CCRI File Report 2

DISTRIBUTION AND PERSISTENCE OF FENITROTHION RESIDUES IN FOLIAGE, SOIL AND WATER IN LAROSE FOREST

By

K. M. S. Sundaram

Chemical Control Research Institute,

Canadian Forestry Service, Environment Canada,

25 Pickering Place, Ottawa, Ont., K1A 0W3.

File Report No. 2

April 1974

TABLE OF CONTENTS

DISTRIBUTION AND PERSISTENCE OF FENITROTHION RESIDUES IN FOLIAGE, SOIL AND WATER IN LAROSE FOREST

By

K. M. S. Sundaram

Chemical Control Research Institute,

Canadian Forestry Service, Environment Canada,

25 Pickering Place, Ottawa, Ont., K1A 0W3.

INTRODUCTION

Organophosphorus insecticides are becoming increasingly important for the control of insect pests in Canadian forest spray programs. Fenitrothion (O, O-dimethyl O-(4-nitro-m-tolyl) phosphorothioate) has been used since 1969 in place of DDT for operational control of spruce budworm (Choristoneura fumiferana Clemens) without causing any gross damage to the forest flora and fauna (Fettes 1968). Yule and Duffy (1972) observed that when the insecticide was applied aerially in New Brunswick forests at the rate of 2 oz/acre, it disappeared rapidly from mixed spruce foliage with a half life of ca 4.5 days but persisted in trace amounts up to a year whereas in soil it disappeared within 32 days.

So far no information is available on the distribution and persistence of the compound in aquatic environments of forest areas. This report summarizes an operational experiment carried out in Larose Forest to study the persistence of aerially applied fenitrothion and its metabolites (the oxon analogue and 4-nitrocresol) in white spruce foliage, soil and water samples collected from sprayed areas.

MATERIALS AND METHODS

Samples

Forest soil, foliage of white spruce [*Picea glauca* (Moench) Voss] and water samples were collected by Dr. C.H. Buckner and Mr. B. McLeod of this Institue from four plots at Larose Forest (Fig. 10), designated as Bee Range (BR), T-1, T-2 and Control (C), and supplied by them for the present investigation.

Foliage and soil samples (*ca* 4 inch depth) were taken from more than one location in each plot and pooled for extraction. In addition, foliage samples from apical, central and basal crowns of spruce trees from the T-1 plot were analysed to study the distribution pattern of fenitrothion residues. Water samples were collected in Mason jars containing screw caps and aluminum foil covers from the four sampling sites, BR (BR-1, pond; BR-2, stream), T-1 (pond), T-2 (pooled samples from three ponds) and C (pond). All the samples were transported immediately to the chemical laboratory

for analysis. Temperature and pH were recorded for each water sample at the site of collection. Prespray samples were taken from all the sampling locations a day before the spray.

Extraction Procedure

Water

In the laboratory, water samples from each sampling site were filtered through a 1-micron porosity sintered glass filter. Aliquots of water (500 ml) were extracted thrice by vigorously shaking for 9 minutes with an equal volume of chemically pure ether in s separatory funnel. After equilibration, the ether fraction was collected quantitatively and combined. The combined extracts were then dried by passing through a 15 g (5 cm) column of anhydrous sodium sulphate, flashed to a small volume and diluted to 0.50 or 1.00 ml with benzene. The fenitrothion was then estimated by GLC without further cleanup.

Diethyl ether was used for solvent partition, although petroleum ether (b.p. 30-60^{o}C), hexane, benzene and chloroform were tried initially and rejected since both the aqueous and nonaqueous phases became strongly emulsified and the separation of phases were not distinct. Partition p-values (fractional amount of the total solute found in the organic phase of an equivolume solvent pair) of Beroza et al (1969) were determined (Table 1) and the values obtained confirmed that the diethyl ether was a suitable solvent for performing this operation.

Table 1

Partition p-values of Fenitrothion at 26.5± 1°C.

Solvent	p-values (%)*
Hexane	94
Pet. ether	93
Chloroform	99
Benzene	98
Diethyl ether	96

* Average of 3 determinations

Foliage

Foliage samples were received in sealed plastic containers and stored in cold room at -10°C until analysis. Samples were defoliated by clipping of twigs with pruners and chopped by grinding machine (Hobart, 84142) into tiny pieces. They were then mixed thoroughly and sub-sampled for chemical analysis and for moisture determination. Moisture was determined by drying, two 10g replicates of each sample at 105°C for 16 hours in a thermostatic oven (AOAC 1955). For residue determination, the method developed by Yule and Duffy (1972) has been used. Two 100g of each composite sample were weighed and extracted with 200 ml of ethyl acetate in a Sorvall-Omini-Mixer (10 min., speed setting 7). The slurry was filtered through a one-inch pad of anhydrous sodium sulphate (ca 50g) into a 500 ml Erlenmeyer flask and flashed to 50 ml. Ten ml of the residue was dissolved in 50 ml of acetonitrile and partioned twice with 25 ml of hexane. The nonpolar layers were discarded and the polar one was flashed to 20 ml, placed on an activated charcoal (6g) - preconditioned Celite 545 (4g) column (i.d. 18 mm) topped with 7g $Na_2 SO_4$ and eluted with 100 ml of 25% benzene in ethyl acetate followed by 100 ml of benzene. The eluate was then flashed to a small volume.

The parent compound and its metabolites (fenitrooxon and 4-nitrocresol) were separated by using a silica gel column (i.d. 12 mm) (Yule and Duffy 1972, Bowman and Beroza 1969) containing 20g of preconditioned silica gel (5% water), sandwiched between 10g of $Na_2 SO_4$ and eluted selectively, first with 60 ml of benzene to give the parent fenitrothion, followed by 120 ml of benzene to yield the 4-nitrocresol and finally with 75 ml of acetone to remove the fenitrooxon.

Soil

Soil samples were received from Larose Forest in plastic bags and stored in cold room (-10°C) until analysis. The sample was thawed, large stones and debris were removed by sifting and mixed thoroughly by hand. A composite sample of approximately 250g was sieved (No. 8 mesh, 2.38 mm opening) and 100g of this soil was used for residue analysis. The extraction, cleanup and isolation methods used, were similar to those of Yule and Duffy (1972). Two 10g aliquots of the soil were used for moisture (AOAC 1955) and pH (Atkinson et al 1958) determinations.

Gas chromatographic analysis

Gas chromatographic analysis of fenitrothion and its metabolites in the foliage, soil and water samples, after complete cleanup and separation, were carried out using a Hewlett-Packard F & M model 810 gas chromatograph equipped with a Tracor flame photometric detector. This specific P or S detector also permitted discriminative and confirmative identification and measurement of the parent and oxon materials.

Operating conditions:

Columns: glass, 4 ft. x 0.25 in.
loadings: (1) 5% OV1; (2) 3.8% SE30; on Chromosorb W, 60/80 mesh, AW-DMCS

Temperatures (°C):		
	injection ports	200
	column oven	185
	transfer line	190
	detector	160

Gas flow (ml./min):	N_2	60
	H_2	150
	O_2	20
	air	50
FPD filters (mu):	P	526
	S	394

Soil and foliage fractions containing the cresol were analysed (Bowman and Beroza 1969) with a Hewlett-Packard Model 5750 gas chromatograph fitted with a 63 Ni electron capture detector. Operating parameters were as follows:

Column: 180 cm. x 4 mm Pyrex glass packed with 20% (W/W) OV-101 on 80-100 mesh Gas Chrom Q preconditioned overnight at 280°C.

Temperatures (°C):	injection ports	210-220
	column oven	190
	detector	280

Carrier gas: argon/methane (95/5%) pressure of 50 psi and flow rate of 50 ml/min.

Instrument settings: Attenuation and range, 16 x 10; pulse rate 50; electrometer 4×10^9 amp. full scale with 1 mv recorder.

The gas chromatographs were standardized on the same day as the samples were analyzed by injecting aliquots (1-5 µl) of

freshly prepared standard solutions of fenitrothion, fenitrooxon and 4-nitrocresol (analytical grades supplied by Sumitomo Chemical Company of Japan), measuring the peak heights, and preparing a calibration curve by plotting peak heights vs concentrations. Quantitative results of the extracted samples were obtained by measuring each of the peak height after injection (2 µl), under the same operating conditions, and reading off the concentration from its calibration curve.

To determine the efficiency of the methods and the overall recoveries of fenitrothion, its oxygen analogue and the nitrocresol, soil, foliage and water samples from the control plot C were fortified with known amounts, extracted immediately through the described procedures and analysed for the concentration of the three compounds by GC. The final recoveries averaged close to 90 percent.

All organic solvents used were either pesticide grade chemicals or freshly distilled in glass. The anhydrous sodium sulphate used was of reagent grade, heated at 150°C overnight and stored in a glass-stoppered bottle.

Laboratory sources (chemicals, glassware, filterpapers, adsorbents etc.) of contamination were found to be minimum.

RESULTS

Fenitrothion content in natural waters collected from the five sampling sites (BR-1, BR-2, T-1, T-2 and C) in Larose Forest

along with their pH and temperature are recorded in Table 2. The insecticide and its oxygen analogue found in spruce foliage collected from T-1 at various longitudinal parts of the tree canopy, together with pooled foliage and control samples are listed in Table 3. Tables 4 and 5 contain similar data for pooled foliage samples from plots T-2 and Bee Range. Moisture content, pH and fenitrothion residues in the soil samples are summarized in Table 6 for plots T-1 and C. Similar data are presented in Table 7 for pooled soil samples from the plots T-2, BR and C.

All samples were collected from various plots at ca 9 a.m. on the collection day to minimize possible errors that may arise in the final evaluation of the concentration of fenitrothion, so that meaningful comparisons could be made. Water, foliage and soil samples from plot C (control) and prespray samples from T-1 (except foliage), T-2 and BR gave negative results for the insecticide residues. A very small amount ($\leq$ 0.010 ppm) of "apparent" fenitrothion was found in the prespray foliage samples from plot T-1 (Table 3). Insecticide concentrations below 0.03 ppb in water samples and concentrations below 0.005 ppm in foliage and soil samples were considered as insignificant and recorded as traces due to the analytical sensitivity of the GC instrument used. Concentrations of the insecticide in water is expressed in ppb (10^{-9}) and for foliage and soil in units of ppm (10^{-6}) "oven dry" mass.

