Intensive Studies of DDT Residues in Forest Soil

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Approximately 6,000 tons of technical DDT were sprayed over 10 million acres of forest land around New Brunswick (N.B.), Canada, between 1952 and 1968, as part of the regional spruce budworm (Choristoneura fumiferana Clemens) control program (MACDONALD, 1966). Intensive ecological research on DDT in the forest environment has been concentrated around the Priceville area of Central N.B. since 1966 (MACDONALD and DUFFY, 1968). The 1,050 acre Priceville plot was selected to represent the locality having the heaviest DDT-dosage record for N.B. forests, namely 70 ounces (oz.) per acre applied between 1956 and 1967.

This paper summarizes intensive studies on the vertical and horizontal distributions of DDT in the forest soil environment at Priceville, and traces qualitative and quantitative changes that have occurred in soil-residue status between 1967 and 1971 (see also YULE, 1970; YULE and SMITH, 1971).

Methods and Materials

Soil description. Soil profiles, prepared close to plots I, II, and III (Fig. 1), were inspected by pedologists, and a summary of their description of the stony orthic-podzol is given in YULE and SMITH (1971). Plot II represented anomalous local soil and topographical conditions caused by creek erosion.

Sampling procedure. Soil profiles were dug to a depth of 36 in. and horizons were sampled horizontally from each freshly exposed face using a one-in. diameter steel auger. Analysis of horizon samples showed that all of the DDT residue occurred in the surface 6 in. of the soil profile (Table 1), and thereafter soil sampling was standardized using a four-in. diameter toothed auger to a depth of 6 in. The auger was stabbed into the soft duff, giving a surface sample 9 sq. in. in area, then rotated as it was pressed down, to break up stones and roots.

Analysis for DDT. Soils were stored at -15°C and extracted in moist "as sampled" state (see YULE and SMITH, 1971). A composite sample of 50 g. sieved moist soil was extracted twice with 100 ml. of a mixture of 2:1 V/V n-hexane:acetone (Burdick and Jackson, Muskegon, Mich., distilled-in-glass grade) in a high speed mixer. The volume of the combined extracts was made up to 300 ml. with hexane and mixed with 600 ml. distilled water in a 1,000 ml. separatory flask. After separation and washing, the combined hexane phases were dried by passing slowly through 2 funnels of anhydrous Na_2SO_4.

