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# Dislodgable Insecticide Residues on Cotton Foliage: Fenvalarate, Permethrin, Sulprofos, Chlorpyrifos, Methyl Parathion, EPN, Oxamyl, and Profenofos

N. A. Buck, B. J. Estesen, and G. W. Ware
*Department of Entomology, University of Arizona, Tucson, Arizona 85721*

It was the purpose of this study to determine the dislodgable or easily removed surface residues of some of the newer insecticides on cotton over a 4-day period following application. Such information is essential in establishing safe reentry intervals for personnel working in treated fields. ESTESEN et al. (1979) compared the dislodgable foliar residues of profenofos (Curacron), fenvalarate (Pydrin), sulprofos (Bolstar), Decis, and endosulfan (Thiodan) on cotton through 96-h post application. This paper extends that series with two separate studies. In the first we obtained the disappearance rates from cotton of fenvalarate, permethrin (Pounce), sulprofos, and chlorpyrifos (Lorsban). In the second we examined methyl parthion with EPN, sulprofos, oxamyl (Vydate), permethrin, profenofos, and methyl parathion with toxaphene.

## METHODS AND MATERIALS

### First Study

Test plots were located in a 6.5 ha block of'Delta Pineland 55'short staple cotton at the Agricultural Experiment Station, Marana, Arizona. Cotton plant heights averaged 48 cm on the day of insecticide applications, July 17, 1978. Plots consisted of 4 treated rows, with 102 cm spacing, 30.5 m long. Sprays were applied at 122 L/ha, at 4 km/h and 276 kPa pressure (13 gal/acre, 2.7 mph, and 40 psi). The manually drawn spray rig treated two rows, using 3 DC 2-13 Spraying Systems nozzles per row. The pressure was maintained from a 6.8 kg $CO_2$ tank with a single-stage regulator.

The formulation and rate of active ingredient (AI) per ha were: Bolstar 6 (6EC) @ 1.1 kg/ha, Pydrin (2.4EC) @ 0.22 kg/ha, Pounce (3.2EC) @ 0.22 kg/ha, and Lorsban (4EC) @ 1.1 kg/ha.

Maximum and minimum air temperatures during the test were July 17, 42° - 24.4°; July 18, 35.6° - 22.8°; July 19, 37.8° - 27.8°; July 20, 37.8° - 25.6°; July 21, 33.9° - 26.7°C. There was a 3 mm rainfall recorded between samplings at 0 and 24 h.

Triplicate samples were collected in each treated plot at 0, 24, 48, 72, 96 h after treatment, with controls collected on 0,

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48, and 96 h. Each sample consisted of 100 leaves punched singly and consecutively from the top, middle and bottom portions of plants in all 4 rows, using 2.54-cm diameter leaf punches. 100 leaf disks for each replicate were placed in labeled jars covered with ice until their return to the laboratory for processing.

Samples were processed according to the protocol for dislodgable residues (IWATA et al. 1977) as follows: leaf disks were transferred to wide-mouth mason jars with 200 mL distilled $H_2O$ containing 8 drops of Sur-Ten detergent diluted 1:50. The sample was shaken on a reciprocal shaker at 200 cpm for 20 min. The extract was decanted into 1-L separatory funnel, and the leaves were reextracted twice more as before. The three aqueous extracts were combined and the insecticide partitioned into 2 100-mL portions of dichloromethane with 1 min shakings. The dichloromethane was dried by passing it through $Na_2SO_4$.

A suitable aliquot of the sample was removed, evaporated to dryness under a stream of nitrogen without heat and taken up in hexane for fenvalarate and permethrin, and benzene for sulprofos and chlorpyrifos.

Fenvalarate and permethrin samples were cleaned on a 2.5 cm height of activated Florisil (120°C for 24 h) in a 22 mm ID column topped with 1 cm of $Na_2SO_4$. After the column was prewashed with 25 mL hexane, sample aliquots were poured on and eluted with 50 mL hexane followed by 50 mL of 5% ethyl acetate in hexane at 2 drops per second.

Fenvalarate and permethrin extracts were analyzed using the methods of ESTESEN et al. (1979). The permethrin carrier gas flow was changed to 90 mL/min for this study. Retention times of fenvalarate and the cis and the trans isomers of permethrin were 6.4, 13.5 and 16.5 min respectively.

