

PERSISTENCE STUDIES OF INSECTICIDES III. ACCUMULATION OF  
FENITROTHION AND ITS OXYGEN ANALOG IN FOLIAGE, SOIL AND  
WATER IN LAROSE FOREST

by

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## INTRODUCTION

Fenitrothion [O,O-dimethyl O-(4-nitro-m-tolyl) phosphorothioate], a broad spectrum organophosphorus insecticide, has been used extensively since 1969 in Canadian Forests for the control of spruce budworm, Choristoneura fumiferana (Clemens). It is usually applied as an aerial spray at economic dosages of 2 to 4 oz. A.I./acre to prevent severe defoliation by the budworm, without causing any noticeable environmental or ecological damage (Fettes 1968).

During the past 5 years, since fenitrothion came into general use as a replacement for DDT in controlling spruce budworm outbreaks in Canadian Forests, its fate and degradation in forest environments has been studied only sporadically and little is known regarding its persistence and accumulation in various components of the forest areas. Yule and Duffy (1972) studied its persistence on balsam fir [Abies balsamea (L.) Mill.] and mixed spruce (Picea spp.) foliage and soil samples collected from New Brunswick forests after an operational spray of the toxicant and found that 50 percent of the initial dosage was lost from the foliage in 4 days and nearly 80% within two weeks. Similar rapid decay was also observed in soil. The behaviour of fenitrothion in the Larose Forest environment, under operational conditions of insect control, was recently studied by Sundaram (1974) by residue analysis of water, soil and white spruce [Picea glauca (Moench) Voss] foliage. The data obtained so far demonstrated that from the point of view

of degradation rates and residue levels in the forest environment, the insecticide, unlike some of the persistent organochlorines, can be regarded as relatively safe and ecologically acceptable. Current studies (Yule 1974) show that contrary to the belief of rapid degradation of the toxicant, under normal operating dosages, e.g., 2 to 4 oz. A.I./acre, fenitrothion persisted and concentrated progressively in measurable amounts (0.02 to 0.80 ppm) in fir foliage collected from New Brunswick forests.

The work presented here is an intensive study on the persistence and accumulation of the insecticide in water, soil, and different coniferous foliage samples [white spruce, Picea glauca (Moench) Voss; red pine Pinus resinosa Ait; white pine, Pinus strobus L.] collected from Larose Forest following three consecutive years of application beginning in 1971. The primary objective is to provide more information on the persistence and accumulation of fenitrothion in forest environments to indicate any possible adverse effects and hazards attributable to its frequent use which may be more subtle and perhaps ultimately more significant, and to determine the need for further research on the toxicant in the physical environment.



#### MATERIALS AND METHODS

The spray plots T-1, T-2 and the control plot C used in the 1972 residue studies (Sundaram 1973, 1974) and an additional plot T-3, used in 1973 tests were selected in Larose Forest for the persistence studies of fenitrothion in soil, water, and foliage. Spray histories of the three plots and the emitted dosage of the insecticide (Table 1) are well documented for the spray period since 1971. Plot T-1 received 3 applications, one in each year, of 4 oz. A.I./acre of aqueous emulsion<sup>\*</sup> of fenitrothion since 1971; T-2 received a similar active ingredient dosage of fenitrothion oil-based formulation<sup>+</sup> in 1972 and 1973 spray season (mid-June). T-3 was sprayed in the middle of June 1973 with a single fenitrothion emulsion formulation similar to the one used in T-1. Samples for the present tests were taken in the third week of May just prior to the start of the 1974 spray program.

Foliage samples from each of the three species (white spruce, red pine and white pine) were collected by clipping branches

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\* Composition by weight percent: Arotex (density 0.94) 1, Atlox 3409 emulsifier (density 1.03) 1+, fenitrothion (tech., density 1.30) 10, rhodamine B indicator dye (tracer) 0.6 and water 87.

+ Composition by weight percent: Fenitrothion (tech.) 53, Arotex type solvents 46+, dye 0.3.

above the midcrown, using a pole pruner, from six randomly chosen trees to be truly representative of each plot. Each twig of the branch was carefully hand clipped and the foliage separated physically according to discrete yearly growth up to 3 years old<sup>\*</sup>. Each such sub-sample of a species in a plot was pooled and reduced by mixing and quartering to 100 g. The composite sample was machine (Hobart) chopped and 20 g duplicates were taken for residue analysis and moisture determination. A general cross-section sample of branches of the three species collected from each plot and processed similarly served as the mixed-age foliage sample (Table 2).

Soil sampling was carried out using a toothed auger to a depth of 6 inches. Six samples were collected randomly from each plot, pooled and processed according to the techniques described earlier (Sundaram 1974). Twenty-gram samples were used for the residue analysis.

Water samples (ca 1 liter) were collected from the ponds in each plot using Mason jars and were partitioned twice with toluene (2 x 200 ml) to extract fenitrothion residues into the toluene phase.

Extraction, clean-up and analysis of foliage, soil and water samples, using gas chromatography were as described by Sundaram (1974). The flame photometric detector (P mode 526 nm optical filter),

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\* Pine foliage sampling posed the problem of age classification due to its ill defined annual growth pattern. Annual rings and shoot growth served as indicators.

which responds with high specificity to phosphorus, was used. Background interferences were less than 0.001 ppm.

