# Soil Toxicity of 2,4-D to Pome Fruit Trees from Herbicide Application<sup>1</sup>

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Abstract. Symptoms of 2.4-D injury were observed on apple and pear trees following commercial herbicide application. This was thought to be due to absorption from the soil. 2,4-D was found to move easily into orchard soils when applied to soil columns and irrigated. Concentrations in excess of 0.5 ppm occurred. Apple trees were damaged by this concentration. 2,4-D is readily inactivated in moist soil or on a moist soil surface. Less than one week is required for deactivation. Although field observations always indicated injury occurred when both 2,4-D and paraquat were applied together, laboratory and greenhouse studies indicated that paraquat did not increase 2,4-D movement or slow its deactivation.

In the spring of 1970 symptoms were noted on some pear trees that resembled hormone-type herbicide damage (Fig. 1, B and C). The weeds under these trees had been spraved the previous summer with 2,4-D plus paraquat. Later in the spring and summer, symptoms were observed in several apple and pear orchards following a weed spray of 2,4-D plus paraquat or 2,4-D plus amitrole (Fig. 1, A and D). In most instances the symptoms were typical of 2,4-D injury (6) but in some cases the only symptom was chlorosis of the terminal leaves of growing shoots and terminal die back (Fig. 1 A). This symptom has not been associated with foliar applied 2,4-D. The non-volatile 2,4-D was applied with standard weed sprayers designed to give minimum drift. All orchards were sprinkler irrigated.

It seemed probable that the injury was due to absorption from the soil. To test this possibility, a solubilized acid formulation of 2,4-D was applied at the rate of 1.68 and 3.36 kg/ha to an area of 4 sq m per tree in 2 orchards with a low pressure sprayer. Spraying was done on a windless day to prevent drift. Within 2 days the plots were sprinkler irrigated with 10 cm of water. Symptoms, especially those shown in Fig. 1 A, appeared on many trees several days later, indicating that 2.4-D had been absorbed from the soil. Davidson and Clay (7) also reported injury to pear trees from a herbicide application of 2,4-D or 2,4,5-T. Their application precluded drift so the herbicide must have been root absorbed since they could detect no volatile herbicide under the trees.

Several studies have been made to determine how readily 2,4-D moves in soils. Crafts (6) states that 2,4-D is not strongly fixed in most soils and that it is subject to leaching. Weber et al. (14) found 2,4-D to be negatively adsorbed by montmorillonite and kaolin which should increase its leachability. Weise and Davis (15) found the amine salt of 2,4-D to leach to a depth of 15 in. in Pullman clay when applied to the soil surface and leached with  $4\frac{1}{2}$  in of water, whereas the ester form remained in the top 3 in. Using percolation tests Crafts (5) found 2,4-D to be retained by some soils but not others. Neither the textural grade nor the parent material gave any clue to the factors affecting retention. Continued leaching with 320 surface cms of water moved the 2,4-D downward in 2 soils but did not completely rid the soil of 2,4-D as determined by bioassay (5). Thus, 2,4-D may be expected to percolate into soils, but it was

not clear what concn could be expected, what concn in the soil would be toxic to apple and pear trees or whether paraquat would affect 2,4-D movement.

Several studies have shown that 2,4-D is readily decomposed in moist warm soils (2, 4, 9, 10). Since the inactivation of 2,4-D is a biological process, it is temp related (1, 2) and proceeds slowly near freezing temp. At 20° to 25°C, 2 to 4 lbs/Ac 2,4-D would be inactivated in about 2 weeks (1). Under orchard conditions a spray would be deposited on the soil surface and the degradation rate there may be expected to be quite different from an incorporated mixture. Brown and Mitchell (2) found that 2 lbs/Ac 2,4-D would be decomposed in 4 weeks at 20% soil moisture but not in 2 weeks when surface applied and not incorporated.