A plot of per cent residual insecticide vs time (t) (days), showing the hydrolytic pattern of fenitrothion, is shown in Fig. 1. Plots T-1 and T-2 showed the exponential but uniform decrease of concentration of the insecticide whereas the samples from BR-1 and BR-2 showed occasional peakings. Figures 2 and 3 show the concentration variations of fenitrothion in water samples collected from the four sampling sites and their correlations with rainfall during the period (June, July 1972) of this investigation. Figure 2 represents the concentration-rainfall correlations for the samples from BR-1 and BR-2 whereas the Fig. 3 shows the same for T-1 and T-2. The rate of loss of fenitrothion residues in foliage from different parts of the tree canopy are represented in Fig. 4, similar data for the pooled samples from the sites T-1, T-2 and BR are given in Fig. 5. Figure 6 shows the residual foliar concentrations of the insecticide-rainfall correlations for the pooled samples from the sites T-1, T-2 and BR. The rate of loss of fenitrothion in soil samples from T-1, T-2 and BR is shown in Figs. 7 and 8 and the corresponding concentration-rainfall correlations are given in Fig. 9.

Table 2

Fenitrothion Content in Natural Water from Various Sampling Sites

Time Relative to Application (Days)	BR-1 t°C	pH	Concentration (ppb)	BR-2 t°C	pH	Concentration (ppb)	T-1 t°C	pH	Concentration (ppb)	T-2 t°C	pH	Concentration (ppb)	Control t°C	pH	Concentration (ppb)
-1*	12.4	7.20	N.D.	16.5	7.10	N.D.	19.2	7.10	N.D.	16.0	7.01	N.D.	14.5	6.95	N.D.
0	12.2	7.10	9.00	16.7	7.05	4.60	19.0	7.28	25.50	-	-	-	15.2	7.12	N.D.
0.5	12.8	7.30	5.60	17.8	7.00	6.70	19.4	7.31	19.00	15.6	7.07	24.00	16.0	6.90	N.D.
1	12.2	7.30	4.30	16.7	6.90	4.30	-	-	-	16.9	7.01	23.50	16.7	6.82	N.D.
2	12.2	7.28	6.50	15.7	7.09	2.60	-	-	-	13.2	7.24	15.30	15.2	7.22	N.D.
3	-	-	-	-	-	-	19.1	6.92	2.10	-	-	-	18.2	7.11	N.D.
4	7.8	7.31	0.50	12.8	7.09	3.80	-	-	-	11.7	7.00	7.77	-	-	-
6	-	-	-	-	-	-	20.0	6.82	0.10	-	-	-	-	-	-
9	13.6	7.35	0.40	20.6	7.53	1.10	-	-	-	20.4	7.20	2.43	14.4	7.35	N.D.
10	-	-	-	-	-	-	18.9	6.99	0.07	-	-	-	-	-	-
20	-	-	-	-	-	-	18.9	7.16	0.03	-	-	-	16.9	7.20	N.D.
21	14.4	6.68	0.30	17.8	6.37	0.03	-	-	-	16.7	6.82	1.17	14.4	7.30	N.D.
27	-	-	-	-	-	-	-	-	-	17.2	6.56	0.73	-	-	-
40	17.2	6.00	T	20.0	5.85	N.D.	26.7	6.69	T	19.6	6.38	T	17.5	7.33	N.D.

* Prespray samples

T=Traces (< 0.03 ppb)

N.D.=Not detected

Table 3

Fenitrothion Residues in Foliage from Plot T-1[+]

Time Relative to Application (Days)	Lower			Middle			Upper			Pooled			Control**		
	Moisture Content %	Fen	Fenox	Moisture Content %	Fen	Fenox	Moisture Content %	Fen	Fenox	Moisture Content %	Fen	Fenox	Moisture Content %	Fen	Fenox
-1*	58	T	N.D.	62	N.D.	N.D.	55	N.D.	N.D.	65	0.010	N.D.	62	T	N.D.
0	58	0.595	N.D.	61	2.770	N.D.	59	3.540	N.D.	67	3.470	N.D.	58	T	N.D.
0.5	62	0.350	N.D.	59	2.050	N.D.	61	2.990	N.D.	62	0.835	N.D.	65	N.D.	N.D.
3	60	0.225	T	62	1.155	T	63	1.750	T	68	0.750	0.050	67	N.D.	N.D.
6	62	0.105	N.D.	61	0.359	T	66	0.177	N.D.	64	0.370	0.010	61	N.D.	N.D.
10	60	0.115	N.D.	65	0.200	0.045	64	0.170	T	62	0.230	T	57	N.D.	N.D.
15	65	0.110	T	61	0.140	0.030	62	0.110	T	59	0.250	N.D.	51	N.D.	N.D.
30	57	0.060	T	57	0.040	T	57	0.040	N.D.	55	0.085	T	58	N.D.	N.D.
45	57	0.050	T	54	0.045	N.D.	59	0.025	N.D.	57	0.060	N.D.	60	N.D.	N.D.
90	48	0.040	N.D.	52	0.030	N.D.	54	0.020	N.D.	53	0.035	N.D.	61	N.D.	N.D.
155	50	0.005	N.D.	50	0.005	N.D.	54	T	N.D.	51	0.005	N.D.	63	N.D.	N.D.

* Prespray samples. Samples contained ca. 0.010 - 0.005 ppm of fenitrothion.

Conc. of residues is expressed in ppm on "oven-dry" mass basis.

T = Traces (< 0.005 ppm)

N.D. = Not detected

** Pooled samples from control plot.

\+ No nitrocresol was found in the samples analysed.

Table 4

Fenitrothion Residues in Foliage from Plot T-2

Time Relative to Application (Days)	Samples (Pooled)			Control		
	Moisture %	Fen	Fenox	Moisture %	Fen	Fenox
-2	62	N.D.	N.D.	58	N.D.	N.D.
0	63	4.200	N.D.	60	N.D.	N.D.
0.5	67	10.855	N.D.	62	N.D.	N.D.
1.5	66	2.705	T	61	N.D.	N.D.
4	68	0.785	T	63	N.D.	N.D.
10	64	0.120	N.D.	58	N.D.	N.D.
21	65	0.085	T	59	N.D.	N.D.
30	61	0.130	N.D.	57	N.D.	N.D.
45	54	0.035	N.D.	61	N.D.	N.D.
90	53	0.015	T	58	N.D.	N.D.
155	46	0.005	T	60	N.D.	N.D.

See the footnotes in Table 3

Table 5

Fenitrothion Residues in Foliage from Bee Range

Time Relative to Application (Days)	Samples (Pooled)			Control		
	Moisture %	Fen	Fenox	Moisture %	Fen	Fenox
-2	60	N.D.	N.D.	57	N.D.	N.D.
0†	56	5.450	N.D.	60	N.D.	N.D.
0.5†	62	11.650	N.D.	61	N.D.	N.D.
1.5	67	7.735	0.025	59	N.D.	N.D.
4	63	2.780	0.050	58	N.D.	N.D.
10	62	0.590	0.035	63	N.D.	N.D.
21	62	0.135	0.020	60	N.D.	N.D.
30	60	0.205	T	53	N.D.	N.D.
45	56	0.015	N.D.	56	N.D.	N.D.
90	54	0.010	N.D.	58	N.D.	N.D.
155	47	0.005	N.D.	63	N.D.	N.D.

See the footnotes in Table 3.

† Insufficient samples.

Table 6

Moisture Content, pH and Fenitrothion Residues in Soil from Plot T-1*

Time Relative to Application (Days)	Site No. 40				Pooled				Control			
	Soil Moisture Percent	Soil pH	Fen	Fenox	Soil Moisture Percent	Soil pH	Fen	Fenox	Soil Moisture Percent	Soil pH	Fen	Fenox
-1	34	5.20	N.D.	N.D.	33	5.10	N.D.	N.D.	37	4.80	N.D.	N.D.
0	35	5.01	0.005	N.D.	35	4.45	T	N.D.	40	5.20	N.D.	N.D.
0.5	37	4.92	T	N.D.	35	5.01	N.D.	N.D.	39	5.11	N.D.	N.D.
3	38	4.45	N.D.	N.D.	38	4.90	N.D.	N.D.	40	4.91	N.D.	N.D.
6	38	4.52	N.D.	N.D.	40	5.03	N.D.	N.D.	37	4.95	N.D.	N.D.
10	40	4.44	N.D.	N.D.	37	5.22	N.D.	N.D.	38	5.22	N.D.	N.D.
15	39	5.00	N.D.	N.D.	39	5.20	N.D.	N.D.	42	5.27	N.D.	N.D.
30	41	5.22	N.D.	N.D.	37	5.17	N.D.	N.D.	40	4.99	N.D.	N.D.
45	45	5.30	N.D.	N.D.	44	4.99	N.D.	N.D.	36	4.86	N.D.	N.D.
90	40	5.05	N.D.	N.D.	30	4.80	N.D.	N.D.	41	5.52	N.D.	N.D.

* No nitrocresol was found in the samples analysed.

T = Traces (< 0.005 ppm)

N.D. Not Detected

Residue concentration is expressed in ppm calculated on "oven-dry" mass basis.

Table 7

Moisture Content, pH and Fenitrothion Residues in Soil from Plots T-2 and Bee Range

Relative to Application (Days)	Bee Range (Pooled)				T-2 (Pooled)				Control			
	Soil Moisture Percent	Soil pH	Fen	Fenox	Soil Moisture Percent	Soil pH	Fen	Fenox	Soil Moisture Percent	Soil pH	Fen	Fenox
-1*	28	5.70	N.D.	N.D.	31	5.68	N.D.	N.D.	29	6.10	N.D.	N.D.
0	-	-	-	-	32	5.70	0.100	N.D.	28	5.92	N.D.	N.D.
0.5	27	5.66	0.030	N.D.	29	5.80	0.030	N.D.	31	5.49	N.D.	N.D.
1.5	23	4.95	0.020	N.D.	-	-	-	-	25	5.66	N.D.	N.D.
4	16	5.20	0.025	N.D.	28	5.74	0.020	N.D.	22	5.49	N.D.	N.D.
10	31	6.09	0.030	N.D.	32	5.50	0.030	N.D.	27	5.71	N.D.	N.D.
21	40	5.98	0.015	N.D.	34	5.60	0.010	N.D.	32	5.99	N.D.	N.D.
30	24	5.83	0.005	N.D.	37	5.44	T	0.010	28	6.25	N.D.	N.D.
45	34	5.85	T	N.D.	31	5.91	N.D.	T	28	5.87	N.D.	N.D.
90	24	5.70	N.D.	N.D.	25	5.72	N.D.	N.D.	31	5.62	N.D.	N.D.