#### RESULTS AND DISCUSSION

The spray history of plots T-1, T-2 and T-3 from which the foliage, soil and water samples were taken for study of fenitrothion persistence is given in Table 1. Plots T-1 and T-3 were treated by aerial spray with fenitrothion emulsion (10%) applied at the rate of 4 oz. A.I./acre. Plot T-1 had this treatment for 3 consecutive years (1971, '72 and '73) and T-3 one application ('73) (Table 1). Plot T-2 had air-spray treatments of fenitrothion applied as an oil solution in 1972 and '73 at a nominal rate of 4 oz. A.I./acre. The plot T-1 received the highest total emitted dosage of 12 oz. A.I./acre for the 3 year period since 1971 whereas T-3 received a single application of only 4 oz. A.I./acre in 1973. The ratio of the total emitted dosage of fenitrothion in each plot, T-1, T-2 and T-3, for the 3 year spray program period beginning 1971 was 3:2:1.

Residue levels of fenitrothion found in the three species of foliage samples (as sampled) comprising single year age classes and mixed-age type, after a three year spray program, one in each year since 1971, are given in Table 2 for each plot. Foliages of white spruce, red pine and white pine contained very low but measurable amounts of fenitrothion (>0.001 ppm) up to 3 year period. The variation of the residue levels among the species studied was not significant. The average insecticide content of the three foliar species according to the number



TABLE 1

SPRAY HISTORY OF PLOTS IN LAROSE FOREST SELECTED FOR SAMPLING

SAMPLING PLOTS	FENITROTHION APPLIED (OZ. A.I./ACRE)	FORMULATION	YEARS APPLIED	NO. OF APPLICATIONS	TOTAL EMITTED * DOSAGE (OZ. A.I./ACRE)
T-1	4	WATER EMULSION	1971, 1972, 1973	3	12
T-2	4	OIL-BASED	1972, 1973	2	8
T-3	4	WATER EMULSION	1973	1	4

\* Under satisfactory meteorological conditions about 25-40% of the active material emitted from aircraft might be expected to be deposited (see Armstrong, J.A. 1973. Forest meteorology and insecticide drift and deposit. Program Review 1973, Chem. Cont. Res. Inst. 12-14; Capizzi, J. and J.M. Witt, Pesticides, Pest Control and Safety on Forest and Range Lands, Proceedings for Pesticide Applicators 1971, Oregon State University and USFS, page 207).



TABLE 2

FENITROTHION RESIDUES <sup>++</sup> FOUND IN WHITE SPRUCE, RED PINE AND WHITE PINE FOLIAGE SAMPLES  
 COLLECTED ON MAY 22, 1974 FROM LAROSE FOREST <sup>++</sup>

PLOTS	WHITE SPRUCE				RED PINE				WHITE PINE			
	FENITROTHION CONTENT (ppm)				FENITROTHION CONTENT (ppm)				FENITROTHION CONTENT (ppm)			
	YEARS AFTER FIRST APPLICATION			MIXED-AGE FOLIAGE SAMPLE	YEARS AFTER FIRST APPLICATION			MIXED-AGE FOLIAGE SAMPLE	YEARS AFTER FIRST APPLICATION			MIXED-AGE FOLIAGE SAMPLE
	3	2	1		3	2	1		3	2	1	
T-1	0.005	0.005	0.003	0.005	0.005	0.008	0.005	0.007	0.011	0.007	N.D.	0.008
T-2		0.014	0.014	0.009		0.011	0.009	0.015				
T-3			0.011	0.006							N.D.	T
AVERAGE FENITROTHION CONTENT (ppm)	0.005	0.010	0.009	0.007	0.005	0.010	0.007	0.011	0.011	0.007	-	0.004

\* Fenitrothion concentration is expressed in ppm of fresh weight of foliage. The average moisture content of the foliage samples was:  
 White Spruce 47%, Red Pine 50%, White Pine 53%

+ Fenitrothion was not found in any of the foliage samples.

N.D. = Not Detectable

T = Traces (<0.001 ppm)

++ Samples from the control plot C did not contain measurable amounts (>0.001 ppm) of Fenitrothion residues, therefore are not recorded.

TABLE 3

FENITROTHION RESIDUES IN SOIL AND WATER SAMPLES\* COLLECTED FROM LAROSE FOREST ON MAY 22, 1974

PLOTS	WATER				SOIL			
	pH	t <sup>o</sup> C	Fenitrothion (ppm)	Fenitrooxon (ppm)	pH	Moisture Content (%)	Fenitrothion (ppm)	Fenitrooxon (ppm)
T-1	6.3	15.7	T	T	5.0	36	N.D.	N.D.
T-2	6.7	16.4	T	N.D.	5.3	24	0.003	N.D.
T-3	6.5	15.2	0.001	N.D.	4.3	39	N.D.	N.D.

\* Sample size: Water 900 ml; soil 20g.

T = Traces (<0.001 ppm)

N.D. = Not Detected

Water and soil samples from the control plot did not contain any detectable fenitrothion residues.

of years sprayed was:

I year	0.005 ppm
II year	0.009 ppm
III year	0.007 ppm

The maximum average level of accumulation of fenitrothion (ca 0.010 ppm) in fresh conifer foliage samples was found to be in the second year. The data recorded in Table 2, although partly lend support to previously reported findings of Yule (1974) of fenitrothion accumulation in conifer foliage, they did not confirm either of the toxicant's foliar concentration level or its increased accumulation in proportion to number of years sprayed as observed in the New Brunswick forests. The accumulation level of the insecticide in fresh foliage at Larose was nearly one hundred times less than the one observed in N.B. forests. Insecticide persistence and its aftermath accumulation are variable and complex properties and are influenced by various environmental (physical and metabolic) factors. They depend particularly on the insecticide dosage, formulation, mode of application, substrate type and growth, rain, temperature, light, humidity, air movement, and various metabolic (enzymic and microbial) and physicochemical processes (Westlake and San Antonio 1960, Linskens et al 1965, Gould 1966). Consequently such a direct comparison of fenitrothion accumulation for two dissimilar locations was neither possible nor valid and it would be unwise to extrapolate unless more information on residue levels is available.



