Bull. Environm. Contam. Toxicol. 25, 608-615 (1980)

Dislodgable Insecticide Residues on Cotton Foliage: Acephate, AC 222,705, EPN, Fenvalerate, Methomyl, Methyl Parathion, Permethrin, and Thiodicarb[1]

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The need continues for establishing safe reentry intervals for persons working in insecticide-treated cotton fields. The compilation and comparison of dislodgable residues of various insecticides may aid in establishing these intervals. BUCK et al. (1980) compared the dislodgable foliar residues of fenvalerate (Pydrin), permethrin (Pounce), sulprofos (Bolstar), chlorpyrifos (Lorsban), methyl parathion, EPN, oxamyl (Vydate), and profenofos (Curacron) on cotton through 96-h post application. This paper extends that series with three separate studies. The first 96-h post application study compares the disappearance rates from cotton of acephate (Orthene), methomyl (Lannate), permethrin, and AC 222,705 (American Cyanamid's experimental compound). The second study compares the 72-h post application disappearance rates from cotton of EPN, methyl parathion, methyl parathion plus Coax (an insect gustatory stimulant wettable powder distributed by Traders Protein Division of Traders Oil Mill Company, Ft. Worth, TX.), methyl parathion plus EPN (Trion 6), and thiodicarb (Larvin 500, previously UC 51762). The third study directly compares the 96-h post application disappearance rates from cotton of the 3 most commonly used pyrethroids, permethrin (Pounce and Ambush formulations) and fenvalerate.

METHODS AND MATERIALS

First Study

Test plots were located in a block of 'Delta Pineland 55' short staple cotton at the Agricultural Experiment Station, Marana, Arizona. Plots consisted of 4 treated rows, with 102 cm spacing, 30.5 m long. Cotton plant heights averaged 49 cm on the day of insecticide applications, July 9, 1979. Sprays were applied at 122 L/ha, at 4.3 km/h, and 276 kPa pressure. The manually drawn sprayer 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 per ha were: Orthene 75S (75% soluble powder) @ 1.1 kg/ha, Lannate L (1.8 #/gal.

[1]Contribution to Regional Research Project W-45, "Environmental Distribution, Transformation, and Toxicological Implications of Pesticide Residues". University of Arizona Agricultural Experiment Station journal series No. 3342.

0007-4861/80/0025-0608 $01.60

liquid) @ 0.50 kg/ha, Pounce (3.2 EC) @ 0.16 kg/ha, and AC 222,705 (30%) @ 0.44 kg/ha.

Maximum and minimum air temperatures during the test were July 9, 42.8°-20°; July 10, 42.8°-20.6°; July 11, 41.1°-20°; July 12, 42.2°-24.4°; and July 13, 41.1°-21.7°C. There was no rainfall during the test.

Triplicate samples were collected in each treated plot at 0, 24, 48, 72, and 96 h after treatment. Controls (one sample for each solvent used) were collected at 0, 48, and 96 h. Each sample consisted of 100 leaf disks, 2.54-cm diameter, taken singly and consecutively from the top, middle, and bottom portions of plants in all 4 rows. Each sample replicate was extracted in the field with 100 mL of the appropriate solvent. The sample was shaken for 1 min, the extract transferred to a labeled storage bottle, the solvent level marked, and the bottles placed in an ice chest until transported to the laboratory refrigerator. The extracting solvents were tap water for acephate and methomyl and redistilled hexane for permethrin and AC 222,705. The AC 222,705 samples were reextracted with 100 mL redistilled methanol. The methanol extracts were stored separately from the hexane extracts. Controls were extracted with tap water or hexane followed by methanol as described above.

