Bull. Environ. Contam. Toxicol. 31, 551–558 (1983)

Dislodgeable Insecticide Residues on Cotton Foliage: Comparison of ULV/Cottonseed Oil vs. Aqueous Dilutions of 12 Insecticides[1]

G. W. Ware, N. A. Buck, and B. J. Estesen

Department of Entomology, University of Arizona, Tucson, AZ 85721

With the renewed interest in ultra-low volume (ULV) applications of pyrethroids using vegetable oil as the carrier, there has also developed a parallel interest in formulations developed especially for ULV application. Additionally, growers and pest control advisers are becoming increasingly interested in the possibility of making ULV applications using insecticides not registered for this use. This poses a new form of reentry problem in that the insecticides are applied in concentrated form, as much as 20-fold, and may degrade at a reduced rate by a different route, or to more toxic metabolites.

In this study it was our purpose to compare the dislodgable residues of the 12 most commonly used insecticides when applied to companion plots of cotton as the typical, low volume spray diluted with water and the ULV.

METHODS AND MATERIALS

Experiment 1 - Pyrethroids

Test plots were located in a block of Deltapine-41 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 plants had an average height of 45 cm the day of the pyrethroid applications, June 28, 1982.

The aqueous sprays were applied at 122 L/ha (13 gal/A), 4.0 km/h (2.5 mph), and 276 kPa (40 psi) pressure using our manually drawn sprayer which treated two rows. The rig was equipped with 3 DC 2-13 Spraying Systems nozzles per row, and pressure was maintained from a 1.1 kg CO_2 tank with a 2-stage regulator.

The ULV sprays were applied with the above manually drawn sprayer equipped with two Micromax^{TM} controlled droplet atomizers spaced 203 cm apart, and pulled at 3.7 km/h (2.3 mph), treating

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[1] Contribution to Regional Research Project W-45, "Environmental Distribution, Transportation, and Toxicological Implications of Pesticide Residues". University of Arizona Agricultural Experiment Station journal series No. 3761.

Experiment 2 - Organophosphates

In the second series of insecticides applied July 12, 1982, the same equipment, cotton field, and experimental design were used. The aqueous sprays were applied with the same sprayer, nozzles, rate, and pressure as described in Experiment No. 1.

They were: Azinphosmethyl (Guthion® 25, 2.0 EC) @ 0.55 kg/ha; methyl parathion (5.0 EC) @ 1.1 kg/ha; sulprofos (Bolstar® 6, 6.0 EC) @ 1.1 kg/ha; and chlorpyrifos (Lorsban 4E, 4.0 EC) @ 1.1 kg/ha.

For the 3.5 L/ha ULV applications, cottonseed oil was again the diluent, except for the chlorpyrifos, which was applied as the experimental formulation Lorsban® XRM-4656 (2 lb/gal) at the rate of 4.7 L/ha (4 pints/A). This was accommodated by treating the plot at the reduced speed of 2.8 km/h. Because of the high rate of ai/ha, compared to the pyrethroids, the ratio of cottonseed oil to formulation was considerably reduced. For instance, azinphosmethyl contained only 33%, methyl parathion 47%, and sulprofos 55% cottonseed oil by volume.

Leaf sampling was as described in Experiment No. 1, and collected at 0, 24, 48, 72 and 96 h after treatment. Sample extraction was as described in Experiment No. 1, except that redistilled benzene was used as the extracting solvent.

Air temperatures were July 12, 40° - 19°; 13th, 40° - 19°; 14th, 41° - 21°; 15th, 40° - 23°; and July 16, 40° - 24°C, maximum and minimum. No rainfall was recorded during this period.

All 4 insecticides were analyzed without cleanup using a Micro Tek MT-220 GC equipped with a flame photometric detector, and the phosphorus mode read at 526 nm. A 102 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. Temperatures were: column, 200°C; detector, 245°C; and inlet, 205°C. For azinphosmethyl, gas flow was 120 mL/min, with retention time (RT) of 4.8 min. Methyl parathion had a RT of 1.7 min with 60 mL/min gas flow. Sulprofos RT was 3.1 min, the sulfone was 8.0 min, and the sulfoxide was 9 - 11 min at 120 mL/min gas flow. Chlorpyrifos RT was 2.4 min at 60 mL/min flow rate.