Sulprofos, its metabolites and chlorpyrifos were analyzed by gc using a flame photometric detector. A 76 cm x 4 mm I.D. Pyrex column containing 2% OV-101 on 100/120 mesh Chromosorb W (H.P.) was used. Quantitation was by peak height. Carrier gas flow was 120 mL/min for sulprofos and metabolites and 60 mL/min for chlorpyrifos. Temperatures for sulprofos and metabolites were: column, 200°C; detector, 220°C; and inlet, 222°C. Temperatures for chlorpyrifos were 195°C, 215°C and 225°C for column, detector and inlet respectively. Retention times were 3.2 min for chlorpyrifos, 3.8 for sulprofos, 9.8 for sulprofos sulfone and 11.8 for sulprofos sulfoxide.

## RESULTS AND DISCUSSION

The results are presented in Table 1 expressed as micrograms of toxicant or metabolite per square centimeter of cotton leaf, one surface only. From the data the effect of the 3 mm rain can not be determined, though it is unlikely that it had a significant influence. In order of their persistence, the 96 h residues were fenvalarate > permethrin > sulprofos > chlorpyrifos. The residues remaining of sulprofos and chlorpyrifos probably would not be efficaceous at 24 h in that they had declined to 22 and 3.6%, respectively. In contrast, fenvalarate and permethrin had 42 and 31% remaining at 24 h. These data support the results of our earlier study.

## METHODS AND MATERIALS

### Second Study

The test plots were located in the same field and variety as the first study, and previously untreated with insecticide. Plant heights averaged 76 cm on the day of application, August 28, 1978. Plot applications were under the same parameters.

The formulation and rate of active ingredient (AI) per ha: methyl parathion and EPN (3+3EC) @ 1.1+1.1 kg/ha, Bolstar (6EC) @ 1.1 kg/ha, Vydate (2EC) @ 0.41 kg/ha, Pounce (3.2EC) @ 0.17 kg/ha, Curacron (6EC) @ 1.1 kg/ha, and toxaphene and methyl parathion (6+3EC) @ 2.2+1.1 kg/ha respectively.

Maximum and minimum air temperatures were: Aug. 28, 39.5° - 17.2°; Aug. 29, 39° - 20°; Aug. 30, 40° - 23.3°; Aug. 31, 36.7° - 25.6°; and Sept. 1, 39.5° - 21.7°C.

Triplicate samples of 100 disks each were collected as in the first study. In the field each sample was extracted with 100 mL of the appropriate solvent for one min. The extract was then transferred to an 8-oz labeled sample bottle, the solvent levels marked, and the jars placed in an ice chest until transferred to the laboratory refrigerator. The extracting solvents were benzene for methyl parathion-EPN, methyl parathion-toxaphene, sulprofos, profenofos, hexane for permethrin and tap water for oxamyl. Controls were extracted with either hexane, benzene or tap water.

EPN, methyl parathion, sulprofos and profenofos were analyzed directly by GLC using the flame photometric detector. The column and gc conditions for sulprofos and its metabolites were the same as in the first study. For the others the column, carrier gas flow rate, and temperatures were the same as those for chlorpyrifos in the first study. Retention times were methyl parathion 2 min, profenofos 3.2 min, sulprofos 3.8 min, sulprofos sulfone 9.8 min, sulprofos sulfoxide 11.8 min, and EPN 13.7 min. A 162 cm x 4 mm I.D. Pyrex column containing 10% DC 200 on 60/80 mesh Gas Chrom Q was used for methyl paraoxon. Carrier gas flow was 60 mL/min and the temperatures were: column, 195°C; detector, 215°C; and inlet 225°C. Retention time was 5.8 min.

Permethrin samples were cleaned and analyzed by ECGC as described in the first study. Oxamyl samples were analyzed using a modified method of HOLT & PEASE (1976). 10 or 20 mL aliquots of sample were diluted to 50 mL with distilled water and extracted twice with 50-mL portions of hexane with 1 min shakings. The hexane was discarded and the aqueous layer placed in a 250-mL beaker. To this was added 5 mL of 1N NaOH. The extract was then placed in a 62-64°C water bath for 1 h. The samples were removed, cooled and returned to separatory funnels and extracted for 1 min with 50 mL chloroform, which was then discarded.

The aqueous samples were then acidified with 6 mL 1N $H_2SO_4$, saturated with 25 g NaCl, and extracted 4 times with 50-mL portions

## TABLE 1

Dislodgable residues expressed as $\mu g/cm^2$ of cotton leaf (one surface only) following application by ground rig. Marana, AZ. July 17, 1978.

