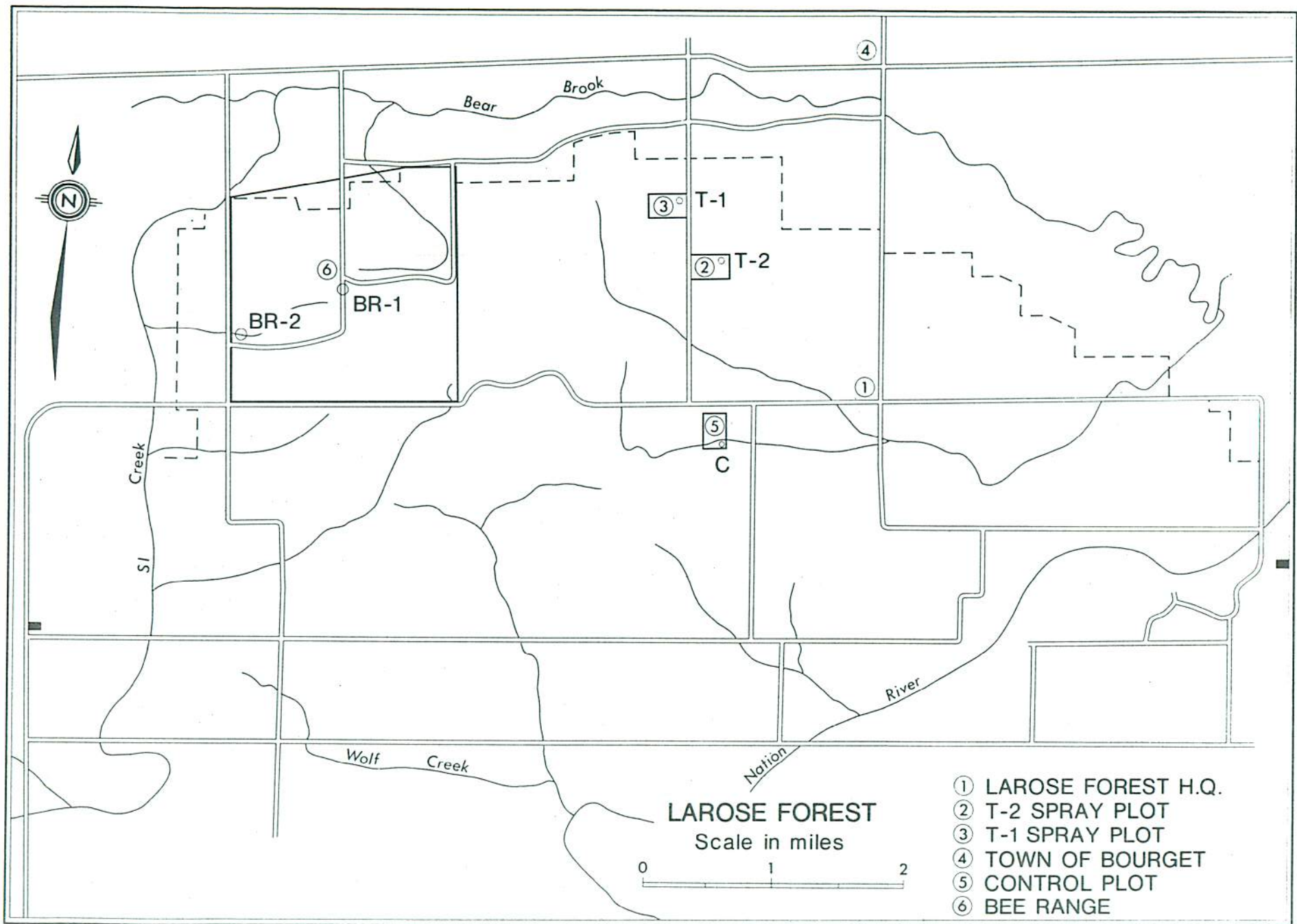


Fig. 1 Plot design for Matacil spraying in Larose Forest - June 1974.

Spruce Foliage (100 g)

1. Sampling and processing.
2. Sorvall homogenization with 2 x 200 ml  $\text{CH}_3\text{CN}$ .
3. Vacuum filtration.
4. Rinsing of residue with  $\text{CH}_3\text{CN}$  (30 ml).

Residue  
(discard)

Filtrate

5. Separation

Filtrate  
(90 g aliquot for  
storage).

Filtrate  
(10 g aliquot)

6. Flash-evaporation (5 ml)
7. Acid-base partition (cleanup)  
(200 ml of 0.5 N  $\text{H}_2\text{SO}_4$ ).
8. Extraction (3 x 50 ml  
ether + 1 x 50 ml  $\text{CHCl}_3$ ).

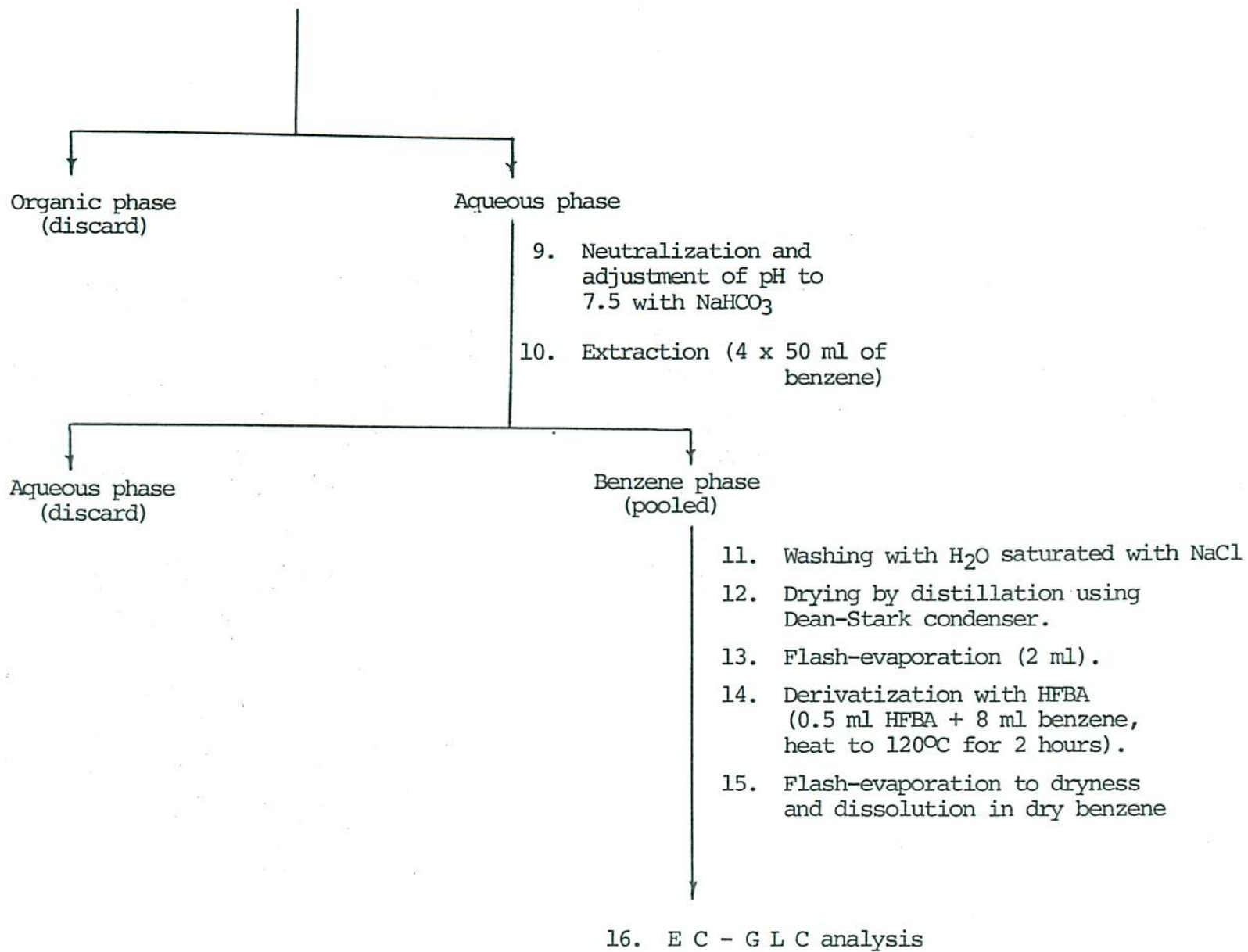
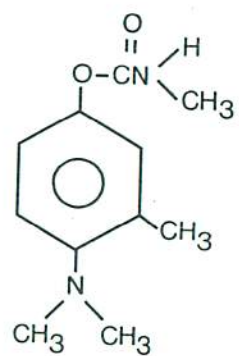


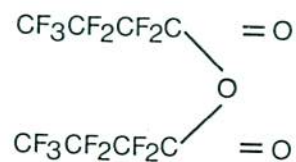
Fig. 2 Schematic representation of extraction and analysis of Matacil in spruce foliage.

