

## Measurement of Aminocarb in Long-Distance Drift Following Aerial Application to Forests

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A major concern associated with aerial forest spraying programs has been the extent of off-target loss of insecticide due to volatilization and aerial drift (Ecobichon 1982). Early deposition studies with DDT revealed that only about 40% of the applied material reached the ground in cleared areas (Symons 1977). The aerial drift of fenitrothion was reported as early as 1971; fenitrothion was detected at considerable distances from the site of application (Yule et al. 1971). Poor deposition of aerially-applied fenitrothion was confirmed in deposition studies that detected levels of  $0.8 \mu\text{g cm}^{-2}$  on collector plates when, in theory, at an application rate of  $210 \text{ g ha}^{-1}$ , the concentration should have approached  $2.1 \mu\text{g cm}^{-2}$  (Wood and Stewart 1976). Fenitrothion residues of the order of  $0.02 - 0.15 \text{ g ha}^{-1}$  have been measured in blueberry fields at distances of 3 - 8 km downwind of sprayed forest tracts (Wood and Stewart 1976). More recent studies with a pesticide simulant revealed airborne concentrations of 6 - 16% of the amount applied at a distance of 7.5 km from the spray site (Crabbe et al. 1980a).

With the current spray technology used in New Brunswick spruce budworm programs Grumman TBM or agricultural-type aircraft fly at a height of approximately 30 m above the forest canopy, and release an aerosol having a mean particle diameter of 100  $\mu\text{m}$ . Within 15 s of release, evaporation of the aqueous portion of the emulsion is effectively complete and the mean particle diameter of the aerosol has shifted downward to 52  $\mu\text{m}$  (Reid, 1979). Large particles enter the forest canopy unperturbed but the smaller particles are carried downwind or even lifted upward as they encounter turbulent conditions produced by local winds and thermal convection. Small droplets can drift for considerable distances; droplets having diameters of 50 - 10  $\mu\text{m}$  can drift from 55 - 13,500 m (Akesson and Yates 1964). This report presents the results of experiments conducted to measure mean concentrations of airborne insecticide at a distance of 2 - 3 km from operational spraying by TBM aircraft and at a height between tree-top level and 130 m above the forest canopy.

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## MATERIALS AND METHODS

Amberlite XAD resins have been used by several workers to obtain concentrated pesticide samples from both air and water (Sherma and Zweig 1985). The air sampling apparatus (Figure 1) was based on a modified high volume air sampler similar to that used by Wiesner and Silk (1982) to measure atmospheric pheromone concentrations. Air was aspirated at 48 litres s<sup>-1</sup> through exchangeable cartridges (10 cm diameter) filled with Amberlite XAD-2 resin. Cartridge depth (1.5 cm) was sufficient to prevent the breakthrough of insecticide vapour ( 1% after 2 min aspiration when the resin was spiked with 40 ug aminocarb) and yet allow the high flow velocities required for near isokinetic sampling whilst flying at 36 - 41 ms<sup>-1</sup>.

The intake end of the sampler was 32mm wide and had a sharpened edge to preserve the laminar air flow and therefore reduce losses of insecticide to the inner walls of the sampling chamber.

The sampler was powered by the 24 V DC aircraft supply through an inverter, and the entire unit was mounted on tracks in the cargo area of a Cessna 172. With the cargo door removed, the unit could be extended into the airstream for sampling or retracted into the cabin for cartridge changes.

Sampling was performed downwind of four large (3,500 - 18,000 ha) spray blocks to which aminocarb (4-(dimethylamino)-3-methylphenyl methylcarbamate) as the formulated product, 'Matacil', was being applied at a rate of 70 g a.i. ha<sup>-1</sup> by a team of three Grumman TBM aircraft flying in echelon formation. The equivalent source strength per TBM team swath (400 m) was nominally 2.85 g m<sup>-1</sup>.