| | Sulprofos 1.1 kg/ha | | | Chlorpyrifos 1.1 kg/ha |
|---|---|---|---|---|
| Hours | Sulprofos | Sulprofos Sulfone | Sulprofos Sulfoxide | |
| 0 | 4.0 | <0.036 | 0.33 | 3.64 |
| 24 | 0.55 | 0.040 | 0.40 | 0.13 |
| 48 | 0.17 | 0.11 | 0.43 | 0.071 |
| 72 | 0.13 | 0.14 | 0.46 | 0.055 |
| 96 | 0.069 | 0.12 | 0.36 | 0.034 |
| Controls | <0.010 | <0.010 | <0.020 | <0.004 |

| Hours | Permethrin 0.22 kg/ha | | | Fenvalarate 0.22 kg/ha |
|---|---|---|---|---|
| | Cis isomer | Trans isomer | Total | |
| 0 | 0.38 | 0.49 | 0.87 | 0.85 |
| 24 | 0.11 | 0.16 | 0.27 | *0.36 |
| 48 | 0.085 | 0.12 | 0.20 | 0.38 |
| 72 | *0.063 | *0.091 | *0.15 | 0.28 |
| 96 | 0.045 | 0.063 | 0.11 | 0.28 |
| Controls | **----- | **----- | **---- | <0.002 |

* average of only two replicates

** no interference from controls

TABLE 2

Dislodgable residues expressed as μg/cm$^2$ of cotton leaf (one surface only) following application by ground rig. Marana, AZ. August 28, 1978.

| | Methyl Parathion + EPN | | | Sulprofos | | | Profenofos |
|---|---|---|---|---|---|---|---|
| | 1.1 kg/ha + 1.1 kg/ha | | | 1.1 kg/ha | | | 1.1 kg/ha |
| Hours | Methyl Parathion | Methyl Paraoxon | EPN | Sulprofos | Sulprofos Sulfone | Sulprofos Sulfoxide | |
| 0 | 4.5 | 0.12 | 5.1 | 5.8 | <0.018 | <0.078 | 3.5 |
| 24 | 0.78 | 0.029 | 2.0 | 2.3 | 0.13 | 0.74 | 1.1 |
| 48 | 0.33* | 0.024* | 1.4* | 1.4 | 0.46 | 1.1 | 0.74 |
| 72 | 0.11 | 0.017 | 0.81 | 0.34 | 0.38 | 0.87 | 0.51 |
| 96 | 0.065 | 0.017 | 0.57 | 0.29 | 0.37 | 0.73 | 0.35 |
| Controls | <0.010 | <0.002 | <0.024 | <0.016 | <0.016 | <0.030 | <0.006 |

| | Toxaphene + Methyl Parathion | | Permethrin | | | Oxamyl |
|---|---|---|---|---|---|---|
| | 2.2 kg/ha + 1.1 kg/ha | | 0.17 kg/ha | | | 0.41 kg/ha |
| Hours | Methyl Parathion | Methyl Paraoxon | cis isomer | trans isomer | Total | |
| 0 | 4.2 | 0.053 | 0.26 | 0.38 | 0.64 | 1.5 |
| 24 | 1.3 | 0.021 | 0.24 | 0.34 | 0.58 | 1.1 |
| 48 | 0.54 | 0.017 | 0.22 | 0.32 | 0.54 | 1.2 |
| 72 | 0.19 | 0.012 | 0.16 | 0.24 | 0.40 | 0.85 |
| 96 | 0.099 | 0.011 | 0.15 | 0.21 | 0.36 | 0.76 |
| Controls | <0.010 | <0.001 | ----** | ----** | ----** | <0.085 |

* average of 2 replicates
** no interferences from controls

of ethyl acetate. The ethyl acetate was then dried through $Na_2SO_4$. To this extract was added 0.1 mL of triethylamine, followed by concentration under a stream of $N_2$ on a warm bath to *ca.* 20 mL. Triethylamine (0.1 mL) was again added and the sample concentrated further to 2 or 5 mL as required for gas chromotography. Recovery standards were carried through the procedure daily.

A 152 cm x 4 mm I.D. Pyrex column containing 10% SP-1200 and 1% $H_3PO_4$ on 80/100 mesh Chromosorb W (H.P.) was used. Carrier gas flow was 120 mL/min at 40 psi. Temperatures were: column, 195°C; detector, 215°C; and inlet, 200°C. Retention time was 9.1 min. Quantitation was by peak height using oxamyl oxime as a standard.

## RESULTS AND DISCUSSION

The results appear in Table 2, expressed as $\mu g/cm^2$ of cotton leaf, one surface only. Toxaphene has a stabilizing influence on methyl parathion which was not seen when methyl parathion was combined with EPN. EPN disappears somewhat less readily than methyl parathion. EPN, sulprofos and profenofos had practically identical residual lives, while oxamyl and permethrin were very similar and the most persistent.

The method of removing leaf surface residues with the most appropriate solvent, which has been used in all of our other dislodgable studies, is far less complicated and much faster than the recommended method used in the first study. Further, we believe that it provides a realistic surface residue picture that is as reliable as the detergent water extraction.

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