Bulletin of Environmental Contamination & Toxicology,
Vol. 9, No. 1,

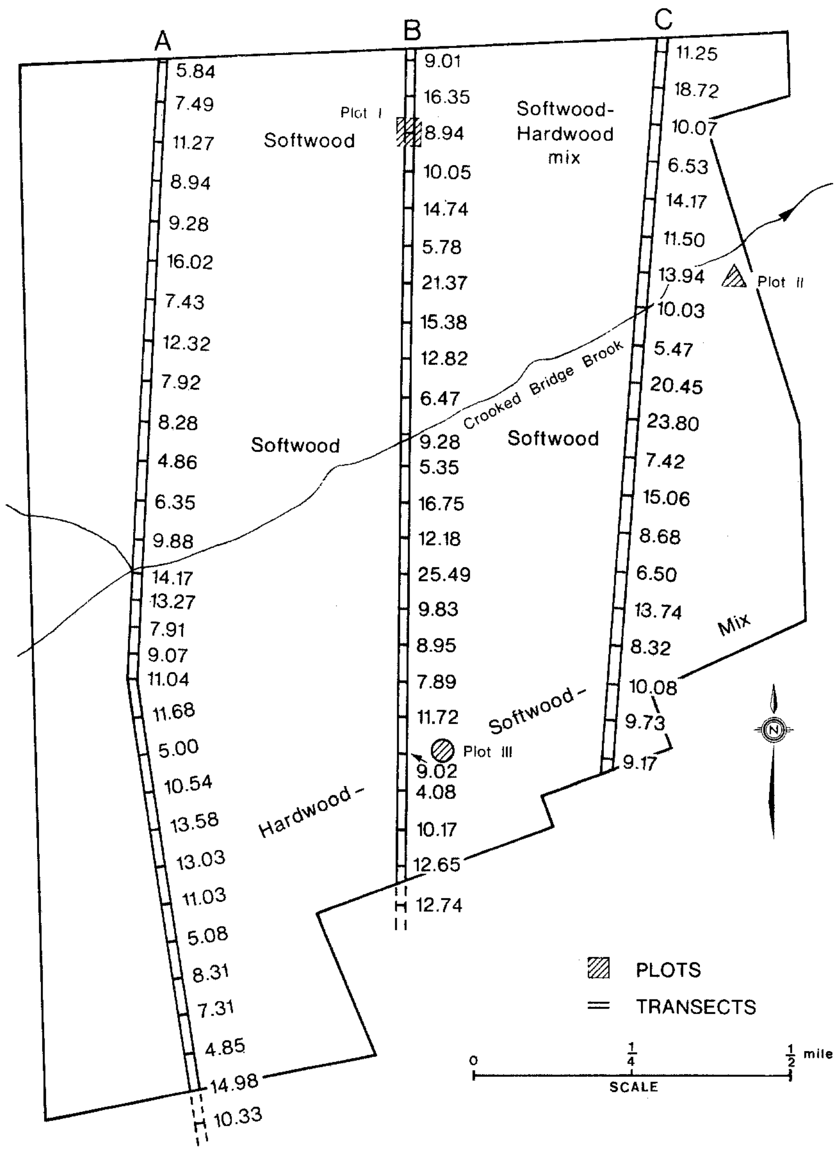

Figure 1. Priceville area diagram showing locations of 3 experimental plots, and transect lines with total DDT residues (1968) at 100-yard intervals (ounces per acre).

Soil extracts were cleaned up using chromatographic columns loaded with 20 g. pre-conditioned florisil with Na_2SO_4 (DUFFY and WONG, 1967). The column was washed three times with 50 ml. hexane, then the 50 g. soil extract was added and eluted twice with 100 ml. 15 per cent (V) benzene in hexane. The eluate (>200 ml.) was collected and reduced to 50 ml. by flash evaporation (1 g./ml.) for gas chromatographic analysis.

Each soil sample was analysed twice by gas-liquid chromatographic techniques, using a Hewlett-Packard 5750 instrument (Avondale. Pa.) fitted with twin columns and twin electron capture (Ni 63) detectors.

Operating conditions were:

Columns: glass, 4 ft. x 1/4 in.; loadings, (1) 3.8 per cent SE30, (2) 4 per cent SE30 with 6 per cent QF_1; on Chromosorb W, 60-80 AW-DMCS.

Temperatures (°C): injection ports 210-220; column oven 185; detectors 250.

Gas flow: 5 per cent methane in argon, (1) 50 ml./min.; (2) 70 ml./min.

Spot checks, mainly for confirmation of identification of DDT's, were made on the same extracts using thin-layer chromatographic analysis (MORLEY and CHIBA, 1964).

Results and Discussion

Units. Residues in soil have been given in several different units in the various studies. Ppm. "as sampled"; includes variables such as stones and water, for ecological interpretation of field situations. Ppm. "ovendry"; represents sieved samples less water, to standardize residues for comparison (e.g. from year to year, or site to site). Ounces per acre; takes account of total sample weight and its surface area, allows both above interpretations, and allows comparison with dosage units (spray histories).

Vertical Distribution of DDT Residues - 1967.

Results in ppm. "as sampled" and "ovendry" units are given in Table 1 for the vertical distribution of total DDT in soil pits located just outside each of the 3 Priceville plots. Two pits were dug at Plot II, one at the bottom of the creek valley, and one at the top of the hill (L and U respectively in Table 1). These investigations showed that DDT residues were largely confined to the surface (organic) layers of soil and had not been leached into the subsoil during the period 1956-67 (see also WOODWELL and MARTIN, 1964; DIMOND *et al.*, 1970).

Horizontal Distribution of DDT Residues - 1968.

