DDT and Copper Residues in a Vineyard Soil

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The accumulation of DDT and copper residues was determined in the soil of a vineyard in which three or four regular sprays had been applied annually for 6- and 12-year periods, respectively. The build-up of DDT in the 0- to 3-inch layer was about 18 pounds per acre in the 6-year program and 27 pounds per acre in the 12-year test. About one half of the total DDT applied over a period of 6 years and two thirds of that applied over a period of 12 years were not recovered from the soil. Only small amounts of DDT were found below the top 3-inch layer of soil. The copper content of this soil was 40 p.p.m. before any sprays were applied. After 6 years, the top 3-inch layer contained twice as much copper, but the second 3-inch layer was unaffected. After 11 years there was about three times the original amount of copper in the top 3 inches of soil and nearly twice as much in the second 3-inch layer.

During the last 15 years many vineyardists in the Chautauqua Grape Belt have used DDT and copper compounds continuously to control insects and diseases. Three or four annual post-blossom DDT sprays were applied in combination with a fungicide. Some form of Bordeaux mixture was used until it was shown *(13)* that Bordeaux sprays in combination with DDT retarded the vine growth of the Concord grape. Since 1952 Ferbam has been the recommended fungicide in the first spray followed by a low soluble copper compound in the second and third treatments.

The question now arises as to how much of these materials may have accumulated in the soil. The literature on DDT contains no reference to residues in vineyard soils. Also, information is lacking on the accumulation of copper from sprays applied for disease control in the Chautauqua district.

Extensive investigations *(1, 6, 8, 9)* have shown that DDT accumulated in different types of soil distributed throughout the United States when it was regularly applied as a pesticide to various crops. Ginsburg *(5)* and Lichtenstein *(9)* both found DDT in amounts ranging up to more than 100 p.p.m. in orchard soils, and smaller but significant quantities in soils planted to corn, potatoes, beans, and other annual crops. The persistence of DDT in 85 different soil types was reported by Fleming and Maines *(4)*. After 8 years of exposure about one half of the original DDT remained. They found that texture and organic content of the soil, cultural practices, environmental conditions, and method of application were factors affecting the persistence of DDT.

Experimental Procedure

Soil samples were obtained in May 1958 from a vineyard upon which accurate and complete records of spraying practices were available from 1946 through 1957. The soil type was Alton gravelly loam. The vines were planted in 1927 and no insecticide or fungicide treatments were known to have been made until 1946.

All sprays were applied with a hooded boom. Detailed data for each year are recorded in Table I. The total

Table I. Detailed Spray Schedule

	Spray Formulas, Lb./100 Gallons					Total Amount Applied, Lb./Acre	
Year	DDT, 50% w.p.[a]	$CuSO_4$, $5H_2O$	Lime, hyd.	Gallonage/Acre	No. of Sprays	DDT	Copper
		12-Year Program, DDT-Bordeaux Mixture					
1946	1.5	2.0	4.0	220	4	6.60	4.40
1947	1.5	2.0	2.0	220	4	6.60	4.40
1948	1.5	4.0	4.0	220	1	1.65	2.20
	1.5	3.0	4.0	220	1	1.65	1.65
	1.5	2.0	2.0	220	2	3.30	2.20
1949		As in 1948		As in 1948	4	6.60	6.05
1950		As in 1948		As in 1948	4	6.60	6.05
1951		As in 1948		As in 1948	4	6.60	6.05
1952	1.5	4.0	4.0	250	2	3.75	5.00
	1.5	2.0	4.0	300	1	2.25	1.50
1953		As in 1952		As in 1952	3	6.00	6.50
1954		As in 1952		As in 1952	3	6.00	6.50
1955		As in 1952		As in 1952	3	6.00	6.50
1956		As in 1952		As in 1952	3	6.00	6.50
1957	1.5	0.0	0.0	As in 1952	3	6.00	0.00
		Totals		10,080	42	75.60	65.50
	DDT	Ferbam	Copper[b]				
		6-Year Program, DDT-Ferbam-Low Soluble Copper					
1952	1.5	1.5	0.0	250	1	1.88	0.00
	1.5	0.0	2.0	250	1	1.88	2.75
	1.5	0.0	2.0	300	1	2.25	3.30
1953		As in 1952		As in 1952	3	6.00	6.05
1954		As in 1952		As in 1952	3	6.00	6.05
1955		As in 1952		As in 1952	3	6.00	6.05
1956		As in 1952		As in 1952	3	6.00	6.05
1957		As in 1952		As in 1952	3	6.00	6.05
		Totals		4800	18	36.00	36.30

[a] Wettable power = w.p.
[b] Metallic copper, 55%.

amounts of actual DDT and metallic copper applied over the 6- and 12-year periods are also given. The application program was changed from four to three annual sprays midway in the 12-year program. Nevertheless, almost the same amounts of DDT were applied in each of the two 6-year periods, because a larger amount of spray was needed for adequate coverage as vine growth increased in the later years. Applications of Bordeaux mixture varied much more than did DDT.

