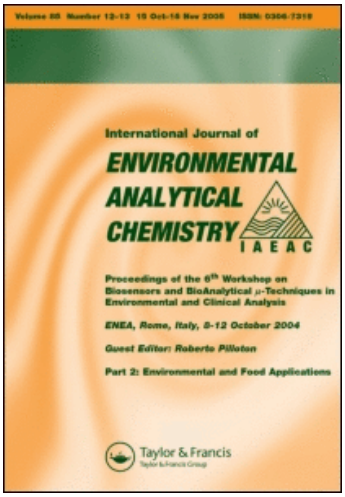

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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M. E. Krzymien[a]
[a] National Aeronautical Establishment, National Research Council of Canada, Ottawa, Ontario, Canada

To cite this Article Krzymien, M. E.(1982) 'Measurement of Atmospheric Fenitrothion and Aminocarb Concentrations Near the Spray Area', International Journal of Environmental Analytical Chemistry, 13: 1, 69 — 84
To link to this Article: DOI: 10.1080/03067318208071584
URL: http://dx.doi.org/10.1080/03067318208071584

Intern. J. Environ. Anal. Chem. 1982, Vol. 13, pp. 69–84
0306-7319/82/1301-0069 $06.50/0

Printed in Great Britain

Measurement of Atmospheric Fenitrothion and Aminocarb Concentrations Near the Spray Area†

M. E. KRZYMIEN
National Aeronautical Establishment, National Research Council of Canada, Ottawa, Ontario, Canada

Fenitrothion and Aminocarb are the insecticides commonly used in spruce budworm control programmes. Significant amounts of the pesticides remain airborne long after completion of aerial spraying and their vapours, as well as aerosol, drift over long distances. Their concentration, dosage, range and residence time were determined using a method described below, which is sufficiently rapid to allow the processing of over 100 samples a day.

Samples of airborne pesticides were collected in glass adsorber tubes 6 mm O.D. × 75 mm, each packed with a 1 cm plug of 60/80 mesh Tenax GC (~25 mg). The capacity of the Tenax adsorber, defined as the maximum air volume which could be sampled before pesticide elution occurred, was determined to be over 700 l for both fenitrothion and aminocarb.

The ambient air was drawn through the adsorber tubes by means of a battery-powered pump incorporated in a sampling device. Three types of these devices were used. The first sampler, designed for unattended operation, had a built-in electronic clock, which allowed us to pre-programme the sampling period and a start time. It sampled air at a rate of 2 l/min, usually for 4 hours, and was used to determine time-integrated concentrations (dosages). The second type of sampler also had the capability for unattended operation. An electronic timing device and a set of valves allowed it to draw air through eight consecutive adsorber tubes for predetermined short periods and was used to measure time-wise variations of concentration. The sampling rate of this device was 1 l/min. When very low concentrations of pesticide were anticipated and time-wise variations of concentration were to be measured, a third type of sampler was used. It sampled air at a rate of up to 8 l/min for short periods of time. An unlimited number of adsorber tubes could be attached consecutively to the sampler by an operator.

The trapped vapours and aerosol were thermally released from the adsorber and transferred by a stream of carrier gas directly into a gas chromatograph (G.C.). The G.C. was equipped with a special adaptor for ease of adsorber coupling, and a 4-port switching valve. A thermoionic specific detector allowed concentrations in the picogram per liter range to be determined with a precision of better than ±10%.

†Presented at the 12th Annual Symposium on the Analytical Chemistry of Pollutants, Amsterdam, 1982.

Eight-stage Anderson 2000 Inc. cascade impactors, modified according to Crabbe *et al.*, were used to measure drop-size distributions of pesticide formulation aerosol in a range of 1–30 μm. To eliminate experimental error caused by evaporation of pesticide from impactor plates, tris (2-ethyl hexyl) phosphate (TEHP) was added to the formulation and drop-size distribution was obtained from the TEHP deposits. The minimum amount of TEHP which could be quantitatively determined with $\pm 5\%$ precision was 20 pg per plate.

KEY WORDS: Fenitrothion, aminocarb, airborne pesticides, GC, aerosol.