See the footnotes in Table 6

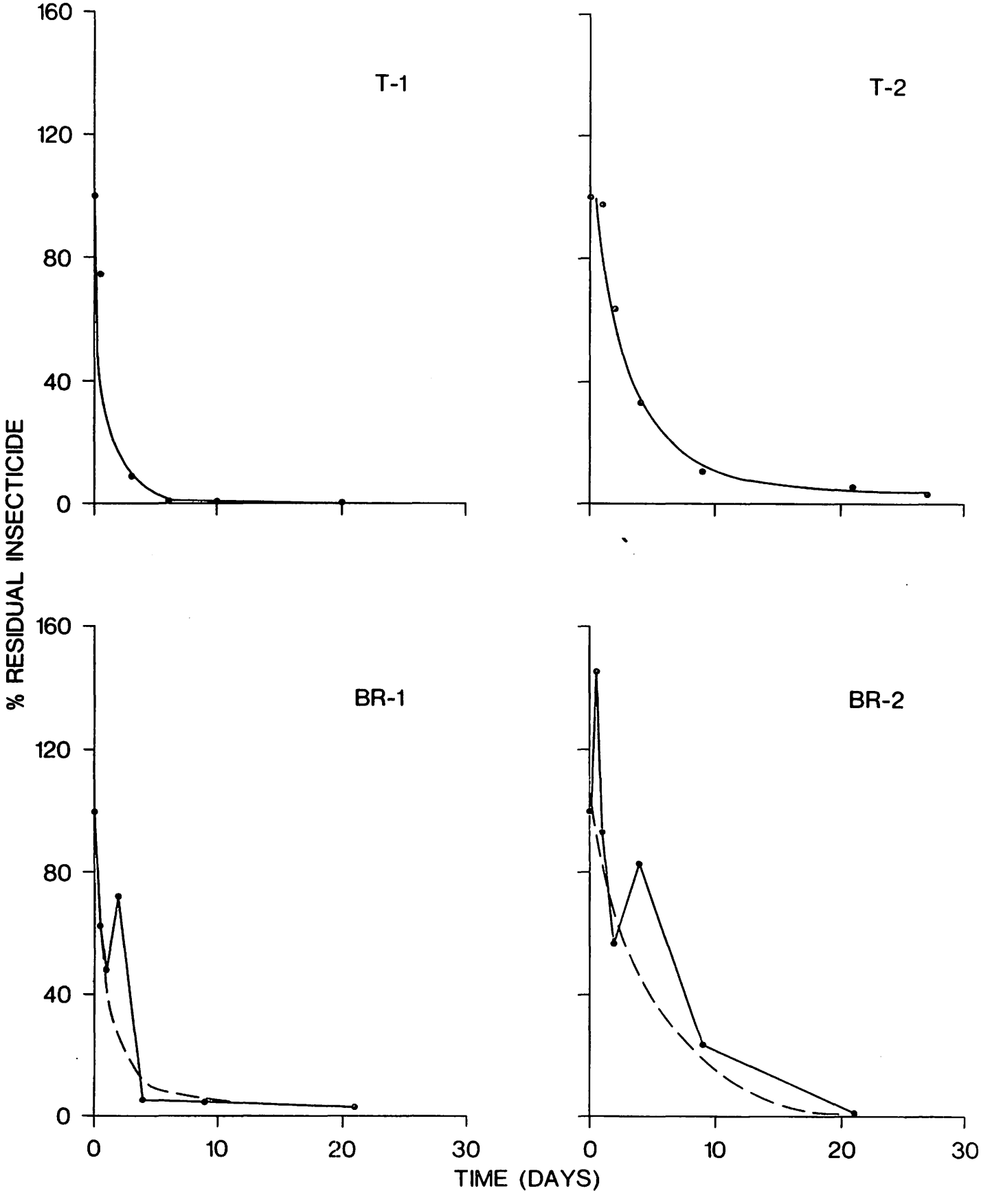


Fig. 1 Residual fenitrothion concentration in water samples

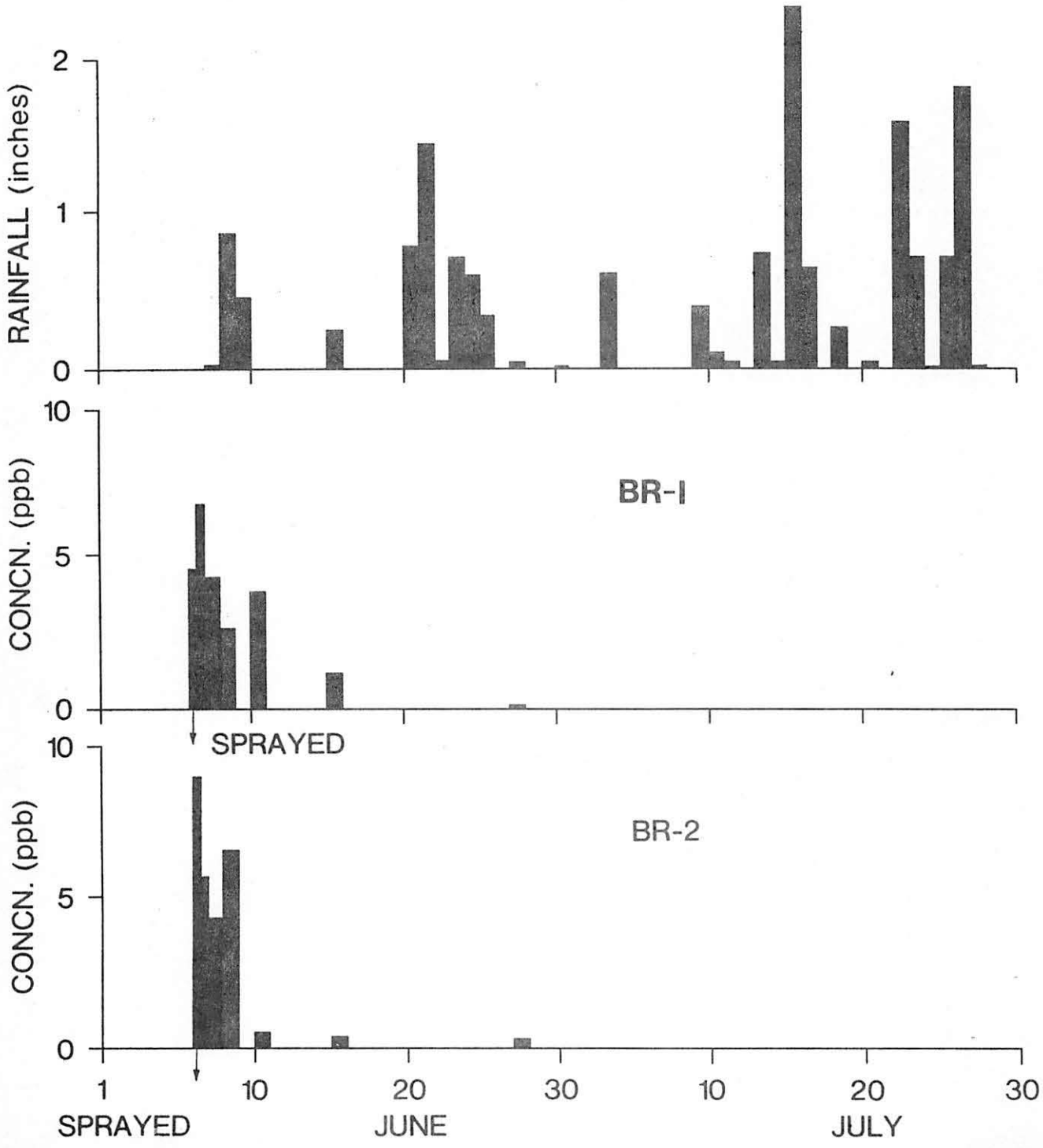


Fig. 2 Effect of rainfall on the concentration of fenitrothion in water samples from BR-1 and BR-2