The exact route by which fenitrothion dissipates from the conifer foliage has only been studied sparsely and is still obscure. The effective mechanism, as pointed out earlier (Yule and Duffy 1972, Sundaram 1974), seems to involve physicochemical factors (primarily climatic parameters) such as hydrolysis, photodegradation, volatilization, temperature, weathering action of humidity, rain and wind rather than metabolic factors. The traces of persistent fenitrothion molecules, being lipophilic were probably absorbed, transported and stored in cuticular waxes<sup>\*</sup> of the conifer foliage resisting leaching, volatilization, photo and biodegradations.

The wax pattern on the conifer foliage changes according to the tree species, their growing conditions and to the age of the foliage (Linskens et al 1965) thus accounting for the variations of residue concentrations observed within the three species studied and the time interval after applications.

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\* Plant waxes, in addition to hydrocarbons, consists of polar components like free alcohols, unsaturated ketones, long-chain aldehydes and glycerol compounds. The cuticle consists of cellulose membrane on top, followed by pectic and cutin layers, the last being loaded with waxy materials. Permeability for fenitrothion is probably through cuticular pores on the foliage, the lipid nature of the cuticle enabling the passage of the polar toxicant molecules to the cutin layer for storage (intracuticular or subcuticular residue) thus resisting ready dissipation by physical and metabolic processes (Linskens et al 1965).



Fenitrothion residues found in soil and water samples collected from Larose Forest are recorded in Table 3. No measurable amounts of fenitrothion and its oxon metabolite were found in soil samples collected from plots T-1 and T-3. Plot T-2 contained small but detectable amount (0.003ppm) of the parent material which most likely reached the forest by foliar leaching during rain and litter fall of needles and twigs. The absence of noticeable residue levels of the toxicant in soil samples was, as pointed out earlier (Sundaram, 1974), due to the rapid chemical and microbial decompositions catalyzed by surface active soil particles, inorganic ions and pH conditions indigenous to the soils and to a lesser extent by various processes mentioned earlier.

No detectable amounts of fenitrothion and its oxygen analog were found in water samples from plots T-1 and T-2. Samples from T-3 contained negligible amounts (0.001 ppm) of the insecticide, the presence and dissipation of which could be accounted for as discussed in soils.

In conclusion, the residue data obtained so far from Larose Forest demonstrated that the fenitrothion insecticide sprayed for insect control, appear to have persisted and accumulated in the foliage of three coniferous trees to small but detectable amounts (0.010 ppm) over a three year period with repeated annual applications at the operational dose (4 oz./A.I./acre) levels. No insecticide build-up was found in

forest soil and surface water samples. Considering the residue levels in the forest environment, fenitrothion still can be regarded as a relatively safe organophosphate insecticide. Increased and prolonged use of this compound would probably warrant the need for a more intensive study of its metabolism and residues in various components of the forest environments to understand fully its ecological implications and its overall impact on the ecosystem.

#### SUMMARY

The residual accumulation of fenitrothion and its oxygen analog was studied in three species of conifer foliage, soil and water samples collected from a forest environment after an operational spray program (4 oz. A.I./acre) comprising three applications, one in each year since 1971. The results indicated that the insecticide persisted and accumulated in foliage to insignificant amounts (ca 0.010 ppm); no build-up was found in forest soils and surface waters. A critical appraisal of the residue concentrations showed that the insecticide would be considered as relatively safe for use in forest insect control and the slight accumulations observed should cause no alarm.

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REFERENCES

- Fettes, J.J. 1968. Chemical control of forest insects by aircraft. Pulp and Paper Mag. of Canada 69(18):90.
- Gould, R.F. 1966. Organic Pesticides in the Environment. Adv. Chem. Series 60, Am. Chem. Soc. Washington, D.C.
- Linskens, H.F., W. Heinen, and A.L. Stoffers. 1965. Cuticula of leaves and the residue problem. Residue Reviews 8: 136-178.
- Sundaram, K.M.S. 1973. Degradation dynamics of fenitrothion insecticide in aquatic environments associated with forest spraying. Proc. Chem. Inst. Canada Water Quality Parameters Symposium, Burlington, Nov. 19-21, 28 pp.
- Sundaram, K.M.S. 1974. Distribution and persistence of fenitrothion residues in foliage, soil and water in Larose Forest. Environ. Canada Forestry Serv. Inf. Report CC-X-64, 43 pp.
- Westlake, W.E. and J.P. San Antonio. 1960. Symp. Nature Fate Chemicals Appl. Soils, Plants, Animals, 105-115 pp.
- Yule, W.N. and J.R. Duffy. 1972. The persistence and fate of fenitrothion insecticide in a forest environment. Bull. Env. Contam. Toxicol. 8(1):10.
- Yule, W.N. 1974. The persistence and fate of fenitrothion insecticide in a forest environment II. Accumulation of residues in balsam fir foliage. Ibid., (in press).

Appendix

Gas chromatographic characteristics of fenitrothion and fenitrooxon are recorded in the following pages for the foliage, soil and water extracts analysed, and the primary standards used in calibrating the GC instrument.