In each case, the sampling aircraft repeatedly flew a designated line parallel to the wind direction i.e., at right angles to the spray lines, from a point 2 km to a point 3 km downwind of the downwind edge of the spray block. Sampling commenced at tree top (approximately 20 m above ground) at the 3 km terminus and continued while the aircraft climbed to approximately 150 m above ground level at the 2 km terminus. The sampler aircraft then turned, the sampler cartridge was exchanged, and the next sampling run commenced while descending from approximately 150 m at 2 km back to 20 m at 3 km (Figure 2). Each sampling interval, ascending or descending, lasted approximately 30 s with turns taking approximately 1 min. In this way, a time sequence of samples from essentially the same air space was obtained. By beginning the sampling as the spray planes were applying the first swath and continuing sampling as they worked progressively further upwind on the block, a

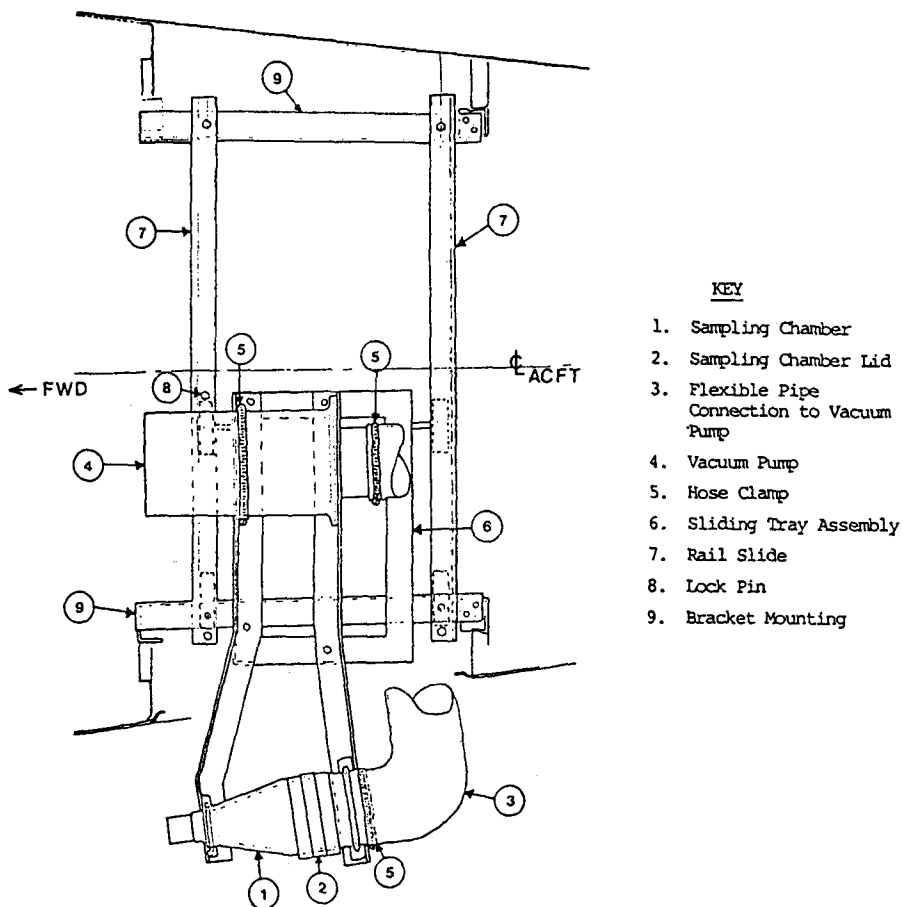


Figure 1. The Air Sampler

measure of mean drift concentration versus time at 2.5 km downwind and approximately 85 m above ground was obtained. A total of twenty samples was collected in each case.

Atmospheric stability, wind speed and wind direction throughout the sampling period were monitored by a ground based meteorological team making Minisonde ascents at approximately 15 min intervals.

A continuously operating tape recorder was used to record the activities of both the sampler and spray aircraft so that scenarios could be reconstructed and analysed.

