Persistence of DDT in Orchard Soils[a/]

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In 1966 we reported that about 88% of the DDT remaining in the soil of two orchards which had been treated since 1946 was in the upper six inches (1). We concluded that contamination of the land adjacent to the orchards was slight, and that losses in underground water were negligible. We have been interested in the further fate of these residues, and, after a 5-year lapse, have collected and analyzed additional samples from the same orchards. This report summarizes our results.

EXPERIMENTAL

Field Plots:

Between 1946 and 1964 the Hood River orchard was treated with 388 lb of DDT and 14 lb of dicofol [4,4'-dichloro-α-(trichloromethyl) benzhydrol] per acre. Additional treatments were: 1965, 15 lb of DDT and 5.7 lb of dicofol; 1966, 11 lb of DDT; and 1967, 2.4 lb of dicofol, for a total of 414 lb of DDT and 22.1 lb of dicofol. The Medford orchard received 169 lb of DDT and 10 lb of dicofol per acre (1947-1964) and 2.16 lb of dicofol in 1965 and again in 1966, for a total of 169 lb of DDT and 14.32 lb of dicofol.

The Hood River orchard is located in the Columbia River gorge in North-Central Oregon where the mean temperature is 50.5°F, and the average precipitation is 29.7 inches. The Medford orchard is located in an interior valley in Southern Oregon where the mean temperature is 53.9°F, and average precipitation is 19.6 inches.

The soil samples were composites made of subsamples from the drip zone of 5 trees, i.e., 5 cores per sample. The samples were taken with a 3/4-inch soil auger at 0 - 6, 7 - 12, 13 - 24, and 25 - 36-inch levels.

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Analytical Methods:

The samples were extracted by shaking for 1 hour with a 1 to 1 mixture of acetone:hexane. The extracts were washed free of acetone and dried with anhydrous sodium sulfate. They were analyzed without cleanup by electron capture gas chromatography using a column of 2 to 1 QF-1-Dow-11 on 100/200 mesh HP Chromosorb W at 180°C. Other details of the analytical method were described earlier (1). Resolution of DDT analogs and metabolites was good except that when residue levels were high TDE appeared as a shoulder on the larger p,p'-DDT peak. Dicofol was converted to its thermal decomposition product, 4,4'-dichlorobenzophenone (DBP).

To measure the soil levels of dicofol and DBP, aliquots of the extracts were given a preliminary cleanup by passage through an activated Florisil column and eluted with 300 ml of 3 to 1 hexane:ethyl ether. The eluates were concentrated and spotted on alumina coated TLC plates which were developed with a 2 to 1 mixture of carbon tetrachloride:hexane. The R_f values in this system were 0.11 for dicofol and 0.50 for DBP. The identity of the two compounds were confirmed by their mass spectra. The adsorbent was scraped from the plates in the appropriate areas, extracted with acetone and quantified by electron capture gas chromatography. The amounts determined by this TLC procedure agreed with those indicated by the DBP peaks in the original GC analysis of the soil extracts.

The sensitivity of the analytical method was 0.01 ppm for all compounds. The reliability of the analytical method was confirmed by analyzing fortified samples. Recovery averaged 89%. The pesticide concentrations were calculated on the basis of dry weight of soil and have not been corrected for recoveries.

RESULTS AND DISCUSSION

The distribution of residues in the soil profile of the two orchards is summarized in Table I. These are probably maximum values because the samples were taken from the drip zone of the trees. Dicofol and DBP analyses are included because of the possibility that one or both of these compounds are metabolites of DDT. The relatively high levels of dicofol and DBP in the upper layers probably reflect the more recent applications of dicofol to the two orchards. The high value for DBP (7.25 ppm) in the 0 - 6 inch zone of the Hood River soil cannot be explained.

