

Residues in Apples Subsequent to Ground Sprays of Endrin

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Four different treatments of endrin as a ground spray were applied on orchards of two varieties of apples at two different seasons. Both picked and dropped fruits from the succeeding apple crop were

analyzed for endrin. Depending on the time applied and amount of endrin, zero to 0.005 p.p.m. was detected in the picked apples as compared to a maximum of 0.028 p.p.m. in the dropped fruits.

Marth (1965) showed that several chlorinated hydrocarbons, including endrin, have residues in various plants. According to Nash (1968), soybeans grown in Hagerstown and Lakeland soils showed endrin-¹⁴C residues in hay and seeds. Saha and McDonald (1967) found 0.015 p.p.m. of endrin in wheat when the toxicant was used on the crop at 2.0 lbs. per acre. Apparently related to insect control for previous crops, soybeans growing on cotton land consistently exhibit endrin residue between 0.10 and 0.17 p.p.m. Endrin residues were found by Dupree and Beckham (1968) in turnips, squash, and lima beans, but not in tomatoes. According to Harris and Sans (1967), carrots absorbed most residue > radishes > turnips > onions. Of the four vegetables, only in carrots did the residue approach tolerance. As a possible cause of soil endrin decline and lack of appreciable translocation, Dazzio (1968) reports microbial degradation of endrin by five organisms, probably by extracellular enzyme action. By means of insect bioassay, Mulla (1960) found that approximately 50% of the endrin on the soil surface was lost after 24 hours at maximum daytime temperatures of 120°F. No assigned reason for the loss is given. Green *et al.* (1967) indicate that endrin does not escape readily in drainage waters. As reported in one study of national waters in the United States by the latter authors, endrin reached maximum in 1964 and then decreased. So far, no previous paper on ground sprayed endrin residue in fruits from orchard trees has been seen by the authors.

PROCEDURES

The orchard selected for the endrin treatments was on a rolling type of mountainous terrain in the portion of the northern Virginia apple belt known as the Chester-Braddock soil area. Granitic rock outcrops are present. The herbaceous cover was about average, and not too dense for successful mouse control by ground spray.

Both Red Delicious and Golden Delicious apple trees, mostly in the same tree lines, were employed in these experiments. Four plots of acre size or larger, depending on availability of full crop trees, were ground sprayed for each variety. Based on times of application and toxicant rates, each of the four plots received a different treatment as shown in Table I. Applications of endrin were made on November 15, 1967, and April 26, 1968, prior to the gathering of the fruit samples on October 26, 1968. Both dropped and hand picked fruit from the trees in the treated and check areas were analyzed for endrin residue.

Two toxicant concentrations of ground spray were used to give treatment rates of the 2.0 lbs. and 4.0 lbs. of endrin per acre. The 2.0 lbs. per acre rate was made with a hand

gun, using 3 pints of emulsible endrin (1.6 lbs./gallon) diluted in 100 gallons of water. The higher 4.0 lb. per acre rate of toxicant was applied in the same manner as the lesser rate, by doubling the concentration to 6 pints of emulsible stock solution to 100 gallons of water. In standard ground spray practice, as here applied, the limb-end to limb-end strip width for the length of the tree line received all of the stated acre rate for the toxicant. The untreated alleys between limb-ends or about one-third of the acre received no endrin at all. In the experimental Marshall Orchard, from which the data in Table I were obtained, no ground sprayed endrin had been applied to the check plots during 1966 and 1967.

The object of spraying, as usual in mouse control, was to contaminate the rodent feed that grows above ground. To reduce the drive and to ensure little or no soil penetration, as is recommended in mouse control, the spray gun was regulated to provide a cone about 3 inches in diameter at the point of contact with the soil surface. The spray impact with the cover was 7 to 10 feet from the operator's position. In spraying, the gun was moved laterally from side to side to thoroughly treat the cover along a full tree-line strip across the plot as wide as the limb spread of the tree. The horizontal lines of spray contact with the cover were about 18 inches apart. The angle for holding the gun produced a ricochet action that effectively contaminated the intervening space between parallel lines of impact.

To obtain samples in the orchard, 40 lbs. of the apples were selected at random, about 6 feet high, from various parts of the tree. Proportionate numbers of fruits came from each of the trees of the sampled variety in each plot. For transport to the laboratory, a smaller sample of 8 to 10 lbs. was selected at random from the 40-lb. lot. Except that dropped fruits were obtained from the ground, samples were assembled exactly as those picked from trees.

