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Tomatoes grown on field plots were treated with aldrin at three levels. After harvesting, the tomatoes were processed by commercial procedures and residues were determined in samples taken from various points in the processing operation. Commercial canning and juicing operations removed approximately 80% of the aldrin and dieldrin res-

imited data are available on the effects of commercial processing on pesticide residues in fruits and vegetables. The effects of commercial and home preparative procedures on the removal of DDT, malathion, and carbaryl from tomatoes (Farrow et al., 1968) and green beans (Elkins et al., 1968), DDT from potatoes (Lamb et al., 1968a), DDT, parathion, and carbaryl from spinach (Lamb et al., 1968b), and parathion and carbaryl from broccoli (Farrow et al., 1969) have been determined. Farrow et al. (1966) demonstrated that p,p'-DDT was partially converted to p,p'-TDE during the processing of canned spinach. Other published work on the effects of processing on pesticide residues are: malathion in apples, gooseberries, plums, strawberries, string beans, and tomatoes (Koivistoinen et al., 1964), azinphosmethyl and DDT in green snap beans (Carlin et al., 1966), DDT and derivatives in green beans (Hemphill et al., 1967), Morestan in papayas (Bevenue et al., 1968), and DDT and derivatives in apples (Baldwin et al., 1968).

The work reported in this paper shows the effects of commercial processing on residues of aldrin and dieldrin in tomatoes. In addition, residues were determined in crops (beets, sweet corn, soybeans) grown the following year on the treated plots.

#### EXPERIMENTAL

**Pesticide Application.** Experimental plots were located near Dresden—a prime tomato growing area of southwestern Ontario. The field used had no history of aldrin or dieldrin applications and was therefore well suited for this study. The soil at this location was classified as a loam containing 15% clay, 43% silt, and 42% sand. Twelve plots (three replications, A, B, and C, of four plots, 1, 2, 3, and 4—for variable aldrin treatment) were planted on May 30–31, 1967. Each plot measured 150 by 30 feet and consisted of 450 tomato plants (variety #1350) planted on 5 by 2 feet spacing.

On August 3rd, two months after planting, the first of six aldrin spray applications was applied. A boom-type sprayer (John Bean R55T) with a 15-foot boom was used to spray aldrin in the form of an emulsifiable concentrate (75 psi pressure). The complete spray program is shown in Table I. Soil samples were taken from all plots prior to the first aldrin spray application. Thereafter, samples were taken 24 hours after each spray application to show the amount of residue idues. Residues in the soil of the treated plots declined rapidly and, after overwintering, were approximately 10% of the former levels. Beets, corn, and soybeans grown on the treated plots did not accumulate appreciable aldrin and dieldrin residues from the soil.

| Table I.         Spray Program for Tomato Plots                          |                     |                     |                     |                     |  |  |
|--|---------------------|---------------------|---------------------|---------------------|--|--|
| Pounds per acre of active ingredient                                     |                     |                     |                     |                     |  |  |
| Date   | Plots<br>1A, 1B, 1C | Plots<br>2A, 2B, 2C | Plots<br>3A, 3B, 3C | Plots<br>4A, 4B, 4C |  |  |
| July 4   | $DDT-2^{a}$         | DDT-2               | DDT-2               | DDT-2               |  |  |
|  | M-22-2.5            | M-22-2.5            | M-22-2.5            | M-22-2.5            |  |  |
| July 20  | M-22-3.5            | M-22-3.5            | M-22-3.5            | M-22-3.5            |  |  |
| August 3   | M-22-3.0            | Aldrin-0.5          | Aldrin-1.0          | Aldrin-2.0          |  |  |
|  |                     | M-22-3.0            | M-22-3.0            | M-22-3.0            |  |  |
| August 14  | M-22-3.0            | Aldrin-0.5          | Aldrin-1.0          | Aldrin-2.0          |  |  |
|  |                     | M-22-3.0            | M-22-3.0            | M-22-3.0            |  |  |
| August 21  | M-22-3.0            | Aldrin-0.5          | Aldrin-1.0          | Aldrin-2.0          |  |  |
| -  |                     | M-22-3.0            | M-22-3.0            | M-22-3.0            |  |  |
| September 1  | M-22-3.0            | Aldrin-0.5          | Aldrin-1.0          | Aldrin-2.0          |  |  |
|  |                     | M-22-3.0            | M-22-3.0            | M-22-3.0            |  |  |
| September 7  | M-22-3.0            | Aldrin-0.5          | Aldrin-1.0          | Aldrin-2.0          |  |  |
|  |                     | M-22-3.0            | M-22-3.0            | M-22-3.0            |  |  |
| September 18   | M-22-3.0            |                     |                     |                     |  |  |
| September 19   |                     | Aldrin-0.5          |                     |                     |  |  |
| •  |                     | M-22-3.0            |                     |                     |  |  |
| September 20   |                     |                     | Aldrin-1.0          | Aldrin-2.0          |  |  |
|  |                     |                     | M-22-3.0            | M-22-3.0            |  |  |
| <sup>a</sup> DDT and M-22 (Maneb) are used in tomato growing operations. |                     |                     |                     |                     |  |  |