Conversion of Matacil to a Stable Gas-Liquid Chromatographic Derivative

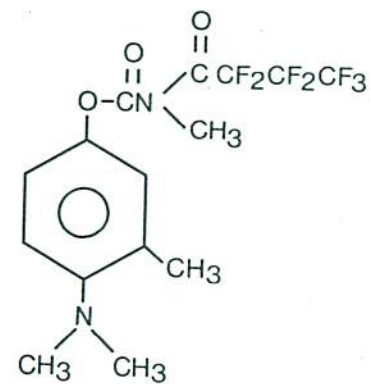


Matacil

+



HFBA



4-(dimethylamino)-3-methylphenyl-N-heptafluorobutyryl-N-methylcarbamate

2. Forest Soil

The procedure adopted for soil was very similar to that for foliage and the aliquot of  $\text{CH}_3\text{CN}$  extract used from step 6 (Fig. 2) onwards for the final analysis corresponded to 50 g of soil instead of the 10 g as in foliage.

3. Natural Waters

The analysis of Matacil in extracted water samples using toluene as the extractant and kept in storage in the frozen state in the dark (see the section on "water" in "Sampling and Extraction") was carried out using steps 11 to 16 (Fig. 2) as in foliage. If the interference due to coextractive impurities was high, then steps 6 onwards were followed in the quantification procedure.

Gas Chromatographic Analysis

Gas chromatographic analysis of Matacil residues present in forest environmental samples after complete cleanup and derivatization were carried out using a Hewlett-Packard Model 5750 gas chromatograph fitted with a Ni 63 electron capture (E.C.) detector. Operating parameters were as follows:

Column: 183 m x 6 mm (6 ft. x 0.24 in.)  
O.D. Pyrex glass packed with  
6% SE-30 on Chromosorb G. 70/80  
mesh, AW-DMCS, preconditioned  
overnight at 190°C.

Temperatures (°C) : Injection port 225  
Column oven 190  
Detector 260

Gas Flow : Carrier gas - Argon / methane  
(95/5%) at pressure 50 psi and  
flow rate of 75 ml/min.  
Purge gas - Argon / methane  
(95/5%) at pressure 50 psi and  
flow rate of 125 ml/min.

Instrument Settings: Attenuation 32  
Range 10  
Pulse rate 150  
Electrometer  $4 \times 10^9$  amp at  
full scale deflection with a  
1 Mv recorder from Linear  
Instruments.

Chart Speed (cm/hr): 76.2 (30 in / hr)  
Retention Time (min): 4.0

The gas chromatograph was standardized on the same day as the samples were analysed by injecting *fresh* HFBA derivatized aliquots (2-5 ul) of Matacil (Fig. 3) (analytical grade supplied by Chemagro), measuring the peak heights, and preparing a calibration curve by plotting peak heights vs concentration (Fig. 4). The calibration was checked intermittently. The extracts of samples from Larose Forest, after derivatization with HFBA were diluted with dry benzene or concentrated

by dry air-evaporation to the desired concentrations for GC analysis. Quantitative results of the extracted and derivatized samples were obtained by measuring each of the peak heights after injection (2 to 4 ul), under the same operating conditions, and reading the concentrations from the calibration curves (Fig. 4). Since the HFBA derivatives were not very stable, the analysis was done immediately after the derivatization\*.

All organic solvents used were either pesticide grade (P.G.) chemicals or freshly distilled in glass. The benzene used in preparing the HFBA derivative was dried using the Dean-Stark apparatus. Being hygroscopic and unstable, the HFBA reagent was stored in a desiccator and a fresh vial was used at each set of experiments. All the chemicals used in the analysis met with the American Chemical Society specifications. The anhydrous sodium sulphate used was of reagent grade from Fisher, heated at 150° overnight and stored in air-tight glass-stoppered bottles.

Laboratory sources of contamination including chemicals, glassware, solvents etc. were found to be negligible during the period of study.

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\* See the footnotes on page 7.



Table I

Analysis of Pond Water Samples for Matacil from Larose Forest

| Sample No. | Days After Application | Matacil conc. (ppb) |
|------------|------------------------|---------------------|
| 1          | Prespray*              | N.D.                |
| 2          | 0.6                    | 2.1                 |
| 3          | 1.0                    | 1.6                 |
| 4          | 2.0                    | 1.5                 |
| 5          | 3.0                    | 1.7                 |
| 6          | 4.0                    | 1.4                 |
| 7          | 7.0                    | 0.6                 |
| 8          | 11.0                   | 0.7                 |
| 9          | 17.0                   | 0.4                 |
| 10         | 32.0                   | T                   |
| 11         | 63.0                   | N.D.                |

N.D. Not Detected

T Traces (< 0.1 ppb)

Minimum detectable limit 0.1 ppb

Average pH of water 5.5

\* Sampled on May 16, 1974, spray date: June 6, 1974.

Table II

Analysis of Stream Water Samples for Matacil from Larose Forest

| Sample No. | Days After Application | Matacil conc. (ppb) |
|------------|------------------------|---------------------|
| 12         | Prespray               | N.D.                |
| 13         | 0.6                    | 1.9                 |
| 14         | 1.0                    | 1.9                 |
| 15         | 2.0                    | 2.6                 |
| 16         | 3.0                    | 1.6                 |
| 17         | 4.0                    | 1.1                 |
| 18         | 7.0                    | 0.9                 |
| 19         | 11.0                   | 1.0                 |
| 20         | 17.0                   | 0.4                 |
| 21         | 32.0                   | T                   |
| 22         | 63.0                   | N.D.                |

Average pH of water 7.1

See the footnotes in Table I

Table III

Analysis of White Spruce Foliage Samples for Matacil from Larose Forest

| Sample No. | Days After Application | Matacil Conc.* (ppm) |
|------------|------------------------|----------------------|
| 23         | Prespray               | N.D.                 |
| 24         | 0.6                    | 0.7                  |
| 25         | 1.0                    | 1.1                  |
| 26         | 2.0                    | 1.3                  |
| 27         | 4.0                    | 2.2                  |
| 28         | 7.0                    | 1.3                  |
| 29         | 11.0                   | 1.0                  |
| 30         | 17.0                   | 0.8                  |
| 31         | 32.0                   | 0.6                  |
| 32         | 64.0                   | N.D.                 |
| 33         | 126.0                  | N.D.                 |

See the footnotes in Table I

\* An artifact appeared in all the foliage samples analysed with the same RT as Matacil. The peak height of the artifact was found to vary with the sampling period and a mean correction factor has been introduced to account for it in the final concentration of Matacil recorded in column 3. Due to this artifact, the minimum detection limit for Matacil in foliage was 0.5 ppm based on 10g aliquots of the foliage. Attempts made to remove the artifact were not successful to date. The average moisture content of the foliage was 48%.

Table IV

Analysis of Soil Samples for Matacil from Larose Forest

| Sample No. | Days After Application | Matacil Conc.* (ppm) |
|------------|------------------------|----------------------|
| 34         | Prespray               | N.D.                 |
| 35         | 0.6                    | N.D.                 |
| 36         | 1.0                    | N.D.                 |
| 37         | 2.0                    | N.D.                 |
| 38         | 4.0                    | N.D.                 |
| 39         | 7.0                    | N.D.                 |
| 40         | 11.0                   | N.D.                 |
| 41         | 17.0                   | N.D.                 |
| 42         | 32.0                   | N.D.                 |
| 43         | 64.0                   | N.D.                 |
| 44         | 126.0                  | N.D.                 |

See the footnotes in Table I.