Plots. Samples were taken at 1 rod (16.5 ft.) intervals in a squared pattern throughout each plot, and residues are given in units in ppm. "as sampled" for ecological interpretation and "ounces per acre" for standardized comparison with dosage and for statistical analysis (Table 2).

Plot reference numbers and letters are similar to those used by MACDONALD and DUFFY (1968).

TABLE 1

Vertical distribution of total DDT residues in soil profiles adjacent to Priceville plots, 1967 (upper - ppm. "as sampled"; lower - ppm. "ovendry")

Horizon		Plot location (Fig. 1)			
Depth (in.)	Class*	I	II_U	II_L	III
Surface	L	4.49 6.87		12.85 21.33	10.76 17.43
			3.01** 5.18		
1	F - H	0.70 1.08		2.15 3.91	0.34 0.51
3	H - Ah	Trace	0.11 0.17	0.40 0.69	0.03 0.04
6	Ae	ND	Trace	ND	ND
12, 18	B				
24, 36	C	ND	(not detectable)		ND
	R				

* LEAHEY (1965) Trace <0.025 ppm.
** moss

TABLE 2

Statistical values for distribution of DDT residues in Priceville plots - 1968.

Statistical parameter	Plot I	 II	 III
		ppm. "as sampled"	
N	22	22	22
Mean	0.58	1.37	0.45
S	0.20	0.87	0.14
SE	0.04	0.19	0.03
		ounces per acre	
Mean	11.09	14.24	9.13
S	3.43	8.06	2.73
SE	0.73	1.72	0.58
χ^2 homogeneity (33.92 at P=0.05)	20.70	95.82	16.71
t test of means (2.024 at P=0.05)	I/II	1.686	
	I/III		2.096
	II/III	2.817	

TABLE 2 (Cont'd)

Plot II regression of DDT residue (y) on elevation (x)	(see MACDONALD and DUFFY, 1968)
Equation	$\hat{Y} = 14.24-0.56(x-\bar{x})$
Correlation coefficient r (0.537 at P=0.01)	-0.69
Analysis of variance, significance of regression F (14.8 at P=0.001)	18.15

In 1968, Plots I and III, representing mixed forest types and gently undulating topography, had uniform distribution of residues (internal X^2 test), and mean total DDT residues of 11.09 and 9.13 oz. per acre, derived from the 70 oz./acre reported as applied to the general area between 1956 and 1967 (Table 4). The means are just significantly different (t test), and this may reflect the effect of hardwood-softwood forest cover (Fig. 1) on the common dosage. The mean of Plot II residue was larger than I and III and significantly different from that of III (t), but its large variance and X^2 show lack of uniformity of residues within the plot and wide confidence limits of the mean of II. A regression of residue (y) on elevation (x) (Table 2), demonstrated that a very significant negative correlation existed between these two parameters (Tables 2 and 3), and this is interpreted as evidence of gravitational transport of DDT residues on inclined land (see also LICHTENSTEIN, 1958; EDWARDS, 1966). The larger average DDT dosage in the creek valley may have arisen due to unique meteorological conditions associated with this localized topographical feature in a generally undulating environment.

Transects. The positions and residue values at 100-yard intervals for transect-sampling of the Priceville area are given in Fig. 1, and statistical parameters for transects are given in Table 3.

TABLE 3

Statistical values for distribution of DDT residues in Priceville area by transect-sampling (Fig. 1) - 1968.

Statistical Parameter	Transect A	Transect B	Transect C	Whole area
	ppm. "as sampled"			
N	30	24	20	74
$\bar{x}$	0.55	0.63	0.58	0.58
S	0.21	0.28	0.26	0.25
SE	0.04	0.06	0.06	0.03

TABLE 3 (Cont'd)

Statistical Parameter	Transect A	B	C	Whole area
	ounces per acre			
$\bar{x}$	9.57	11.54	11.73	10.79
S	3.15	5.00	4.86	4.36
SE	0.58	1.02	1.09	0.51
X^2	30.08	49.87	38.27	128.72
(value at P=0.05/N)	(43.77)	(36.42)	(31.41)	(95.08)
t test of means (value at P=0.05)	A/B 1.764 ; (2.009)	A/C 1.910 ; (2.013)	B/C 0.127 (2.019)	

These show general heterogeneity within transects (X^2) with no special localized aberrations such as the creek valley (Table 2) to explain their lack of internal uniformity (see also DIMOND et al., 1970). However, the means of combinations of pairs of transects are not significantly different, and the whole area mean (10.79 oz./acre) is a reliable estimate of the average residue remaining in Priceville soils in 1968 from the area treatment of 70 oz./acre accumulated between 1956 and 1967.

