

## Vapour Phase Photochemistry of Fenitrothion and Aminocarb

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Pesticide residues resulting from spray drifts during application enter the atmosphere by vaporization from soil, plant and water surfaces (WHEATLEY 1973). With the advent of aerial application of pesticides, there has been considerable interest in evaluating drifts from spray operations. This interest stems from the concern with the environmental contamination and from the search for a more efficient way of conducting spray programs.

Evaporation of water from a sprayed formulation occurs even at high relative humidity (CUNNINGHAM et al. 1962); evaporation decreases the average particle diameter and thereby increases the opportunity for long distance drift. Also, pesticide vapours are produced which can remain in the atmosphere for extended periods of time. The wavelengths responsible for photoconversions of pesticides in the lower atmosphere are in the range 290 to 400 nm; these wavelengths possess sufficient energy (99-72 Kcal/mole) to cause photoconversions (CROSBY & MOILANEN 1974, MOILANEN & CROSBY 1977, LEITIS & CROSBY 1974, SODERQUIST et al. 1974). Oxidants such as ozone, hydroxyl radicals and oxygen tend to enhance photoconversion in the vapour phase.

This work reports the findings of atmospheric photochemical study of spray drifts in which aminocarb and fenitrothion vapours were irradiated under controlled laboratory conditions, and in actual field conditions.

### EXPERIMENTAL

**Materials.** Fenitrothion (95% purity) and aminocarb (97% purity) were obtained from Chemical Services, Inc., West Chester, PA 19380 and used without further purification. Fenitrothion formulation (11% fenitrothion, 1.5% atlox 3409F, 1.5% dowanol, 13% nonylphenol, and 82% diluent oil 585 were supplied by the New Brunswick Forest Protection Agency (FPA). Spectrograde solvents were used. Ethyl acetate was used to clean the laboratory photoreactor, and also for Soxhlet extraction of the Porapak Q adsorbent, used for sampling the field atmosphere.

The Grumman TBM Plane used in the spray program and the meteorological equipments used to measure the relative humidity, wind-speed and wind direction were all provided by FPA. Sunlight intensities were measured by a Western illumination metre, Model 756 with a quartz filter.

Vapour-drift field experiment. Formulations were sprayed separately by a Grumman TBM flying at an estimated altitude of 24 m. The fenitrothion formulation was applied along a 600 m swath line in seven passes over a period of 12 min. The Matacil formulation was also applied along the same 600 m swath line in five passes over a period of 10 min. Four sampling stations were set up at 50, 230, 405, and 672 m downwind from the centre of the swath line and the air was sampled continuously while the aircraft made applications.

Low and high volume samplers contained 2 and 20g respectively of pre-Soxhlet extracted Porapak Q. Station one had 3 low volume samplers operating at 35 L/min and the other three stations each had one high volume sampler operating at flow rates of about 900 L/min. Sampling time for each station was about 10 min.

Tests were run between 10:40 and 11:50 AM on July 25, 1979; average temperature, relative humidity, wind speed and direction were as follows: 23.8°C, 65%, 9.2 km/h, 220°. Average sunlight intensity during the spray operation was about 8000 ft-candles.

Field Sample Analysis. Samples were packed in a dry ice box, transferred to the laboratory and stored in the freezer until ready to be analysed. The Porapak adsorbents were Soxhlet-extracted with 250 mL portions of ethyl acetate. Extracts were filtered, concentrated and analysed by gas chromatography (GC) equipped with thermionic specific detector and by high-performance liquid chromatography (HPLC). GC conditions were as follows: 1.8 m x 4 mm (id) glass column, packed with 3% SE-30 on 80/100 mesh Chromosorb Q at 190°C and a flow rate of 40 mL/min. HPLC analysis was performed with fixed UV (254 nm) absorbance detector. The column was 30 cm x 4 mm id Micropak MCH 10 (packed with 10 µm C18 µBondapak). The mobile phase was acetonitrile - water (80:20) in the reversed phase mode. Solvent flow was 1 mL/min at ambient temperature and all organic solvents were HPLC-grade: water was distilled and deionized before being used.

Laboratory Vapour-Phase Photolysis. Fenitrothion and amino-carb (10-15 mg) were placed on a glass dish in a 50-L reaction chamber, according to CROSBY & MOILANEN (1974). The base of the reactor was heated to about 85-90°C to promote vaporization of the insecticide, and dry air, either with or without ozone, was passed through the photoreactor at a rate of 190 cm<sup>3</sup>/min.

Pesticide vapours were irradiated with a collimated beam of light from a Varian Model VIX-300, a 300-watt Xenon arc illuminator with up to 2 watts of UV (200-400 nm) output and equipped with a Varian Model R300-1 lamp holder and a Varian PS 300-1 power supply.

The ozone was generated in the air stream going into the photoreactor by passing air through a quartz flow tube irradiated by a Pen Ray ultraviolet lamp. The ozone concentrations were measured iodometrically by sampling the air exiting the photoreactor and was found to be  $0.35 - 0.45 \pm 0.05$  ppm.