Experiment 3

The last set of 4 insecticides was applied on July 19, 1982, under the same conditions as previously described. The aqueous sprays were methidathion (Supracide® 2E, 2.0 EC) @ 1.1 kg/ha; chlordimeform (Galecron® 4E, 4.0 EC) @ 0.138 kg/ha; EPN (5.0 EC) @ 1.1 kg/ha; and methomyl (Lannate® L, 1.8 lb/gal water-miscible liquid) @ 1.0 kg/ha.

For the 3.5 L/ha ULV applications, cottonseed oil served as the diluent for EPN and chlordimeform. For methomyl, the new ULV formulation, (Lannate® LV, 2.4 lb/gal water-miscible liquid) was

4 rows simultaneously. The flow rate was regulated at 3.5 L/ha (3 pints/A) using a Spraying Systems Tee Jet® flow regulator orifice plate No. 4916-12, at 138 kPa (20 psi) and a 200 mesh screen, operated at 5000 RPM. The atomizers were powered by a 12-volt deep-cycle marine battery. With these settings the droplets ranged from 70 to 90µm, according to Micromax Operation Manual.

The insecticide formulation and rate of ai/ha were: Fenvalerate (Pydrin®, 2.4 EC) @ 0.22 kg/ha; permethrin (Pounce®, 3.2 EC) @ 0.22 kg/ha; flucythrinate (Pay-Off®, 2.5 EC) @ 0.088 kg/ha; and cypermethrin (Cymbush®, 3.0 EC) @ 0.066 kg/ha. For the ULV applications, each pyrethroid formulation was diluted with an appropriate amount of once-refined cottonseed oil to give the designated ai in 3.5 L/ha.

Maximum and minimum air temperatures during the test were June 28, 40° - 19°; 29th, 37.8° - 21°; 30th, 36° - 22°; July 1, 36° - 14°; 2nd, 37° - 14°; 3rd, 37.8° - 16°; 4th, 36° - 17°; 5th, 33° - 21°; and July 6, 28° - 21°C. There was 3.0 mm of rainfall immediately before the last sampling.

Triplicate leaf samples were collected from each plot at 0, 28, 96, and 192 h after treatment. Controls were collected at 0 and 192 h. Each sample consisted of 100 leaf discs, 2.54 cm diameter, taken singly and consecutively from the top, middle, and lower portions of plants in all 4 rows. Each sample replicate was extracted in a field shelter with 100 mL of redistilled hexane, by shaking for 1 min. The extract was transferred to a labeled storage bottle, the solvent level marked, and the bottles placed in an ice chest for transport to the laboratory for refrigeration.

Pyrethroid extracts were cleaned on a 2.5 cm plug of activated Florisil (120° for 24 h) covered with a 1.0 cm layer of Na_2SO_4, in a 22 mm I.D. column after prewetting with 50 mL of hexane. Sample aliquots were eluted with 100 mL of 4% ethyl acetate in hexane at 2 drops/sec, except flucythrinate, which was eluted with 10% ethyl acetate.

Extracts were analyzed on the Micro Tek MT-220 equipped with a ^{63}Ni electron capture detector. Permethrin was analyzed on a 104 cm x 4 mm I.D. Pyrex column packed with 3% SP-2330 on 27% Chromosorb W (A.W.) and 70% Chromosorb W (H.P.). Nitrogen flow was 70 mL/min with temperatures: column, 195°C; detector, 250°C; and inlet, 210°C. Retention times (RT) were 10.0 min for the cis and 12.5 min for the trans isomers.