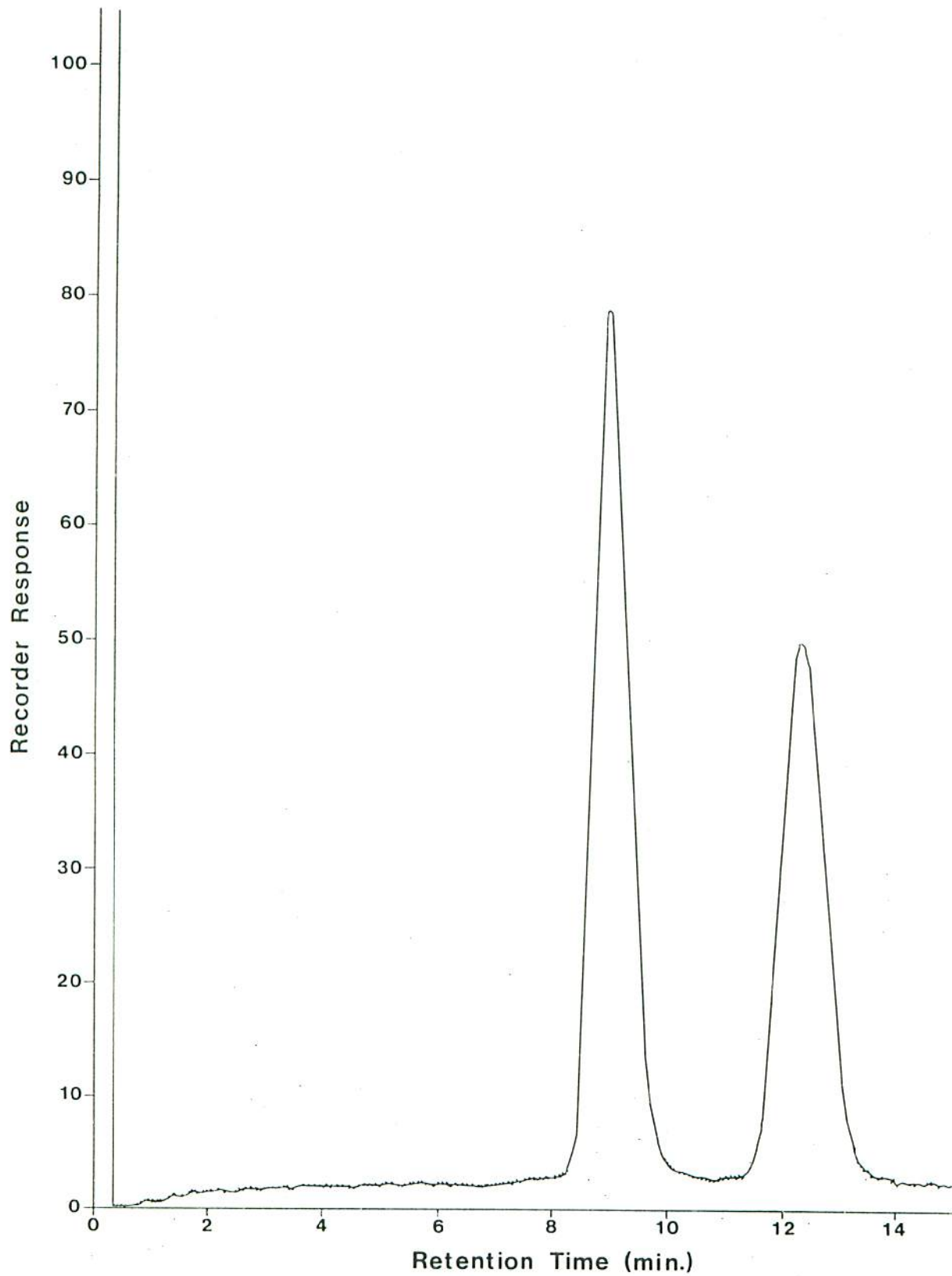


Fig. 1. Gas chromatogram of fenitrooxon (20 ng) and fenitrothion (12 ng) in benzene (for GC conditions see Sundaram 1974).