Permethrin extracts 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 100 mL of 4% ethyl acetate in hexane at 2 drops per second. Permethrin was analyzed by GLC using the Micro Tek MT-220 equipped with a ^{63}Ni electron capture detector. The 104 cm x 4 mm ID Pyrex column was packed with 3% SP-1200 on a mixture of 27% Chromosorb W(A.W.) and 70% Chromosorb W(H.P.). Nitrogen carrier gas flow was 100 mL/min and temperatures were 218°C, 210°C, and 270°C for inlet, column, and detector respectively.

A 20- or 30- mL aliquot of the aqueous methomyl extract was acidified with 0.5 mL 1 N H_2SO_4 and extracted twice with 20-mL portions of redistilled hexane. The aqueous phase was then hydrolyzed by adding 20 mL 6.25 N NaOH and heating in a covered water bath (64°-68°C) for 1 h. The sample was cooled and extracted with 50 mL chloroform. The aqueous phase was acidified with 5 mL 25.2 N H_2SO_4, 10 g NaCl was added and it was extracted 4 times with 30-mL portions of ethyl acetate. The ethyl acetate was dried thru Na_2SO_4, 0.1 mL triethylamine was added, and the solvent was concentrated under N_2 to ca 50 mL. At this time 0.1 mL more triethylamine was added and the extract was concentrated to < 5 mL and then transferred to a graduated centrifuge tube. The methomyl was analyzed by GLC on a Micro Tek MT-220 equipped with a flame photometric detector in the sulfur mode. The 152 cm x 4 mm ID Pyrex column contained 10% SP-1200 and 1% H_3PO_4 on 80/100 mesh Chromosorb W(H.P.). Nitrogen carrier gas flow was 60 mL/min and inlet, column, and detector temperatures were 225°, 185°, and 210°C respectively. Quantitation was by peak height using methomyl oxime as a standard.

Acephate was partitioned from water into dichloromethane by taking a 25-mL aliquot of water extract, salting it out with 9g NaCl, and shaking with 100 mL dichloromethane for 1 min in a separatory funnel. The aqueous layer was extracted twice more with 50-mL portions of dichloromethane each time. The combined dichloromethane extracts were dried through Na_2SO_4 and evaporated to just dryness.

The residue was taken up in ethyl acetate and transferred to a graduated centrifuge tube to await gc analysis. The above described gc was equipped with a flame photometric detector in the phosphorus mode. The 99 cm x 4 mm ID Pyrex column contained 2% Reoplex 400 on 80/100 mesh Gas Chrom Q. The nitrogen carrier flow was 60 mL/min. The inlet, column, and detector temperatures were 218°, 195°, and 210°C respectively.

RESULTS AND DISCUSSION

The results are presented in Table 1 expressed as micrograms of toxicant per square centimeter of cotton leaf, one surface only. In order of their persistence, the 96 h residues were AC 222,705 > permethrin > acephate > methomyl. With 58% AC 222,705 remaining vs 40% for permethrin, it appears as if this new pyrethroid bears consideration for further tests.

METHODS AND MATERIALS
Second Study

Test plots were located in a field of 'Delta Pineland 55' short staple cotton on a private farm in Marana, Arizona. The plots were set up and sprays applied as described in the first study. Cotton plant heights averaged 68 cm on the day of insecticide applications, August 21, 1979.

The formulation and rate of active ingredient per ha were: methyl parathion (4 EC) @ 1.1 kg/ha, EPN (4 EC) @ 1.1 kg/ha, methyl parathion (4 EC) + coax @ 1.1 kg/ha + 1.1 kg/ha, Trion 6 (3 #/gal EPN + 3 #/gal methyl parathion) @ 0.55 kg/ha + 0.55 kg/ha, Larvin 500 (4.18 #/gal) @ 1.1 kg/ha.

Maximum and minimum air temperatures during the test were Aug. 21, 37.8°-15.6°; Aug. 22, 38.3°-17.2°; Aug. 23, 38.9°-18.3°; and Aug. 24, 40.0°-18.9°C. No rain fell during the test.