Fenvalerate, cypermethrin and flucythrinate were analyzed using a 33 cm x 4 mm I.D. Pyrex column packed with 5% SE 30 on 100/120 mesh Chromosorb W (H.P.). Nitrogen flow was 95 mL/min with temperatures: column, 200°C; detector, 270°C; and inlet, 220°C. RTs were flucythrinate, 6.0 min; cypermethrin, 7.0 min, and fenvalerate, 7.5 min.

applied undiluted. Methidathion, because of its low weight/volume formulation, was also applied undiluted but at the rate of 4.7 L/ha to achieve the 1.1 kg/ha.

Leaf samples were collected at 0, 24, 48, and 72 h after spraying. Sample extraction was as in Experiment No. 1, using tap water for methomyl, redistilled hexane for chlordimeform, and redistilled benzene for EPN and methidathion.

Air temperatures were July 19, 37° - 23°; 20th, 38° - 24°; 21st, 38° - 23°; and July 22, 35° - 22°C. There was 11.3 mm of rainfall immediately before the last sampling.

EPN and methidathion were analyzed without cleanup on the MT-220, under the parameters described in Experiment No. 2. The EPN and EPN-oxon RTs were 4.2 and 3.6 min, respectively at 120 mL/min. That of methidathion was 2.7 min at 70 mL/min.

Methomyl extracts were hydrolyzed and analyzed by glc as described by Ware et al. (1980) with the following exceptions: A single hexane partitioning was done on the tap water extracts, the chloroform extraction was eliminated, and the last aqueous phase, after making alkaline to 0.1 N NaOH and hydrolyzing on a steam bath, was extracted 3 times, instead of 4, with ethyl acetate. Recoveries were 67% in conversion efficiency using this method.

Chlordimeform extracts were analyzed according to a method adapted from Voss et al. (1973). The derivatized product was analyzed using a 60 cm x 4 mm I.D. Pyrex column packed with 5% Dexsil 300 on 100/120 mesh Chromosorb W (H.P.). Nitrogen flow was 70 mL/min with temperatures: column, 100°C; detector, 250°C; and inlet, 218°C. RT was 3.5 min. Quantitation was by peak height.

RESULTS AND DISCUSSIONS

The results of Experiment No. 1 are presented in Table 1 expressed as micrograms of toxicant per square centimeter of cotton leaf, one surface only. The initial deposits from the Micromax™ ULV application were noticeably less than their companion aqueous sprays, averaging only 61%. This holds true in the next 2 experiments. The cottonseed oil obviously enhanced the residual life of all 4 pyrethroids, resulting in 38% of their initial deposits remaining after 8 days, while only 20% of the emulsions remained.

The results of Experiment No. 2 are presented in Table 2. Chlorpyrifos was not diluted with cottonseed oil, since it was formulated for ULV. Its residue was enhanced at 24 h by the ULV, but not beyond that. Azinphosmethyl was unchanged with the oil carrier, while methyl parathion was extended as ULV to 24 h, by inhibiting its conversion to the oxon. Sulprofos dissipated and was converted to the sulfone at an accelerated rate with cottonseed oil. This resulted in approximately twice the sulfone and one-half the sulfoxide of the emulsion at 4 days.

TABLE 1

Dislodgable residues expressed as $\mu g/cm^2$ of cotton leaf (one surface only) following application by ground rig. Marana, AZ. June 28, 1982

	Fenvalerate 0.22 kg/ha		Permethrin 0.22 kg/ha		Flucythrinate 0.088 kg/ha		Cypermethrin 0.066 kg/ha	
Hours	EC	ULV	EC	ULV	EC	ULV	EC	ULV
0	1.16	.97	1.18	.55	.41	.30	.32	.14
48	.69	.71	.71	.55	.28	.24	.20	.09
96	.48	.66	.43	.39	.18	.22	.14	.08
192	.24	.40	.19	.21	.08	.13	.07	.04
Controls	<.004		<.02		<.004		<.004	
	(21)*	(41)	(16)	(38)	(20)	(43)	(22)	(29)

* percent of initial residues remaining 192 h after application.