TABLE I

Vertical Distribution of DDT Analogs and Metabolites in Orchard Soils, 1970

Soil level, inches	Pesticide concentration, ppm					
	p,p'-DDT	o,p'-DDT	p,p'-DDE	p,p'-TDE	Dicofol	DBP
			Hood River			
0 - 6	33.1	5.59	7.61	1.59	2.44	7.25
7 - 12	7.25	1.20	0.97	0.18	2.32	0.87
13 - 24	1.08	0.17	0.19	0.02	0.50	0.19
25 - 36	1.02	0.11	0.12	0.01	0.36	0.07
			Medford			
0 - 6	14.35	2.99	2.50	1.40	3.58	0.86
7 - 12	1.79	0.36	0.38	0.21	0.98	0.09
13 - 24	0.69	0.11	0.12	0.07	0.32	0.06
25 - 36	0.32	0.07	0.07	0.05	0.13	0.05

A comparison of these results with those obtained in the 1965 experiments, expressed as percent increase or decrease, is given in Table II. There was a substantial decrease in the amount of DDT and its analogs in the top 6 inches, about 30% in both orchards. About 29% (Medford) and 36% (Hood River) is due to downward movement. Apparently the remainder was lost by evaporation or by degradation to products not detected by our method. There was a sharp increase, percentagewise, in the pesticide residues found at the 25-36-inch level.

TABLE II

Changes in Vertical Distribution of Total DDT, 1965 - 1970[a/]

Soil level, inches	Hood River		Medford	
	Change, µg/sample	Change, %[b/]	Change, µg/sample	Change, %[b/]
0 - 6	- 7129	- 31	- 2425	- 30
7 - 12	+ 1994	+ 159	- 77	- 6
13 - 24	- 321	- 16	+ 471	+ 136
25 - 36	+ 861	+ 247	+ 307	+ 331
0 - 36	- 4595	- 18	- 1724	- 17

a/ Includes analogs and metabolites of DDT from Table I, this article, and Table II and III of Terriere, et al. (1).
b/ As percent of 1965 levels.

The changes in the levels of DDT analogs and metabolites are examined more closely in Table III. The largest losses occurred in p,p'-DDT residues and the largest gains were in dicofol-DBP residues. The data for TDE are erratic, showing a decrease in Hood River and an increase in Medford. This may be due to analytical difficulties in those samples where DDT concentrations were high.

TABLE III

Changes in the Amounts of DDT Analogs and Metabolites, 1965 - 1970

Pesticide	Hood River		Medford	
	Change, µg/sample[a/]	Change, %[b/]	Change, µg/sample[a/]	Change, %[b/]
p,p'-DDT	- 6881	- 35	- 2600	- 37
o,p'-DDT	- 643	- 24	- 140	- 14
p,p'-DDE	+ 798	+ 46	+ 210	+ 36
p,p'-TDE	- 670	- 57	+ 155	+ 52
Dicofol-DBP	+ 2801	+ 196	+ 727	+ 77

a/ Sum of residues in the entire 3 foot core.
b/ As percent of 1965 levels.

An interesting aspect of the data of Table III is the increase since 1965, on the total sample basis, in the amount of dicofol-DBP. Since both orchards were treated with additional dicofol during this period, 8.1 lb/acre in Hood River and 4.32 lb/acre in Medford, this increase might be expected. However, during the same period the Hood River orchard received an additional 26 lb/acre of DDT, and in the soils of both orchards both p,p'- and o,p'-DDT decreased markedly. These results suggest two possibilities regarding the dicofol-DBP residues; in soil these compounds are more stable than DDT, or they are metabolites or degradation products of DDT. The latter possibility is supported by Lichtenstein, et al. (2) who report traces of dicofol in soil treated earlier with DDT.

One of the most interesting aspects of these results is the similarity in the residue trends seen in the two locations. The net loss in the 5-year period in the Hood River soils amounts to 18% and in the Medford soils to 17%. This is in spite of differences in climate, soil type, and cultural practices. The Hood River soil is a sandy loam and, in the orchard studied, is not cultivated. The Medford soil is clay adobe which, in this orchard, is kept free of vegetation by regular cultivation.

It is clear from this and our previous study that the DDT residues in these soils attained a threshold level within a few years after its regular use began. The decline in total residues is proceeding at a rate of about 3.5% per year, based on those present in 1965, with an additional loss of the amounts added since 1965.

We have been unable to locate other reports of similar investigations, but our results are confirmed in part by Harris et al. (3) who show that DDT in orchard soils range from 25 to 138 ppm and by Duffy and Wong (4) who found DDT up to 20 ppm in orchard soils. The decline of DDT residues in soils is confirmed by a Mississippi study (5) which showed that an initial residue of 2300 ppm declined by 30 to 50% in a 20-year period.

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