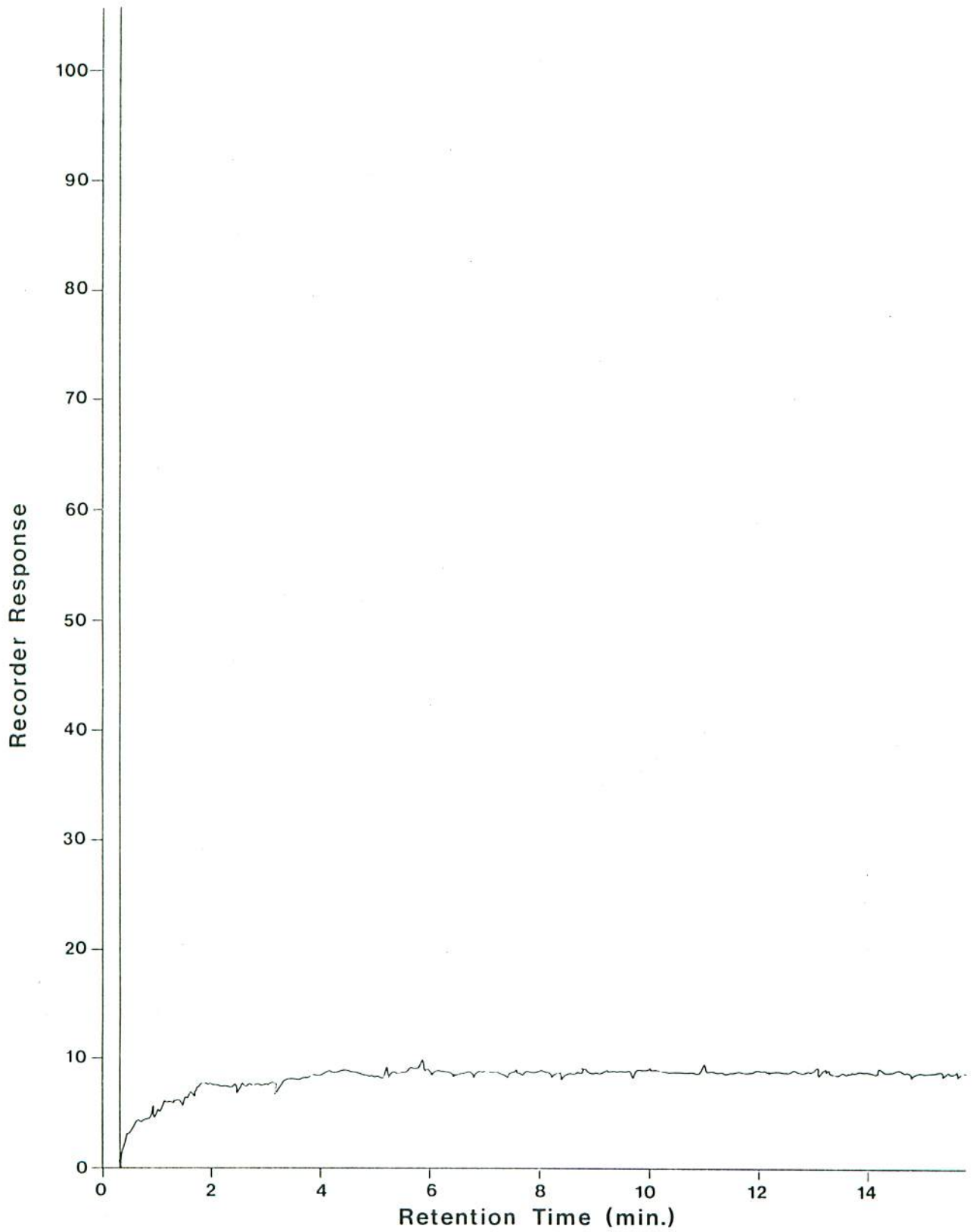


Fig. 2. Gas chromatogram of an extract of untreated conifer foliage (mixed-age).

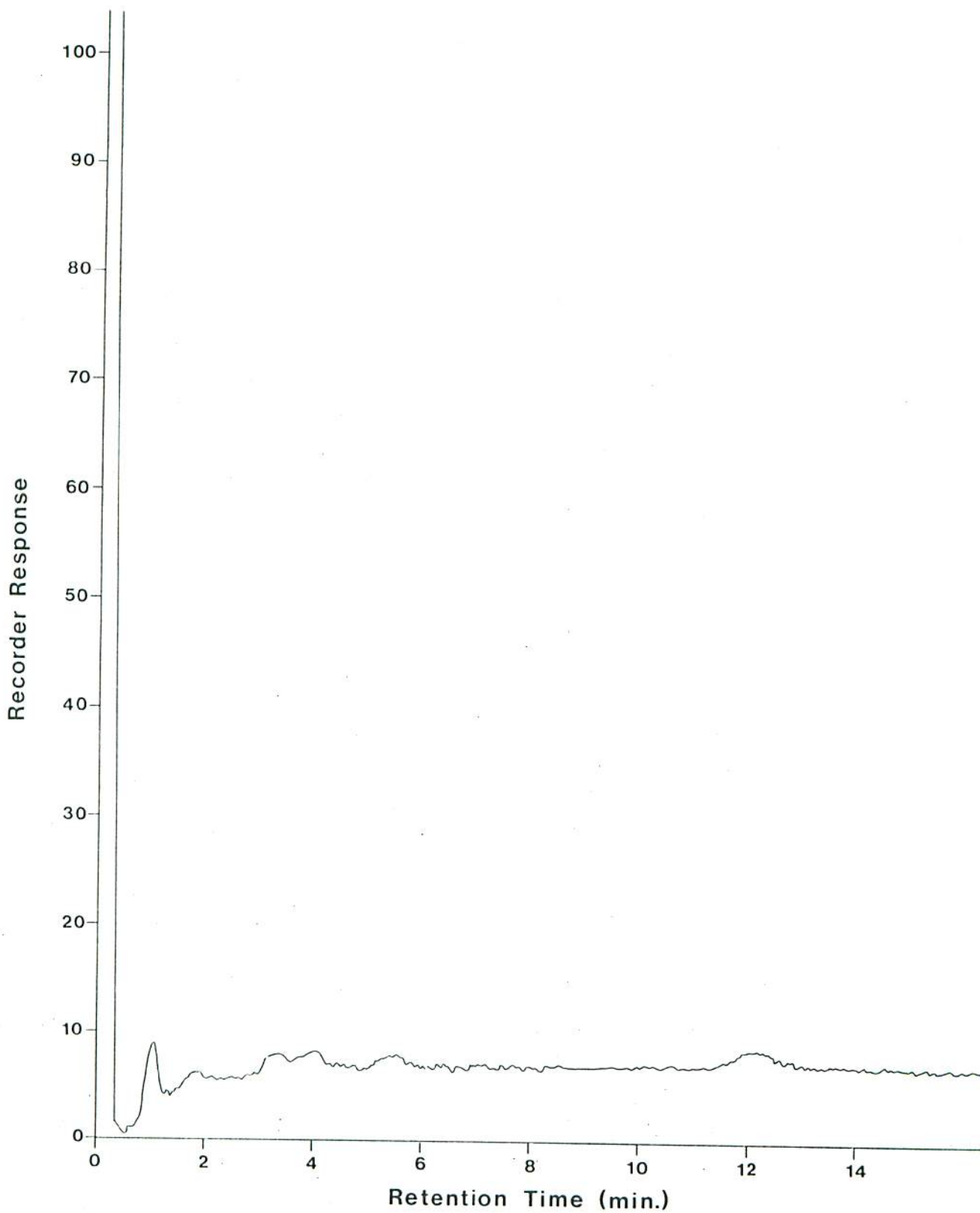


Fig. 3. Gas chromatogram of white spruce (mixed-age) foliage exposed to fenitrothion application (Plot T-1).

