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Persistence of Formulated Fenitrothion in Distilled, Estuarine, and Lake Water Microcosms in Dynamic and Static Systems*

Pearl Weinberger,[1] R. Greenhalgh,[2] D. Sher,[1] and M. Ouellette[1]

[1]*Biology Department, University of Ottawa, K1N 6N5 and* [2]*Chemistry and Biology Research Institute, Agriculture Canada, Ottawa, Ontario K1A 0C6*

Reports of the widespread distribution of xenobiotic residues in the global system are increasing in number (BUTLER 1966; RISEBOROUGH et al. 1978; HOLDEN 1970 a,b). In Canada, fenitrothion represented 40% of all pestidical chemicals used in the years 1968-1979 inclusive (SYMONDS 1977). Its mode of degradation *in vitro* by hydrolosis (ZITKO & CUNNINGHAM 1974; MAGUIRE & HALES 1980; GREENHALGH et al. 1980) and photolysis (MARSHALL et al. 1974; OHKAWA et al. 1974) in both distilled water and buffer solutions have been well documented. Similarly, degradadation, partitioning, and accumulation in limited field and laboratory microcosms have also been followed (WEINBERGER et al. 1981; MOODY et al. 1978; LAKSHMINARAYANA & BOURQUE 1980).

The present study with natural lake and estuarine water, follows the degradation and partitioning of fenitrothion in a dynamic system simulating a stream with 3 sampling sites flowing into a lake, or an estuary into a bay. The chemical interactions were examined at three pH values representative of those found naturally in the Maritimes and Eastern Ontario, namely pH 4.5, 6.8, and 8.5. Fenitrothion was added as a formulation with Atlox and the tank mix prepared by addition of Aerotex or Dowanol. The experimental variables permitted an assessment to be made of whether the degradation of fenitrothion was modified by the type of water (lake or estuarine), pH of the medium, and/or the adjuvants with which fenitrothion was mixed.

MATERIALS AND METHODS

Chemicals: Technical grade fenitrothion (98% purity) and methoxy-^{14}C labelled fenitrothion were gifts from Sumitomo Chemical Co., Japan. Ring labelled fenitrothion (specific activity 14.5 mCi/mmole) was purchased from New England Nuclear Co., U.S.A. Aerotex, a petroleum distillate, Atlox, an anionic detergent and Dowanol (dipropylene glycol methyl ether), were gifts from Texa-Co Oil, Texas Chemical Co. and Dow Chemical Co., repesctively. 3-methyl-4-nitro phenol was purchased from Aldrich Chemical Co. Ethyl iodide and ScintiVerse scintillation cocktail were bought from Fisher Chemical Co.

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Water: In parallel experiments, deionized glass-distilled water (pH 6.5), lake, or estuarine water was used in the model river system. Lake water (pH 7.5, specific conductance 61±2μMHO/cm) was taken from Lac Bourgeois, Quebec, filtered through glass wool, and stored at 4°C until required (WEINBERGER et al. 1982). Estuarine water (pH 7.5, specific conductance 49±2μmMHO/cm, density 1.018 g/cc) was obtained from New Brunswick, and stored frozen until used. 1N HCl or 1N NaOh was added to these waters to provide water samples of pH 4.5 and pH 8.5.

Conductivity: Measurements were made with an Industrial Instruments model-RA-2A conductivity meter.

Tank mix: Two tank mixes, (Aerotex or Dowanol), were used each having field proportions of pesticide to adjuvants. They were added to a fenitrothion/Atlox formulation in the ratio of 11:1.5: 1.5 (w/v/v) respectively. The components were suspended in water and administered as an emulsion

Dynamic Stream/Estuary Models: The systems were maintained at 25±1°C and consisted of a 50-L feeding reservoir, three 1-L round-bottom flasks designed to represent upstream, midstream, and downstream locations and a 50-L collection reservoir. These were connected by a 21.4 m of coiled glass tubing (7mm id). All waters were collected in the collection reservoir and used for immediate mass balance determinations. A variable speed peristaltic pump controlled the flow of water into the upstream flask into which the pesticide tank mix was added. Air pressure controlled the flow of water through the coils to a rate of 85 mL/m, fluorescent lights (Sylvania) provided an illumination intensity of 1500 LUX over the spectral range of 360 to 700 nm. The diffusion and flow in the system were initially determined by monitoring the concentration of "potassium permanganate". These profiles provided the templates for comparison with the flow of the pesticide. Post-treatment, a minimum of 7 samples were taken from each sampling site.

Static Lake/Estuarine Models: The water in the collection reservoirs were used in the static systems. Parallel sets which were exposed to 5K LUX fluorescent light or natural sunlight were sampled at least twice daily. Dark controls provided the hydrolysis data. All experiments were repeated at least 3 times.

Treatments: Tank-mix fenitrothion enriched with the ^{14}C ring-labelled fenitrothion was pulsed into all systems to a final concentration of 2.5 ppm.

Analytical: Fenitrothion and its derivatives were extracted from water using ethyl acetate (non-polar fraction). The polar and non-polar fractions were quantitated by gas chromatography, and products confirmed by thin layer chromatography and scintillation counting as referenced (WEINBERGER et al. 1981).