INTRODUCTION

Fenitrothion (0,0-dimethyl 0-(3-methyl-4-nitrophenyl) phosphorothioate) has been aerially sprayed to control spruce budworm (Choristoneura fumiferana Clem.) in New Brunswick for almost 15 years. Aminocarb (4-dimethylamino-3-methylphenyl methylcarbamate) was introduced in 1971 and in 1979 it was sprayed over 98% of protected areas. Its share dropped to 15.5% in 1980 and it was not used in 1981. Over 1.5 million hectares (15000 km^2) of infested forest in New Brunswick are sprayed annually with the insecticides. For example, 104 tons of aminocarb and 304 tons of fenitrothion were sprayed in 1978. Understandably, such a large scale operation causes significant concern over its environmental and health impact. The concern is associated mainly with atmospheric drift and subsequent off-target fallout of the spray.

The drift of agricultural chemicals has been recognized and well documented.[1,2,3] Yule *et al.*[4] measured atmospheric contamination following forest spraying with fenitrothion. The samples, collected on Florosil filter-column linked in series with a bubbler containing dimethylformamide, were analyzed by a modified total phosphorus method.[5] Some specific analyses for fenitrothion were performed on DMF samples using gas chromatography.

The effect of atmospheric stability on long range drift of fenitrothion was studied by Crabbe *et al.* in 1979[6] and the same group measured atmospheric fenitrothion concentrations near the spray area in 1980.[7] The analytical procedure for determination of fenitrothion in ambient air was reported in 1979.[8] It was later modified and applied to collection and analysis of a great number of air samples in a field laboratory.

Szeto and Sundaram reported a method for direct chromatographic determination of aminocarb in foliage, forest soil and fish tissue.[9] Determination of aminocarb in air, however, has not been reported yet.

This paper describes methods for analysis of airborne aminocarb and fenitrothion which allow for determination of the total concentration of airborne pesticides as well as the concentrations of aerosol and vapour separately. Also a brief description of a sampling grid and a few results of air monitoring are presented.

EXPERIMENTAL PROCEDURES

Vapour and aerosol collection

Airborne fenitrothion and aminocarb were collected in glass adsorber tubes 76 mm × 6.3 mm O.D. packed with a 10 mm plug of Tenax GC 60/80 mesh, secured in place by two screens made of 150 mesh nickel gauze. Ambient air was drawn through the tube by a constant-flow air pump at a rate of up to 1 l/min. Designed for unattended operation, the battery-operated pump could be preset to turn on up to 24 hrs ahead of time and to turn off after a selected time period by an incorporated electronic clock. It was used to determine dosage (time integrated concentration) of a pesticide when temporal variations of concentration were not of interest. The latter were determined using a sequential sampler, which had eight ports to accept eight adsorber tubes, a pump and eight on/off solenoid valves activated by a clock. The pump drew air sequentially through consecutive adsorbers for a preset period of time (1–99 minutes) at a constant flow rate of 1 l/min. It was also battery powered (Fig. 1).

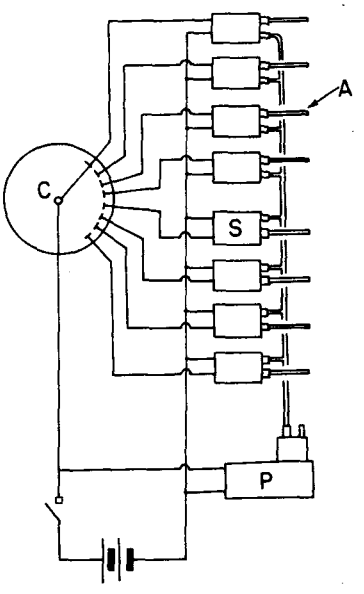

FIGURE 1 Schematic view of sequential sampler. C—Clock, S—Solenoid Valve, A—Adsorber Tube, P—Pump.

The adsorber tubes were analyzed for pesticides using thermal desorption and gas chromatography.