Triplicate samples were collected from each treated plot at 0, 24, 48, and 72 h after treatment. Control samples (one for each solvent used) were collected at 0 and 48 h. The sampling, extracting, and handling procedures were the same as in the first study. Redistilled benzene was used to extract all samples except thiodicarb, which was extracted with redistilled acetone. Controls were extracted with either benzene or acetone.

All methyl parathion- and EPN- containing samples were analyzed directly by GLC with no cleanup. The Micro Tek gc was equipped with a flame photometric detector in the phosphorus mode. The 98 cm x 4 mm ID Pyrex column contained 5% SE-30 on 100/120 mesh Chromosorb W(H.P.) Nitrogen carrier flow was 60 mL/min and temperatures for inlet, column, and detector were

TABLE 1

Dislodgable residues[a] expressed as ug/cm^2 of cotton leaf (one surface only) following application by man-pulled ground rig. Marana, AZ. July 9, 1979.

Hours	AC 222,705 0.044 kg/ha			Permethrin 0.16 kg/ha			Methomyl[f] 0.50 kg/ha	Acephate[g] 1.1 kg/ha
	Hexane Extract[b]	Methanol Extract[c]	Total	Cis Isomer[d]	Trans Isomer[e]	Total		
0	0.20	0.037	0.24	0.39	0.49	0.88	1.1	4.8
24	0.18	0.032	0.21	0.30	0.37	0.67	0.15	3.6
48	0.17	0.028	0.20	0.24	0.32	0.56	0.10	2.2
72	0.14	0.030	0.17	0.19	0.24	0.43	0.031	1.4
96	0.12	0.020	0.14	0.16	0.19	0.35	0.017	1.0
Controls	<0.003	<0.0006	<0.004	<0.01	<0.01	<0.02	<0.008	<0.008

[a] Average of triplicate samples

[b] No correction made for Florisil cleanup recovery range of 88-100%

[c] No correction made for Florisil cleanup recovery range of 93-98%

[d] No correction made for Florisil cleanup recovery range of 92-100%

[e] No correction made for Florisil cleanup recovery range of 97-100%

[f] No correction made for average hydrolysis recovery of 76.2% (range 69.9-82.8%)

[g] No correction made for average partitioning recovery of 93.3% (range 87.4-104%)

225°, 210°, and 236°C respectively. The EPN oxon was analyzed on a 156 cm x 4 mm ID Pyrex column containing 10% DC 200 on 60/80 mesh Gas Chrom Q. Carrier gas flow was 120 mL/min and inlet, column, and detector temperatures were 230°, 210°, and 223°C respectively.

A 10-mL aliquot of the thiodicarb acetone extract was pipetted into a beaker, 0.2 mL ethylene glycol added, and the acetone evaporated off. The residue was taken up in 30 mL distilled water, 0.5 mL 1 N H_2SO_4 added, and the thiodicarb was hydrolyzed to methomyl oxime as described in the first study for methomyl analyses. The gc analysis of the oxime was performed under conditions identical to that in the first study.

RESULTS AND DISCUSSION

The results of this study are presented in Table 2 expressed as micrograms of toxicant or metabolite per square centimeter of cotton leaf, one surface only. In order of their persistence, the 72 h residues were thiodicarb > EPN > methyl parathion. The EPN and methyl parathion residues substantiate our earlier results. Thiodicarb appears as an extremely persistent chemical with virtually no loss 72 h post application. This persistence indicates that thiodicarb is not degraded under Arizona field conditions and warrants further study as an insecticide.

METHODS AND MATERIALS
Third Study

Test plots were located in a block of Stoneville 213 short staple cotton at the Agricultural Experiment Station, Marana, Arizona. The plots were set up and sprays applied as described in the first study. Cotton plant heights averaged 85 cm on the day of insecticide applications, September 4, 1979.

The formulations of the pyrethroids were: Pounce (3.2 EC), Ambush (2.0 EC), and Pydrin (2.4 EC). All were applied at the rate of 0.22 kg AI/ha.