Toxicity of soil 2,4-D to plants is difficult to determine because of its short persistence. Bruns and Clore (3) showed that 'Concord' grapes were injured when the soil concn exceeded 0.5 ppm. Lange and Crane showed that 2,4-D concn up to 0.5 ppm in nutrient solutions had little toxic effect on several deciduous fruit tree seedlings (12). Davidson and Clay did not determine soil concn of 2,4-D that were associated with injury to pear trees (7).

The purpose of this study was to determine 2,4-D concn and the distribution pattern that might be expected in sprinkler irrigated orchards and to determine the influence of paraguat on the pattern since all cases of toxicity involved a combination of the 2 herbicides. It was also our purpose to check deactivation rates and to estimate tolerable 2,4-D concn in the soil supporting pome fruit trees.

## **Materials and Methods**

Soil from 2 orchards showing symptoms of apparent 2,4-D injury were collected and stored moist. The soil from both sites was Supplee sandy loam, some characteristics of which are given in Table 1. Soil 3 represents a good orchard soil which was added for comparison. All soil samples were collected from the 15 to 45 cm depth.

Soil columns 60 cm long were made by taping together aluminum cylinders 7.5 cm dia. x 5 cm long with plastic electrical tape. The column was filled with dry soil and thoroughly wetted and allowed to drain overnight. Herbicides were added to the top of the soil, then water was added to the soil surface to provide a total of 5, 10 or 15 cm of leaching water. Leaching proceeded under about 1 cm head. The herbicides added were either 2,4-D alone or 2,4-D mixed with paraquat or amitrole. Concentrations used were 1, 10 or 100 times that applied in the field. The rate of 2,4-D application was 1.5 lb/ac (1.68 kg/ha) for the 1x concn based on the surface area. A min of 5 replicated columns were used to test each material, combinations of materials, rate of application or amount of leaching.

Commercial solubilized 2,4-D acid (Amchem 638)<sup>5</sup> was used in all columns except those which specifically tested the rate of

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<sup>&</sup>lt;sup>5</sup>The use of commercial products does not constitute an endorsement of these products by the University.

<sup>&</sup>lt;sup>6</sup>Paraquat <sup>14</sup>C was supplied by the Chevron Chemical Company.

movement of the amine (Pennwalt Pennamine). Commercial amitrole and paraquat were used.

After leaching was complete, the column was dismantled, each 5 cm section was dried at 80°C, weighed and assayed for 2,4-D, paraquat or amitrole. Bioassay was based on hypocotyl length of 10 cucumber seeds planted in the soil moistened to field capacity, after 4 days incubation at 26°C. The amount of 2,4-D present was estimated by comparing length of the hypocotyl with control samples planted at the same time in soil containing graduated amounts of 2,4-D. The method is sensitive to 0.1 ppm 2,4-D.

More exact information on the concn of 2,4-D in the soil was obtained by mixing <sup>14</sup>C 2,4-D with the solubilized acid before leaching. After drying at 80°C and weighing each section, 5 g of



- Fig. 1. A. Terminal die back on 6-year-old Bartlett pear following a soil application of 2,4-D at the rate of 3.36 kg/ha and sprinkler irrigated within 48 hours.
  - B. Distorted leaves and shoots of d'Anjou pear in an orchard where 2,4-D had been applied to the soil at the rate of 1.68 kg/ha.
  - Swollen nodes of d'Anjou pear following 2,4-D application to the soil.
  - D. Abnormal growth of apple following soil application of 2,4-D.

	pH	Organic matter	% Sand	% Silt	% Clay	C.E.C. Me/100g	% Base saturation
1. Supplee sandy loam	7.0	0.5	61.8	32.4	5.8	6	83
2. Supplee sandy loam	6.3	0.6	55.0	35.2	9.8	8	74
3. Ritzville silt loam	7.4	0.4	34.0	55.0	11.0	16	90
	Anal	yses by Washingto	on State Soil T	esting Labora	atory		

soil were weighed into a scintillator vial, 10 ml of scintillation mixture was added, the vial was thoroughly mixed and counted. It was determined that c/m/g soil increased linearly with the amount of 14C 2,4-D added over the range used in this experiment.