Aerosol collection

Eight-stage Anderson 2000, Inc. cascade impactors, modified according to Crabbe *et al.*[7] were used to measure the drop size distribution of the pesticide spray. The impactors were operated at a flow rate of 7 l/min, which is one quarter the manufacturer's design value, on order to shift the drop size spectrum of the collected aerosol upward by a factor of two. At this reduced flow the drop size range was 30 μg (stage 0) to 1 μm (stage 7) and covered the greater portion of a drop size spectrum generated by an aircraft spray vortex, still including droplets which are usually inhaled by humans ($d < 5\,\mu$m). The mass distribution was obtained from deposits of tris (2-ethylhexyl) phosphate (TEHP) which was added to the spray mixture in the amount of about 10 g/l.

After a sample was collected the impactor plates were rinsed with about 3 ml of acetone. The acetone solution was concentrated to 100 μl, and 5 μl aliquots were injected directly into the gas chromatograph without preconcentration on the adsorber (10).

Gas chromatography

A Tracor Model 160 gas chromatograph, equipped with a Perkin–Elmer Nitrogen–Phosphorus detector and Hewlett–Packard 3390A integrator, was used throughout the project. It was modified to accept the adsorber tubes and to provide a means for thermal release and transfer of collected material to the GC column. A schematic view of the gas chromatograph is presented in Fig. 2. Operating conditions were as follows:

Fenitrothion and TEHP:

Column: 2 m × 3 mm O.D. nickel tube packed with Ultra-Bond 20 M 80/100 mesh.

Temperature:	Oven	200°
	Adsober Heater	320°
	Detector	230°

Carrier gas: nitrogen at a flow rate of 20 ml/min.

Detector: N-P selective, H_2—3 ml/min, air—100 ml/min, glass bead heater setting—640.

Aminocarb:

Column: 1 m × 3 mm O.D. nickel tube packed with Ultra-Bond 20 M 80/100 mesh.

Temperature:	Oven	160°
	Adsorber Heater	260°
	Detector	230°

Carrier gas: nitrogen at a flow rate of 30 ml/min.

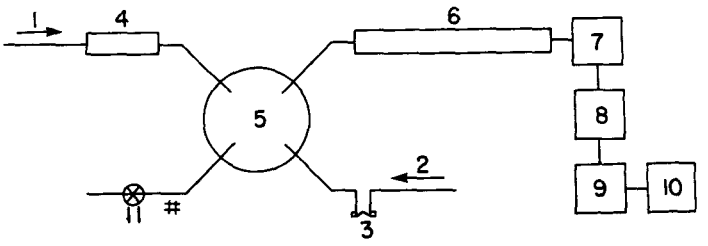

FIGURE 2 Schematic view of the gas chromatograph. 1,2—Carrier Gas, 3—Septum, 4—Adsorber, 5—4-port Switching Valve, 6—Column, 7—Nitrogen-Phosphorous Detector, 8—Electrometer, 9,10—Integrator and Printer-Plotter, 11—Restriction.

Detector: N-P selective, $H_2 - 3$ ml/min, air—100 ml/min, glass bead heater setting – 630.

Sampling grid

The sampling grid for the fenitrothion experiment was located entirely in spruce-fir forest. The U-shaped grid was oriented for westerly winds (prevailing winds in the area), with the spray line completing the square (Fig. 3). The downwind sampling lines extended 700 m and the cross-wind sampling line was 750 m long. Samplers were positioned every 50 m along the lines, 1.5 m above ground level.

For the aminocarb experiment the sampling grid comprised a crosswind spray line with crosswind sampling arcs at 400, 1200 and 3600 m downwind. On the first two arcs, sampling stations were located ± 300 m from the grid centreline, while at 3600 m they were located at ± 750 m from the centreline (Fig. 4). The samplers were positioned on TV masts 15 m above ground level.