DDT Residue History, 1968-71.

Plots. The data for 1968 (Fig. 2) were derived from 22 samples from each of the three plots, and statistics are given in Table 2. However, the average plot residues for 1969, 70 and 71 were derived from 8 pooled samples.

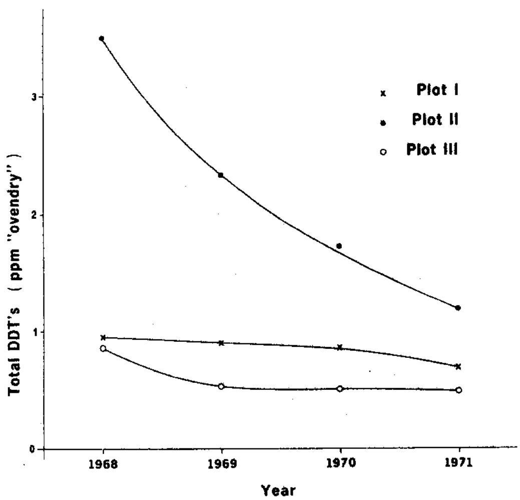

Figure 2. DDT residues in Priceville plot soils over 4 years.

Accurate interpretation of residue history beginning from 1968 (the year after DDT-treatment ceased) is difficult, considering the mixture of ages of residues comprising the starting total at that time. This makes "half-life" estimates unreliable since rates of loss appear to be variable (Fig. 2). However, in case an approximate forecast might be useful, then if the average slopes for DDT residues found in Plots I and III were extrapolated to 50 per cent value (Fig. 2), a "half-life" estimate of less than 10 years would be obtained for these forest soils (see also DIMOND _et al._, 1970).

It is evident (Fig. 2) that larger residues were lost at a greater rate, and also that rates of loss within the 3 plots were variable. There was no evidence from this Priceville study that DDT residues in soil increased significantly for the first few years after cessation of forest spraying, then declined (cf. WOODWELL and MARTIN, 1964), although contaminated foliage did continue to fall to the ground for several years (this was established by collecting and analyzing the accumulated debris from snow drifts in Spring), (see also MACDONALD and DUFFY, 1968).

Residue composition and significance. No further breakdown products of DDT were found under analytical conditions set for pp'DDT, DDE and DDD, and op'DDT. The composition of DDT residues in Priceville soil for 1968 agreed quite closely between plots and transects (Table 4), but some qualitative change with time is evident from the historical data (see also DIMOND _et al._, 1970).

TABLE 4

Compositions of DDT residues in Priceville soils at various locations and times

Location	Year	Residue compositions (%) op'DDT	pp'DDE	pp'DDD	pp'DDT
Transects	1968	8	7	T	85
Plot I	1968/71	9/11	6/9	T	85/80
Plot II	1968/71	9/9	8/8	T	83/83
Plot III	1968/71	8/9	8/10	T	84/81

T < 1%

The proportion of pp'DDT in the total residue decreased from 1968-71, while pp'DDE, and to a lesser extent op'DDT, proportions appeared to increase. No significant amount of pp'DDD was found in these forest soils, and Plot II again demonstrated anomalies in the lack of change in residue composition with time.

Acknowledgements

The author acknowledges with appreciation the co-operation received from staff of the Forest Research Laboratory, Fredericton, N.B. and Forest Protection Ltd., Campbellton, N.B. The technical assistance of G. Smith, R. Fox and D. Bonnett is gratefully acknowledged.

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