Movement of paraquat and paraquat-2,4-D mixtures were determined by adding 14C paraquat<sup>6</sup> to commercial paraquat and adding to the top of soil columns. These were 2 cm diam and 50 cm long glass tubes. The soil was packed into the columns, wetted and excess water allowed to drain overnight. The herbicide was added and followed with 15 cm water. When leaching was complete the soil was extruded with air pressure and the column cut into 2.5 cm section, placed on planchettes, dried, weighed and counted in a gas flow proportional counter.

Persistence of 2,4-D was determined by weighing sufficient field moist soil into pint-size covered plastic containers to equal 180g of air dry soil. 2,4-D was added to equal 5 and 10 ppm thoroughly mixed. Additional water was added to bring the moisture content to 18%. The soils were incubated at 10, 20 and  $30^{\circ}$ C. At one week intervals 4 replicate containers from each 2,4-D concn at each temp were bioassayed as described above.

To determine the disappearance rate of 2,4-D on the soil surface, moist soil was weighed into straight-walled, metal soil moisture boxes as described above. These were arranged in a single file and sprayed with a field weed sprayer. The concn of 2,4-D in the containers as determined by bioassay were 0, 2.52, 5.04 and 12.6 kg/ha based on the surface area. The samples were incubated at  $25^{\circ}$ C without stirring, then at weekly intervals 5 replicate boxes from each 2,4-D concn were stirred, made to 18% moisture and bioassayed. An additional surface 2,4-D application and 2,4-D plus paraquat was made on moist soil with a field weed sprayer as described above. The concn of 2,4-D applied was 1.68 kg/ha as determined by bioassay and the paraquat rate was 1.12 kg/h a. Incubation was completed as described above and bioassays were made at weekly intervals.

Soil toxicity of 2,4-D was determined by transplanting young apple seedlings from peat moss into soil having measured amounts of 2,4-D. A further check was made by mixing 2,4-D acid with soil to give concn ranging from 0 to 2.0 ppm, then adding water to form a paste. The soil solution was then extracted with 30 pounds of air pressure and the extract added to undisturbed seedlings growing in peat moss. Finally, the toxicity was evaluated by displacing the soil solution from potted seedlings by thoroughly leaching with 2,4-D solutions. The concn were: 0, 2.5 and 5 ppm. The field capacity was 20% which resulted in a 2,4-D concn of 0, 0.5 and 1.0 ppm respectively, based on the air dry soil.

## Results

The position of greatest  $^{14}C$  activity in the soil column was assumed to coincide with the highest 2,4-D concn. In soil columns where both the bioassay and  $^{14}C$  counts were made this assumption was justified (Fig. 2). Because of the limited time required for leaching, dismemberment of the soil column, and drying at  $80^{\circ}C$  where biological activity stopped, very little breakdown of 2,4-D could have taken place. In all calculations of 2,4-D concn, it is assumed that breakdown was negligible.

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The depth of movement of the 2,4-D, whether added alone or as a mixture with paraquat or amitrole, is given in Table 2. Neither the paraquat nor the amitrole had any measurable effect on the 2,4-D movement (P = 0.01). The distance 2,4-D moved was approx a linear function of the amount of leaching water added. There was some difference among the 3 soils in the depth of 2,4-D movement which appeared to be related to the soil water holding capacity.

Based on the findings in soil columns, 2,4-D applied immediately before a sprinkler irrigation would be concd at 13 to 15 cm with 5 cm of water, 20 to 25 cm with 10 cm of water, and 36 to 40 cm with 15 cm of water. On the average, over 75% of the 2,4-D would occur in a 10 cm zone. There was practically no retention of 2,4-D in these soils as indicated in Fig. 2. Some



Fig. 2. Concentration of 2,4-D in the soil as measured by 14C and length of cucumber hypocotyl in the same column of Ritzville silt loam. Ten times normal field rate (16.8 kg/ha) was added and the column was leached with 15 cm of water. Length of hypocotyl curved broken line; 14C curved solid line.

Table 2. Effect of water application on the average depth of movement of	ľ
2,4-D in columns containing 3 orchard soils.	

