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Analysis of Environmental Samples for Constituents of an Aromatic Solvent Used in Fenitrothion Spray Formulations

C. W. Howse, E. J. Hale, and R. J. Maguire*
Process Research Division, National Water Research Institute,
Canada Centre for Inland Waters, 867 Lakeshore Road, Burlington, Ontario, Canada L7R 4A6

Fenitrothion (O,O-dimethyl-O-[4-nitro-m-tolyl]phosphorothioate)has been used since 1969 in New Brunswick, Canada for control of the spruce budworm (Choristoneura fumiferana [Clemens]) in the province's forests. Millions of hectares have been sprayed annually at dosages of 150 - 300 g active ingredient per hectare. The routes and rates of environmental transformation and disappearance of fenitrothion are subjects of a great deal of interest (NATIONAL RESEARCH COUNCIL OF CANADA 1975, 1977).

Fenitrothion spray formulations used in New Brunswick are typically composed of about 11% (w/w) technical fenitrothion (>95% pure), 1.5% aromatic solvent (e.g., Aerotex 3470), 1.5% emulsifier (e.g., Atlox 3409F) and 86% water (COCHRANE and MAYBURY 1977). The solvent Aerotex 3470 contains mainly alkylated derivatives of benzene and naphthalene boiling between 340 and 700°F, and the composition has been partially elucidated (SAFE et al. 1977a, 1977b). The emulsifier Atlox 3409F contains a blend of nonionic and anionic detergents (SAFE et al. 1977b).

In recent years it has become apparent that an assessment of the environmental impact of a pesticide should include not only an account of its distribution and persistence but also that of all potentially toxic adjuvants in the pesticide formulation. For example, CROCKER et al. (1976) have shown that certain emulsifiers which have been used in fenitrothion spray formulations in New Brunswick are capable of enhancing viral activity in young mice; there may be a connection between exposure to such emulsifiers in fenitrothion spray formulations and the occurrence of Reye's syndrome (encephalopathy and fatty degradation of the viscera) in children.

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* to whom to address correspondence

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In the course of a study on the distribution and persistence of fenitrothion and its transformation products in aquatic systems, we collected pre- and post-spray air, water and sediment samples in central New Brunswick in May 1977; these samples have also been analyzed for the components of the aromatic solvent used in the spray formulation and these results are reported in this article.

METHODS

Samples were taken from a stagnant pond about 0.3 m deep in an uninhabited forested area 8 km due south of the confluence of the Cains and southwest Miramichi rivers (lat. 46°C, 40'; long. 65°, 50') before and after a spray of 1500 g/ha emulsion of composition as described above. It is customary to spray forest tracts twice annually, with the sprays about a week apart; the spray monitored in this study was the second one, which occurred 7 days after the first spray.

Sampling and extraction methods were those which had been shown to be suitable for fenitrothion; it is acknowledged that some components of the spray formulation may not be quantitatively extracted by macroreticular resins or amenable to gas chromatographic analysis (i.e., either eluting with the solvent or not at all). Only the subsurface bulk water samples and air samples were analyzed for Aerotex constituents. Subsurface bulk water samples were collected in 1 ℓ glass-stoppered bottles; the water was quickly passed through 15 cm x 0.75 cm diameter columns of XAD-2 resin (JUNK et al. 1974) in the field, and the wet resin was stored at 4°C until extraction. Water samples were taken in triplicate at 20 times from 4 days pre-spray to 3 days post-spray. Air samples were taken qualitatively, merely by exposing petri dishes (10 cm diameter) of wet XAD-2 resin to the atmosphere for varying periods of time. These time periods varied from 1 day before the spray to 4-hour intervals after the spray.

The XAD-2 resin samples of air and water, and appropriate blanks, were extracted with toluene, dried, concentrated and analyzed by flame ionization gas chromatography (GC) and gas chromatography-mass spectrometry (GCMS). The GC used was a Hewlett-Packard 5700A, with a 2 m x 2 mm 10% OV-1 column, temperature programmed in the following fashion: 80°C for 8 min, then to 240°C at 8°C/min. Similar conditions were used for GCMS, and two systems were used: (i) a Finnigan 1015-C (electron impact at 70 ev) with PDP-8 computer and the Cyphernetics spectral library, and (ii) a Finnigan 4000 (electron impact at 70 ev) with INCOS 2300 data system, a spectral enhancing program (ENHA), and the NIH-EPA spectral library.

Samples of Aerotex 3470, Atlox 3409F and fenitrothion were kindly supplied by Texaco Canada Ltd., Atlas Chemical Co. and Chemagro Ltd., respectively. All other standards were obtained commercially. Pesticide grade solvents were used throughout this study.