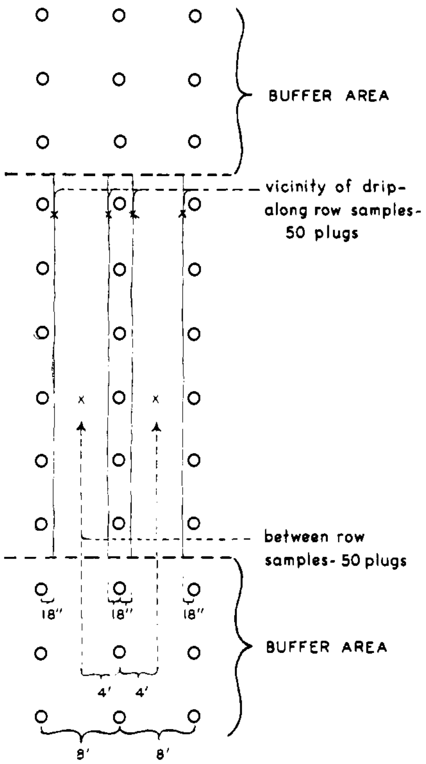

Figure 1. Individual plot arrangements, showing vineyard locations from which soil samples were taken

Treated and untreated plots were randomized and replicated four times. In recognition of the changed fungicide recommendations in New York State, a new spray program using ferbam and low-soluble copper materials with the same amounts of DDT was begun in 1952. Four new plots for this 6-year program were obtained by dividing each of the previously untreated 6-row replicates into two three-row plots. The remaining three-row plots continued to serve as untreated controls. The original treated plots were continued in the 12-year program with the changes noted in Table I.

The location at which soil plugs were taken with respect to vines and rows is shown by the diagram in Figure 1. Samples of soil designated as having been taken "along the rows" were made up of soil plugs from a strip about 36 inches wide. Soil plugs comprising samples from "between rows" were taken along a line approximately one half the distance between rows.

Each cylindrical soil plug was $1^5/_8$ inches in diameter, 3 inches long, and contained a volume of 6.22 cubic inches. To obtain the 3- to 6-inch soil layer, a second sampler was inserted in the same hole after the first 3-inch plug had been removed. Fifty such plugs were taken from each plot and the weight recorded. The sample was then sifted through a $^1/_4$-inch hardware screen to remove stones and plant debris. After mixing, two 500-gram subsamples were air dried and the loss in weight was recorded. In this way, the final results could be expressed on a unit weight basis as parts per million of air dried soil, or on a unit volume basis as pounds per acre of soil 3 inches deep.

Fifty grams of the air-dried soil were extracted with acetone for 4 hours in a Soxhlet apparatus. An aliquot of acetone extract equivalent to 5 grams of soil was evaporated to dryness in an air stream and analyzed by the Schechter-Haller method (*11*) as modified by Downing and Norton (*3*). The DDT reference standard was selected by the Entomological Society of America and contained 78% of *p,p'* isomer and 22% of *o,p'* isomer. The average composition of technical grade DDT is similar to this standard and no correction for the *o,p'* isomer was attempted. Schechter *et al.* (*11*) found that DDE [1, 1' dichloro-2,2' bis-(*p*-chlorophenyl) ethylene], the primary decomposition product of DDT, gives a red color instead of the blue characteristic of DDT. Both DDT and DDE were determined in the same solution by measuring the absorbance at 597 and 520 mμ and using the differential method of analysis of Knudson *et al.* (*7*). Ninety-five per cent recovery of known amounts of DDT and DDE added to soil was demonstrated. No chromatographic cleanup of the extract was necessary, and no correction was made for the apparent insecticide content of the soil.

The copper analyses were made by digesting one gram of soil samples with acid and using the colorimetric method of Strafford, Wyatt, and Kershaw (*12*).

Results

DDT and DDE analyses of soil samples taken at 0- to 3- and 3- to 6-inch depths are given in Table II. In general there is rather close agreement between replicates in amount of DDT

Table II. Recoveries of DDT and DDE from a Vineyard Soil after Treatment of the Vines with a Standard Spray Schedule over Periods of 6 and 12 Years

Treatment Period	Replicate No.	0- to 3-Inch Soil Layer: DDT P.P.M.	DDT Lb./3-inch A	DDE P.P.M.	DDE Lb./1-inch A	3- to 6-Inch Soil Layer: DDT P.P.M.	DDT Lb./3-inch A	DDE P.P.M.	DDE Lb./3-inch A
					Samples from along Row				
1952–57	1	21.8	20.1	4.4	3.7	0.0	0.0	0.2	0.2
	2	19.2	16.3	1.2	1.0	0.3	0.4	0.0	0.0
	3	19.6	17.1	3.6	3.0	3.7	3.5	0.8	0.8
	4	21.1	16.8	1.6	1.4	1.5	1.5	0.4	0.4
Av.		20.4	17.6	2.7	2.3	1.4	1.4	0.4	0.4
1946–57	1	30.0	28.9	3.8	3.1	1.1	1.3	0.2	0.2
	2	28.6	23.6	7.8	6.4	1.4	1.4	0.0	0.0
	3	31.0	27.3	3.8	3.1	1.1	1.0	0.0	0.0
	4	35.8	27.8	6.2	5.0	2.3	2.1	0.0	0.0
Av.		31.4	26.9	5.4	4.4	1.5	1.5	0.05	0.05
					Samples between Rows				
1946–57	1	20.5	14.8	6.0	4.3				
	2	28.2	20.2	3.0	2.6				
Av.		24.4	17.5	4.5	3.5				
Untreated	1	1.5	1.3	0.0	0.0	0.15	0.15	0.0	0.0