Chemical Analysis. The vaporized insecticides and their mobile photoproducts were trapped in about 130 mL of ethylene glycol in a gas bubbler and then extracted from the ethylene glycol by the procedure of SHERMA & SHAFIK (1975). Experiments were run under four different conditions: (a) dark without ozone, (b) dark with ozone, (c) light without ozone, (d) light with ozone. Knowing the concentration of insecticide material vaporized in the photoreactor, the fraction remaining after photolysis, and assuming first-order kinetics for photoconversion of the vaporized insecticide, rate constants and half-lives of photoconversions were estimated for fenitrothion and aminocarb.

## RESULTS AND DISCUSSION

Table 1. Summary of Field Data for Fenitrothion and Aminocarb

Station	Insecticide	Number of Spray Passes	Volume of Air Sampled ( $m^3$ )	Amount of Material ( $\mu g$ )	Residence Time (min)
1	F	7	1.6	0.17	0.6
2	F	4*	13.0	21.7	1.7
3	F	7	31.0	12.3	3.6
4	F	7	30.0	36.8	5.1
1	A	5	3	0.71	0.6
2	A	5	22	81.3	1.3
3	A	5	20	3.55	2.7
4	A	5	33	5.62	4.5

\* Sampler failure during first three passes.

F = Fenitrothion, A = Aminocarb

Table 2. Vapour-Phase Photolysis of Fenitrothion and Aminocarb

Condition	Insecticide	Photolysis Times (days)	Determinations	Rate Constant ( $\text{min}^{-1}$ )	Half- Life (min)
Light/no ozone	F	4	2	0.011	61+11
Light + ozone 0.45+ 0.05 ppm	F	4	2	0.29	24+3
Dark + ozone 0.35+ 0.05 ppm	F	4	2	0.002	433+4
Dark/no ozone	F	4	1	---	---
Light/no ozone	A	4	2	0.018	38+2
Light + ozone 0.45+ 0.05 ppm	A	4	2	0.024	29+ 3
Dark + ozone 0.35+ 0.05 ppm	A	4	2	0.002	347+10
Dark/no ozone	A	4	1	---	---

F = Fenitrothion, A = Aminocarb

Table 1 gives the results of the field work. The assumption is made that, under the field conditions of moderate relative humidity (65%) and air temperature ( $23.8^{\circ}\text{C}$ ), the spray droplets would quickly evaporate, favouring increased insecticide vapour concentration in the atmosphere at the downwind sampling stations. However, the possibility exists that these insecticides were sampled as fine aerosols and vapours. The methodology applied in this work does not differentiate between insecticide vapours and aerosols.

A further assumption made in this study is that the vaporized insecticides disappear in the atmosphere in an exponential decay fashion with time, since other variables that might affect the rate

constants, e.g. temperature, moisture, wind and solar radiation do not vary appreciably over the photolysis period.

The results of the field experiment by SONDERQUIST et al. (1975), showed that parathion vapour in California atmosphere had a short half-life, 2 to 5 min. Since fenitrothion is structurally similar to parathion, the half-lives in this study were also expected to be short if appreciable amounts of the spray formulations evaporated to give fenitrothion and aminocarb vapours.

Field sample extracts analysed for fenitrothion, carboxy fenitrothion, 3-methyl-4-nitrophenol, 5-methyl fenitrothion, 4-dimethylamino-3-methylphenol and 4-formylamino-3-methylphenol by GC and HPLC, yielded no detectable amounts of photoproducts. The absence of photoconversion products, therefore, suggests that sprayed formulations did not evaporate to favour a high concentration of fenitrothion and aminocarb vapours, which would then photodegrade much more rapidly.

Fenitrothion showed a measurable conversion to fenitrooxon in the dark with ozone present. Thus the conversion was due to thermochemical oxidation. Thermochemical oxidation in the dark to 4-dimethylamino-3-methylphenol occurred with aminocarb vapour in the presence of ozone at room temperature.

Table 2 gives the rate data for fenitrothion and aminocarb under all three experimental conditions. For both insecticides, the photolysis rate increased with the introduction of ozone into the photoreactor, and both compounds were thermochemically oxidised, although at very slow rates.

Half-lives were computed for the laboratory experiments based on the rate of decrease in concentration of the vaporized insecticide with time. From accurate gas chromatographic estimates of the fenitrothion and aminocarb concentrations before and after photolysis, reasonable rate constant values are calculated, and hence the half-lives. The half-lives estimated in the laboratory experiments lend further support to the assumption that these insecticides would undergo appreciable photoconversion in the atmosphere, if they were in the vapour phase during the short-range drift study.

A look at the ultraviolet spectra of these insecticides indicates low extinction coefficients in ethanol at the wavelength region between 290 and 400 nm, hence the low probability of undergoing extensive photoconversion in a short-range drift study. However, extensive photoconversion can still occur in a short-range

drift situation depending on environmental factors such as the concentration of ozone or other oxidants, photosensitizers and third bodies like dust particles.

#### ACKNOWLEDGEMENTS

I thank the New Brunswick Research and Productivity Council and the New Brunswick Forest Protection Agency for financial support. Also, helpful suggestions and discussion with C. Wiesner and P. Silk are gratefully appreciated. I thank C. Henderson for technical assistance.

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Accepted May 21, 1981