The grids described here are presented as examples only. In studies of the effect of atmospheric stability and swath width on pesticide drift and on target deposition a number of different grids were used.[6,7,11]

Spray formulations

The spray formulations were those used in operational forest treatment except for the addition of tris(2-ethyhexyl)phosphate (TEHP). It was added as a tracer to determine aerosol concentration and drop size distribution from cascade impactor deposits. Unlike fenitrothion and aminocarb, TEHP, owing to its extremely low vapour pressure and chemical stability, can be sampled with a cascade impactor for prolonged periods of time (1–2 hrs) without appreciable losses.[10]

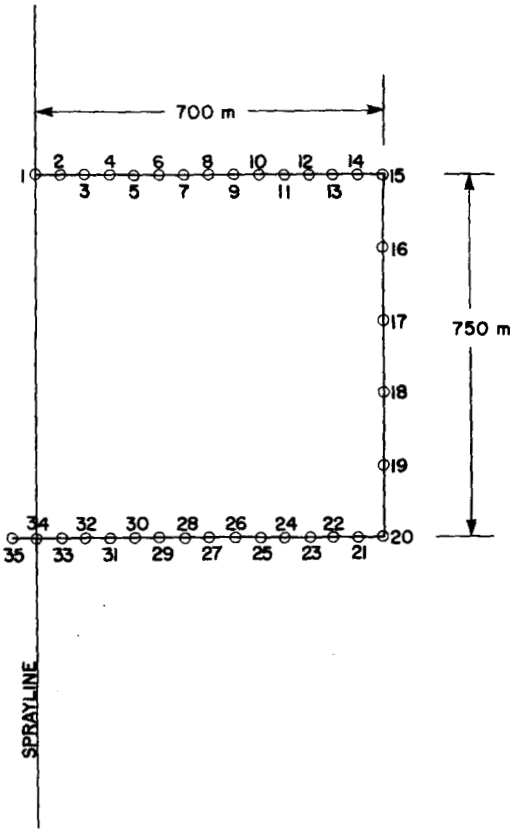

FIGURE 3 Sampling grid for fenitrothion experiment.

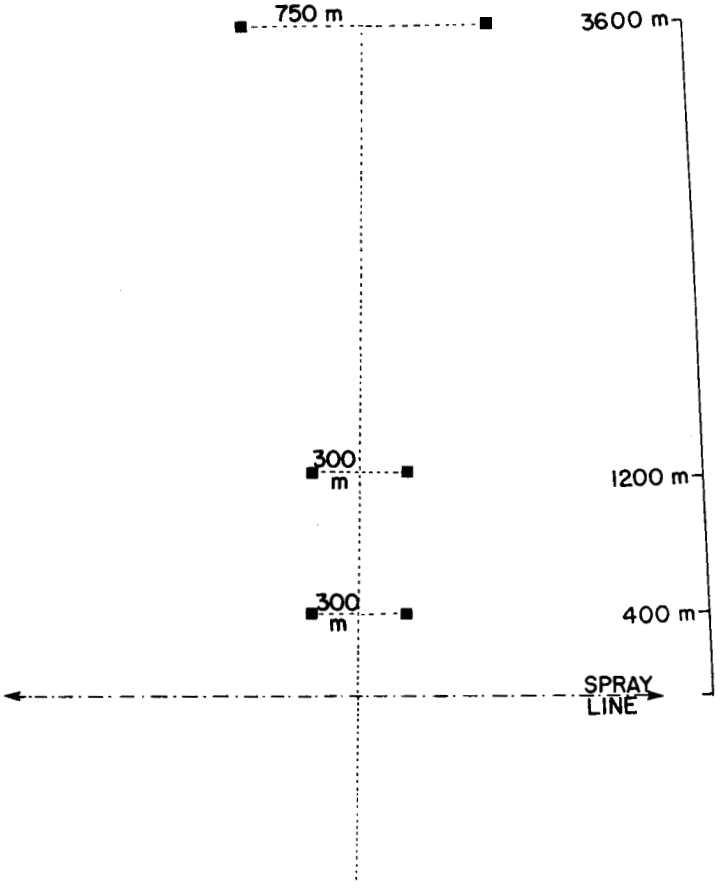

FIGURE 4 Sampling grid for aminocarb experiment.

The aqueous fenitrothion formulation comprised 11.1% fenitrothion, 2.2% TEHP, 1.7% Atlox (emulsifier) and 1.7% Dowanol (solvent), by volume.

The aminocarb formulation was a 585 Diluent oil solution containing 4.7% aminocarb and 12% nonyl phenol.

RESULTS AND DISCUSSIONS

Analytical procedure

Tenax GC was chosen as an adsorbing material after a careful examination of other materials, such as OV-101 coated platinum mesh and OV-1 on Chromosorb W, which were previously used for similar applications.[8,10] It efficiently trapped fenitrothion and TEHP and permitted a reasonable release temperature.

