# DDT Residues in a Vineyard Soil After 24 Years of Exposure[1]

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Many vineyards in the New York Chautauqua Grape Belt have been treated with DDT sprays for about 25 years. Each season's dose has usually been distributed in 3-4 post-blossom sprays to give a yearly total of 4-6 lbs. active ingredient per acre. A certain portion of the spray lands directly on the soil or enters the soil indirectly through runoff, contaminated leaf and fruit drop, etc.. This DDT is then subjected to volatilization and degradation by physical, chemical and biochemical means.

In 1946 an experiment was initiated to follow the fate of DDT in a typical Chautauqua vineyard soil. Careful records were kept with respect to the time and amount of DDT applied to vines in randomized plots. After 6 and 12 years of continuous DDT applications, soil samples were taken and analyzed for DDT and DDT degradation products. The results of these analyses indicated that most of the DDT residues were confined to the top 3-inch layer; that about half of the DDT applied over a 6-year period was not recovered from the soil; that two-thirds of the DDT applied over a 12-year period was not recovered from the soil; and that the only degradation product present in the soil was DDE (1). This paper reports the findings from soil samples taken from vineyard plots sprayed annually for 24 years with DDT.

## METHODS

Most of the conditions and methods used in this study have been described previously (1). Samples were taken from a vineyard planted in 1927 in Alton gravelly loam soil. Prior to 1946, the soil was not subjected to any known insecticide or fungicide treatments. In the 12-year period from 1946-1957, 4 replicate plots received 75.6 lbs. of DDT per acre with an additional 89.25 lbs. per acre applied from 1958 to 1969. Thus, these plots received 164.85 lbs. per acre of DDT over a 24-year period. Another 4-plot series was sprayed with 36 lbs. of DDT per acre over the 6-year period 1952-1957 with another 18 lbs. per acre applied from 1958-1960 (54 lbs. per acre in a 9-year period).

Soil samples from the DDT plots and from untreated plots were taken in the spring of 1971. Fifty 0-3 inch plugs and fifty 3-6 inch plugs were removed from an area half-way between the rows of vines and from an area along the drip-line near the base of the vines. Each group of 50 plugs was mixed thoroughly, weighed,

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screened, and reweighed. Two 500 g. subsamples were airdried and reweighed to determine the moisture content of the soil.

The procedure used previously for DDT analysis involved a Soxhlet extraction and Schechter-Haller determination (1). For this study, a 100 g. sample of airdried soil plus enough water to make a slurry were placed in a one l. erlenmeyer flask. Then 600 ml. of 3:1 petroleum ether:isopropanol was added and the contents were mixed for 5 min. with a wrist-action shaker. The liquid was decanted into a one l. separatory funnel and mixed thoroughly with 150 ml. of water. After separation of the layers, the water-isopropanol fraction was removed and the remaining fraction was reextracted 2 more times with 150 ml. of water to remove almost all of the alcohol. The petroleum ether fraction was dried over anhydrous sodium sulfate.

Detection of DDT and DDE was accomplished by injecting a portion of the petroleum ether extract into an Aerograph Hy-Fi Model 550-B gas chromatograph equipped with an electron-capture detector. The column was 3' x 1/8" and was packed with 5% Dow 11 on 60-80 mesh Gas-Chrom Q. The column-detector temperature was 195°C and the injection block was 220°C. Recovery from spiked DDT soil samples averaged 95%. Several soil samples were analyzed by the old procedure (1) and the results were very similar to those found with the gas chromatography procedure.

## RESULTS AND DISCUSSION

The amount of DDT and DDE found in the 0-3 and 3-6 inch soil samples is shown in Table 1. For comparative purposes, results from previous analyses are also given in the table. All values represent the average of 4 replicate plots.

The samples for the 6- and 12-year periods were taken in the spring following the last treatment year. In the case of the 24-year treatment period, the samples should have been removed in the spring of 1970, but there was a delay until the spring of 1971. However, there was no DDT applied in 1970. Thus this delay should not have any drastic effect on the results so that the 24-year values can be compared with the 6- and 12-year values. However, samples for the 9-year period (1952-60) were also taken in the spring of 1971. Even though there were no further applications of DDT to these plots after 1960, this delay in sampling must be considered in the interpretation of these results.

Several trends became evident when comparing data for the 6-, 12-, and 24-year treatment periods. First of all, the percentage of the total residue recovered as DDE increases with time. Considering the total 0-6 inch soil layer, only 12% of the residue was DDE after 6 years of treatment. The percentage increased slightly after 12 years, but by 24 years DDE represented 27% of the recovered residues. These results indicate that DDT is slowly degraded to DDE and that DDE is somewhat more persistant in the

vineyard soil than is DDT. Conversion of DDT to DDE has been shown to occur in other soils (2).

Secondly, the percentage of DDT and DDE recovered from the soil with respect to the amount of DDT applied to the vineyard decreases with time. Using a formula which considers the area along the row and between the row and the spacing of vines, the actual loss of DDT in terms of the amount applied can be calculated (1). In the 6-year period, about half of the DDT applied to the vineyard was recovered from the soil as DDT and DDE; after 12 years of spraying only 33% was recovered; and after 24 years, only 22% could be recovered. Thus, the DDT loss rate from the soil probably exceeded the accumulation rate over the 24-year period.