TABLE 2

Dislodgable residues expressed as ug/cm^2 of cotton leaf (one surface only) following application by ground rig. Marana, AZ. July 12, 1982

	Sulprofos 1.1 kg/ha								Azinphosmethyl 0.55 kg/ha	
	EC				ULV				EC	ULV
Hours	SUL	-SO	$-SO_2$	TOTAL	SUL	-SO	$-SO_2$	TOTAL		
0	4.9	.44	.02	5.4	2.6	.40	.03	3.0	2.2	1.6
24	2.2	.86	.33	3.4	.7	1.6	.18	2.5	.94	.75
48	.75	.93	.82	2.5	.16	1.8	.36	2.3	.58	.44
72	.34	.72	.94	2.0	.04	1.3	.34	1.7	.37	.28
96	.15	.61	1.0	1.8	.02	1.2	.39	1.2	.26	.20
Controls	$<$.001	$<$.004	$<$.01						$<$.002	

	Methyl Parathion 1.1 kg/ha						Chlorpyrifos 1.1 kg/ha	
	EC			ULV			EC	ULV
Hours	THION	-OXON	TOTAL	-THION	-OXON	TOTAL		
0	4.7	.04	4.7	3.9	.01	3.9	2.9	1.7
24	.29	.03	.31	.82	.05	.87	.30	.58
48	.08	.01	.09	.24	.04	.28	.19	.20
72	.03	.01	.04	.08	.03	.11	.13	.07
96	.02	.003	.02	.03	.03	.06	.08	.03
Controls	$<$.003	$<$.003					$<$.002	

TABLE 3

Dislodgable residues expressed as $\mu g/cm^2$ of cotton leaf (one surface only) following application by ground rig. Marana, AZ. July 19, 1982

	Methidathion 1.1 kg/ha		Methomyl 1.0 kg/ha		Chlordimeform 0.138 kg/ha	
Hours	EC	ULV	EC	ULV	EC	ULV
0	5.1	4.2	1.3	1.2	.053	.031
24	1.4	2.4	.066	1.3	.029	.029
48	.34	1.2	.049	.15	<.002	<.002
72	.08	.08	*	*	*	*
Controls	<.002		<.03		<.002	

* no samples collected

	EPN 1.1 kg/ha					
	EC			ULV		
Hours	EPN	-OXON	TOTAL	EPN	-OXON	TOTAL
0	4.8	.02	4.8	3.3	<.01	3.3
24	1.8	.09	1.9	.86	.01	.87
48	.77	.05	.82	.34	<.01	.34
72	.36	.00	.36	.11	<.01	.11
Controls	<.01	<.01				

TABLE 4

Percent of initial residue remaining 48 hours after application as aqueous dilution and as ULV. Marana, AZ. June 25-July 19, 1982

	EC	ULV
Permethrin	60	100
Flucythrinate	68	80
Sulprofos	46	77
Fenvalerate	59	73
Cypermethrin	62	64
Methidathion	6.6	29
Azinphosmethyl	26	27
Methomyl	3.8	12.5
Chlorpyrifos	6.5	12
EPN	17	10
Methyl parathion	1.8	7.2
Chlordimeform	.0	.0

The results of Experiment 3 are presented in Table 3. Because methomyl and chlordimeform have such short field lives, residue samples were collected only through 48 h. The chlordimeform residue was extended measurably through 24 h in cottonseed oil. Methomyl, in the form of the new ULV formulation, Lannate® LV, was greatly extended through 48 h. The ULV methidathion was applied as its basic formulation, undiluted, which increased its residual life substantially through 48 h. No benefit was seen in the ULV application of EPN by cottonseed oil.

A summary of the 3 studies is presented in Table 4 as the influence of ULV on the residual levels at 48 h compared to the typical aqueous dilutions of the 12 insecticides. The permethrin ULV value at 100% is unlikely but should be rather like fenvalerate and flucythrinate. These data, with Table 1, demonstrate clearly the enhanced residual life of all tested pyrethroids by using vegetable oil as the carrier. Of the remainder, only sulprofos and methidathion have enhanced residues when applied as ULV over 48 h. Chlordimeform, the most volatile of the 12, is extended through 24 h by the oil carrier (Table 3).

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Accepted June 6, 1983