\* An artifact of smaller magnitude appeared in soil samples but was not considered very significant.

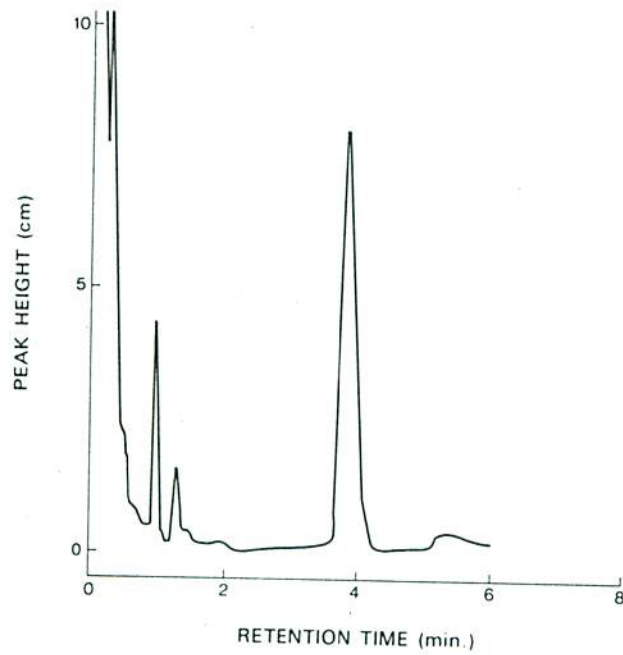


Fig. 3 Gas chromatogram of 5.0 mg of Maticil  
Peak height 8.2 cm, R. T. 4.0 min.

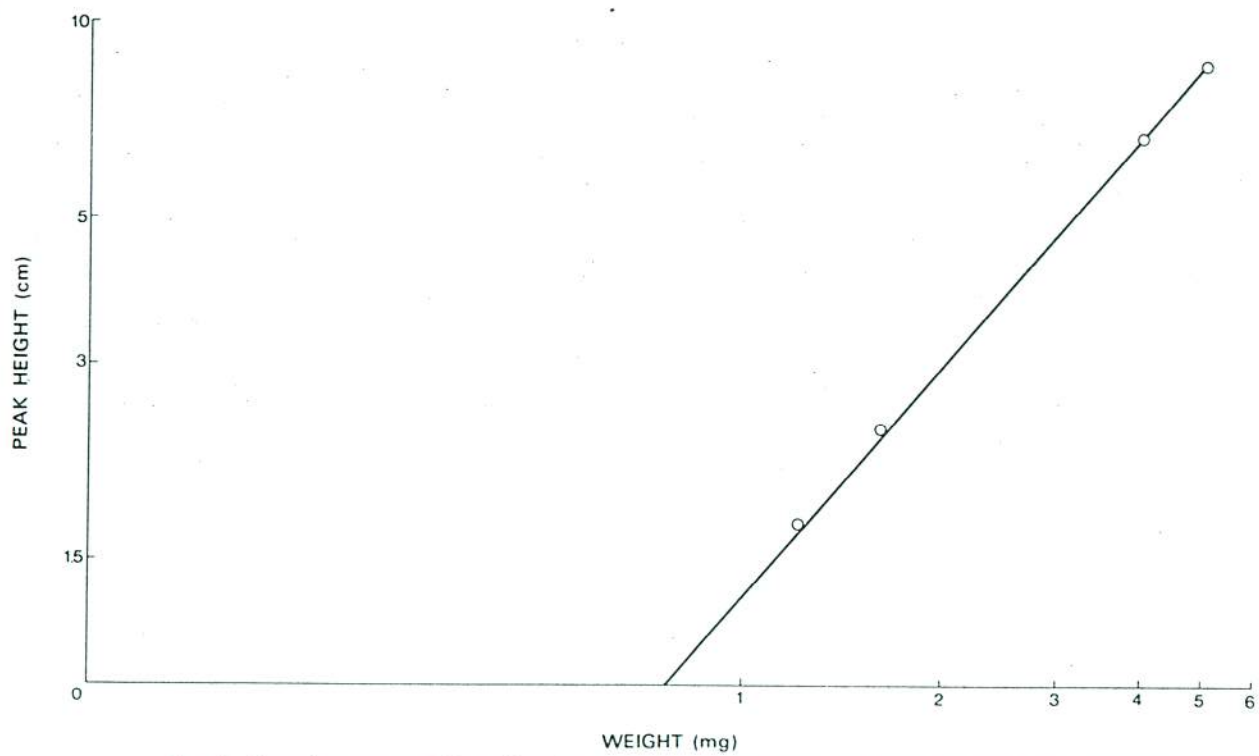


Fig. 4 Gas chromatographic calibration curve for Maticil obtained with the Ni-63 E.C. detector

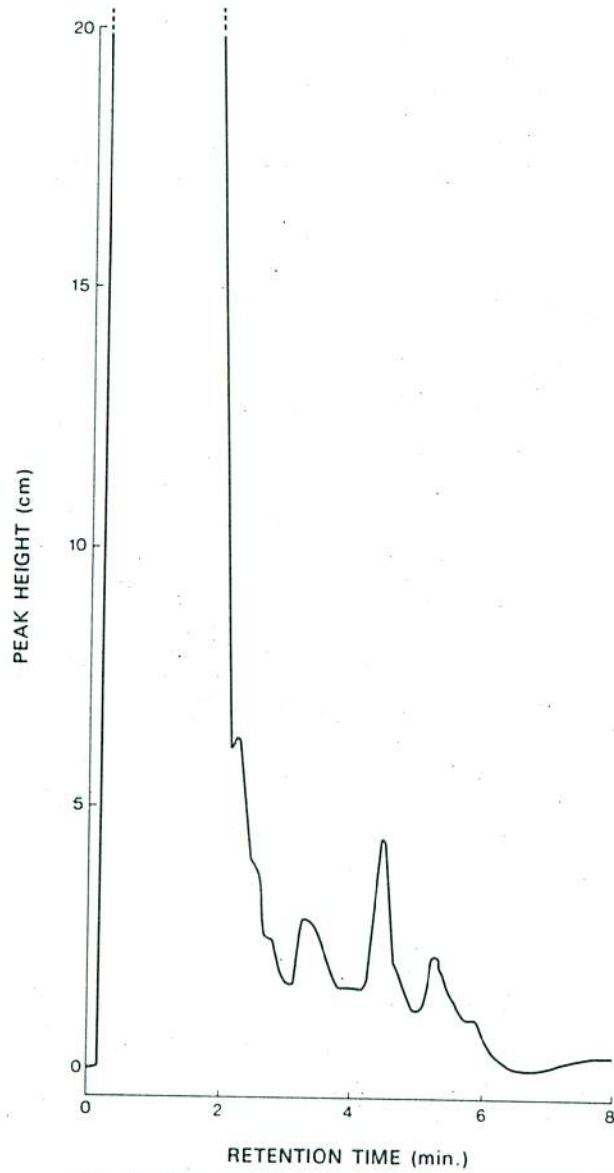


Fig. 5 Chromatogram of a derivatized extract of pond water fortified with Matacil at the level of 1.0 ppm