Efficiency of the adsorber (breakthrough volume) was determined by passing fenitrothion and TEHP vapours through two adsorbers connected in series. A stream of air-diluted vapours was generated by a continuous-flow vapour source.[12] The concentration of fenitrothion and TEHP in the stream was approximately 3 ng/l and 30 pg/l, respectively. This mixture was sampled at a rate of 1 l/min for increasing periods of time until fenitrothion was detected on a second (backup) adsorber. This happend after about 13 hrs of sampling, which corresponds to about 780 l sample volume. Since the field experiments sampling times never exceeded 4 hrs and in most cases was limited to 2 hrs, the efficiency of the Tenax GC adsorber was more than adequate for trapping fenitrothion and TEHP.

A similar test was conducted for aminocarb vapour, which was generated at a concentration of about 0.3 ng/l. The Tenax GC adsorber is even more efficient for trapping aminocarb than it is for trapping fenitrothion. After 24 hrs of sampling at a rate of 1 l/min (1440 l sample) no aminocarb or its degradation product was found on a backup adsorber.

In the remote, sparsely populated area, where the experiments were performed, the air was clean and not many interfering contaminants were expected. Nonetheless, the adsorbers were tested for their ability to trap possible interfering compounds. A number of air samples were collected a few days before the forest was sprayed with insecticides. Their analysis produced negative results—no interfering peaks were found.

The compounds added to the formulations as solvents or emulsifiers do not interfere for they do not contain nitrogen or phosphorus, or at present at much lower concentrations than active ingredients.

Finally, a number of tests were conducted to determine possible loss of collected fenitrothion or aminocarb during the period of time between

collection of the sample and its subsequent analysis. No significant losses were observed when samples of fenitrothion and aminocarb were stored over the weekend in capped adsorbers in polyethylene bottles.

Fenitrothion recovery, defined as the ratio of a response factor (amount/peak area) calculated for adsorber-deposited fenitrothion to that of fenitrothion injected via the septum (without trapping) was about 75% and remained constant over the range of 0.1 ng to over 100 ng. Recovery of TEHP was close to 100%.

Recovery of aminocarb, however, was very poor. About 90% of aminocarb deposited on a Tenax GC adsorber was lost (Figs. 5a and 5b).

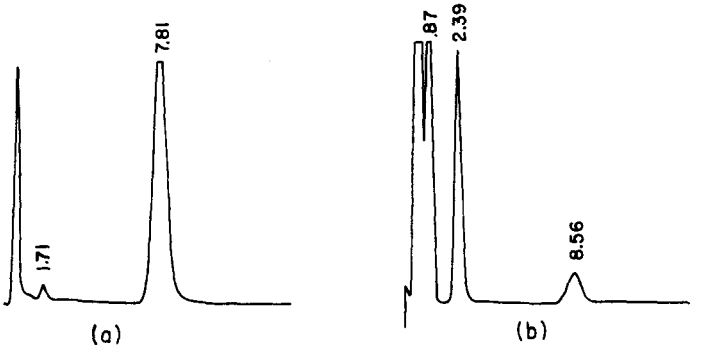

FIGURE 5 Aminocarb chromatogram. a—injected via septum, b—deposited on Tenax GC and thermally desorbed.

Wheeler and Strother[13] found that aminocarb breaks down during chromatographic analysis at a temperature above 180°. Percentage breakdown varies with temperature and column packing and can be as high as 50% at 205° on an OV-17 column. Levesque and Mallet[14] investigated chromatographic behaviour of aminocarb and its seven possible degradation products and found, to the contrary, no significant degradation of aminocarb when chromatographed on OV-17 at 185°.