RESULTS AND DISCUSSION

Analysis of Aerotex 3470

While this work was in progress SAFE *et al.* (1977b) reported on the analysis of components of Aerotex, first by separation into 4 fractions by thin layer chromatography, then by gas chromatographic-mass spectrometric analysis of each fraction. They positively identified 7 compounds (1,2,3,5-tetramethylbenzene, naphthalene, 1- and 2-methylnaphthalene, and 1,5-, 2,3- and 2,6-dimethylnaphthalene) and made tentative structural assignments for about 60 others; it appears that Aerotex 3470 has a complex composition of isomeric alkylated naphthalenes, benzenes, bibenzyls, fluorenes and phenanthrenes, as well as the parent hydrocarbons (with the exception of benzene and biphenyl).

We compared the Aerotex 3470 with environmental samples by gas chromatography directly without a prior separation by thin layer chromatography. The chromatogram is very complex and contains about 45 peaks, many of which are unresolved, and many of which probably contain more than one compound. Positive identifications were made by GCMS (using multiple and specific ion detection), and co-chromatography with authentic samples, for 5 compounds: n-propylbenzene, 1,2,4,5-tetramethylbenzene, naphthalene and 1- and 2-methylnaphthalene. Tentative identifications were made for another 40 compounds as described in Table 1.

TABLE 1

Partially Identified Constituents of Aerotex 3470

4	C_3-alkylbenzenes
4	C_4-alkylbenzenes
4	C_5-alkylbenzenes
3	C_6-alkylbenzenes

TABLE 1 (continued)

Partially Identified Constituents of Aerotex 3470

3	C_2-alkylnaphthalenes
5	C_3-alkylnaphthalenes
4	C_4-alkylnaphthalenes
	anthracene
	a methylanthracene
	biphenyl
4	C_1-alkyldiphenylmethanes
5	C_2-alkyldiphenylmethanes
1	C_3-alkyldiphenylmethane

Most of the compounds shown are alkylated benzenes and naphthalenes; the designation C_4-alkyl, for example can mean 4 methyls, 2 ethyls, 1 propyl plus 1 methyl and so forth. Inadequate chromatographic separations and the unavailability of authentic isomeric standards made positive identifications impossible in many cases.

Analysis of Atlox 3409F

The emulsifier contains some solvent oil in addition to anionic and nonionic detergents; p-cymene, naphthalene and 2-methylnaphthalene were positively identified by GCMS and co-chromatography with authentic samples.

Analysis of Environmental Samples

Figure 1 shows the flame ionization chromatogram (under conditions described above) of a subsurface water sample taken 48 hours before the spray. There are about 40 peaks, many of which are not well resolved and which may represent more than one compound. The GCMS runs were made under identical conditions. Four compounds were positively identified by mass spectral confirmation and co-chromatography with authentic samples; these are tetralin, naphthalene, 1- and 2-methylnaphthalene. Table 2 lists the positive and tentative identifications of some peaks of the chromatogram which account for 82 area per cent of the total chromatogram, exclusive of solvent.

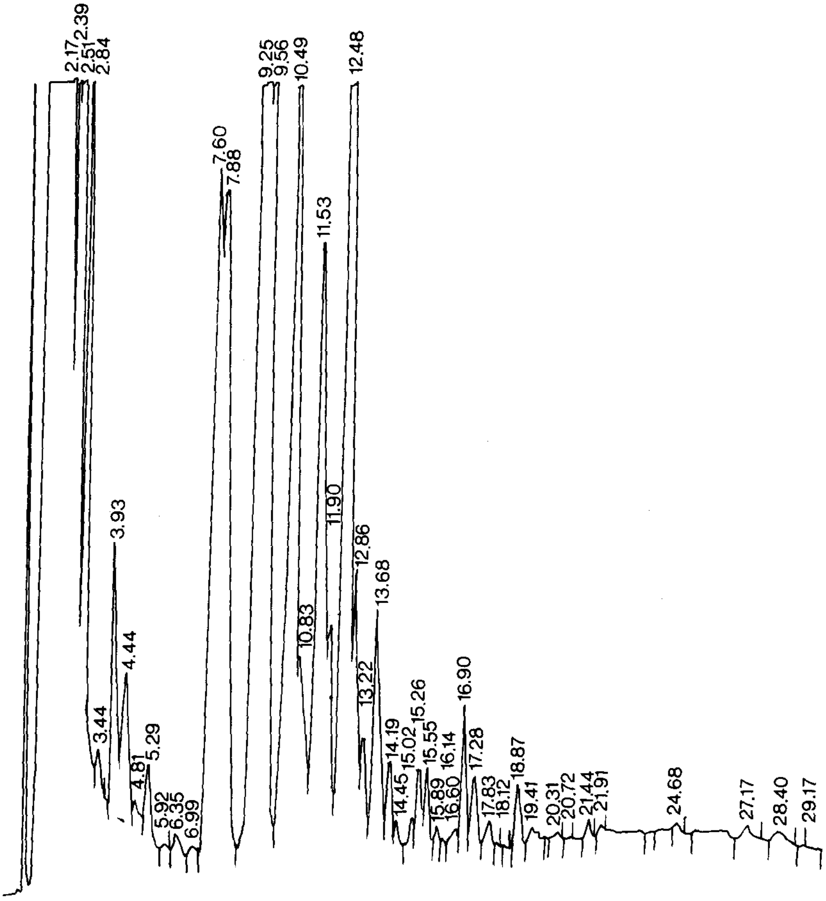

Fig. 1. Flame ionization chromatogram of an extract of a pre-spray bulk subsurface water sample.