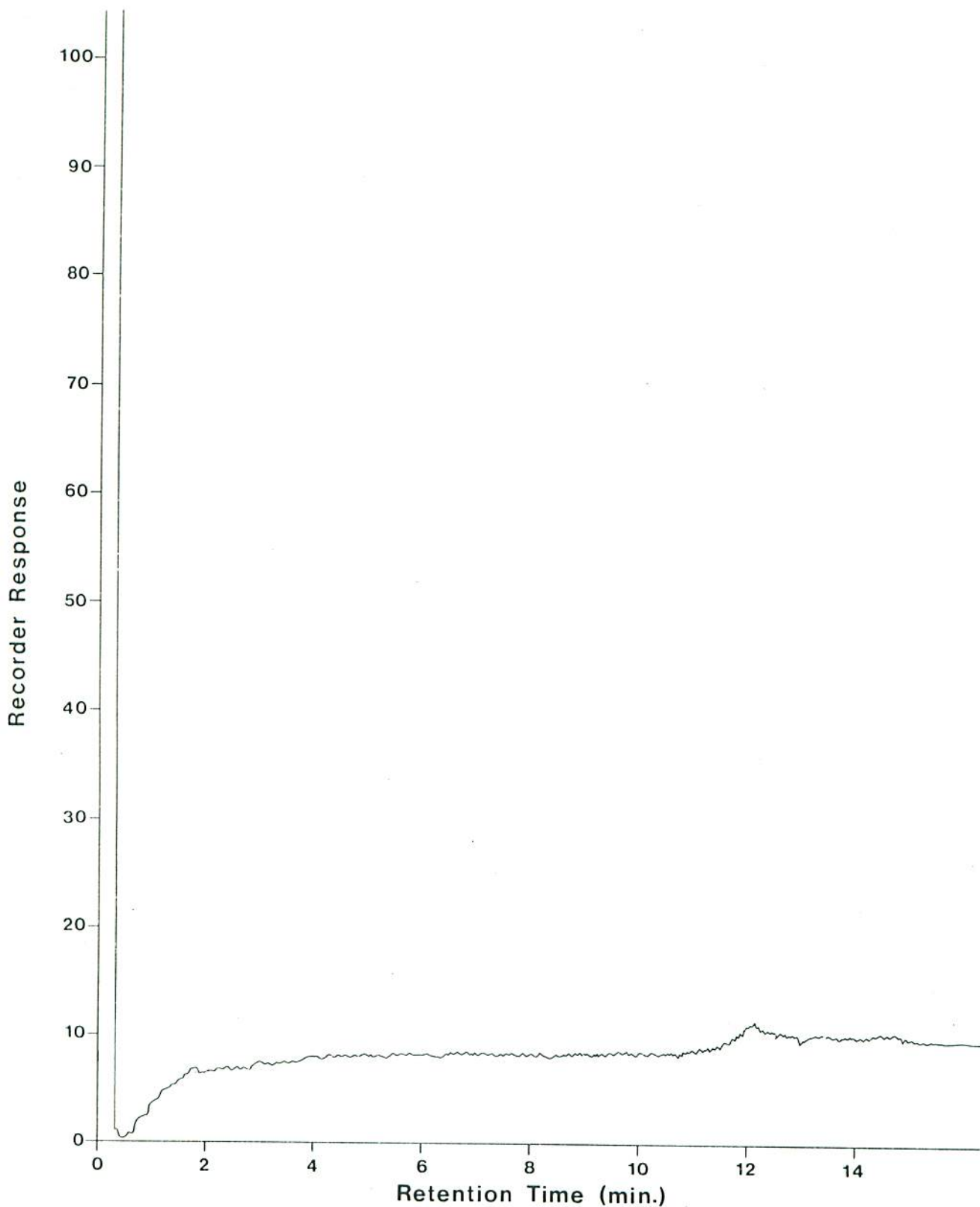


Fig. 4. Gas chromatogram of red pine foliage (mixed-age) collected from fenitrothion treated area (Plot T-1).