building up in the soil. Samples were taken just prior to pre-winter ploughing (October, 1967), in the spring and throughout the summer of 1968 to monitor the residue loss. In October 1968, approximately one year after the last spray application, samples were taken at various depths (0-2inches, 2–4 inches, 3–6 inches, and 6–9 inches) to determine the distribution of the residues in the soil. The plots treated with 2 pounds of aldrin per acre were selected for analysis, so that any differences in pesticide content would be more readily detected.

A sampling procedure similar to that described by Harris *et al.* (1966) was used to take 10 pounds of six-inch cores from each plot. After thorough mixing, a 3-pound subsample of each was stored at  $-10^{\circ}$  F in glass jars pending analysis.

**Commercial Processing.** Twenty-four hours after each spray application, commencing with the second spray (eleven weeks after planting), samples of tomatoes were taken to determine the rate of accumulation of residues resulting from repeated spray applications. After the final aldrin spray, 400 pounds of tomatoes from each plot were harvested and brought to a major canning plant to be processed.

The tomatoes were processed on the factory lines, within 30 hours of the last aldrin spray application. Tomatoes were dumped into a water flume and conveyed to washing tanks.

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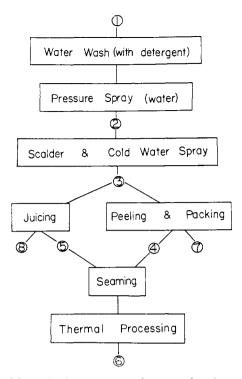


Figure 1. Tomato processing operation showing sampling points (circulated numbers)

Fisan 500 detergent was used. They emerged on inspection rollers and passed under fresh water sprays (approximately 40 pounds pressure). After inspection and trimming, the tomatoes entered a scalder which subjected them to steam followed by more cold water sprays. (This loosens the skin in preparation for hand-peeling and packing.) Part of the produce was peeled and packed into 19-ounce cans. The remainder passed into a chopper and juice extractor, and the juice obtained was used to top off the cans just prior to closure and thermal processing (30 minutes at 240° F).

After processing, the cans were cooled promptly in water to a temperature of 90–100 $^{\circ}$  F.

Figure 1 shows the tomato operation and the points at which samples were taken during the processing. All tomato samples (including final canned samples) were immediately stored at  $-10^{\circ}$  F until analyzed.

**Subsequent Crops.** To determine if the soil in the tomato plots, sprayed with aldrin in 1967, would transfer significant residues to subsequent crops, three different crops—beets, sweet corn, and soybeans—were planted on these plots in 1968. These crops were selected since they are commonly grown in the area and represent a root crop and two seed crops. The crops were harvested when mature and analyzed for residues.

Analytical Methods. Aldrin and dieldrin residues in tomatoes, beets, and corn were determined after acetonitrile extraction and cleanup on a Darco G60-Solka Floc column (McLeod *et al.*, 1967). Residues were determined in soybeans after extraction with 35% H<sub>2</sub>O in acetonitrile (Bertuzzi *et al.*, 1967), partitioning into hexane, and elution with 25% methylene chloride in hexane from a Florisil (deactivated with 2% water) cleanup column. Residues in soils were extracted with acetone-hexane (1:3) with subsequent removal of the acetone fraction. No cleanup of the soils was necessary.

A Varian Aerograph 1522B gas chromatograph, equipped with an electron capture detector (H<sup>3</sup>) and a 4-foot  $\times$  <sup>1</sup>/<sub>4</sub>-inch glass column packed with 5% QF-1 and 4% SE-30

| Table II. | Aldrin and Dieldrin Residues in Raw Tomatoes 24 |
|-----------|---|
|           | Hours after Each Spray Application              |
|           | Residues in P.P.M.ª                             |