Siilarly, a chromatogram presented in Fig. 5a does not indicate presence of significant amounts of degradation products. The chromatogram of aminocarb thermally desorbed from Tenax GC (Fig. 5b), however, shows that about 90% of deposited aminocarb was lost and it demonstrates the presence of at least three decomposition products with retention times of 2.39, 0.87 min and one peak unresolved from a solvent. The 2.39 min peak is very well shaped and clearly separated; it is probably 4-amino-3-methyl phenol. It is apparent from Fig. 5b that the compound exhibits good response to a nitrogen-specific detector and there is linear relation between the size of the peak and amount of aminocarb deposited on the

Tenax GC adsorber over a wide range of 0.9 ng to 157.5 ng (Fig. 6). The degradation process is reproducible under the conditions of the analysis, as indicated by data presented in Table I. The peak can, therefore, be used for quantification aminocarb.

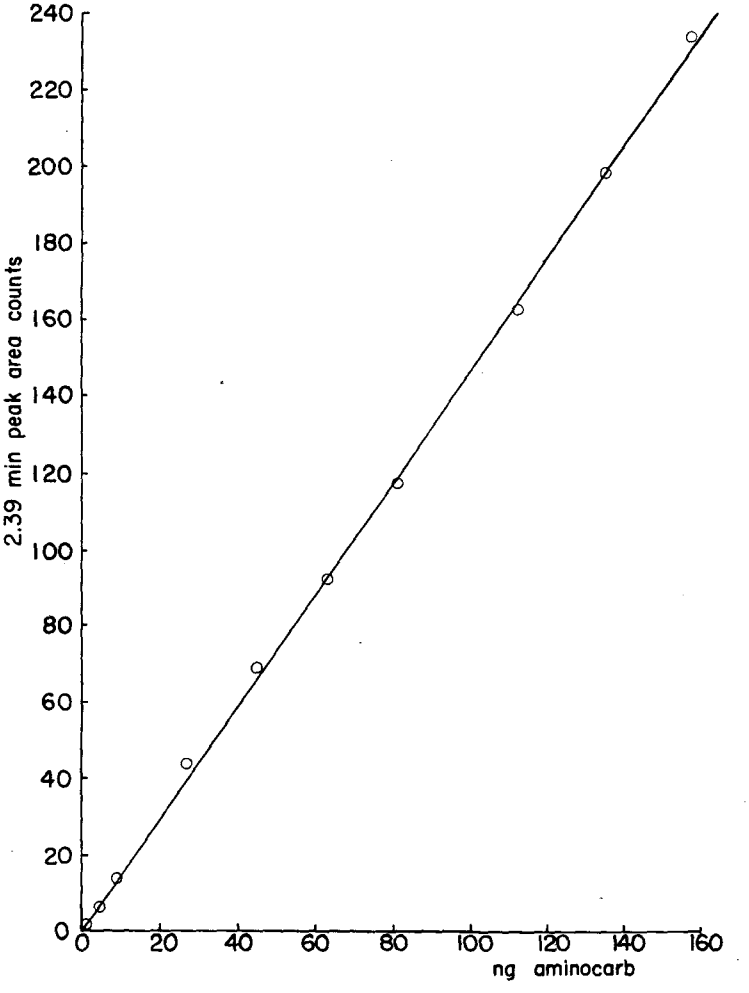

FIGURE 6 "2.39 min" peak area as a function of the amount of aminocarb deposited on Tenax GC adsorber.

The Ultra-Bond 20 M column chosen for analysis does not cause degradation of aminocarb (Fig. 5a) and separates aminocarb and its degradation products at a relatively low temperature of 160°. At this

TABLE I

Degradation of aminocarb on Tenax GC adsorber

Amount of aminocarb deposited ng	2.39 min peak area counts	Average counts	S.D. counts ±	R.S.O. ±%
0.9	58131	55458	4298	7.8
	53831			
	50187			
	59682			
4.5	301510	288030	17832	6.2
	267810			
	294770			
9	680500	683247	37076	5.4
	771620			
	647620			
27	2194100	2182300	11421	0.5
	2181500			
	2171300			
45	3361600	3445567	72866	2.1
	3492200			
	3482900			
63	4708200	4613467	92213	2.0
	4524000			
	4608200			
81	5713100	5870200	136162	2.3
	5943300			
	5954200			
112.5	8255400	8165500	249798	3.1
	8357800			
	7883300			
135	10015000	9959333	49753	0.5
	9919200			
	9943800			
157.5	1.1392×10^7	1.1773×10^7	378000	3.2
	1.1635×10^7			
	1.2287×10^7			
	1.1777×10^7			

temperature the retention time of aminocarb is not excessively long so the analysis can be completed in about 9 min, including change of adsorbers.