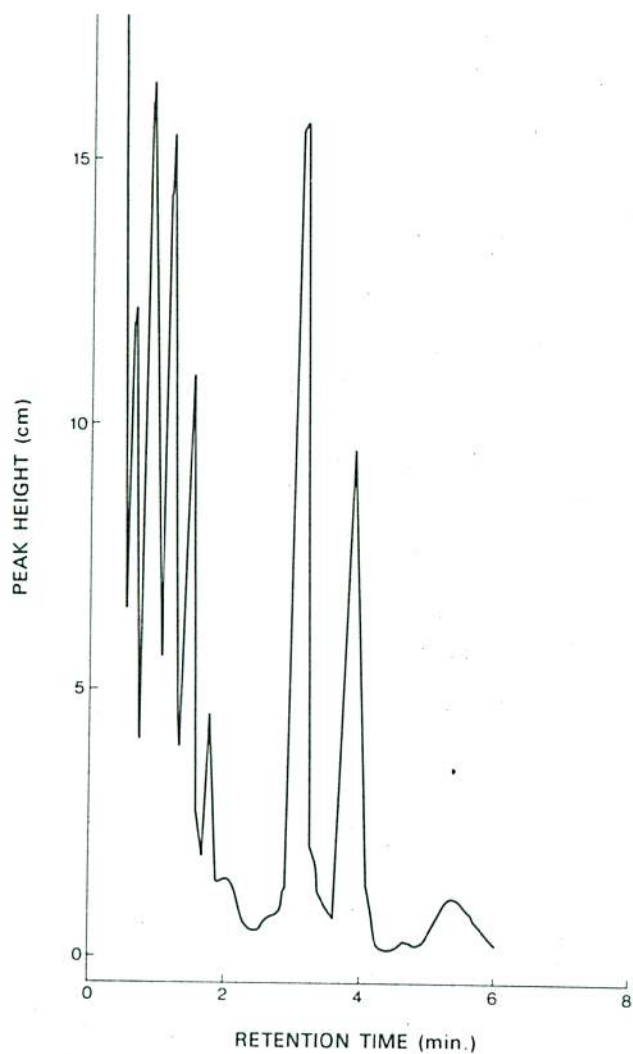


Fig. 6 Chromatogram of a derivatized extract of spruce foliage after fortification with Matacil at the level of 1.0 ppm



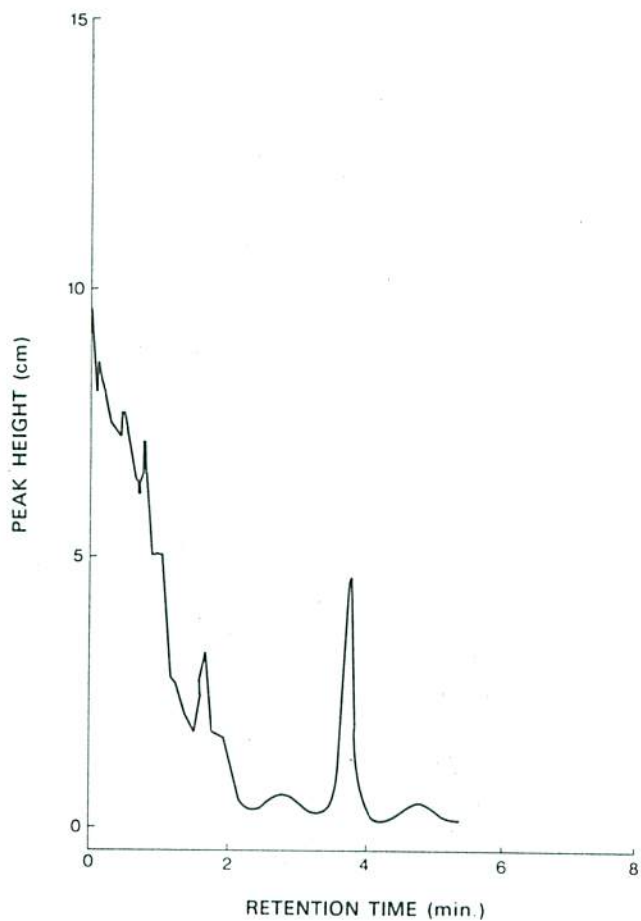


Fig. 7 Chromatogram of a derivatized extract of soil after fortification with Matacil at the level of 1.0 ppm