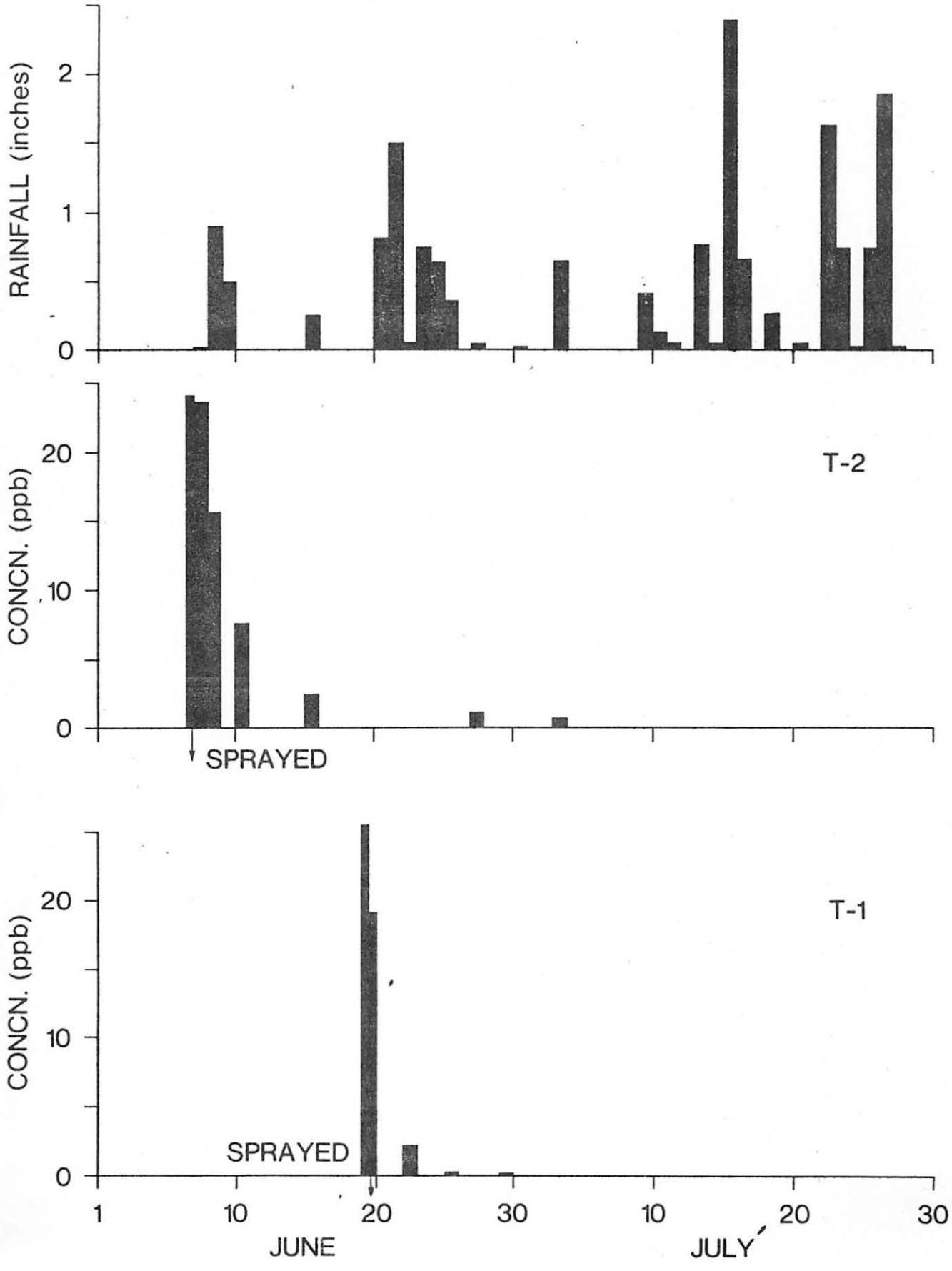


Fig. 3 Effect of rain fall on the concentration of fenitrothion in water samples from T-1 and T-2