TABLE 2

Identification of Components of Pre-Spray Bulk Subsurface Water Sample

Peak No.	Retention time, min. (uncorrected)	Assignment	Area %
5	3.93	C_3-alkylbenzene	0.1
6	4.44	C_3-alkylbenzene	0.4
7	5.29	C_3-alkylbenzene	0.5
10	6.35	C_4-alkylbenzene (possibly p-cymene)	0.1
12	7.60	C_4-alkylbenzene (t-butyl or s-butyl)	6.2
13	7.88	C_4-alkylbenzene (t-butyl or s-butyl)	8.3
14	9.25	a methyl-2,3-dihydroindene	25.7
15	9.56	a methyl-2,3-dihydroindene	8.0
16[1]	10.49	1,6-dimethyldecalin	6.4
16a	10.83	a methyl-2,3-dihydroindene	
19	11.90	tetralin[2]	1.5
20	12.48	naphthalene[2]	20.3
22	13.68	benzothiophene	2.4
25	15.26	2-methylnaphthalene[2]	0.2
26	15.55	1-methylnaphthalene[2]	0.3
28	16.90	C_2-alkylnaphthalene	0.1
29	17.28	C_2-alkylnaphthalene	0.4
30	18.87	C_2-alkylnaphthalene	0.8
31	21.44	1,1-diphenylethane	0.1

[1] shoulder

[2] identity confirmed; all other identifications are tentative.

As was the case for the Aerotex sample, inadequate chromatographic separations and the unavailability of authentic isomeric standards precluded positive identifications in many cases. In addition, other peaks in Fig. 1 which are not shown in Table 2 either contained too little material for a good mass spectrum or they contained a mixture of substances such that identification could not be made; the use of capillary columns would have been helpful in the latter case.

The concentrations in water of the 4 compounds whose identities were confirmed were: naphthalene, 1.5 ppm; 1- and 2-methylnaphthalene, 15 ppb each; and tetralin, 100 ppb.

It is important to note that these compounds were present in water before the spray. That the compounds did not come from the first spray 7 days earlier is demonstrated by the observation that pre- and post-spray water samples contained the same components, with the exception of fenitrothion, at the same concentrations (the post-spray samples showed a fenitrothion peak which disappeared smoothly with time). It appears that there is simply not enough Aerotex 3470 sprayed to significantly alter the chromatogram. A sample calculation shows that, at a nominal spray rate of 1500 g/ha emulsion containing 2% Aerotex into a 1 m^2 x 0.3 m section of pond, and assuming thoroughly mixed conditions, there would be 10 ppb total Aerotex. If naphthalene were 20% of that, as indicated by Table 2, then there would be 2 ppb naphthalene added to the existing 1.5 ppm; the addition is insignificant.

Water samples taken from a nearby stream and the air samples confirmed these observations; the pre- and post-spray chromatograms are identical, with the exception of the fenitrothion peak in the post-spray samples.

The source of the compounds shown in Table 2 is therefore unclear. They could be present naturally in forested aquatic systems, or perhaps they are introduced from the atmosphere. The area as much as 50 km upwind is relatively uninhabited. Most of the compounds of Table 2 have, however, been identified in drinking water, lake and river water, effluent streams and contaminated wells (BURNHAM *et al*. 1972; GROB 1973; SHACKELFORD and KEITH 1976).

Relatively little work has been done on the toxicity of oil components to freshwater organisms; however, it has been claimed that the most toxic components of oil to marine organisms are the mono- and bicyclic aromatic hydrocarbons (NEFF and ANDERSON 1975). ANDERSON *et al*. (1973) showed that clams and oysters accumulated significant amounts of naphthalene, 1- and 2-methylnaphthalene, dimethylnaphthalenes and tetralin; depuration experiments showed that such compounds were also relatively readily excreted. With the exception of tetralin, these compounds were toxic to sheepshead minnows, brown shrimp and grass shrimp at concentrations between 0.08 and 5.1 ppm (ANDERSON et al. 1974). For both species of shrimp, the dimethylnapthalenes were shown to be the most toxic, with 24-hr LC_{50} values of 80 ppb for brown shrimp and 700 ppb for grass shrimp. Other LC_{50} values for these compounds were in the range 1 - 3 ppm.

Not all the components of Aerotex 3470 were even tentatively identified in the environmental samples, perhaps because they were present at too low a concentration. It is possible that some of these unidentified constituents are quite toxic to aquatic organisms. However, it is clear from these results that the potentially toxic naphthalene and 1- and 2-methylnaphthalenes did not originate from the spray formulation. Regardless of their origin, their presence is a matter of some concern and is a subject of continuing investigation on our part.

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