RESULTS AND DISCUSSION

Dynamic Stream/Estuarine Models: A typical flow profile is shown in Fig. 1. Maximum concentrations in the mid- and downstream locations were 34 and 30%, respectively, of the starting concentration in the upstream station after 8 and 15 min., respectively. The pesticide passed through the system within 1.0 h.

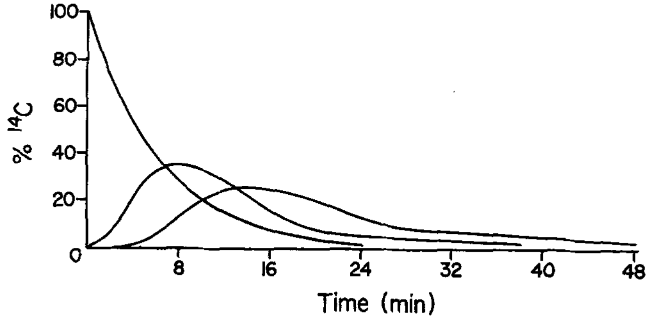

Fig. 1 Persistence of Aerotex/Atlox formulated fenitrothion in the aqueous phase in the upstream (O) midstream (Δ) and downstream (□) stations in the lake water pH 6.8

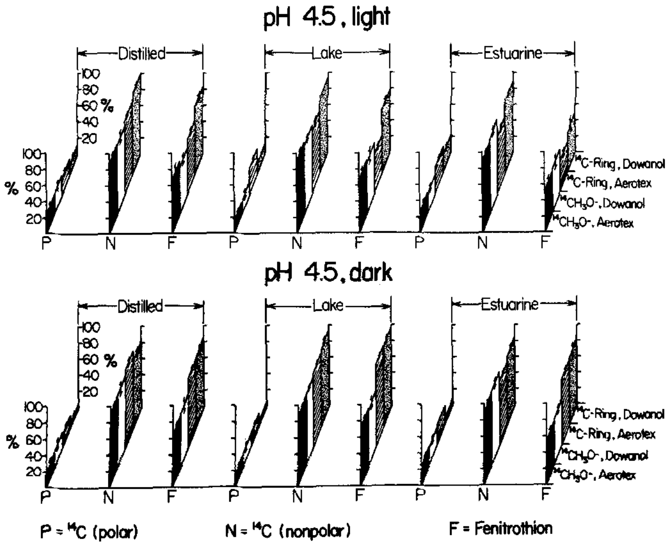

Fig. 2 Light and dark systems 7 days post treatment (pH 4.5). % distribution of fenitrothion (F), polar (P) and non polar (N) fractions in distilled and natural waters.

The Aerotex and Dowanol tank mixes in all 3 waters (distilled, lake and estuarine) and at each of the 3 levels of pH (4.5, 6.8 and 8.5) followed the dye flow profile, as shown by analyses and ^{14}C counts.

No fenitrothion degradation products were observed. All ^{14}C remained extractable by ethyl acetate. In all systems, 1 h post-treatment, mass balance as determined by GC and LSC were quantitative (96±4%) indicating that no chemical breakdown of fenitrothion has occurred. Dilution and elution were the sole factors governing the concentration of fenitrothion in the dynamic model ecosystem. Essentially, the pesticide washed downstream and accumulated in a downstream location, representing the lake or estuarine bay.

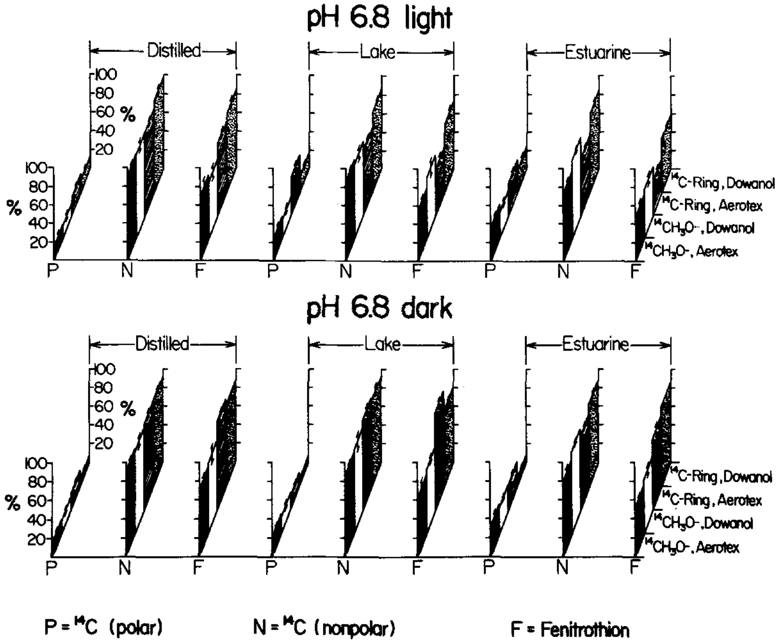

Fig. 3 Light and dark systems 7 days post treatment (pH 6.8). % distribution of fenitrothion (F), polar (P) and non polar (N) fractions in distilled and natural waters.