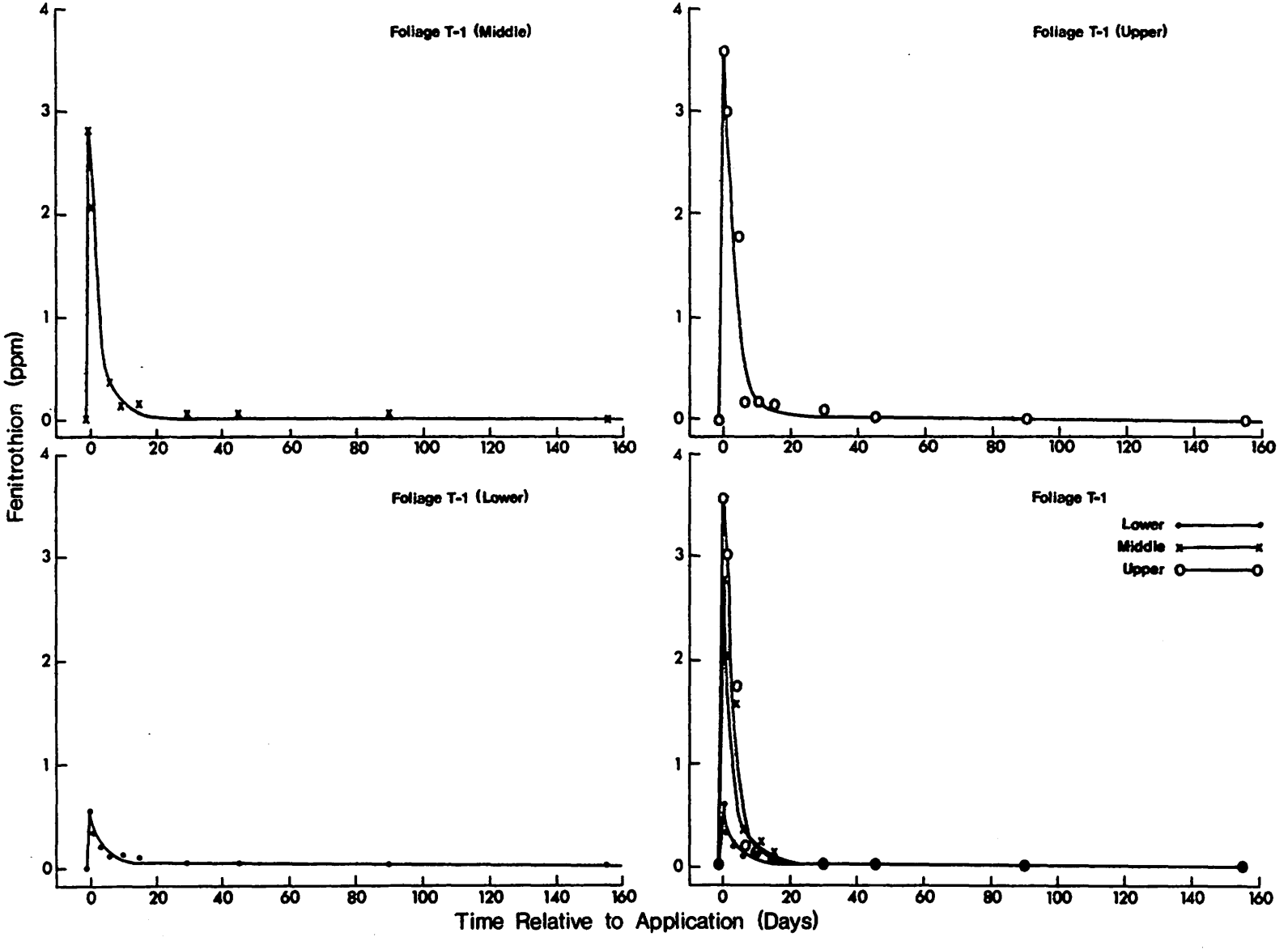


Fig. 4 Fenitrothion concentration in foliage from different parts of tree canopy

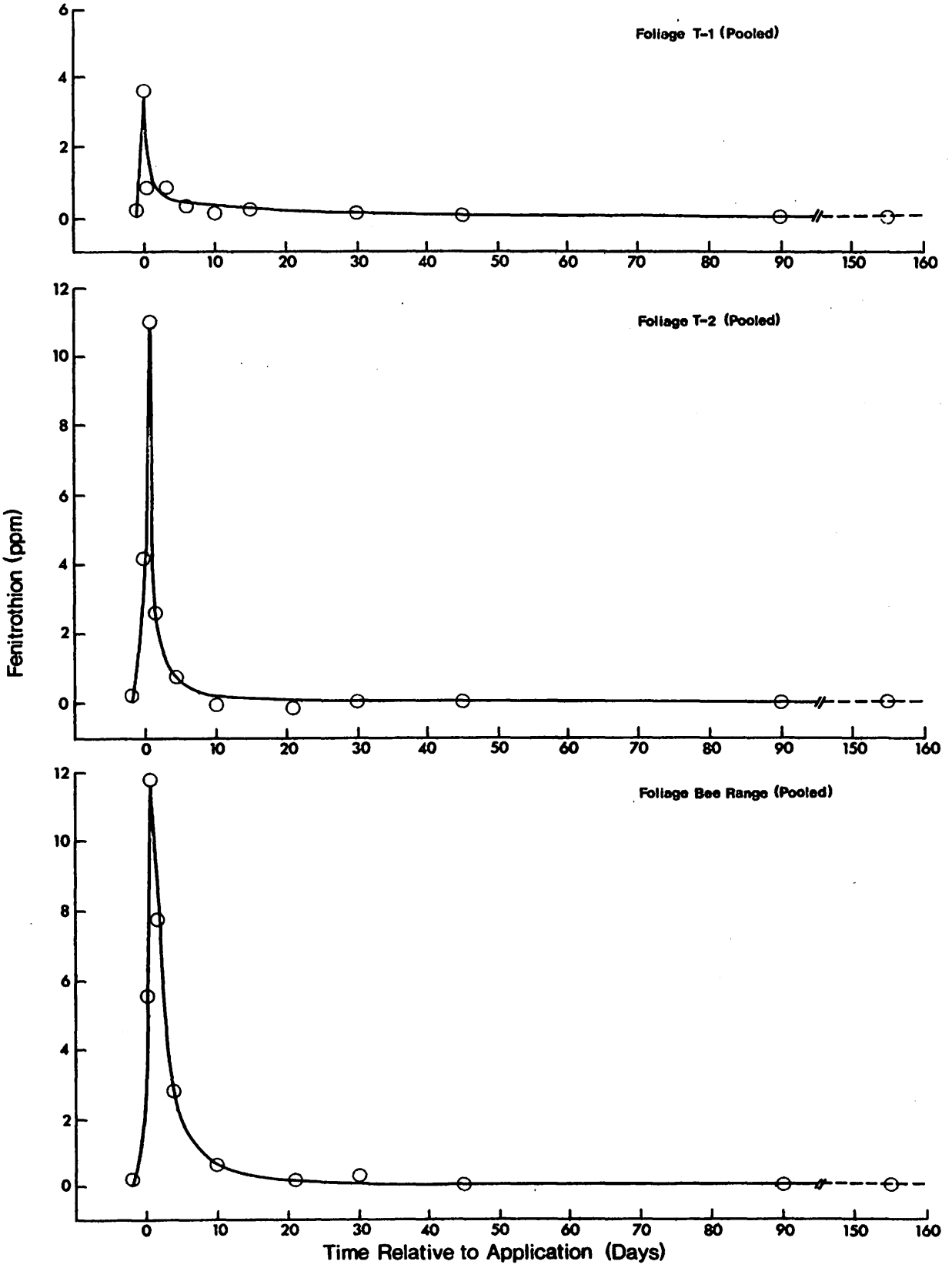


Fig. 5 Loss of fenitrothion in foliage samples from T-1, T-2 and BR

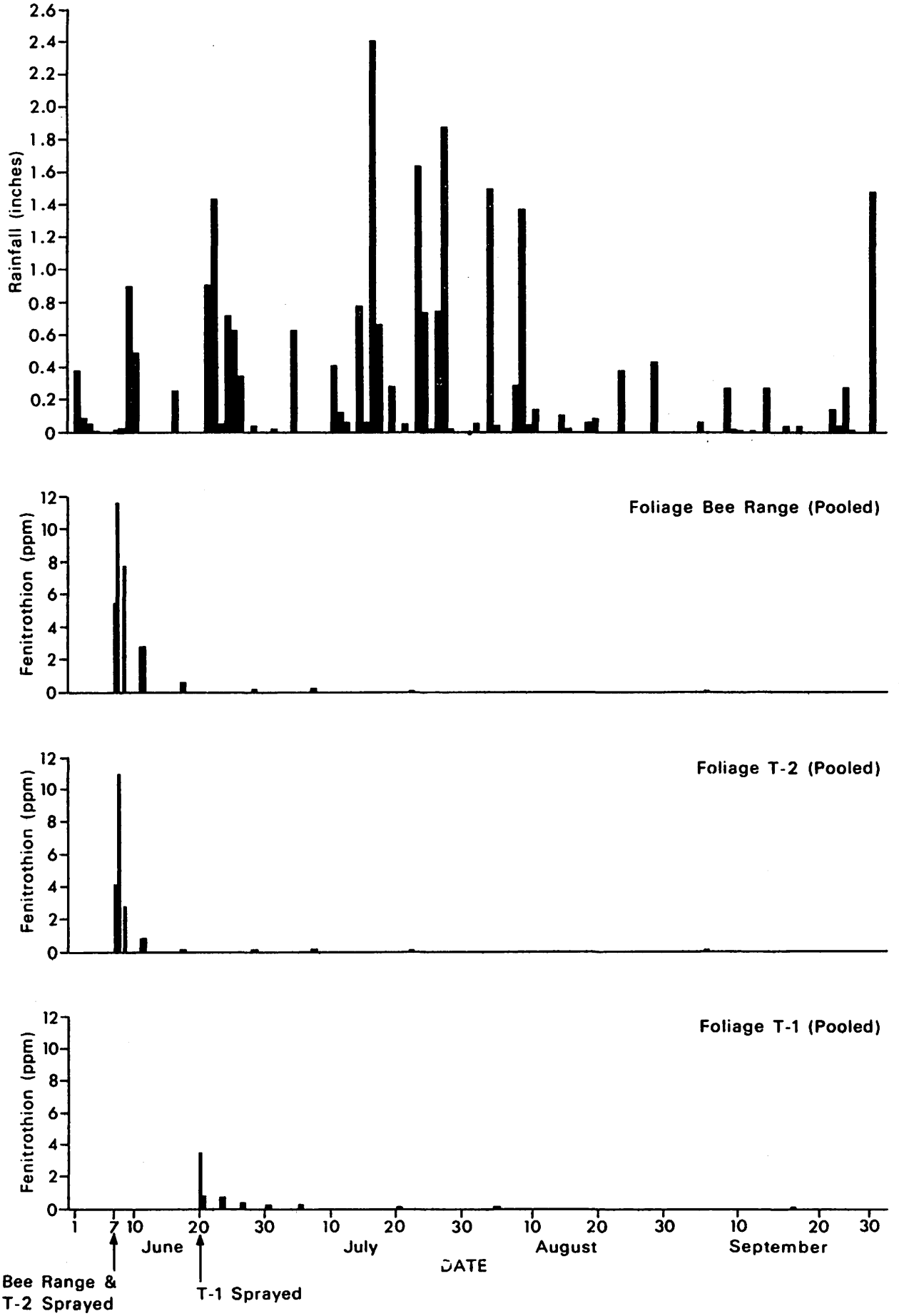


Fig. 6 Effect of rainfall on the concentration of fenitrothion in foliage samples from T-1, T-2 and BR