found along the rows. This 36-inch strip would have the maximum deposit where drip from vines, run-off from the sides of the hooded boom, and deposits weathered from the foliage accumulated in the soil. In the top 3 inches of soil, the average accumulation of DDT was 17.6 pounds per acre in 6 years and 26.9 pounds per acre in 12 years. Only 1.4 to 1.5 pounds of DDT per acre were found at the 3- to 6-inch level. In the unsprayed plots 0.1 to 1.3 pounds per acre were recovered after 12 years. The latter figure is somewhat in excess of the precision of the method.

Data on copper residues accumulating after 6 and 11 years are presented in Table III. Copper normally present amounted to about 40 p.p.m. This value was not deduced from the values presented in Table III. After 6 years, the amount of copper was about doubled in the top 3-inch layer of soil, whereas there was little change in the amount present in the 3- to 6-inch layer. In the 11-year plots, the copper found in the 0- to 3- inch layer of soil was three times, and in the 3- to 6-inch layer twice the amounts normally present.

Table III. Accumulation of Copper in Vineyard Soil after Treatment of the Vines with a Standard Schedule over Periods of 6 and 11 Years

Treatment	Replicate No.	0- to 3-Inch Soil Layer Copper Residue		3- to 6-Inch Soil Layer Copper Residue	
		P.P.M.	Lb./3-inch A	P.P.M.	Lb./3-inch A
		Samples from along Rows			
1952–57	1	107	98	43	41
	2	92	78	50	49
	3	113	99	42	40
	4	87	69	27	26
Av.		100	86	41	39
1946–56[a]	1	126	121	78	88
	2	158	130	95	94
	3	125	110	50	49
	4	142	110	70	67
Av.		138	118	73	75
		Samples from between Rows			
1946–56[a]	1	98	71		
	2	95	68		
Av.		97	69		
Untreated	2	41	36	41	36

[a] Application of copper fungicides was discontinued after 1956.

Discussion

The data in Table II do not show the actual loss of DDT in terms of the amount applied. However, this can be calculated when the spacing of vines is known, Figure 1. The area designated as along the rows is 37% and that as between rows is 63% of the total area. To calculate the amount of DDT per acre of vineyard, multiply the amounts of DDT and DDE in pounds per acre for the two areas sampled by their respective fraction of the total area and add the products. Such a calculation yields a value of 25.3 pounds of combined DDT and DDE per acre after 12 years of treatment and represents 33% of the DDT applied during that period. In the 6-year period, only about half the DDT applied was lost.

There are a number of conditions which exist in vineyards which are likely to influence the extent to which DDT residues accumulate in the soil. One such factor is sunlight. Lindquist, Jones, and Madden (*10*) and Chisholm *et al.* (*2*) reported that DDT decomposed more rapidly when exposed to sunlight. Grape vines, because of the system of training, afford relatively little shading of the soil as compared to the shading in peach and apple orchards. Thus, there is more exposure of the DDT present in the soil to direct sunlight. Furthermore, the number of diskings, four to six or more per season, provides clean type cultivation, especially during the part of the growing season when there is a minimum of rainfall. Undoubtedly such a practice tends to increase the exposure of DDT residue to sunlight.

Between the rows where no spray was applied, 17.5 pounds of DDT per acre were found in the 0- to 3-inch layer of soil. Disk cultivation to a depth of 2 to 3 inches probably accounts for the horizontal redistribution of the spray residue in the soil.

Although the physical properties of this soil were favorable to leaching, 92% of the total DDT recovered remained in the top 3 inches of soil and only 8% had penetrated into the 3- to 6-inch soil layer. In this connection, Ginsburg and Reed (*6*) reported that in orchard soils, most of the DDT was found in the top 4-inch layer, corresponding roughly to the depth of cultivation. For field crops such as corn and potatoes, DDT was not all in the top soil layer, but fairly uniformly distributed throughout the plow depth layer of 0 to 9 inches. They concluded that DDT did not penetrate downward in the soil by leaching action, but only by mechanical mixing.

The only known decomposition product of DDT recovered from this soil was DDE. Others products such as dichlorodiphenylacetic acid and dichlorobenzophenone were not detected. Appreciable amounts of DDE were found only in the top soil layer. In the 6-year plots, the weight ratio of DDE to DDT was 1:8 and in the 12-year plots it was 1:6.

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