Ultra-Bond 20 M also separates fenitrothion and TEHP, although this analysis requires a 2 m column and 200° oven temperature (Fig. 7). The analysis time is also about 9 min.

The short analysis time is important in the field experiment when over 100 samples must often be processed in a day.

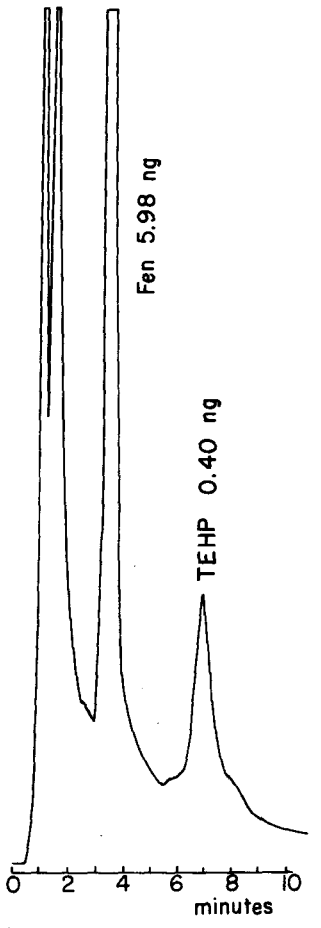

FIGURE 7 Chromatogram of an air sample taken with automatic sampler; sampling rate 1 l/min; sampling time 2 hrs.

Field tests

Results presented here are only to exemplify the usefulness of the above-described analytical procedure for monitoring airborne fenitrothion and aminocarb. Complete results and their discussion in relation to atmospheric conditions and topography have been published in a number of reports.[6,7,11]

Fig. 8 illustrates the fenitrothion dosage pattern at 1.5 m above ground level in the forest up to 700 m downwind of an aircraft spray swath. The dosages shown were measured over about 1 hr following the spray and

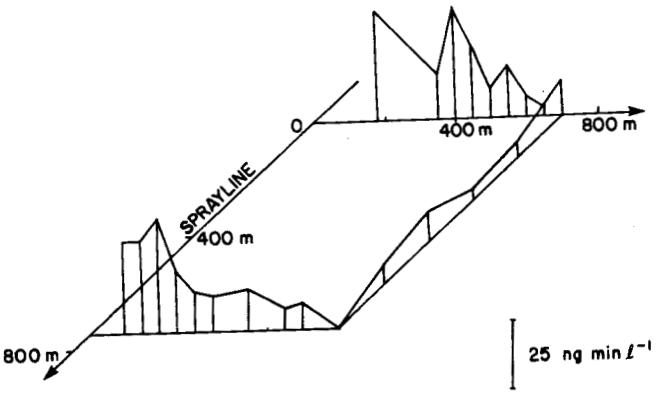

FIGURE 8 Dosage profiles of fenitrothion measured at 1.5 m above ground level in a spruce forest downwind of a spray line. Line source strength = 6 g m^{-1} of fenitrothion.