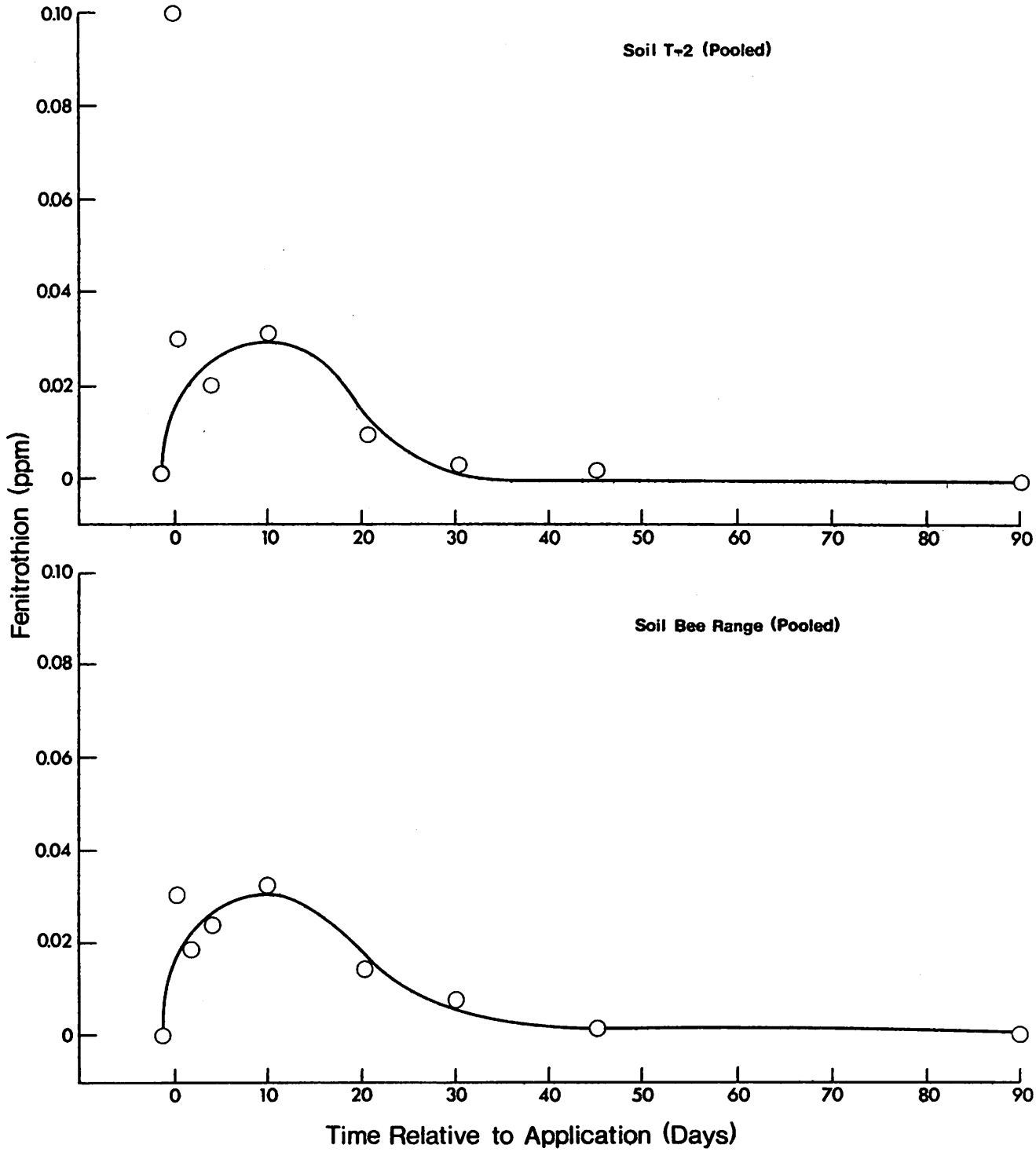


Fig. 7 Loss fenitrothion in soil samples from T-2 and BR

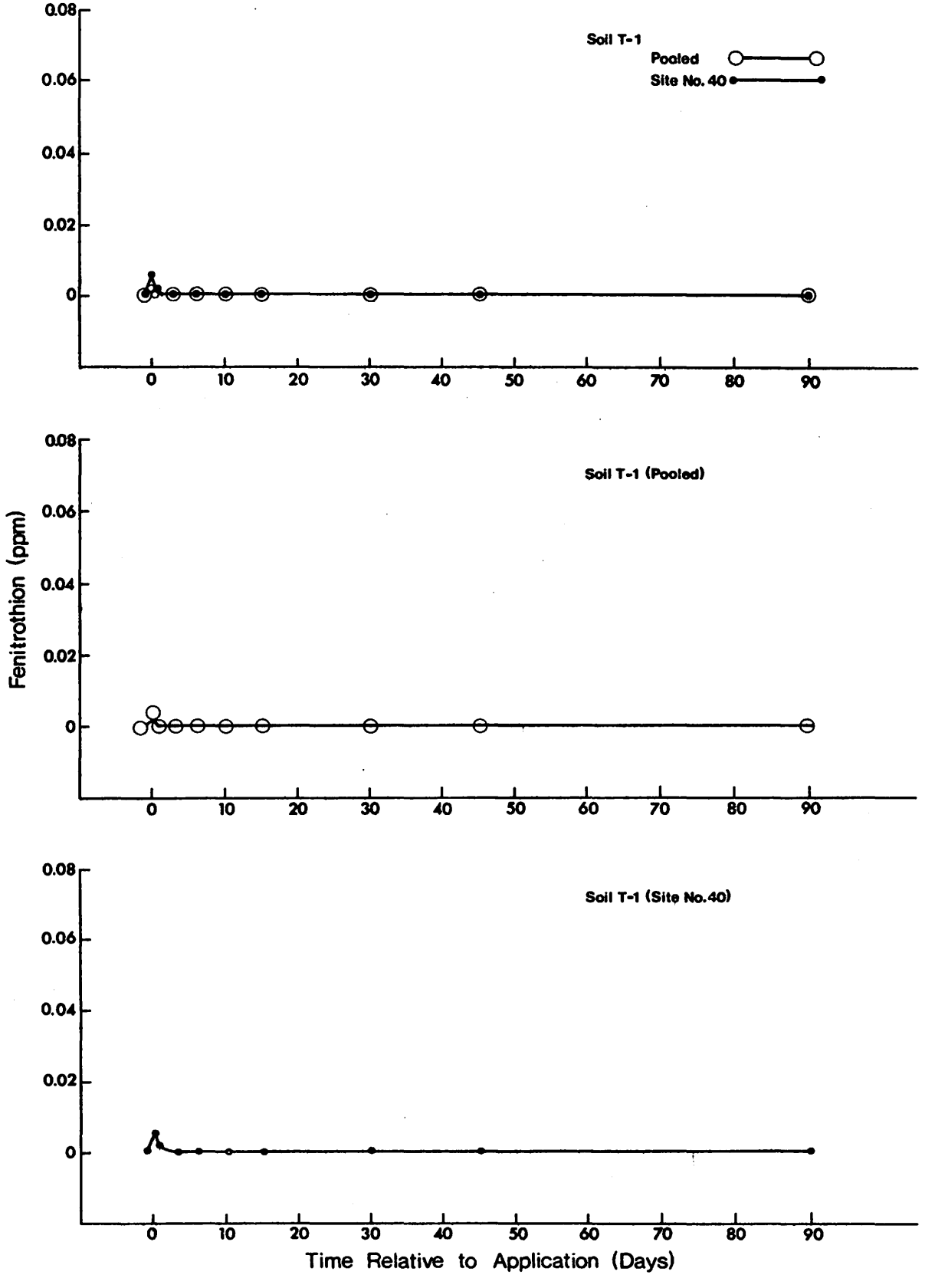


Fig. 8 Loss of fenitrothion in soil samples from T-1

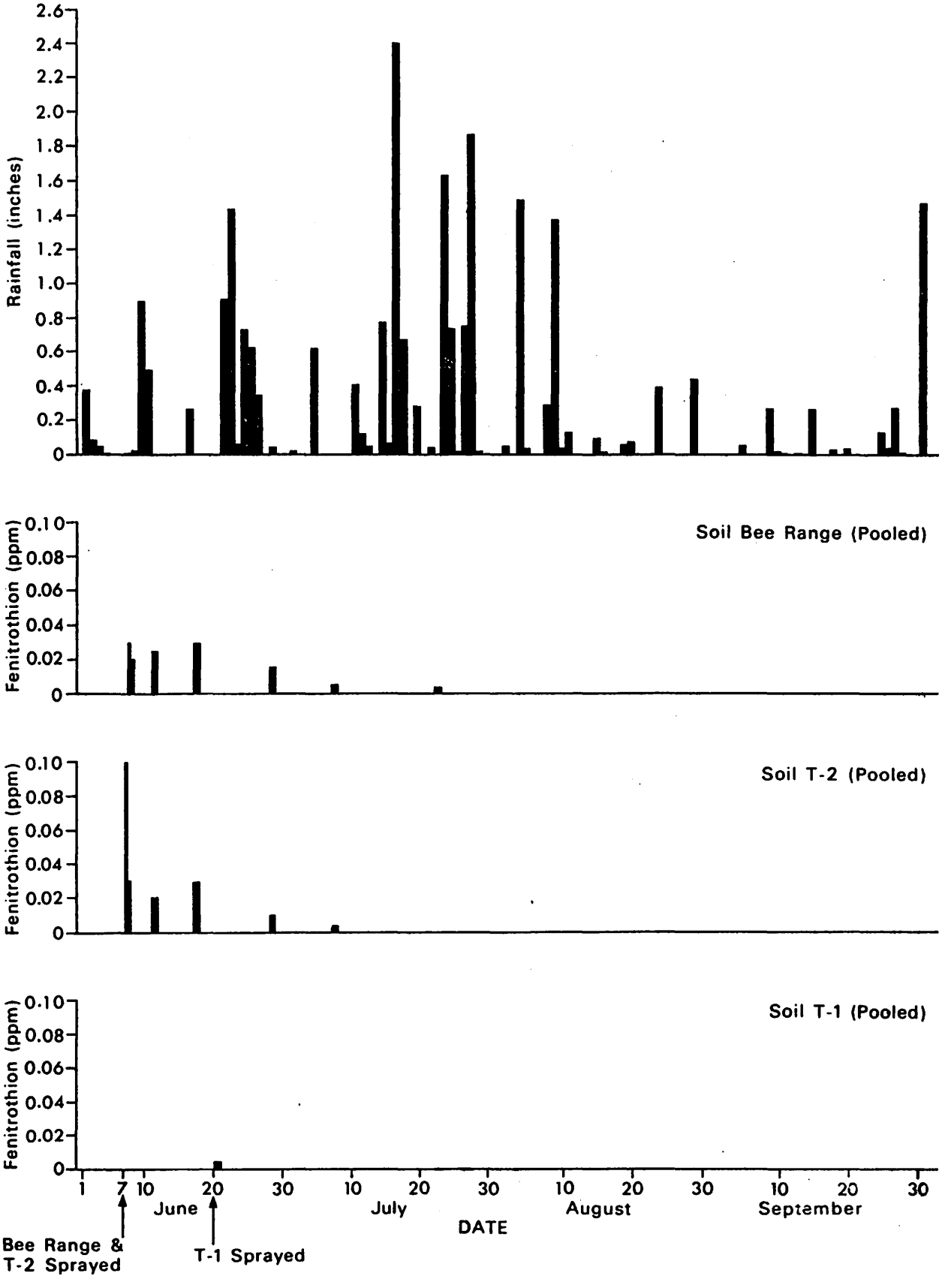


Fig. 9 Effect of rainfall on the concentration of fenitrothion in soil samples from BR, T-2 and T-1

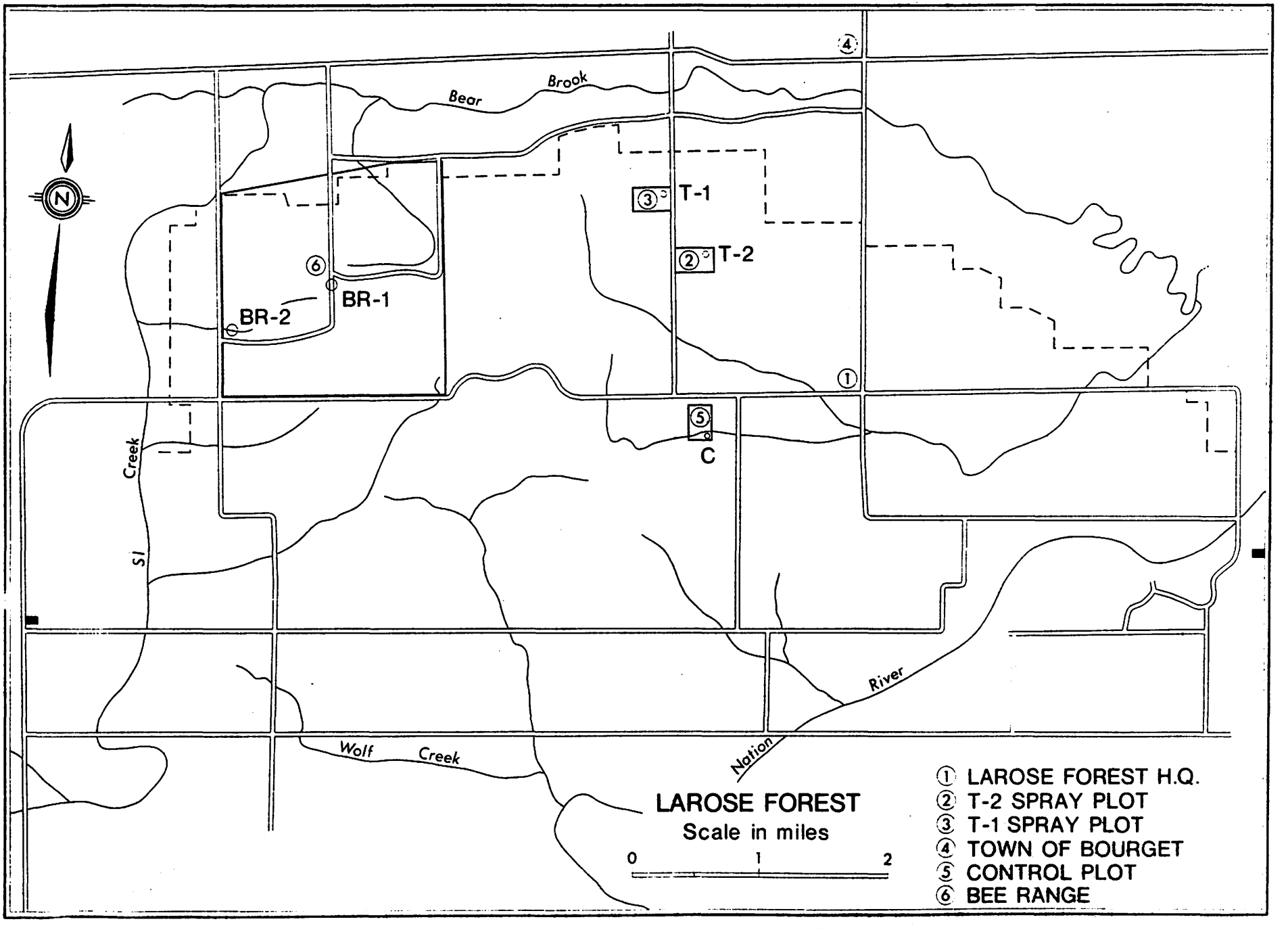

Bear Brook
T-1
T-2
BR-2
BR-1
C
Creek
51
River
Wolf Creek
Nation
LAROSE FOREST
Scale in miles
0 1 2
① LAROSE FOREST H.Q.
② T-2 SPRAY PLOT
③ T-1 SPRAY PLOT
④ TOWN OF BOURGET
⑤ CONTROL PLOT
⑥ BEE RANGE

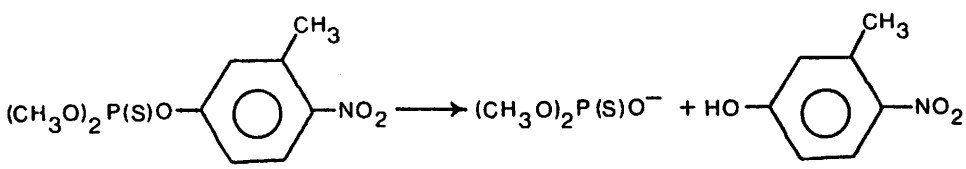
Fig. 10

DISCUSSION

1. Water

The results in Table 2 show the fenitrothion content in water samples collected at various intervals from the ponds (BR-1, T-1 and T-2) and stream (BR-2) in Larose Forest. The initial concentrations in BR-1, T-1 and T-2 were 9.00, 25.50 and 24.00 ppb respectively whereas the samples from BR-2 (stream) contained only 4.60 ppb; the low concentration was probably due to transport of the pesticide by flowing water before the sampling was done.