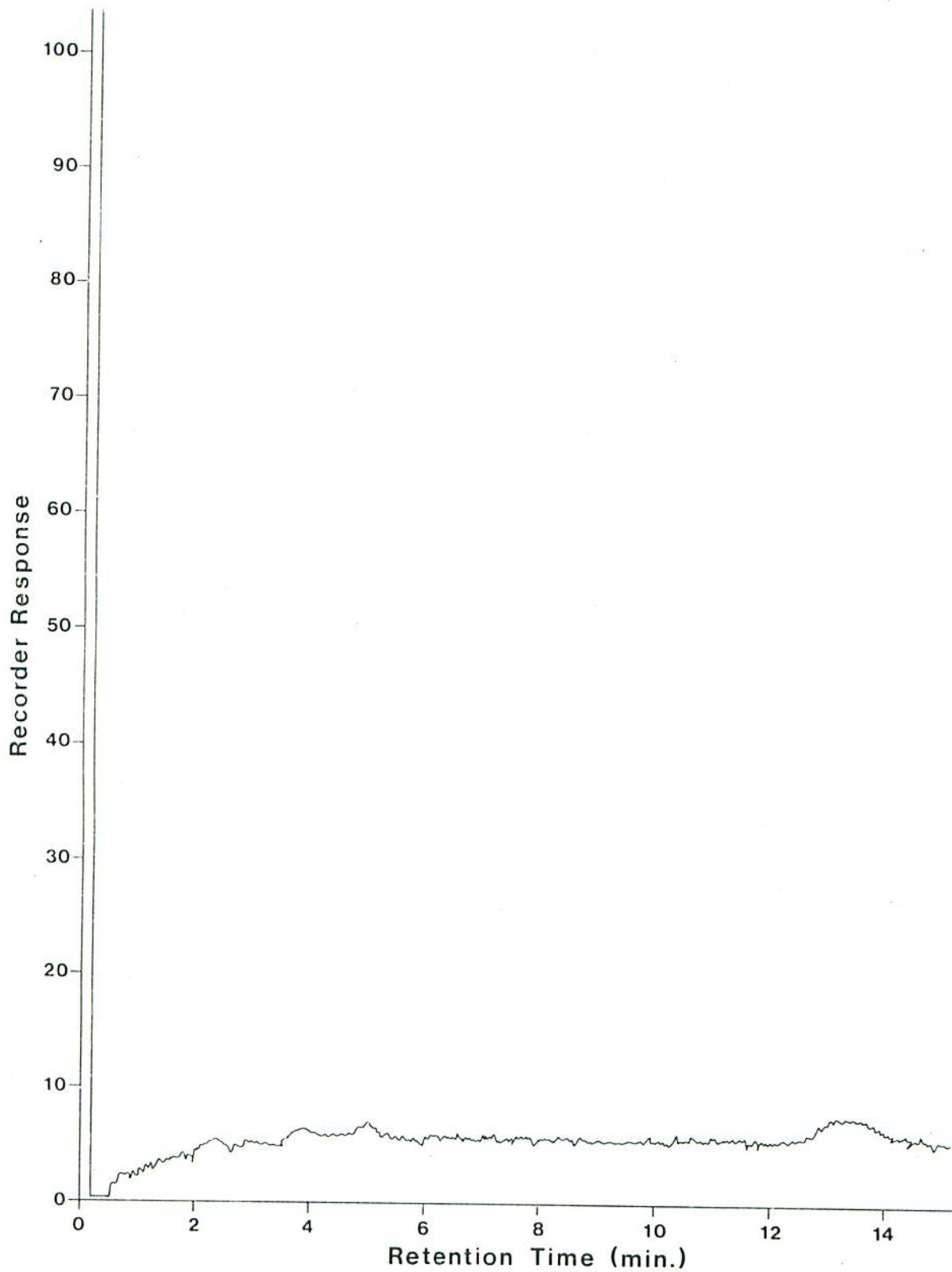


Fig. 5. Gas chromatogram of white pine foliage (mixed-age) collected from fenitrothion sprayed area (Plot T-1).