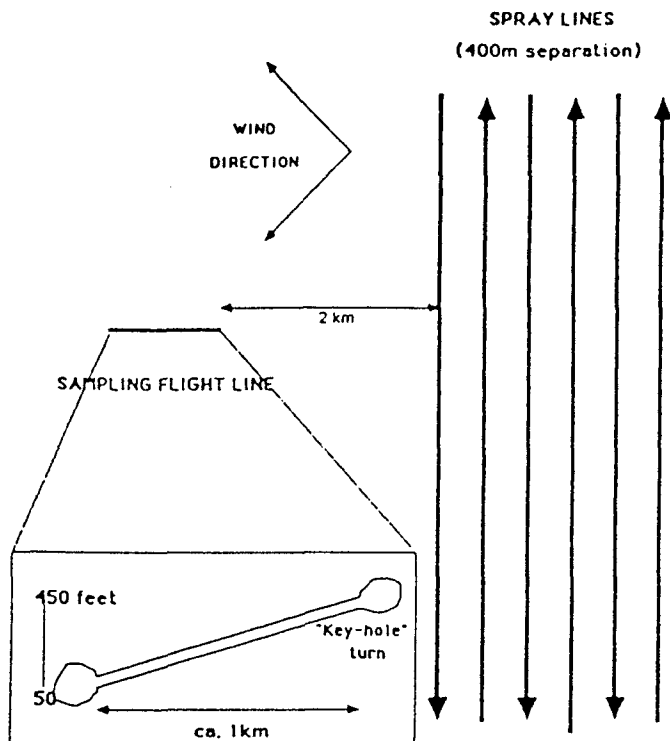


Figure 2. Diagrammatic Representation of Sampling Scenarios

Sample cartridges were returned to the laboratory and the resin stored in screw topped mason jars at a temperature of 2 - 4°C prior to processing. Emptied cartridges were washed in ethyl acetate and refilled with fresh resin for re-use.

Each resin sample was poured into a 30 cm X 25 mm id glass column containing 60 mL of ethyl acetate and allowed to soak for 20 min. After this time, the column was drained and the resin was eluted with three more 60 mL aliquots of ethyl acetate over a period of 15 - 20 min. Any solvent not draining freely from the column after elution with the third aliquot was blown through using a stream of nitrogen. All extracts were combined and the solvent was evaporated to not less than 10 mL by using a rotary evaporator with a water bath temperature of 25°C; 0.5 g of mineral oil was added to each sample prior to evaporation to act as a keeper. Samples were further evaporated to 1 mL under a stream of nitrogen in a water bath at 18°C. By this technique, desorption efficiency recoveries of 4 ug of aminocarb from fortified resin were essentially quantitative ( $x = 100.8\% \pm 4.7$ ;  $n = 3$ ).

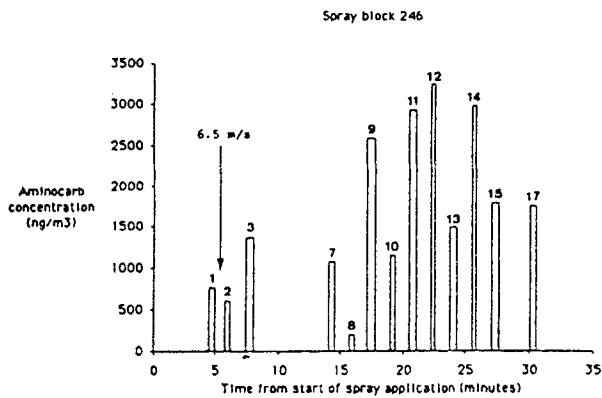
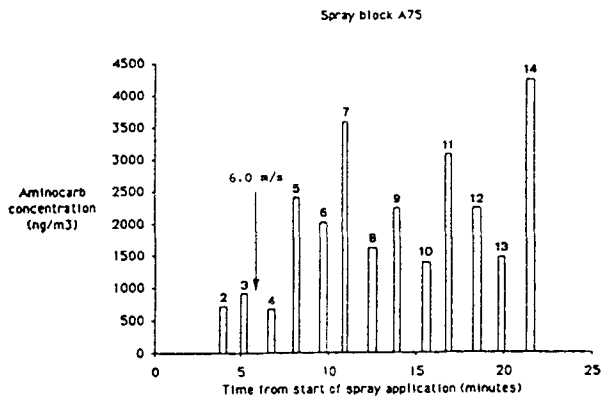
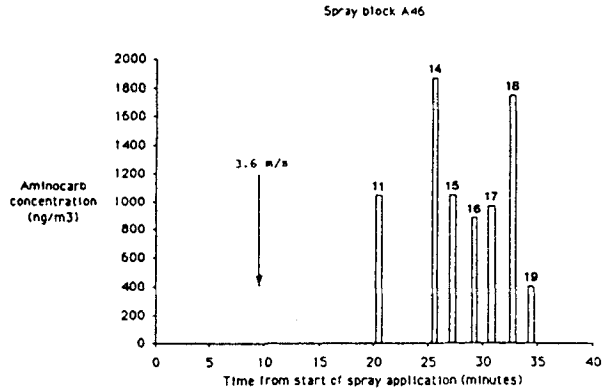
It was found that samples were contaminated and had to be cleaned up prior to analysis by gas chromatography. Each 1 mL sample extract was poured onto a mini column containing 1.0 g of 5% deactivated Florisil that had been washed by elution with 3 mL of ethyl acetate and subsequently with 3 mL of toluene. The 1-mL sample extract was allowed to soak into the column for approximately 15 min. The column was then eluted with 2 mL of toluene, 1 mL of toluene/ethyl acetate mix (2:1) and 2 mL of ethyl acetate, respectively. The eluates were combined and made up to a total sample volume of 5 mL with ethyl acetate. This technique effectively removed background contaminants and with three replicates gave 89.9%, 79.1% and 87.1% recoveries of added aminocarb (10 ug).