The dissipation of fenitrothion in aquatic environments is primarily due to the oxidative desulfuration of the thiono (P=S) to the phosphate (P=O) group followed by hydrolysis (O'Brien 1960, Ruzicka et al 1967) according to the following scheme



The optimum conditions for this hydrolytic breakdown are the pH (> 5.5) and the temperature (> 20°C) of natural waters (Faust and Suffet 1966). The conversion of P=S to P=O is accompanied by

chemical and enzymic oxidation increasing the hydrolyzability of fenitrothion. Natural waters provide enzymic oxidation opportunity by aquatic fauna and chemical oxidation is afforded by dissolved oxygen. The free energy changes (ΔG_o) for such oxidative reactions accompanied by hydrolysis are highly negative for various organophosphorus insecticides (Faust and Hunter 1971) confirming their instability in aquatic media. In the present study, the overall concentration of the insecticide diminished rapidly (Fig. 1) by chemical and biological degradation to negligible amounts (< 0.03 ppb) within a period of 40 days. The temperature and pH of the aqueous solutions varied between 11.7 to 26.7°C and 5.85 to 7.53 (Table 1) respectively, thus facilitating the hydrolysis of the insecticide under natural conditions existing in the forest.

The concentration variations of fenitrothion in the stagnant water samples from BR-1 and the stream BR-2 was greatly influenced by rainfall during the period of study (Fig. 2). During heavy rains, runoff waters from land carried with them the insecticide increasing its concentration in ponds and streams. Soon after spraying the pesticide on June 7, a rainstorm of medium intensity (Fig. 2) caused variations in the concentrations of fenitrothion in BR-1 and BR-2 due to water movement; consequently an apparent correlation existed between the concentrations of the insecticide and the daily rainfall. The high peaking, an increase

of ca 46% in fenitrothion concentration in BR-2 on the +0.5 day sample (Fig. 1), was caused by the high insecticide load carried into the stream from the surrounding land by runoff water and the fenitrothion washed into the stream from foliage and duff. Pesticide-laden dust in the atmosphere must also have been precipitated by sedimentation and rainfall. Similar increase in the residue level was also observed in BR-1 on the second day, perhaps due to the surface drainage from forest lands and partial localization of fenitrothion within the pond. The residue concentration in T-2 diminished gradually from a peak value of 24.00 ppb measured after 0.5 day, to traces at an interval of 40 days. The gradual decrease in concentration was probably due to the composite of portions taken at different points minimizing the errors in sampling. Though the initial amount of fenitrothion was very high in T-1 (25.50 ppb), decline in the concentration was very rapid (Fig. 2) probably due to the heavy rainfall (4.06 inches in a week from June 20th to 26th) after the spray on June 20th (Fig. 4) which caused considerable exchange of water due to runoff, causing dilution. Following this sharp decline was the more gradual drop in residue concentrations. An examination of the results in Table 2 show that the overall pattern of accumulation and disappearance of fenitrothion residues in all the four sampling sites were rather similar with minor variations as discussed

above, and the insecticide concentration diminished to traces (< 0.03 ppb) within a period of 40 days. It is also worthwhile to note that the amounts found initially were far below the acceptable residue level of 0.100 mg/l (0.1 ppm) (1972) of fenitrothion.

The fate and effects of fenitrothion and its metabolites on aquatic flora and fauna are still obscure. O'Brien (1967) Menzie (1969), Sundaram and Sundaram (1969) observed that the oxidative breakdown (oxon) pathway of fenitrothion normally results in increased toxicity. Field studies (Faust and Suffet 1966) suggested that parathion, a familiar member of the organophosphorus group of pesticides, structurally similar to fenitrothion, persisted in natural aquatic environments for a considerable period of time and transported from one area to another by surface runoff and caused extensive fish kill but eventually dissipated by physicochemical and biodegradation routes. Most likely fenitrothion, like parathion, was lost from the aquatic environment through various processes such as volatilization, codistillation, degradation by chemical, microbiological and photochemical means, erosion and weathering resulting from heavy rains (Norris and Moore 1970). Among these various physical and metabolic factors affecting the fate of fenitrothion, probably hydrolysis and biodegradation by various microorganisms are the major sources for the loss of fenitrothion from forest aquatic environment. The factors that activate the

hydrolysis are the presence of various aquocations as catalysts (Sandi 1958) in natural waters, pH, temperature (O'Brien 1960) and variations in the ionic strength (rate of hydrolysis increases with ionic strength of a solution due to primary salt effect) (Ruzicka et al 1967) of the water samples.

The kinetics of disappearance of fenitrothion in aqueous systems under controlled conditions, was found to obey the first order reaction with the rate of disappearance proportional to the amount present (Sundaram 1973). The aquatic environment in the present study was a dynamic system in which fenitrothion concentration was affected by physical, metabolic and environmental factors, consequently the dissipation of the insecticide did not obey the first order and the kinetic half life was not evaluated. An approximate estimation of the half-lives was obtained, ignoring the peakings, from the exponential decay curves given in Fig. 1. The half-lives (days) obtained were low (BR-1 = 0.75, BR-2 = 3.50, T-1 = 0.25 and T-2 = 2.50), confirming the rapid dissipation of the pesticide in the aquatic environment at Larose Forest. The relatively high $t_{0.5}$ of the BR-2 was due to leaching of the pesticide from the land into the stream during rains.

2. Foliage

The persistence of fenitrothion and its metabolites (fenitrooxon and 4-nitrocresol) in the foliage samples collected

from the sampling sites T-1, T-2 and BR was determined upto 155 days after the aerial application. The residue concentrations in pooled samples were found to be high and varied from 3.470 T-1 to 11.650 (BR) ppm (Tables 3-5). All the samples showed highest concentration either on the 0 (T-1) or 0.5 (T-2 and BR) day after spraying. Prespray samples from T-1 showed 0.010 ppm of fenitrothion as residual concentration. All control samples were completely free from the insecticide residues.

Fenitrothion in the foliage samples decreased rapidly with time (see Fig. 5). The short persistence of the residues in T-1 was probably due to heavy rains on June 20, after spraying (Fig. 6) which eluted the insecticide from tree canopy. In all the three samples, approximately half the initial fenitrothion deposit was lost within 2 days ($t_{1/2}$ for T-1 and T-2, 1.5 and BR 2.5 days) and 95 per cent within 10 days after spraying. Yule and Duffy (1972) have reported the half-life of fenitrothion in forest foliage to be about 4 days compared to the present value of ca 2 days. Persistence is a variable property and is affected by various environmental factors (climate, rainfall, etc.), pesticide formulation and mode of application; hence such a comparison is not possible for two dissimilar locations. After a period of 10 days, the residue levels in all the samples were more persistent (Nigam 1970, Yule and Duffy 1972) in spruce foliage

than was anticipated from its fate in various other plants (Miyamoto and Sato 1965, Sumitomo 1968, Mollhoff 1968, Bowman and Beroza 1969, Leuck and Bowman 1969, Sundaram and Sundaram 1969). By the end of 155 days, the residue levels in all the samples decreased to 0.005 ppm.

Fenitrothion residues in various parts of tree canopy - upper, middle and lower - in plot T-1 (Table 3), showed appreciable differences. The upper part of the tree canopy received maximum amount 3.540 ppm, nearly six times more than the lower part (0.595 ppm) but the rate of degradation (Fig. 4) was high in the former. After 5 days, only 5% of the fenitrothion sprayed remained in the upper part compared to 18% in the lower canopy. The low persistence in the upper part of the tree canopy, which has been exposed to sunlight, was probably due to photodegradation, volatilization and elution by rain fall.

The oxon metabolite was found in small amounts usually 1.5 days after spray operation, (Tables 3-5), the maximum concentration being ca 1% of the parent compound. It disappeared more rapidly than the insecticide. No residue of the 4-nitrocresol was found in all the foliage samples analysed. The rapid loss of fenitrothion and the absence of appreciable amounts of metabolites confirmed the view of Yule and Duffy (1972), that the effective mechanism of dissipation of fenitrothion in spruce foliage from forest areas under operational conditions, was primarily due to

physical factors such as volatilization, photodegradation, weathering action of humidity, rain and wind rather than metabolic factors, acting on external surface deposits. The poor penetration of the toxicant into the foliage, not only accounted for its minimal *in vivo* degradation but also for its poor systemic action. The remaining low (*ca* 0.005 ppm) but more persistent insecticide molecules, probably were absorbed and stored in cuticular waxes of the spruce foliage resisting leaching, volatilization, photo and biodegradations.

Contrary to this hypothesis, it is also likely, unless proved otherwise, that the disappearance of fenitrothion in spruce foliage may not be through oxidative desulfuration forming the oxon followed by hydrolysis to yield the cresol and phosphate moities and or primarily by physical factors as assumed so far, but may be through an enzymatic O-dealkylation and hydroxylation (Hollingworth 1970) leading to the formation of hydrophilic products accumulating in the substrate tissues to be released at a latter time. Suprisingly few investigations have been carried out on the metabolism of fenitrothion in forest trees in spite of its wide usage in spray operations.

The results recorded in Tables 3-5 were analysed according to a first order or a pseudo first order kinetics using the expression

$$\ln [A] / [A]_0 = - kt$$

where $[A_o]$ the initial concentration of the insecticide on zero day,

[A] the concentration after time t and k is the rate constant. Plots of ln [A] / [A_o] vs t were nonlinear showing that the disappearance of fenitrothion in spruce foliage did not obey the rate law, [an observation contrary to that of Ebeling (1963), Ruzicka et al (1967) and Sundaram et al (1972)] probably due to nonuniform distribution and the rapid loss of the toxicant (see Fig. 5) by various physical factors causing the breakdown to be independent of the concentration of fenitrothion.