Water applied			
(cm)	1	2	3
5	14.0 cm	14.5 cm	11.4 cm
10	25.0 cm	24.6 cm	24.5 cm
15	38.6 cm	34.8 cm	35.4 cm

columns showed a slight retention at the soil surface which was probably due to the toluene used to dilute the  $^{14}C$  2,4-D. Since there was almost no soil retention of 2,4-D, the distribution pattern of 1, 10 and 100x concn were not different.

A limited study was made with an amine salt. Its movement was not different from the acid. Field observations indicated that injury to growing trees was similar when either of 2 commercial amine salts or the acid were used. Since these soils had a high degree of base saturation, it is probable that both the acid and amine salt reacted to form the Ca salt in which form the 2,4-D moved.

Paraquat added alone invariably remained in the upper 5 cm section of the soil column regardless of the paraquat concn or the amount of leaching water added. Bioassay showed no toxicity to cucumbers even with 100 times normal field concn. This permitted an assay for both chemicals when <sup>14</sup>C paraguat was added with non-radioactive 2,4-D. A more precise determination of  $^{14}C$  paraquat movement was made with a column of lesser diam. Paraquat added at the rate of 2.4 mg per column remained in the top 2.5 cm section, but when added at the rate of 240 mg it penetrated to 5 cm or 24 g of soil. When 240 mg paraquat was added with 360 mg of 2,4-D paraquat was detected at 7.5 cm or 36 g of soil. Paraquat probably did form a salt with 2,4-D in the spray tank but reacted with the soil as a base and had no measurable effect on 2,4-D movement. The effect of 2,4D on paraquat movement is not readily explained, but the effect is so slight that it can be detected only in the presence of extremely high concn of both materials.

Amitrole was also retained in the upper 5 cm section of the soil column and 2,4-D had no measurable influence on its movement. Bioassay for amitrole showed no effect on cucumber growth at 1x or 10x concn but the 100x did reduce the length of cucumber hypocotyl.

Deactivation of 2,4-D activity in Supplee sandy loam treated with 5 or 10 ppm 2,4-D and incubating at 20 or  $30^{\circ}$ C was complete in 1 week. At  $10^{\circ}$ C the percentage loss of activity of 2,4-D after 1, 2 or 3 weeks of incubation is shown in Table 3. It is apparent that 2,4-D that carried into the soil by an irrigation following weed spraying would be lost in less than 1 week in warm soils and less than 2 weeks in relatively cold soils.

Table 3. Percent loss of activity of 2,4-D in the soil incubated at  $10^{\circ}$ C and 18% moisture.

	Weeks of incubation				
Concn 2,4-D	1	2	3		
	SOIL I				
5 ppm	80	100	100		
10 ppm	10	94	98		
	SOIL II				
5 ppm	100	100	100		
10 ppm	95	100	100		

The rate of decomposition on the soil surface prior to an irrigation may be a prime factor in 2,4-D use in the orchard. The rate of loss of activity is shown in Table 4. The normal commercial application rates of 1.68 to 2.24 kg/ha of 2,4-D would be essentially gone in 1 week on a warm, moist soil surface. In a second trial where 2,4-D was applied with and

without paraquat lacking incorporation, the 2,4-D lost 97% of its activity in 1 week and 100% in 2 weeks. Paraquat did not affect the deactivation rate.

Table 4. Percent loss of activity when 2,4-D was applied to the soil surface by a weed sprayer and incubated at  $26^{\circ}$ C.

Concentration		Weeks of	fincubation	
kg/ha	1	2	3	4
		Perce	ent	
2.52	99	100	100	100
5.04	95	100	100	100
12.6	25	90	95	100

When small apple seedlings were transplanted into soil containing graded amounts of 2,4-D, 1 of 5 plants was killed with 0.5 ppm; 3 of 5 showed severe toxicity symptoms at 1 ppm; 5 of 5 were killed at 2 ppm. Seedlings growing in peat were not affected by treatment with saturation extracts from soils having 0.25 ppm 2,4-D, showed temporary growth stoppage with extracts from soils having 0.5 ppm 2,4-D, and were killed with extracts of 1.0 ppm or higher.