Maximum and minimum air temperatures during the test were Sept. 4, 42.2°-20.6°; Sept. 5, 41.1°-22.2°; Sept. 6, 38.3°-23.3°; Sept. 7, 40.6°-23.9°; and Sept. 8, 39.4°-22.2°C. A very light sprinkle of rain fell between the 48- and 72- h samplings.

Four replicate samples and control samples were collected as described in the first study. The sampling, extracting, and handling procedures were the same as in the first study. All samples and controls were extracted with redistilled hexane. Aliquots of these samples were cleaned on Florisil columns as described for the permethrin samples in the first study.

Permethrin extracts were analyzed by GLC as described in study one. Fenvalerate extracts were analyzed by GLC as described by ESTESEN et al. (1979). The column was 33 cm in length for this study and the nitrogen carrier flow was 70 mL/min with column temperature of 210°C.

TABLE 2

Dislodgable residues[a] expressed as ug/cm^2 of cotton leaf (one surface only) following application by man-pulled ground rig. Marana, AZ. August 21, 1979.

Hour	Methyl Parathion[b] 1.1 kg/ha	Methyl Parathion[b] and Coax 1.1 kg/ha	Trion 6 0.55 kg/ha + 0.55 kg/ha		
			Methyl Parathion[b]	EPN[b]	EPN Oxon[b]
0	4.7	5.1	2.3	2.6	0.060
24	0.49	0.52	0.18	0.71	0.069
48	0.15	0.12	0.062	0.48	0.037
72	0.063	0.063	0.040	0.38	0.028
Control	<0.0014	<0.0014	<0.0014	<0.006	---[c]

Hour	EPN 1.1 kg/ha		Thiodicarb[d] 1.1 kg/ha
	EPN[b]	EPN Oxon[b]	
0	5.9	0.045	4.7
24	2.2	0.126	4.8
48	1.2	0.076	4.8
72	0.82	0.047	4.7
Control	<0.006	---[c]	<0.008

[a] Average of triplicate samples

[b] No recovery studies run

[c] No interference in controls

[d] No correction made for average hydrolysis recovery of 78.1% (range 71.6-83.5%)

TABLE 3

Dislodgable residues[a/] expressed as ug/cm^2 of cotton leaf (one surface only) following application by man-pulled ground rig. Marana, AZ. September 4, 1979.

Hour	Pounce 0.22 kg/ha			Ambush 0.22 kg/ha			Pydrin 0.22 kg/ha
	Cis Isomer	Trans Isomer	Total	Cis Isomer	Trans Isomer	Total	
0	0.32	0.39	0.71	0.43	0.47	0.90	0.93
24	0.30	0.37	0.67	0.36	0.37	0.73	0.77
48	0.26	0.34	0.60	0.32	0.34	0.66	0.71
72	0.24	0.30	0.54	0.28	0.28	0.56	0.65
96	0.22	0.26	0.48	0.20	0.19	0.39	0.61
Controls	<0.01	<0.01	<0.02	<0.01	<0.01	<0.02	<0.01

[a/] Average of 4 replicates.

RESULTS AND DISCUSSION

The results are presented in Table 3 expressed as micrograms toxicant per square centimeter of cotton leaf, one surface only. In order of their persistence, the 96 h residues were Pounce > fenvalerate > Ambush. Pounce and fenvalerate had 67% and 66% remaining residue respectively while Ambush had declined to 43%. At 24 and 48 h post-application the remaining fenvalarate and Ambush residues were very similar, 83% vs 80% and 77% vs 72%. The Pounce formulation of permethrin definitely has a longer residual life in Arizona fields than the other two commonly used pyrethroids.

ACKNOWLEDGMENTS

The assistance of Union Carbide Agricultural Products Company and American Cyanamid Company in providing the analytical standards and analysis methods of thiodicarb and AC 222,705 respectively is gratefully acknowledged.

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