As a check treatment, additional to those in the experimental Marshall Orchard, fruits of Red Delicious, Golden Delicious, Rome, and Stayman samples were harvested from trees in the nearby Barton Orchard, which had the same insecticidal and fungicidal program as the Marshall Orchard plots. Similarly, as a further check, Red Delicious and Golden Delicious were picked from the Linden Orchard in the vicinity. The Linden orchard received no pesticidal sprays for the two preceding years. Neither of these two neighboring orchards had ever been ground sprayed with endrin. By the analytical procedure employed, traces of endrin were found in the samples for each variety from the two vicinal orchards. A trace represents any amount found below 0.0005 p.p.m. Levels under this amount were below the linearity of the detector. The linearity of the detector for endrin was between 0.0005 and 0.002 p.p.m. The sensitivity of the detector is not dependable outside the above endrin range. By trial and error, the required dilutions of test samples were deter-

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Table I. Endrin Residues in Drops and in Hand Picked Apples from the Marshall Orchard after Ground Sprays for Pine Mouse Control

Date of fruit harvest—October 26, 1968

Analysis Number	Date Ground Spray Applied		Total Endrin Applied, lbs./acre	Sample Source	Endrin Recovered in Fruit, P.P.M. ^a	
	November 1967 (lbs./acre)	April 26, 1968 (lbs./acre)			Golden Delicious	Red Delicious
1	0	0	0	Picked	Trace ^b	Trace
2	0	0	0		Trace	Trace
1	0	0	0	Drops	Trace	Trace
2	0	0	0		Trace	Trace
1	2.0	0	2.0	Picked	Trace	0.005
2	2.0	0	2.0		Trace	Trace
3	2.0	0	2.0		0.002	Trace
1	2.0	0	2.0	Drops	Zero	Zero
2	2.0	0	2.0		Zero	Zero
1	0	2.0	2.0	Picked	0.002	Trace
2	0	2.0	2.0		0.003	0.003
						0.003
						0.002
1	0	2.0	2.0	Drops	0.028	0.006
2	0	2.0	2.0		0.022	0.008
3	0	2.0	2.0		0.020	
4	0	2.0	2.0		0.020	
1	2.0	2.0	4.0	Picked	Trace	Trace
2	2.0	2.0	4.0		Trace	Trace
3	2.0	2.0	4.0		Trace	
4	2.0	2.0	4.0		0.003	
1	2.0	2.0	4.0	Drops	0.006	0.006
2	2.0	2.0	4.0		0.007	0.006
3	2.0	2.0	4.0		0.005	
4	2.0	2.0	4.0		0.007	
1	0	4.0	4.0	Picked	0.005	0.002
2	0	4.0	4.0		0.003	Trace
1	0	4.0	4.0	Drops	0.022	0.013
2	0	4.0	4.0		0.023	0.018
3	0	4.0	4.0		0.020	0.014

^a Endrin standard: Eight trials with endrin spiked fruits free of the toxicant gave a recovery range between 72% and 89.7%.

^b A trace is the range from 0.0005 to less than 0.002 p.p.m.

mined to bring the endrin content within the range of the above linearity. Calculations based on dilutions gave the endrin content of original samples. Eight trials with spiked endrin in fruits grown in orchards not receiving endrin gave a recovery range between 72% and 89.7%.

From the orchard samples, 5 pounds of apple fruit were chosen at random for grinding in a Hobart food chopper. After the ground material was thoroughly mixed, a withdrawn 50-gram sample was freeze dried for approximately 24 hours. The dried sample was then analyzed by means of a modified version of Samuel's method (1966) for chlorinated and thiophosphate residues. The modification consisted of freeze-drying the samples to prevent the possible loss of residues by heat drying. To remove the heavy waxes from the apple fruit, quadruple acetonitrile-hexane partitioning was used in place of the recommended double partitioning.

Apples were prepared for analysis by freeze drying the samples, followed by the above modification, of Samuel's method (1966) for endrin. A 30-gram sample (freeze dried) was blended in an Omni-mixer with 25 ml. of water and 50 ml. of 95% ethyl alcohol for 2 minutes, followed by blending

with 100 ml. of hexane for an additional 2 minutes. The sample was centrifuged twice, the hexane layer was retained and quadruple partitioned (acetonitrile-hexane) to remove waxes and lipids from the sample. Acetonitrile was evaporated and the sample run through Samuel's No. 5 column with methylene chloride to remove pigments or any remaining waxes. The methylene chloride was evaporated, the sample taken up in hexane and injected into a 4% SE-30-6% QF-1 GLC column.

RESULTS AND DISCUSSION

From the November 15, 1967, standard mouse control treatment of 2.0 lbs. of endrin per acre as shown in Table I, only zero to 0.005 p.p.m. of endrin persisted in the fruit at the 1968 harvest time, which was approximately 11 months later. Detection of similar traces of endrin below 0.0005 p.p.m. in orchards where ground sprays had never been employed points to the low persistence levels of endrin, as applied to mouse controls in late autumn.

The late April 1968 endrin treatment ensured a probable

maximum persistence of endrin residue beyond label permitted use of the toxicant. In 1968 the toxicant was applied after petal fall, when the leaves and fruits were initially forming. A slight wind at the time favored spray drift. Dropped apples from the April period plots showed a range from 0.005 to 0.028 p.p.m., which is substantially lower than the 0.04 p.p.m. point at which the USDA would consider action against fruit with such residues. The quantities of residue for picked fruit from the April plots ranged from traces to 0.005 p.p.m., to give a maximum of $\frac{1}{8}$ of the 0.04 p.p.m. level.

CONCLUSION

As judged by the permissible residue standard of 0.04 p.p.m. actionable level, no significant endrin residue persisted

in either picked or dropped fruits harvested from any of the ground sprayed plots.

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