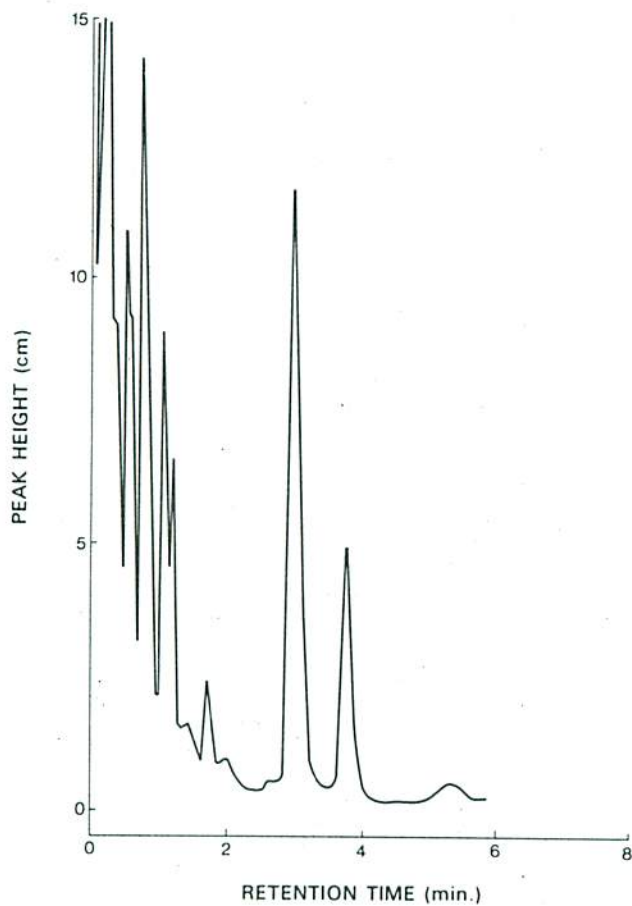


Fig. 8 Gas chromatogram of a derivatized extract of prespray spruce foliage

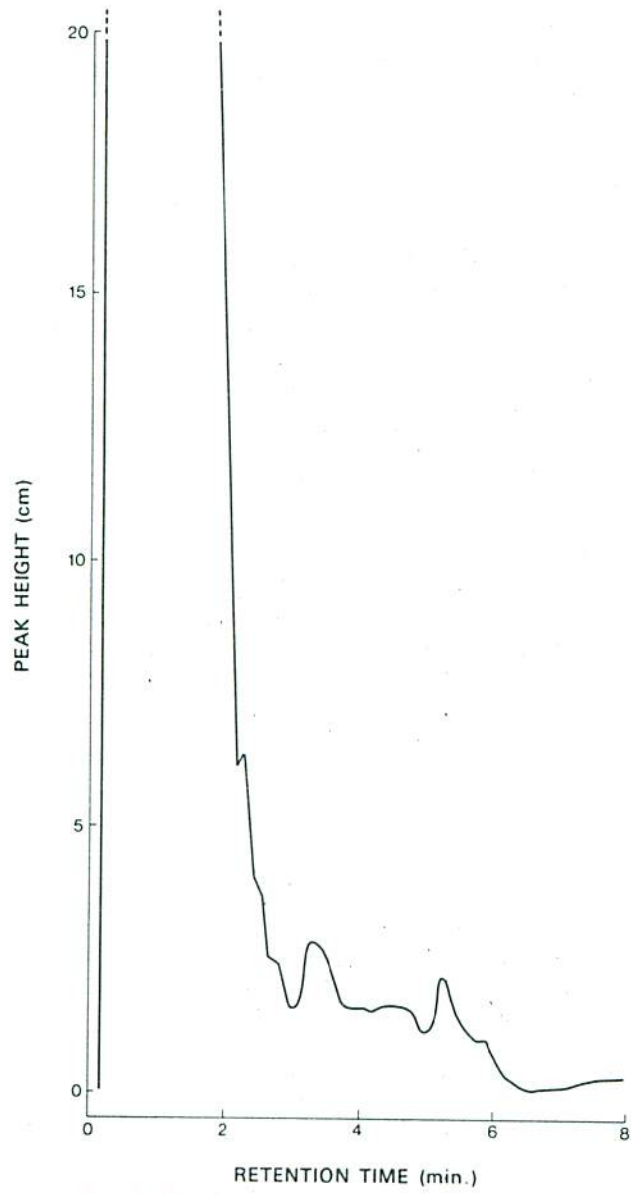


Fig. 9 Gas chromatogram of a derivatized extract of prespray pond water

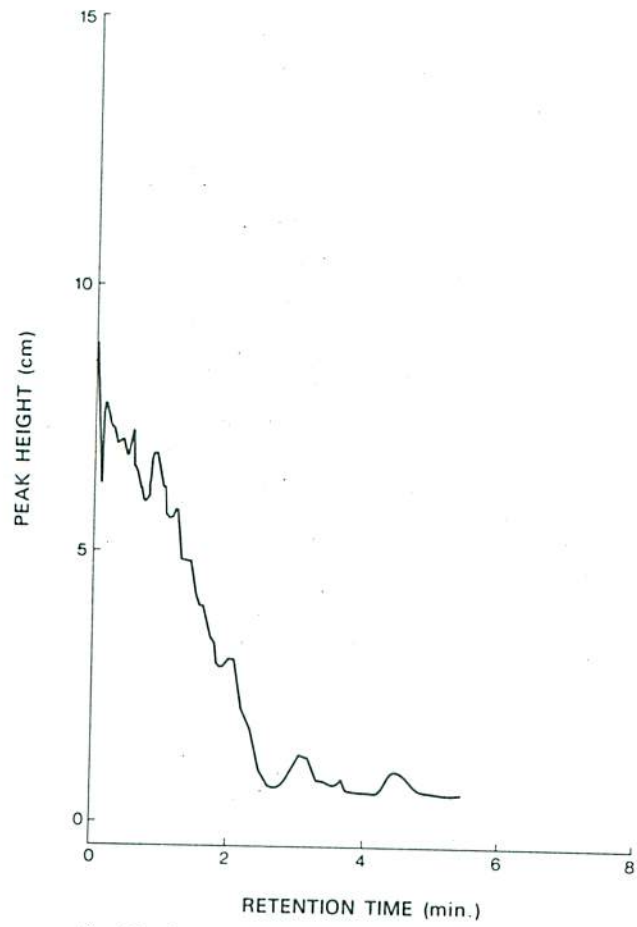


Fig. 10 Gas chromatogram of a derivatized extract of prespray Larose forest soil

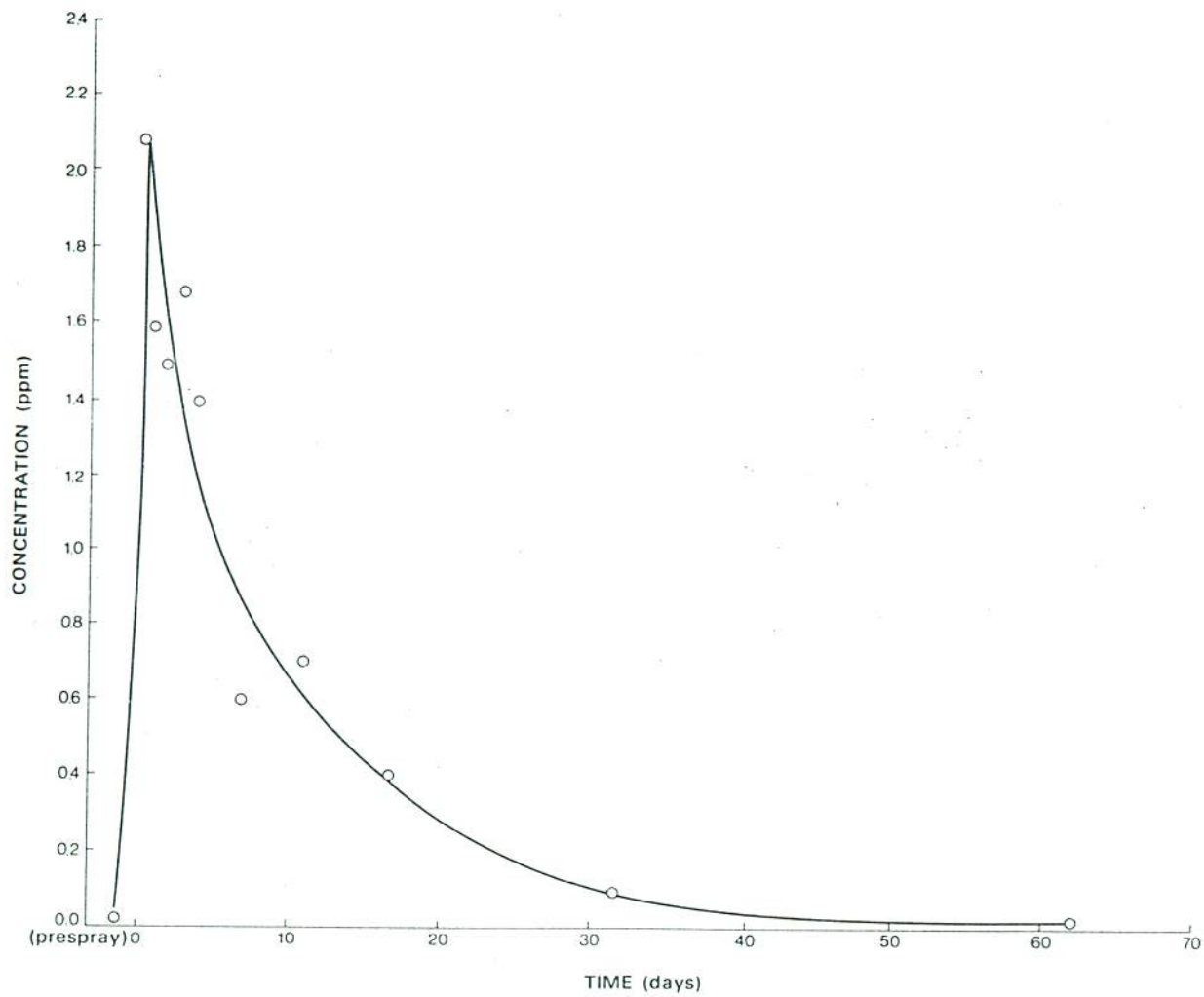


Fig. 11 Matacil degradation curve obtained with pond water samples from Larose forest