Samples were analysed on a Hewlett-Packard 5840 gas chromatograph equipped with a nitrogen/phosphorus detector and autosampler. A 1.85 m X 5 mm i.d. glass column packed with 3% SE-30 on 80/100 mesh Gas-Chrom Q was used throughout. Helium was used as the carrier gas at 40 mL min<sup>-1</sup> at a column oven temperature of 190°C. Duplicate 2- $\mu$ L injections of each sample were made with standards injected at frequent intervals.

## RESULTS AND DISCUSSION

Results of the analyses from three of the four operational spray blocks sampled are given in Figure 3. Individual sample concentrations ranged from 0.0 - 4.2 ug m<sup>-3</sup> with the highest concentration measured corresponding well with values obtained in earlier experiments (Crabbe et al. 1980a, 1985).

The spraying of block A75, an evening spray, began in an unstable atmosphere and was completed under slightly stable conditions. Block 246 was sprayed under deteriorating, early morning, inversion conditions. In each graph of Figure 3, the arrow indicates the time when, according to the available meteorological data, the first insecticide should have been anticipated in air samples. In the experiments on blocks A75 and 246, there was good agreement, the insecticide appeared only in one or two air samples prior to the anticipated time of arrival. In the third experiment (block A46), an evening spray application made under developing inversion conditions, aminocarb was not encountered in the sampling zone until some time after the anticipated time of arrival. In the fourth experiment (not shown), insecticide was detected in only 3 of the 20 samples. Aminocarb concentrations of < 0.1 ug/m<sup>3</sup> were measured at 27, 37 and 42 min after spraying was initiated. At the start of this experiment, windspeeds were marginally higher than in the other trials but decreased with the development of an atmospheric inversion. Under these conditions of increasing atmospheric stability, no satisfactory explanation could be found to account for the poor yields of insecticide in the sampling zone compared to those obtained in the other experiments. The number of TBM team swaths flown in the four experiments were 11, 11, 17 and 9, respectively.



Arrows denote calculated arrival time of first swath in sampling region based on the mean wind speed indicated.

Numbers above columns denote sample cartridge number.

Figure 3. Atmospheric aminocarb concentrations in samples from spray blocks A46, A75 and 246

It is concluded that there is long range transport of pesticide, either as vapour or as aerosol particles which do not impinge upon the forest canopy. The results of this study agree favourably with those of other investigations where pesticides and simulants were applied aerially to forest tracts (Crabbe et al. 1980a,b; Crabbe and McCooeye 1985). Variations in drift concentrations were found not to correlate with minor changes in atmospheric conditions. It is concluded that, unless changes in conditions are particularly extreme, differences in drift will be relatively minor. Factors other than atmospheric conditions, e.g., spray release height, may be more important operational considerations in the aerial application of pesticides.

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