| Date<br>(1967)          |                    | <sup>1</sup> / <sub>2</sub> Pound/<br>Acre | 1 Pound/<br>Acre | 2 Pounds/<br>Acre |  |
|-------------------------|--------------------|--|------------------|-------------------|--|
| August 15               | Aldrin<br>Dieldrin | 0.02<br>ND                                 | 0.03<br>T        | 0.05<br>T         |  |
| August 22               | Aldrin<br>Dieldrin | 0.01<br>T                                  | 0.04<br>T        | 0.14<br>0.01      |  |
| September 2             | Aldrin             | 0.02                                       | 0.05             |                   |  |
| September 8             | Dieldrin<br>Aldrin | T<br>0.03                                  | T<br>0.03        | 0.09              |  |
| September 19-21         | Dieldrin<br>Aldrin | T<br>0.02                                  | Т<br>0.04        | T<br>0.08         |  |
|                         | Dieldrin           | 0.01                                       | 0.02             | 0.02              |  |
| $^{a}$ T = <0.01 p.p.m. | ND = no            | t detected.                                | — = not sa       | mpled.            |  |

 
 Table III. Removal of Aldrin and Dieldrin Residues from Tomatoes by Commercial Processing

 Dieldrin eine DBMG

| <b>Residues in P.P.M.</b> <sup><math>a</math></sup> |                    |  |   |   |  |  |
|---|--------------------|--|---|---|--|--|
|   |                    | <sup>1</sup> / <sub>2</sub> Pound/<br>Acre | 1 Pound/<br>Acre                            | 2 Pounds<br>Acre                            |  |  |
| Raw unwashed  | Aldrin<br>Dieldrin | 0.03<br>T                                  | 0.03<br>T                                   | 0.08<br>0.02                                |  |  |
| After pressure<br>spray                             | Aldrin<br>Dieldrin | 0.02<br>T                                  | $0.03 \\ 0.02$                              | 0.09<br>0.04                                |  |  |
| After scalder<br>& cold water                       | Aldrin<br>Dieldrin | 0.01<br>T                                  | $\begin{array}{c} 0.04 \\ 0.02 \end{array}$ | $\begin{array}{c} 0.04 \\ 0.03 \end{array}$ |  |  |
| spray<br>Skinned                                    | Aldrin<br>Dieldrin | ND   | T   | 0.01  |  |  |
| tomatoes<br>Topping juice                           | Aldrin<br>Dieldrin | ND<br>T<br>T                               | ND<br>0.01<br>T                             | T<br>0.02<br>0.02                           |  |  |
| Final product                                       | Aldrin<br>Dieldrin | T<br>T                                     | T<br>T                                      | 0.01<br>0.01                                |  |  |
| $^{a}$ T = <0.01 p.p.m.                             | ND = no            | t detected.                                |   | -   |  |  |

coated on acid washed Chromosorb W, 60/80 mesh, was used to obtain quantitative data. The column was operated at a temperature of 200° C and a  $N_2$  flow rate of 120 ml. per minute.

Thin-layer chromatography was used for qualitative confirmation of the results. The adsorbent was Silica Gel GHR, 250  $\mu$  thick, with 10% benzene in hexane as mobile solvent, and a silver nitrate spray reagent was used for detection of residues.

### RESULTS AND DISCUSSION

Data for all samples are mean values of individual results obtained from the triplicated plots.

**Residues in Field Tomatoes.** Data obtained on residues in tomatoes sampled 24 hours after each spray application are shown in Table II. Since aldrin degrades under field conditions to dieldrin, samples were analyzed for both aldrin and dieldrin residues. The results in Table II show that no appreciable accumulation on the raw tomatoes occurred as each spray was applied.

After the sixth spray application (on September 19–20), the tomatoes were harvested. Tomatoes receiving 1/2 pound/acre of aldrin and those receiving 1 pound/acre did not contain aldrin and dieldrin residues in excess of the current Canadian tolerance of 0.1 p.p.m. (The Food and Drug Act and Regulations, 1968.) Tomatoes sprayed at 2 pounds/acre contained residues at approximately the tolerance level.

**Residues Removed during Commercial Processing.** Residue data for samples taken throughout the processing lines are shown in Table III. The commercial processing removed all

## Table IV. Aldrin and Dieldrin Residues in Waste Solids of the Tomato Processing Line

Residues in P.P.M.

|   |                    | <sup>1</sup> / <sub>2</sub> Pound/<br>Acre | 1 Pound/<br>Acre | 2 Pounds/<br>Acre |
|---|--------------------|--|------------------|-------------------|
| Tomato skins                            | Aldrin<br>Dieldrin | $0.14 \\ 0.05$                             | 0.24<br>0.08     | 0.36<br>0.13      |
| Pulp residue<br>from juice<br>extractor | Aldrin<br>Dieldrin | 0.31<br>0.09                               | 0.67<br>0.30     | 1.32<br>0.60      |