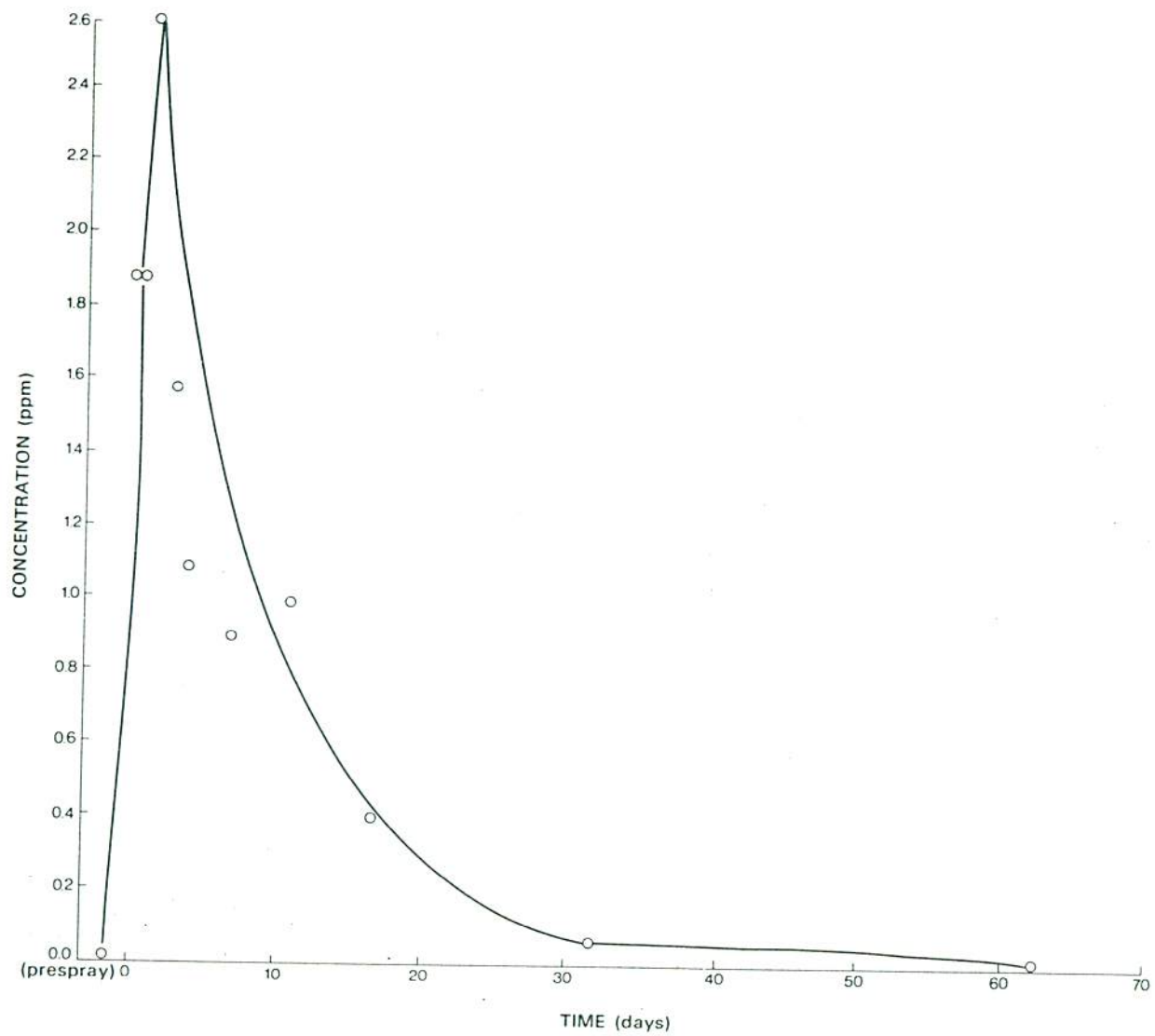


Fig. 12 Degradation of Matacil from stream water in Larose forest

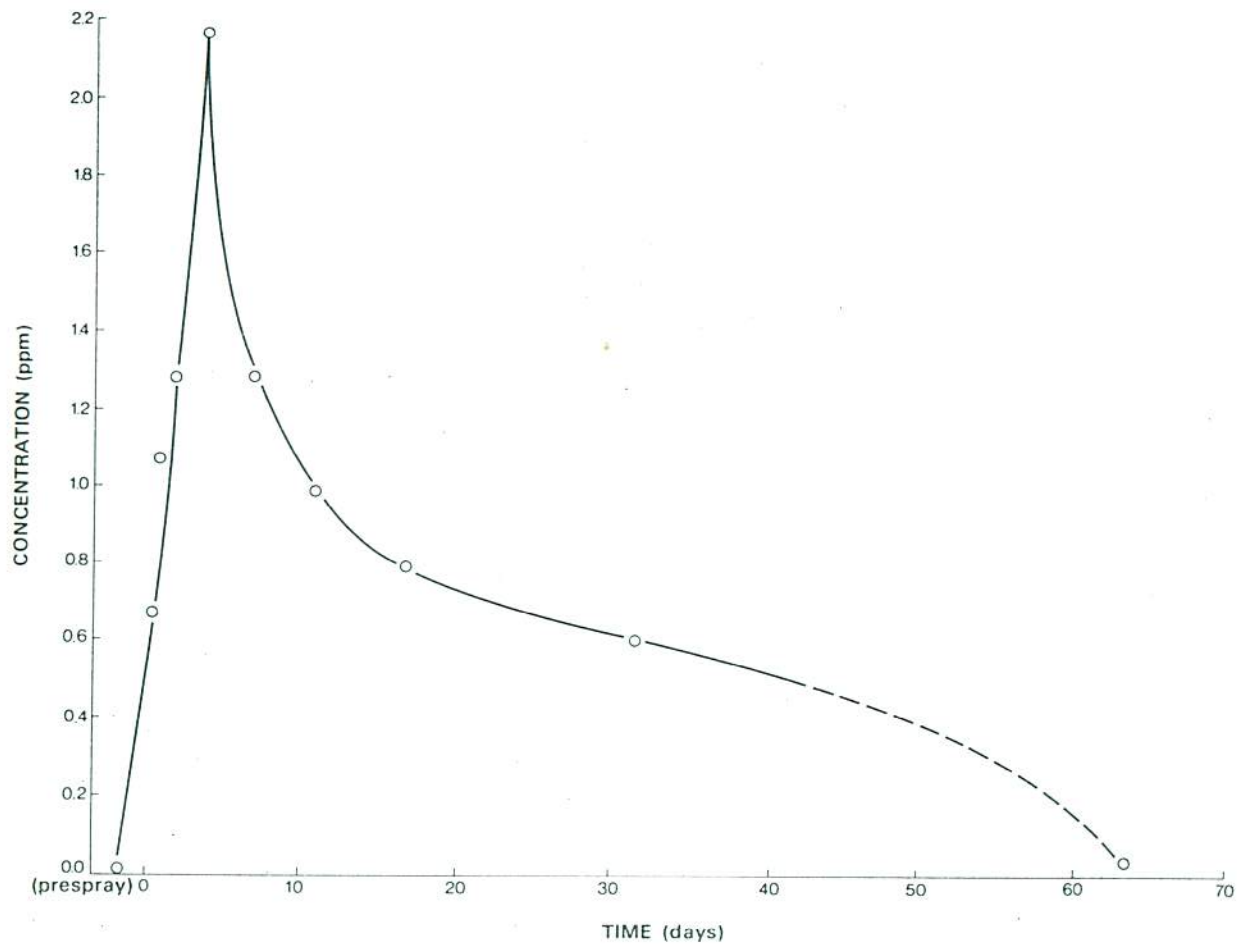


Fig. 13 Dissipation of Matacil in spruce foliage after aerial application

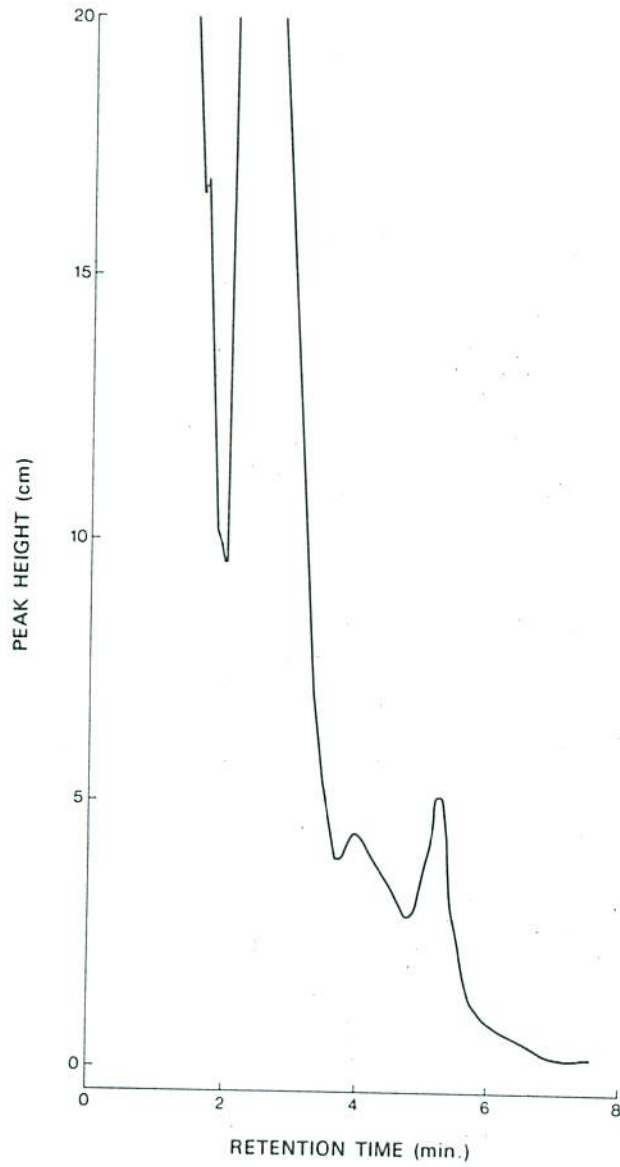


Fig. 14 Gas chromatogram of an extract of 4.0 mg of untreated fish after derivatization