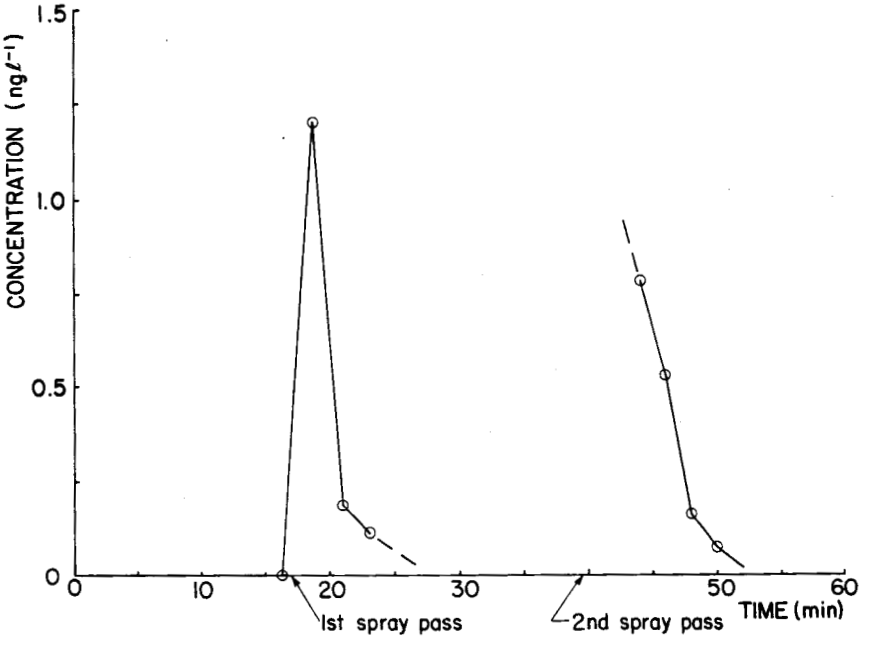

FIGURE 9 Concentration of fenitrothion at 1.5 m above ground level in a spruce forest 100 m from a spray line. One aircraft spraying at 3 g m^{-1}.

comprise mostly aerosol with some vapour from volatilisation of the heavy deposits at the spray line. A systematic decrease from about 40 ng min l^{-1} at the spray line to about 8 ng min l^{-1} 700 m downwind was observed. The substantial variations are a reflection of the random shielding effect of the individual trees. The effect is particularly distinct on the north sampling line where the forest was not uniform. The line source strength in the test was about 6 g/m of fenitrothion arising from two passes by an aircraft.

Sequential samplers allowed the determination of timewise variations of concentration. As illustrated in Fig. 9, two concentration maxima were determined due to two passes by an aircraft.

The aerosol drop size distribution diagram presented in Fig. 10 reveals that most of the fenitrothion formulation is dispersed into droplets below 10 μm in diameter.

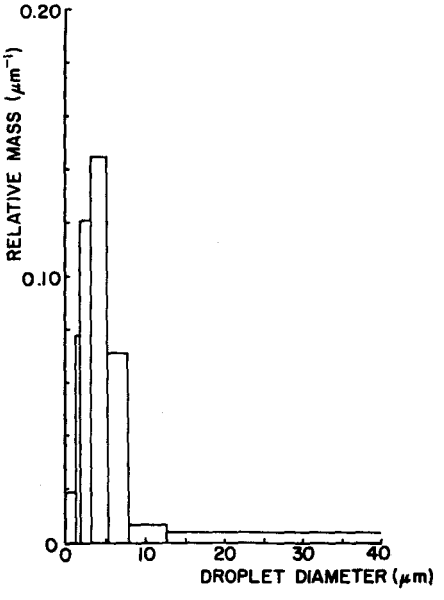

FIGURE 10 Distribution of droplet size in spray drift cloud at 500 m downwind of spray line.

Table II summarizes the results obtained in the aminocarb experiment. The samples were collected over a 1 hr period following the aircraft pass. The dosages systematically decrease from 60 ng min l^{-1} at 400 m downwind to 0.5 ng min l^{-1} 3600 m downwind. There are also minor variations with height. The dosage difference across the sampling arc (east

TABLE II

Total airborne aminocarb measured near the spray area

Sampler location	Height above ground level	Amount of aminocarb collected	Dosage
	m	ng	ng min l^{-1}
4000 E	15	30	54.6
	3	33	60.0
400 W	15	17	30.9
	3	16	29.1
1200 W	30	2.3	4.2
	17	3.2	5.8
	15	3.4	6.2
1200 E	15	4.2	7.6
3600 E	15	0.64	1.2
3600 W	15	0.26	0.5

and west sides) reflect wind direction diagonal to the centreline and, to a lesser extent, shielding effect of individual trees.

Acknowledgements

The author sincerely appreciates the cooperation of Drs. L. Elias and R. S. Crabbe of the Unsteady Aerodynamics Laboratory. Dr. Elias designed the samplers; Dr. Crabbe designed the sampling grids and coordinated the experiments with atmospheric conditions.

Special thanks are due to Mrs. McCooeye who traced the figures presented in this paper.

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