TABLE 1

Recovery of DDT and DDE from vineyard soil after treatment of the vines with a standard spray schedule over periods of 6-24 year

| Treatment period | Lbs. DDT applied/acre | lb./0-3" acre DDT | lb./0-3" acre DDE | lb./3-6" acre DDT | lb./3-6" acre DDE | lb./0-6" acre DDT | lb./0-6" acre DDE |
|---|---|---|---|---|---|---|---|
| | | Along dripline | | | | | |
| 1952-57[a] | 36.0 | 17.6 | 2.3 | 1.4 | 0.4 | 19.0 | 2.7 |
| 1946-57[a] | 75.6 | 26.9 | 4.4 | 1.5 | 0.05 | 28.4 | 4.45 |
| 1946-69 | 164.9 | 29.8 | 11.0 | 4.3 | 1.5 | 34.1 | 12.5 |
| 1952-60 | 54.0 | 19.2 | 2.9 | 2.6 | 0.5 | 21.8 | 3.4 |
| Untreated ('69) | | 5.3 | 2.6 | 1.3 | 0.6 | 6.6 | 3.2 |
| | | Between row | | | | | |
| 1946-57[a] | 75.6 | 17.5 | 3.5 | - | - | - | - |
| 1946-69 | 164.9 | 17.3 | 6.9 | 4.4 | 1.6 | 21.7 | 8.5 |
| 1952-60 | 54.0 | 15.8 | 2.6 | 3.3 | 0.6 | 19.1 | 3.2 |
| Untreated ('57)[a] | | 1.3 | 0.0 | 0.15 | 0.0 | 1.45 | 0.0 |
| Untreated ('69) | | 3.2 | 1.7 | 1.3 | 0.8 | 4.5 | 2.5 |

a/ Results taken from reference 1.

A third comparison concerns the amount of residue in the 0-3 inch soil layer with respect to the amount in the 3-6 inch layer. Considering the results along the dripline, 92% of the recovered DDT and DDE was in the 0-3 inch layer after the first 6 years of treatment. This did not vary considerably with results for the 12-year (95%) or 24-year (88%) periods. Samples taken from

between the rows for the 24-year period indicate that 80% of the recovered pesticide was in the top 3-inch layer. Thus, although the physical properties of the vineyard soil were favorable to leaching, most of the DDT and DDE remained in the top 3 inches of soil. This lack of downward migration by DDT has been demonstrated in a number of other soils (3).

There are differences in the amount of residues recovered from along the dripline compared to those recovered between the rows. As expected, in both the 12- and 24-year periods, most of the DDT and DDE was present in the dripline area. This strip from the base of the vine to the outer leaves should receive the maximum deposit because of drip from vines, run-off from the sides of the hooded boom sprayer, and residues from weathered foliage accumulated in the soil. Other than spray drift, deposition between the rows was probably due to disk cultivation which resulted in some horizontal redistribution of the soil residues.

Finally, there is an increase in the amount of DDT recovered from the untreated check plots with respect to time. The 1957 check samples were taken after 12 years of DDT spraying in nearby plots. Although low levels of DDT were found in the top 3 inch check soil, no DDE was present. (It is probable that some DDE was in this soil. Either the level was below detectable amounts or some error in procedure prohibited its detection). After 24 years, the residues of DDT in the check plots increased considerably, were also present in the 3-6 inch layer, and contained DDE. Although the amount of DDT sprayed in the second 12-year period was somewhat higher than the amount sprayed from 1946-57, this would not account for all of the increase. It was probably just a combination of physical factors, such as spray drift, erosion, etc., which caused the increase.

It is more difficult to analyze results from the 1952-60 treatment period. Although the plots were exposed to annual DDT sprays for 9 years, residue samples were taken 10 years after the last treatment. The percentage of the total residue present as DDE in the 0-6 inch soil layer is almost exactly the same as that found in the 12-year study (13.5%). On the other hand, the amount of DDT and DDE recovered from the soil represented 43% of the applied DDT, a figure which falls half-way between the percentages found for the 6- and 12-year periods. Finally, the distribution of residues between the 0-3 inch and 3-6 inch soil layers is very near that found for the 24-year treatment period (88% in the top layer along the dripline and 83% in the top layer between the row). From these results it appears that after DDT treatment ceased, the rate of DDT decomposition and volatilization was slower than it was in plots under continuous exposure to DDT.

A number of conditions exist in a vineyard which may be primarily responsible for the fate of an applied pesticide. Because of the system of training grape vines, little shading of the soil occurs so that exposure of soil residues to direct sunlight is considerable. Furthermore, the clean type cultivation,

with 4-6 shallow diskings per season, increases exposure to sunlight even more. In addition, the disking spreads the residues throughout the top 2-3 inches of soil giving maximum contact with soil microorganisms and with the atmosphere. However, the only known degradation product of DDT recovered in this study was DDE. Other products, such as TDE or dicofol, have been recovered in other soil studies (2,4). Thus, it appears that the DDT applied to the vineyard soil used in this investigation was either volatilized or slowly degraded primarily to DDE.

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