

Residue Studies with Silvex in Apples¹

by R. B. LEIDY

*N. C. Dept. of Human Resources
Environmental Sciences Section
Pesticide Residue Laboratory
Raleigh, N. C. 27611*

and

*M. D. JACKSON, W. A. SKROCH, and T. J. SHEETS
Pesticide Residue Research Laboratory
and Department of Horticultural Science
North Carolina State University
Raleigh, N. C. 27607*

Brambles (*Rubus* sp.), horsenettle (*Solanum carolinense* L.), Virginia clematis (*Clematis virginiana* L.), goldenrod (*Solidago* sp.), poison ivy (*Rhus radicans* L.), buckhorn plantain (*Plantago lanceolata* L.), broadleaf plantain (*Plantago major* L.), wild strawberry (*Fragaria* sp. L.), and other perennial broadleaf weeds and woody plants have been a problem for many years in apple orchards throughout the Appalachian region. Some of these species have increased in numbers following several annual applications of herbicides that control annual weeds (SCHUBERT, 1971; SKROCH et al., 1974) and consequently have become major problems to apple producers.

AMS (ammonium sulfamate), 2,4-D [(2,4-dichlorophenoxy)acetic acid], dichlobenil (2,6-dichlorobenzonitrile), and paraquat (1,1'-dimethyl-4,4'-bipyridinium ion) are labeled for weed control in apple orchards. AMS controls poison ivy; and 2,4-D, dichlobenil, and paraquat are effective against several of the broadleaf perennial weeds. Other means of control are necessary for species that are not controlled by AMS, 2,4-D, dichlobenil, and paraquat. Because silvex [2-(2,4,5-trichlorophenoxy)propionic acid] effectively controls many of these weeds (SCHUBERT, 1972; SKROCH, unpublished results), the studies reported herein were conducted to develop residue data to aid in the registration of this herbicide for use in apple orchards.

Materials and Methods

Plots were established in 1972 in a 20-year-old apple orchard in a Halewood loam soil near Waynesville, North Carolina. Aqueous sprays of four formulations of silvex (isooctyl ester, propylene glycol butyl ether ester, butoxyethanol ester, and acid), each at 1.1, 2.2, and 4.5 kg/ha, were applied to the ground cover and to the base of apple tree trunks August 16, 1972. A stop-drop spray containing 15 ppm of silvex was applied September 4, 1972 (14 days before the first harvest). Each plot contained one apple tree ('Richard Delicious') and all treatments were replicated three times. Residue samples consisting of 30 to 33 apples per sample were collected from each plot 33 and 49 days after application of the herbicidal spray.

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In 1973, plots were located near Fletcher, North Carolina on a Hayesville loam. Aqueous sprays of the propylene glycol butyl ether ester of silvex were applied at rates of 1.1, 2.2, and 4.5 kg/ha to one-tree plots of 'Red Delicious' or 'Golden Delicious' apples on June 13, July 17, and August 14, 1973. Samples for residue analysis were collected from all plots September 12, 1973; therefore, time intervals of 29, 57, and 91 days between application and harvest were included. The age of trees, application method, and sample size were the same as for the Waynesville location.

Daily maximum and minimum temperatures and rainfall were recorded at each location.

Apples were received in the laboratory within 24 hr after harvest. Each sample of 30 to 33 apples (4 to 5 kg) was ground in a Hobart Food Grinder, and a subsample was transferred to a glass jar and frozen at -18°C . For recovery studies, various amounts of silvex (0.05, 0.10, 0.50, and 1.0 ppm) were added to 25-g samples of ground apple, and the herbicide was extracted by the method of CHOW et al., (1971) with the following modifications: 25 ml of water were added instead of 100 ml; $0.2\text{ N H}_2\text{SO}_4$ was used to acidify the filtrate; the ether extract was filtered through anhydrous sodium sulfate and concentrated to approximately 10 ml on a water bath with Kuderna-Danish evaporators; the column eluate was acidified with $0.2\text{ N H}_2\text{SO}_4$; the ether extract was filtered as before and concentrated to 1 to 2 ml on a water bath; air was used to blow the extract to dryness; and the dried extract was methylated with BF_3 -methanol for gas chromatographic analysis.

A gas chromatograph fitted with a ^{63}Ni electron capture detector was used for the analyses. The following operating conditions were employed: inlet temperature, 240°C ; detector temperature, 190°C ; and oven temperature, 185°C . Columns were 183 X 0.63 cm (6 ft X 1/4 inch) glass U-tubes packed with 4% SE-30 + 6% QF-1 on Gas Chrom Q (60/80), and nitrogen was the carrier gas (100 ml/min). Fifty-nine apple samples were extracted and analyzed as above with 0.05 ppm of silvex as the low detectable limit. A recovery of 0.10 ppm was included with each set of samples. The retention time of the silvex methyl ester was 1.5 minutes, and the peak height method was used to quantitate results.

Results and Discussion

Temperature and rainfall were near normal at the Waynesville location during the 1972 experimental period.

For the 1973 tests at Fletcher, temperatures were near normal during the first and third months; during the second month the average monthly temperature was about 3°C above the 10-year

average. Rainfall was near normal during the experimental period except for the first month after the July spraying when rainfall was about 1.7 times the 10-year average for the period.

Table 1 shows the recoveries of silvex added at various levels to control samples. The average recovery for these 16 samples was 91% with a range of 52 to 104%. Four blanks were higher than normal which contributed to the wide variation.

TABLE 1

Silvex recovered from apples to which known amounts were added immediately before extraction.^{a/}

| Amount added (ppm) | Number of samples | Amount recovered | |
|--------------------|-------------------|------------------|-----------|
| | | Average (%) | Range (%) |
| 0.05 | 2 | 66 | 52 - 80 |
| 0.10 | 10 | 90 | 68 - 100 |
| 0.50 | 2 | 92 | 85 - 100 |
| 1.00 | 2 | 99 | 94 - 104 |

^{a/} All values were corrected for blank; the overall average was 91%.

The effects of 2-weeks of storage at 3°C on methylated sample extracts are shown in Table 2. These data show no changes in amounts of silvex recovered and indicate that samples can be analyzed 2 weeks after extraction if they are refrigerated.

Silvex was not detected in any of the samples from either the 1972 or 1973 tests; the lowest detectable limit was 0.05 ppm. These results indicate that spraying the ground cover and the bases of the tree trunks in apple orchards with silvex in amounts up to 4.5 kg/ha will not produce detectable levels of residue in the apples. Also, the modified method used to extract silvex gave good recoveries at the sub-ppm level.

TABLE 2

Effects of a 14-day storage on the recovery (%) of silvex from methylated sample extracts.^{a, b/}

| Amount added (ppm) | Storage time | |
|--------------------|--------------|-------------|
| | 0 days (%) | 14 days (%) |
| 0.05 | 52 | 60 |
| 0.10 | 84 | 68 |
| 0.50 | 100 | 112 |
| 1.00 | 94 | 90 |
| Average | 82 | 82 |

^{a/} Extracts were stored at 3°C in tubes with ground-glass stoppers and wrapped in aluminum foil.

^{b/} All values were corrected for blank.

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