Static Lake/Bay Models: a) 5k LUX light. Generally, the photolysis and hydrolysis of fenitrothion was unaffected by pH or waters. Desmethyl fenitrothion and 3-methyl-4-nitro phenol were the major degradation products, Figs. 2-4. Aerotex in the tank mix led to an augmentation of the polar fraction.

b) Natural Sunlight. In all systems, despite some variability within the first hour, 80% of the pesticide was photolyzed to polar derivatives within 6 h, Figs. 5-6.

With the Aerotex mix alone, N-formyl- and N- acetylamino-fenitrothion were identified in the organic fraction and quantitatively represented 1% of the original pesticide load.

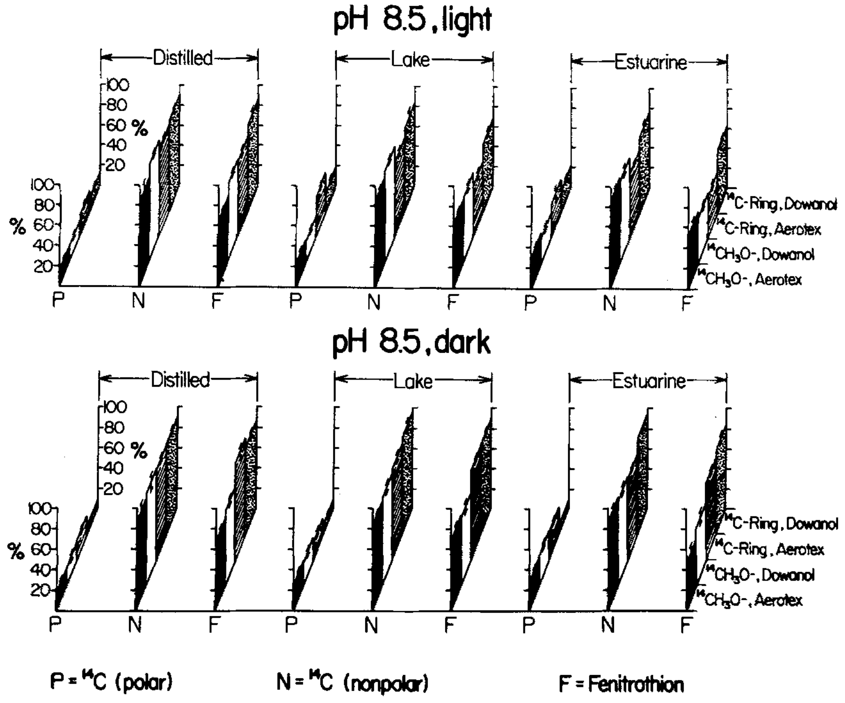

Fig. 4 Light and dark systems 7 days post treatment (pH 8.5). % distribution of fenitrothion (F), polar (P) and non polar (N) fractions in distilled waters.

Degradation in estuarine water was greater than in the other waters, the implication being that the ions and/or microflora in the estuarine waters played an important role in the chemical degradation (ZEPP 1980; MANHEIM et al. 1972; GIBBS 1977).

This study highlights two facts, namely, that sites downstream of spray areas are highly vulneralbe to pesticide perturbations, and laboratory studies on the chemical degradation of pesticides involving distilled water may have only marginal relevance to processes taking place in natural waters. In our present study, the ionic complement of the estuarine water interacting with the adjuvants in the tank mix (Aerotex or Dowanol) contributed more to the degradation of fenitrothion than pH changes.

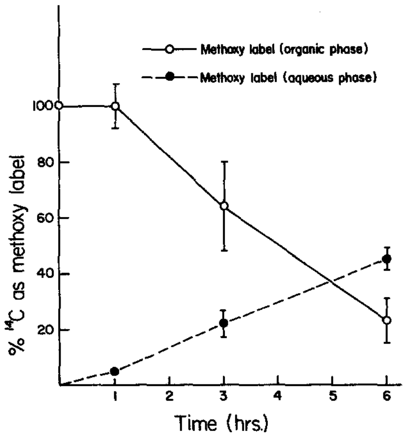

Fig. 5 Solar photolysis of non-formulated fenitrothion in distilled water, pH 6.8

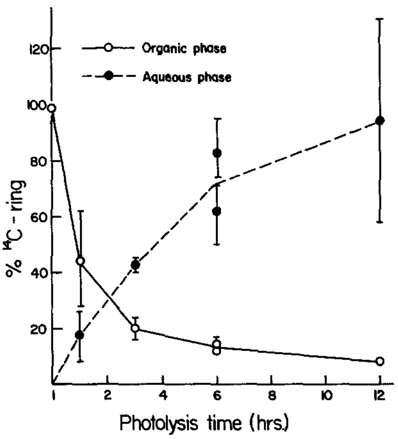

Fig. 6 Solar photolysis of non-formulated fenitrothion in distilled water, pH 6.8

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