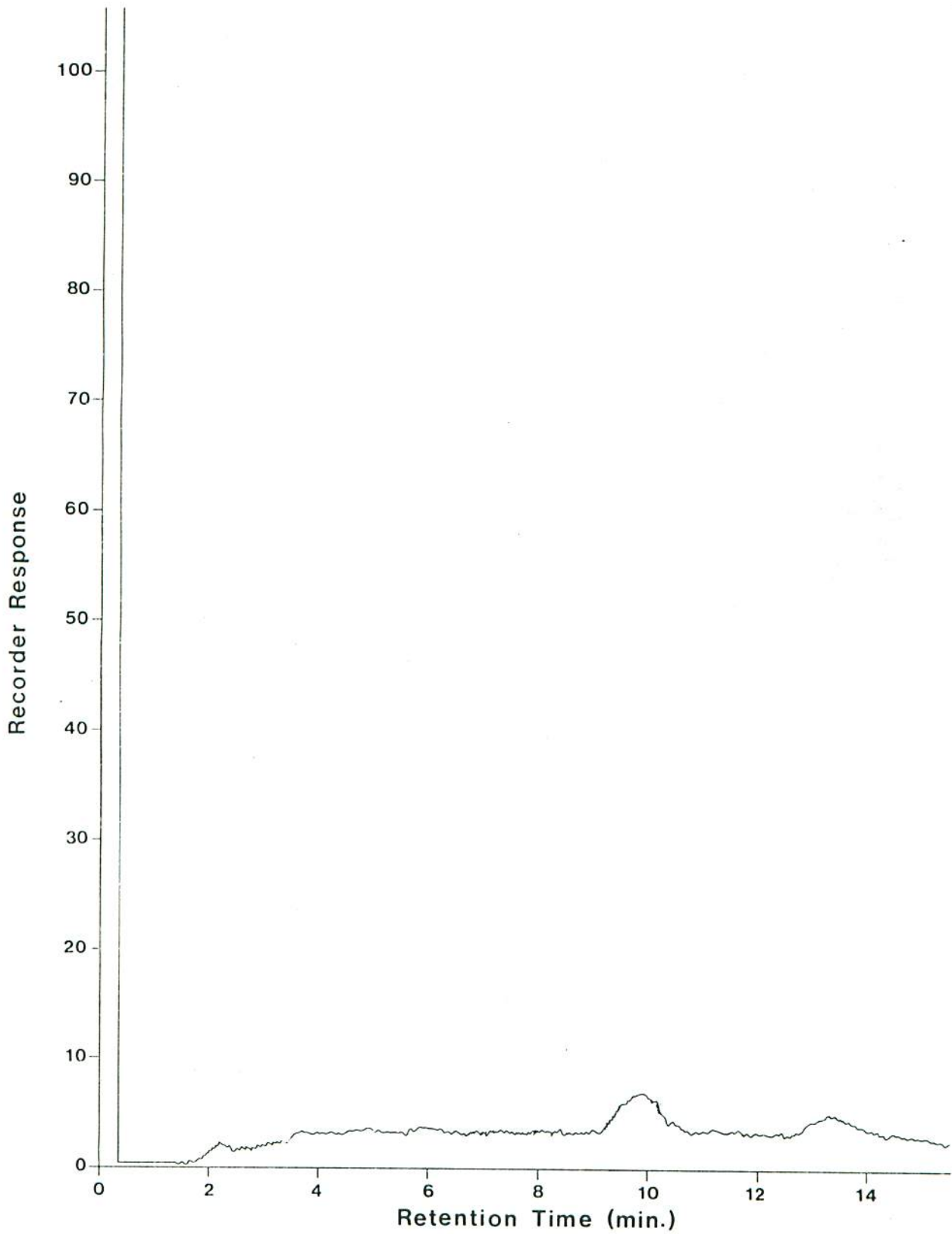


Fig. 6. Gas chromatogram of water samples (pond) collected from Plot T-1.

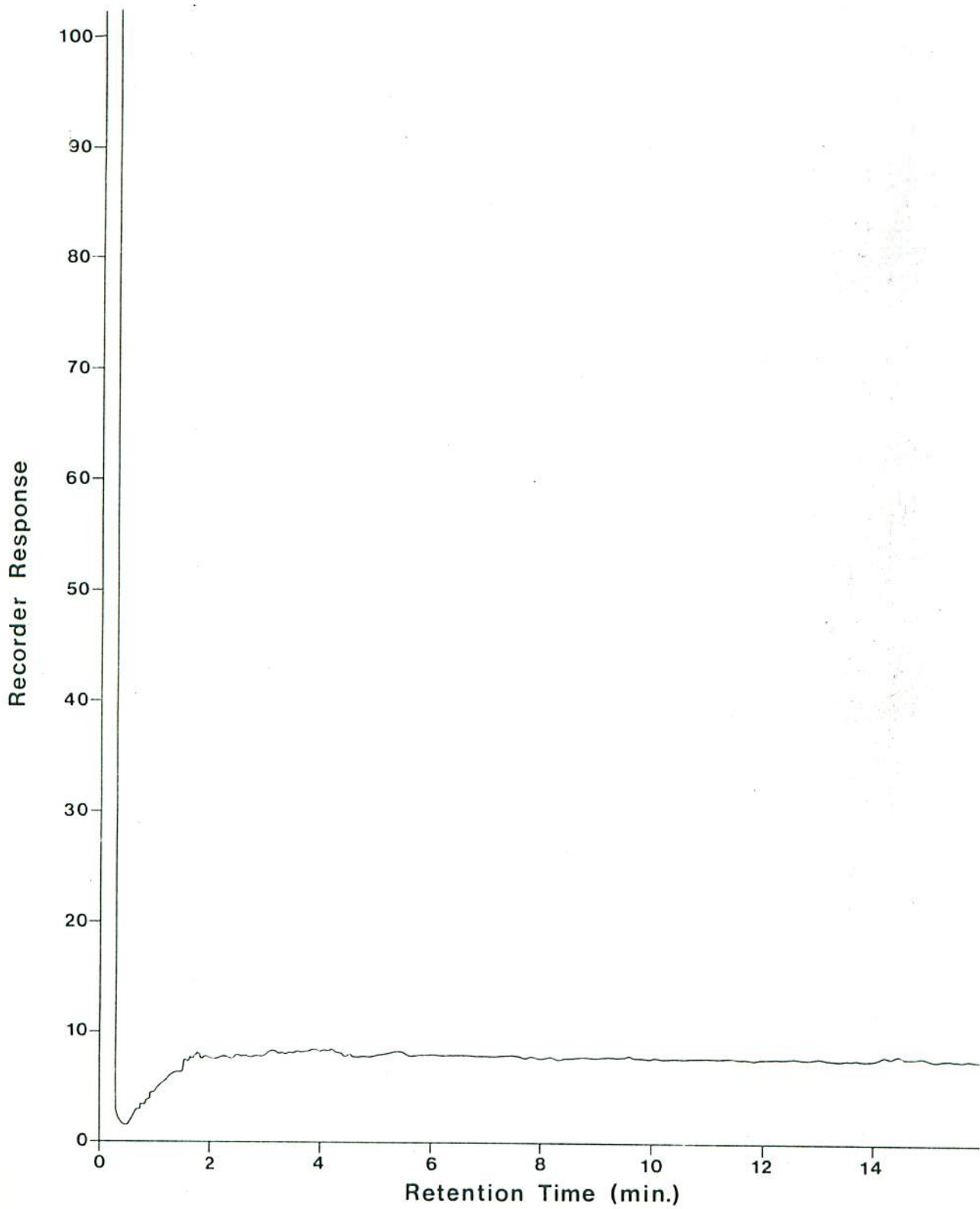


Fig. 7. Gas chromatogram of soil sample collected from Plot T-1.