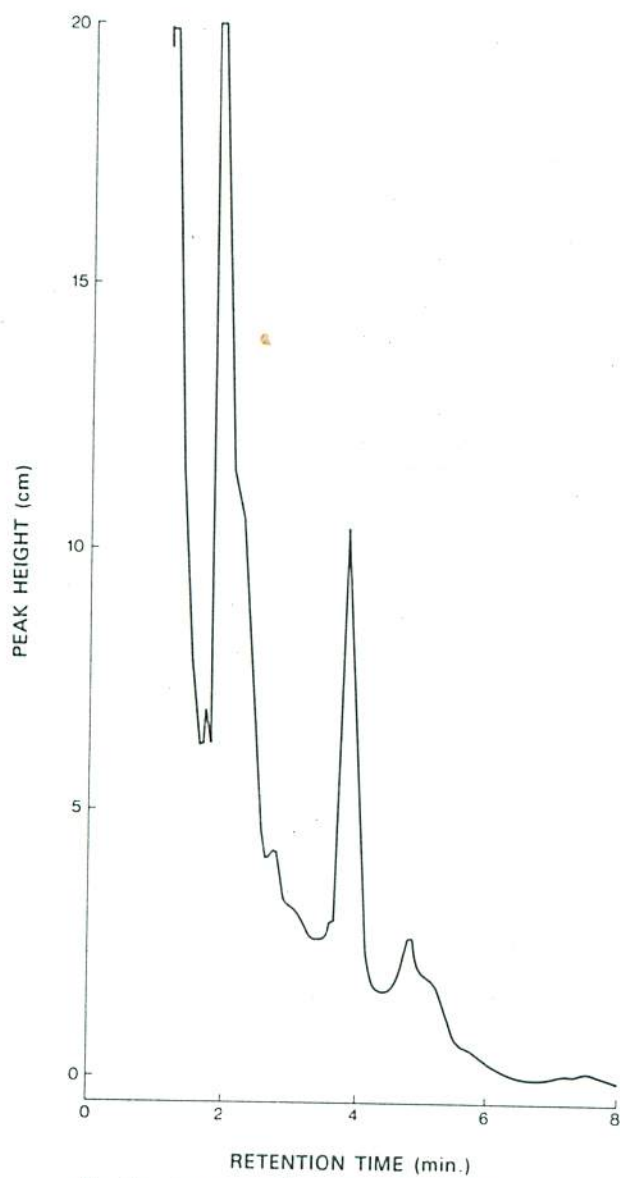


Fig. 15 Gas chromatogram of an extract of fish fortified with Matacil before extraction at the level of 0.5 ppm

## RESULTS AND DISCUSSION

### Sensitivity of the Analytical Method

The method developed by Duffy (pers. comm.) was evaluated by analysing multiple samples of distilled water, spruce foliage and forest soil fortified with known amounts (1 to 2 ug/g) of Matacil. Average recoveries of the insecticide ranged from  $101 \pm 3\%$  in water,  $97 \pm 5\%$  in soil to  $89 \pm 8\%$  in foliage. At low fortification levels (0.5 ug/g and below), the method was found to be reasonably sensitive and satisfactory for analysing water and soil samples but limited in the case of foliage due to poor cleanup.

Similar interferences were also observed while analysing the fortified natural waters for Matacil without going through the cleanup steps outlined in Fig. 2. The GLC response to derivatized Matacil standard is shown in Fig. 3. A retention time (RT) of 4 min. was observed for the derivative. Similarly the chromatographic profiles for the fortified extracts of the insecticide from pond water, foliage and soil samples are given in Figs. 5, 6 and 7, respectively. The background interferences in all these chromatograms, as could be seen from Figs 5 to 7, are appreciably high showing that the extraction, separation and cleanup operations carried out were adequate but not excellent.

The GLC response for the prespray foliage sample is given in Fig. 8 wherein a symmetrical peak with the same RT as Matacil is observed as an artifact. Although the area had never been sprayed before with the insecticide, the peak height of the artifact was found to vary with time i.e. with the age of the foliage. With newly flushed foliage in

early summer, the concentration of the component causing the artifact was found to be high. It diminished gradually with time as the foliage matured and persisted in small amounts to the last day of sampling when the foliage became old. All attempts to eliminate the interference by altering the extracting solvent, experimental conditions, derivatization techniques etc. were unsuccessful. No such artifacts were found either in the prespray water or soil samples (Figs. 9 and 10). Due to the presence of this artifact in foliage, the minimum detectable limit for Matacil in the substrate, is 0.5 ppm on a 10 g weight basis. Attempts made to improve the sensitivity were not successful. Probably more emphasis should be placed in future on alternative extraction, cleanup, derivatization and quantitation methods if we require a much lower detection limit than 0.5 ppm in foliage.

The recovery studies of Matacil made in water and soil samples showed that the analytical method described here is accurate, reproducible and reasonably sensitive and is suitable for estimating the insecticide residues in these two forest components. The lower limits of detection for Matacil in water and soil were 0.1 ppb and 0.1 ppm respectively showing that the method is satisfactory and sensitive enough to analyse for the low levels of the insecticide usually found in these samples collected from the forest environment after spraying.

Current explorative studies made at this laboratory using a Hall nitrogen-detector in place of an electron capture detector to improve the lower detection limit of Matacil in forest components, did not give much improvement except by shortening the method considerably by eliminating the need of a derivative. Additional experimentation is

required to evaluate the usefulness of these two detectors in the quantitation of Matacil.

In conclusion, the analytical methodology developed, in spite of its shortcomings, *e.g.* it is time-consuming, expensive, and lacks high selectivity, sensitivity and precision is satisfactory and could be used in practice for routine analysis of large numbers of forest environmental samples usually received during spray operations provided good financial and technical support are readily available.

#### Persistence of Matacil in Natural Waters

The results of the chemical assay of Matacil residues found in pond and stream water samples collected from Larose Forest are given in Tables I and II respectively in units of ppb (parts per billion). The concentrations of the insecticide on 0.6 day were 2.1 and 1.9 ppb respectively and these values are found to be far below the acceptable residue level of 0.1 mg/l (0.1 ppm) of carbamates in Canadian drinking water standards (1972). The residue levels decreased curvilinearly to traces (< 0.1 ppb) after 32 days. The residue concentration in the pond diminished gradually (Fig. 11) following nearly a first-order kinetic behaviour whereas the dissipation process of the insecticide in stream water was comparatively less rapid (71% decrease in 4 days in pond water *versus* 42% decrease in stream) and uneven probably due to foliar washings by rain and runoff waters from land which carried the insecticide with them showing usually higher residue levels on the second and eleventh day (Table II, Fig. 12) samples. An examination of the results in Tables I

and II show that the overall pattern of accumulation and disappearance of Matacil residues in the two sampling sites were rather similar with minor variations as discussed above, and the insecticide concentration diminished to traces ( $< 0.1$  ppb) within a period of 32 days.

The fate and effects of Matacil on Canadian forest aquatic systems are still obscure. It is likely that the material was lost from the aquatic environment through various processes such as volatilization, codistillation, degradation by chemical, microbiological and photochemical means, erosion and weathering resulting from heavy rains. Among these various physical and metabolic factors affecting the fate of Matacil, probably hydroxylation, hydrolysis and biodegradation by various microorganisms are the major sources for the loss of the chemical from forest aquatic environments.

Since the aquatic environment is a dynamic system at near equilibrium conditions, the dissipation of the insecticide did not strictly obey any rate equation and therefore the kinetic half-life was not evaluated. An estimation of the half-lives was obtained, ignoring the peakings, from the exponential decay curves given in Figs. 11 and 12. The half-lives (days) obtained were 4.4 for the pond and 8.7 for the stream water samples. The high value for stream water was caused, as mentioned earlier, by the high insecticide load carried into the stream from surrounding land by runoff water and washings from foliage and duff.

### Persistence of Matacil in Spruce Foliage

The persistence of Matacil in spruce foliage collected from the spray area was determined up to 126 days using the analytical method described and the data are recorded in Table III in units of ppm "as sampled" including the variables such as moisture and volatile terpene components. Such data are useful for ecological interpretations under actual field conditions.

Since an artifact appeared in the spruce blank as well as in the 126 day sample with the same RT as the HFBA derivative, a mean correction factor was introduced to account for it in all the final residue data recorded in Table III. This also reduced considerably the detection limit of Matacil (0.50 ppm) in spruce foliage; otherwise a sensitivity of 0.02 ppm could be reached easily as is the case for fenitrothion (Sundaram 1974) determination in conifers. Instead of using the strongly polar acetonitrile as extractant, the use of less polar ethyl acetate could minimize the presence of coextractive impurities including the artifact thereby reducing the background interference in GC analysis. It is also worthwhile to research and develop alternative derivatization techniques to eliminate the presence of coextractive impurities in the final analysis.