#### Table V. Aldrin and Dieldrin Residues at Various Depths in the Soil<sup>a</sup>—October 1968

| Residues in P.P.M. |   |        |        |                    |
|--------------------|---|--------|--------|--------------------|
|                    | 0–2   | 2–4    | 4-6    | 6–9                |
|                    | Inches                                      | Inches | Inches | Inches             |
| Aldrin             | $\begin{array}{c} 0.05 \\ 0.05 \end{array}$ | 0.14   | 0.05   | 0.0 <mark>9</mark> |
| Dieldrin           |   | 0.12   | 0.05   | 0.08               |
|                    |   |        |        |                    |

" Soil (Plots 4A, 4B and 4C) had been sprayed with aldrin at 2 pounds/ acre six times during the summer of 1967 (Table I).

#### Table VI. Aldrin and Dieldrin Residues in Crops Grown in Soil Sprayed with Aldrin the Previous Year Residues in P.P.M.

| Residues in F.F.M.   |          |          |                                       |                     |                      |
|--|----------|----------|---------------------------------------|---------------------|----------------------|
| Date<br>Harvested  | Crop     |          | ${{{\rm Pound}}\over{{\rm Acre}^a}}/$ | 1<br>Pound/<br>Acre | 2<br>Pounds/<br>Acre |
| July 22/68   | Beets    | Aldrin   | ND                                    | Т                   | 0.01                 |
|  |          | Dieldrin | ND                                    | Т                   | Т                    |
| September 4/68   | Corn     | Aldrin   | ND                                    | Т                   | 0.01                 |
|  |          | Dieldrin | ND                                    | Т                   | Т                    |
| October 23/68  | Soybeans | Aldrin   | ND                                    | Т                   | Т                    |
|  |          | Dieldrin | ND                                    | Т                   | Т                    |
| <sup><i>a</i></sup> 1967 Spray rates. $T = \langle 0.01 \text{ p.p.m.} \text{ ND} = \text{Not detected}$ . |          |          |                                       |                     |                      |

but small amounts of the residues present on the raw produce. The residue levels in the final product were approximately 20% of those in the raw produce. Partial removal was effected by the washing and scalding operations. The remainder of the residue was removed with the skins. Residue data for the waste solids resulting from the peeling and juicing operations

(Table IV) confirm the presence of the residue in the skins and pulp residue from juice extractor which do not form part of the final product. These data are in agreement with those of Farrow *et al.* (1968) that showed that commercial canning and juicing operations removed virtually all DDT, malathion, and carbaryl residues from tomatoes.

Accumulation and Dissipation of Aldrin and Dieldrin Residues in Soil. The analytical results from the monitoring of the soil expressed as p.p.m. and calculated on an oven-dry basis are shown graphically in Figure 2. Both the aldrin and dieldrin levels in the soil increased during the spraying period. After six spray applications, most of the residue was found in the undegraded state as aldrin, with dieldrin less than 10% of the total residue.

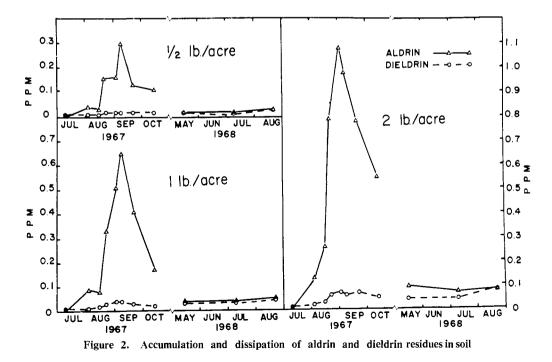
Three weeks after the final aldrin spray application, the total residue in the soil had diminished significantly with aldrin forming a smaller proportion of the residues than before (85–90%). The pesticide level in the top 6 inches of the soil decreased significantly during the winter to approximately 10% of its former level. The residue remained at this low level throughout the summer months. It should also be noted that during the winter the proportion of aldrin in the residues decreased from approximately 90% to 60%.

The data for the soil samples taken at various depths are shown in Table V. The data indicate that the residues are fairly evenly distributed throughout the top 9 inches of the soil, although there is a higher concentration in the 2-4 inch layer.

Uptake of Aldrin and Dieldrin from Aldrin Treated Soil by a Variety of Crops. The results of the analyses are shown in Table VI. The crops did not pick up appreciable residues from the soil. The concentration of residues found in the crops was approximately 10% of the concentration found in the top 6 inches of the soil.

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