Potted apple seedlings treated with solutions of 2,4-D showed growth response indicated in Table 5. This treatment showed toxicity similar to that where seedlings were planted in soils of known concn or where saturation extracts were added to plants in peat. Three of the plants in pots leached with 2.5 ppm 2,4-D solution resumed growth after 3 weeks.

Table 5. Effect of replacing the soil solution with 2,4-D solution growth of potted apple seedlings.

Concentration of	Avg length of shoot produced after Treatment		
2,4-D solution $+^{2}$	14 days	34 days	
ppm	(cm)	(cm)	
0	9.2 a <sup>y</sup>	12.4 a	
2.5	8.5 a	10.1 b <sup>x</sup>	
5.0	6.2 b	6.1 c <sup>W</sup>	

 $^{2}$ +Equivalent concn in the soil is 1/5 of the solution added.

<sup>y</sup>Numbers in a column followed by different letters have statistical significance at 5%.

x2 of 5 plants with dead terminals.

w3 of 5 plants with dead terminals.

The distribution pattern of 2,4-D in soil columns fits into the idealized curves described by Hartley (11) for a soluble substance that does not react with the soil. Extrapolation of these curves to field conditions is not justified because of the greater uniformity of soil in columns and faster application rate of the leaching water. In the field the chemical leaches with more dispersion; consequently the concn is lower. In an attempt to more closely simulate field conditions, water was applied to 2,4-D on soil columns as an intermittent mist. Five columns were leached for 48 hours under a measured application of 7.5 to 10 cm of applied water. The distribution pattern was not greatly different from that of Fig. 2, although the band of 2,4-D concn was 10 to 20 cm instead of 10 cm or less. Under field conditions 2,4-D might be applied to a soil after a loss of about 50% of its available water. To simulate this condition, 5 soil columns were dry packed and 2,4-D applied to the dry surface, then irrigated with an intermittent mist. Again the curves were similar to Fig. 2 and over 75% of the 2,4-D was found concd in a band less than 20 cm broad. Under laboratory conditions the 2,4-D moved down into the soil profile and was present in concn in excess of 0.5 ppm from a lx application. Similar concn should be expected in the field in soils that do not leave a strong structural and profile development and the water is uniformly applied with sprinkler irrigation. That apple trees did show symptoms of 2,4-D injury after field application of 2,4-D plus a

Deactivation of 2,4-D in soil proceeds at a rapid rate. The data reported here is similar to that of other investigators except that most investigators report a slower breakdown rate. Audus showed that the rate of inactivation increases with repeated application (1). The soils used in this work have had several field applications of 2,4-D which can account for rapid deactivation. Even surface deactivation is faster than that reported by Brown and Mitchell (2). They report slow to almost no deactivation in dry soil. Deactivation on a dry soil surface was determined only by field sampling sprayed plots. These plots showed almost no loss of activity in a 2 month period while the soil was maintained dry. It may be concluded that orchard weed spraying with 2.4D should be done only when the soil surface is moist or immediately after an irrigation to allow a few days for the soil to deactivate the herbicide.

No effort was made to determine the soil concn toxic to pear trees. It is apparently quite low as Davidson and Clay (7) found pears to be injured when apples sprayed at the same time were not. This data reported above indicates that about 0.5 ppm is the limiting concn for apples. This figure is similar to that reported by Bruns and Clore (3) for grapes and is consistent with the data of Lange and Crane (12) who found a nutrient solution concn of 0.5 ppm to be non-toxic.

#### Conclusion

Sprays of 2,4-D under apple and pear trees can result in soil concn sufficiently high to damage the tree if sprinkler irrigation follows application. To avoid tree injury, application should be made while the surface soil is moist and a few days allowed for the herbicide to decompose. Although field observation implicated paraquat as a contribution to injury in some manner, no such effect was found. Paraquat did not increase penetration into the soil nor decrease the rate of 2,4-D deactivation.

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