3. Soil

The forest floor is usually considered a major receptor of aerially applied spray materials, but the fenitrothion content found in the soil samples from plots T-1, BR and T-2, up to an average of 4 inch depth were low (Tables 6 and 7), ranging from 0.005 (T-1) to 0.100 (T-2) ppm, far less than the amount found in the foliage. The insecticide concentration decreased steadily with time (Figs. 7 and 8). At the end of 45 days after spraying, nearly all the toxicant reached the forest floor had disappeared. Slight variations in soil concentration recorded in Table 7, apart from the gradual disappearance, may be due to the input of fenitrothion to the forest floor from litter fall of needles and twigs originally subjected to the spray, foliar leaching by rainfall, soil movement resulting in overland flow of water and sediment and, most likely to unavoidable contamination during sampling. The slow

disappearance of the insecticide was probably due to its adsorption on soil mineral or organic matter. Soil samples from T-2 showed traces of the oxon metabolite (0.010 ppm) after an interval of 30 days. Apart from this single observation, no measurable amount of the breakdown products were found in all the other soil samples. Therefore it appears that under operational conditions of forest protection, no significant amount of the insecticide and its breakdown products (oxon and cresol) persisted for a considerable length of time.

Mechanism of disappearance of fenitrothion from forest floor included volatilization*, leaching+ through soil profile by water, degradation by various physicochemical processes including sunlight and biological means. Among these, a combination of chemical and bacterial degradations and volatilization from the soil surface probably play vital parts. Miyamoto et al (1966) observed the bacterial conversion of fenitrothion to its

---

* It has been calculated that a pesticide with a molecular weight (m.w.) of 200 and vapour pressure (v.p.) of 10^{-4} mm Hg (fenitrothion, m.w. 277; v.p. 6×10^{-6} mm Hg at 20°C) could lose as much as 20 Kg ha^{-1} $month^{-1}$ from an inert surface during a temperate summer, whereas usual amounts applied are in the region of 1-2 kg ha^{-1}.

\+ Two cm of rain provides 2×10^{5} kg of water per hectare, enough to dissolve 1 kg ha^{-1} of a pesticide with a solubility of 5 ppm.

amino analogue and desmethyl derivatives under aerobic conditions within 24 hours. Forest soils were moist (Tables 6 and 7) (moisture content ca 40%) favouring microbial and chemical decompositions. The soil samples were acidic with a pH range of 4.44 to 4.99. The acidic condition of the soils seems to influence the degradation of the insecticide. Preliminary studies by the author showed that systems with high hydrogen ion concentrations inhibited the degradation of fenitrothion. Further research is necessary to evaluate critically the loss of the insecticide from forest soil.

SUMMARY

Distribution and persistence of fenitrothion residues in foliage, soil and water from Larose Forest collected at intervals after the aerial application were studied, after solvent extraction and necessary cleanup, by GLC analysis.

The initial insecticide concentration in the foliage varied from 3.470 to 11.650 ppm. Approximately half the deposit was lost within 2 days and 95% within 10 days. The upper part of the tree canopy was the maximum receptor of the spray deposit but the rate of disappearance was high. The residues persisted in detectable amounts (0.005 ppm) up to 155 days due to their absorption and storage in cuticular waxes. The oxon metabilite was found only in traces for a short period and the 4-nitrocresol was not detected. The mechanism of dissipation of the insecticide appeared to be due to physical factors (volatilization, photodegradation, weathering etc.) rather than metabolic processes, consequently the decay process did not obey first-order rate law.

The fenitrothion content in the soil samples were low ranging from trace amounts (< 0.005) to 0.100 ppm and disappeared within 45 days. No measurable amounts of the breakdown products were found. Mechanism of disappearance of the toxicant from forest soil included volatilization, leaching, chemical and microbial decompositions. Soil moisture and pH influenced chemical and biological transformations of the insecticide.

Initial fenitrothion content in natural waters collected from three ponds in Larose Forest ranged from 25.50 to 9.00 ppb whereas the stream water contained only about 6.70 ppb. The residue levels fluctuated due to erosion and leaching from rainfall and runoff from land. The overall concentration of the insecticide diminished rapidly by dilution and by various physicochemical and microbiological degradation to negligible amounts (< 0.03 ppb), far below any known toxic level, within a period of 40 days. In addition to physical and metabolic factors, salt content of the water and various climatic parameters would had appreciable influence on the rapid dissipation of the compound. Consequently the loss of fenitrothion in the natural aquatic environment did not follow first-order kinetics. The half-lives were found to be low ranging from 0.25 to 3.50 days signifying that the compound as a pesticide has little persistence in the natural water environments of forest areas.

Under Larose Forest conditions, residues of fenitrothion degraded rapidly in foliage soil and water when applied aerially at the rate of 2 oz/acre as an aqueous emulsion. Findings from this study are in reasonable agreement with those for the same chemical used in N.B. forests. The compound had low persistence, hence environmentally safe to be used as an insecticide to control forest pests.

ACKNOWLEDGEMENTS

The work reported herein was part of a cooperative programme initiated by C.H. Buckner of the Vertebrate Biology Section of this Institute to study the longterm effects of chemical control practices on the ecology and populations of small forest vertebrates. The author is indebted to him and to B.B. McLeod for collecting and supplying all the foliage, soil and water samples used in this investigation.

The technical assistance of G.G. Smith, W O'Brien, P. Davis and M. O'Connell is gratefully acknowledged.

Appreciation is extended to W.N. Yule, C.H. Buckner, J.A. Armstrong and W.W. Hopewell for reviewing the manuscript.

In conclusion, the author is thankful to Dr. J.J. Fettes for his continued interest in this research project.

LITERATURE CITED

A.O.A.C. 1955. Official Methods of Analysis (8th ed.), A.O.A.C., Washington, D.C., 1008 pp.

Atkinson, H.J., G.R. Giles, A.J. MacLean and J.R. Wright. 1958. Chemical methods of soil analysis. Contrib. No. 169 (rev.). Chem. Div., Sa. Serv., CDA, Ottawa, Ont., 90 pp.

Beroza, M., M.N. Inscoe and M.C. Bowman. 1969. Distribution of pesticides in immiscible solvent systems for cleanup and identification and its application in the extraction of pesticides from milk. Residue Reviews 30:1.

Bowman, M.C. and M. Beroza. 1969. Determination of Accothion, its oxygen analog and its cresol in corn, grass and milk by gas chromatography. J. Agr. Food Chem. 17:271.

Ebeling, W. 1963. Analysis of the basic processes involved in the deposition, degradation, persistence and effectiveness of pesticides. Residue Reviews 3:35.

Faust, S.D. and I.H. Suffet. 1966. Recovery, separation and identification of organic pesticides from natural and potable waters. ibid. 15:44.

Faust, S.D. and J.V. Hunter. 1971. Organic compounds in aquatic environments. Marcel Dekker, Inc., New York. pp 341-376.

Fettes, J.J. 1968. Chemical control of forest insects by aircraft. Pulp and paper Mag. of Canada 69(18):90.

Hollingworth, R.M. 1970. The dealkylation of organophosphorus triesters by liver enzymes. In O'Brien, R.D. and I. Yamamoto (eds.): Biochemical toxicology of insecticides. Academic Press, New York. pp 75-92.

Leuck, D.B. and M.C. Bowman. 1969. Persistence of O, O-dimethyl O-4-nitro-m-tolyl phosphorothioate, its oxygen amalogue and its cresol in corn and grass forage. J. Econ. Entomol. 62:1282.

Menzie, C.M. 1969. Metabolism of Pesticides. U.S. Bureau of sport, fisheries and wildlife, special scientific report - wildlife No. 127, Washington, D.C. pp 487.

Mollhoff, E. 1968. Beitrag zur Frage der Ruckstande und ihrer Bestimmung in Pflanzen nach Anwendung von Praparaten der E605 - und Agritox - Reihe. Pflanzenschutz - Nachrichten Bayer 21:331.

Miyamoto, J. and Y. Sato. 1965. Determination of insecticide residues in animal and plant tissues. II. Metabolic fate of sumithion in rice plant applied at the preheading stage and its residue in harvest grains. Botyu-Kagaku 30:45.

Miyamoto, J., K. Kitagawa and Y. Sato. 1966. Metabolism of organophosphorus insecticides by Bacillus subtilis with special emphasis on Sumithion. Jap. J. Exp. Med. 36:211.

Nigam, P.C. 1970. Summary of laboratory evaluation of insecticides against forest insect pests during 1970. Dept. Fisheries and Forestry, Chemical Control Research Institute, Inf. Rept. No. CC-X-5, pp 10.

Norris, L.A. and D.G. Moore. 1970. The entry and fate of forest chemicals in streams. Proceedings of a symposium on forest land uses and stream environment, Organ State University, p. 138.

O'Brien, R.D. 1960. Toxic Phosphorus Esters. Academic Press, New York.

O'Brien, R.D. 1967. Insecticides, Action and Metabolism. Academic Press, New York.

Ruzicka, J.H., J. Thomson and B.B. Wheals. 1967. The gas chromatographic determination of organophosphorus pesticides. Part II. A comparative study of hydrolysis rates. J. Chromatog. 31:37.

Sandi, E. 1958. Reduction of parathion induced by light. Nature 181:499.

Sumitomo Chemical Co. 1968. Sumithion data collection -1, Osaka, Japan. pp 138.

Sundaram, A. and K.M.S. Sundaram. 1969. Studies on the translocation pattern, persistence characteristics and metabolic pathway of Sumithion [0, 0-Dimethyl-0-(3-methyl-4-nitrophenyl) phosphorothioate] in the cocoa tree Theobroma cacao L. Ghana Jour. Sci. 9(2):96.

Sundaram, K.M.S., G.G. Smith, W. O'Brien and D. Bonnett. 1972. A preliminary report on the persistence of methoxychlor for the control of white pine weevil in plantations. Dept. Env., Can. For. Serv. Inf. Rept. No. CC-X-31, pp 27.

Water Report. 1972. Guidelines for water quality objectives and standards. Dept. Env., Inland Waters, Tech. Bull. No. 67, pp 156.

Yule, W.N. and J.R. Duffy. 1972. The persistence and fate of fenitrothion insecticide in a forest environment. Bull. Env. Contam and Toxical. 8(1):10.