Spruce foliage contained 0.7 ppm of Matacil after 0.6 day of spraying and the value gradually increased up to a maximum of 2.2 ppm after 4 days (Table III). After this period, the residue levels decreased exponentially and disappeared completely after 64 days, probably due to various physical and environmental factors as observed earlier for fenitrothion (Sundaram 1974).

A plot of the Matacil concentration in ppm *vs* time (days) representing the dissipation pattern of the chemical is shown in Fig. 13. A maximum residue level of 2.2 ppm is obtained on the fourth day after spray application which then decreased exponentially showing an approximate half-life of 5.6 days for Matacil in spruce foliage.

#### Matacil Residues in Forest Soil

The forest floor is usually considered a major receptor of aerially applied spray materials. In the present investigation it is found that from the operational spraying by aircraft of 70 g AI/ha (1 oz AI/acre), surface forest soil up to an average of 10 cm depth did not contain any detectable level of Matacil (0.1 ppm) on and after 0.6 day of application. The small amount of the toxicant, if it reached the forest floor could have been degraded rapidly by various physicochemical and biological means before the sampling was done.

#### Extension of the Method to Analyse Matacil in Fish Tissues

The increasing utilization of Matacil in Canadian forest spray programs has prompted CCRI to initiate research on studying the long term effect and environmental significance of the insecticide on various non-target species of fauna and aquatic organisms inhabiting the forest and exposed to the toxicant. To this end, it became necessary to extend the analytical method for quantifying Matacil in various biological components of the forest. As a start, fish were chosen as the substrate to represent the biological component and the analytical method discussed earlier was used to quantify the spiked Matacil residues present in them.

Fish samples (rainbow trout - *Salmo gairdnerii*) were collected from a Matacil-free lake in Quebec, cut into pieces, mixed well and 10 g aliquots in triplicate were fortified with 2, 5 and 10 ug of Matacil and extracted using 2 x 50 ml of acetonitrile in a Sorvall Omni-Mixer homogenizer. The insecticide concentration present in the spiked fish tissues was estimated by following the analytical steps outlined in Fig. 2. The average recovery of the insecticide in the nine samples studied was 98% with a coefficient of variation of 4. The minimum detection limit was found to be 0.5 ppm at the above concentration range, using a 10 g aliquot. The chromatographic profiles for the blank and spiked extracts of fish are given in Figs. 14 and 15 respectively to evaluate and to assess the magnitude of the artifact and background interference compared to other substrates analysed earlier. In spite of these difficulties, the analyses of Matacil in fish tissues were comparatively simpler and more precise than in spruce foliage.

Further work is in progress on the detection and quantitation of Matacil in fish and amphibian samples collected from ponds, streams and lakes exposed to the spray deposit and attempts are being made to extend the method to analysing insect materials and avian tissues.



### SUMMARY AND CONCLUSIONS

The direct application of gas chromatography is generally unsatisfactory for the quantitation of Matacil because of the on-column decomposition of the molecule and the weakness of detector response. These difficulties have been averted by converting the molecule to a stable heptafluorobutyric anhydride (HFBA) derivative which gave good response to an electron capture (EC) detector. Using this technique, an analytical methodology has been reported to determine Matacil residues in spruce foliage, forest soil and natural waters.

The method was evaluated and rigorously assessed by adopting it to analyse the forest environmental samples spiked with Matacil. The steps included are solvent extraction, acid/base and aqueous/non-aqueous partitions, cleanup, derivatization and final determination using EC chromatography. Average recoveries of the insecticide were from  $101 \pm 3\%$  in water,  $97 \pm 5\%$  in soil and  $89 \pm 8\%$  in spruce foliage with sensitivities 0.1 ppb, 0.1 ppm and 0.5 ppm respectively. The low sensitivity in foliage was due to an artifact appearing with the same retention time as the Matacil derivative. The method is tedious, imprecise and costly but workable and could be adopted after suitable refinements for routine residue analysis of forest samples.

Distribution and persistence of Matacil residues in spruce foliage, forest soil and natural waters from Larose Forest collected at intervals after an experimental aerial application of 70 g AI/ha (1.0 oz AI/acre) were studied. The 0.6 day insecticide concentration in the pond and stream water samples were 2.1 and 1.9 ppb respectively, and disappeared through physical and biological processes below the limits

of analytical sensitivity (0.1 ppb) within 32 days. The rate of disappearance was slow and uneven in stream samples due to foliar washings by rain and runoff waters from land. The half-lives (days) of both samples were different ranging from 4.4 and 8.7 for the pond and stream waters respectively. The initial (0.6 day) concentration of Matacil in spruce foliage was found to be 0.7 ppm and the value increased to a maximum of 2.2 ppm after 4 days. After this period, the residue levels decreased exponentially with a half-life of 5.6 days and disappeared completely after 64 days probably due to physical and environmental factors. No measurable amounts of Matacil were found in the post-spray soil samples.

The provisional studies made so far at CCRI show that under the Larose Forest conditions, residues of Matacil degraded reasonably fast from spruce foliage, forest soil and natural waters when sprayed by aircraft at the emitted rate of 70.0 g AI/ha. The compound seems to have low persistence and could be considered acceptable for use as an insecticide to control forest pests. More affirmative statements require an indepth and extensive study to be made on the fate of this chemical in various components of the forest environment.

RESUME

La chromatographie en phase gazeuse (C.P.G.) ne peut être appliquée de façon satisfaisante pour la détermination du Matacil, à cause de l'instabilité du composé sur colonne et d'une faible réponse du détecteur. Ces difficultés sont surmontées en faisant un dérivé d'anhydride d'heptafluorobutirique (HFBA), qui a une bonne réponse sur le détecteur à capture d'élection (EC). Suivant cette technique, une méthode analytique a été mise au point pour la détermination du Matacil dans les feuillages d'épinette, dans le sol forestier ainsi que dans l'eau.

Cette méthode qui inclue d'abord l'extraction avec un solvant approprié ainsi que des partitions aqueuse/non aqueuse, formation du dérivé et enfin l'analyse quantitative par C.P.G. a été appliquée dans l'eau, le sol et les feuillages d'épinettes, avec un pourcentage de récupération de  $101 \pm 3\%$ ,  $97 \pm 5\%$  et de  $89 \pm 8\%$  et une limite de détection de 0.1 ppb, 0.1 ppm et de 0.5 ppm respectivement. Cette faible limite de détection dans le feuillage est due à une interférence qui a le même temps de rétention que le dérivé de Matacil. Cette méthode est longue, mais moyennant quelques modifications, peut être adoptée, sur une plus grande échelle, pour l'analyse d'échantillons provenant de la forêt.

Suite à une pulvérisation aérienne de Matacil (1.0 oz IA/acre) sur "Larose Forest", sa distribution ainsi que sa persistance fut étudiée dans le feuillage d'épinette, le sol, ainsi que dans l'eau. Après 0.6 jour, la concentration de l'insecticide se situe dans l'eau d'étang et de ruisseau à 2.1 et 1.9 ppb respectivement, et disparaît en 32 jours en dessous de 0.1 ppb. La vitesse de disparition est lente dans l'eau de

ruisseau, due aux lavages du feuillage et du sol par la pluie. Le temps de demi vie en jour est de 4.4 dans l'eau d'étang et 8.7 dans l'eau de ruisseau. Dans le feuillage la concentration passe de 0.7 ppm après 0.6 jour, pour atteindre un maximum de 2.2 ppm, 4 jours plus tard. Suite à cette période, la disparition est exponentielle avec une demi vie de 5.6 jours, pour ensuite disparaître complètement après 64 jours.

D'après cette étude, le Matacil est dégradé assez vite dans l'environnement forestier quand il est appliqué à 70.0 g IA/ha par pulvérisation aérienne. Ce composé semble avoir une faible persistance et peut être considéré acceptable pour le contrôle de pestes dans la forêt. Néanmoins d'autres études plus approfondies sont nécessaires afin de bien comprendre son comportement dans cet environnement.

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