Bull. Environ. Contam. Toxicol. (1991) 47:355–361

Environmental Contamination and Toxicology

Pyrethroid Insecticides and Formulations as Factors in Residues Remaining in Apparel Fabrics after Laundering

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Worker exposure to pesticides can be limited by the use of protective clothing. Pesticide residue in garments can be lowered or removed with the selection of the most appropriate combination of laundering factors. Higher wash temperature, prerinsing, prewash additives, using heavy-duty liquid or phosphate-built detergents, daily laundering, and multiple launderings are proven to be helpful for removal of pesticide residue from fabrics (Laughlin and Gold, 1988). Repellent finishes on protective apparel fabrics decrease pesticide absorption; however, these finishes may hinder pesticide removal in laundering (Laughlin and Gold 1989).

The textile substrate (garment) is an important consideration in the completeness of removal of pesticide residues in laundering. While a fabric's fiber content does not affect removal of pesticide residues (Easley *et al.* 1983; Laughlin *et al.* 1986), fabric weight may contribute to after-laundering residue retention. Leonas and DeJonge (1986) report that the heavier fabrics prevented pesticide penetration better than the lighter fabrics. Kim *et al.* (1982), in a study of two very different fabric weights, found that the heavier fabric retained more residues after laundering than did a very light weight fabric.

The pesticide itself contributes to problems in residue removal. Keaschall *et al.* (1986) reported differences in residue remaining after laundering among the chemical classes of organophosphates, organochlorines, and carbamates. Differences in refurbishment requirements among chemicals within the same class have been identified (Keaschall *et al.* 1986; Lillie *et al.* 1981).

The formulation of a pesticide affects residue remaining after laundering. Laughlin *et al.* (1985) reported that the encapsulated and wettable powder formulations of methyl parathion were more easily removed than the emulsifiable concentrate formulation. Easley *et al.* (1983) found that the ester formulation of 2,4-D was more difficult to remove than the more highly water-soluble amine formulation.

Few studies have examined detergent concentration relative to pesticide residues. Hild *et al.* (1989) concluded that as detergent concentration increased, the amount and percent of pesticide residue remaining after laundering decreased. At the highest concentrations, a plateau was evident. Obendorf and Klemash (1982) reported similar results. Very little work has used the pyrethroids, a class of pesticide in increasing use.

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MATERIALS AND METHODS

This study was undertaken to determine effective laundry methods for the removal of the pyrethroid insecticides, cyfluthrin and cypermethrin of wettable powder and emulsifiable concentrate formulations from fabrics. Fabric weight and fabric finish may affect the removal of the pesticides.

The study was designed as four experiments, each a 2 x 2 x 2 x 4 in factorial design: fabric factors of weight (10 oz/yd^2 and 14 oz/yd^2) and finish (unfinished and repellent finished); and laundry factors of detergent type (heavy-duty liquid and phosphate) and detergent concentration (0.5×, 1.0×, 1.5× and 2.0×). The four experiments were completed with one of the following: 1) cyfluthrin emulsifiable concentrate, 2) cyfluthrin wettable powder, 3) cypermethrin emulsifiable concentrate, and 4) cypermethrin wettable powder, respectively. In all four experiments, the laundry procedures remained constant: use of a prewash spray (0.250 μL), water volume (150 mL), use of distilled water, agitation, laundry procedure, and temperature of washing and rinsing (50°C).

Fabrics were cut into specimens measuring 8 cm x 8 cm then spiked with pesticide solutions of 0.1% active ingredient (AI). The emulsifiable concentrate (EC) formulation of cyfluthrin [(RS)-α-cyano-4-fluoro-3-phenoxybenzyl (1RS, 3RS: 1 RS, 3RS)-3-(2,2-dichlorovinyl)-2,2-dimethycyclopropanecarboxylate (IUPAC)] was 24.3% AI. Its wettable powder (WP) formulation was 20.0% AI. The EC formulation of cypermethrin [(RS-α-cyano-3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate (IUPAC)] was 25.3% AI and its WP formulation was 40.0% AI. The insecticide solution was pipetted onto each fabric specimen in amounts of 200 μL. The contaminated specimens were air dried.

Each specimen was treated with 250 μL of a prewash spray product (Spray-n-Wash®[1]). Then specimens were laundered in an Atlas Launder-Ometer for 12 minutes and rinsed for 5 minutes and 3 minutes. Four levels of detergent concentration were used: 0.0× (or laundered without detergent), 0.5×, 1.0×, and 1.5× (where × = manufacturer's recommendation), made up to 150 ml volume for laundering each specimen. The two detergents were a heavy-duty liquid (Cheer®[1]) and a phosphate (powdered Cheer®[1]) (PHOS). After laundering, specimens were allowed to air dry, then extracted and prepared for analysis.

Pesticide residue was based on area counts done on a Varian Series 3400 gas chromatograph with an eletron capture detector at 240°C, 260°C, and 325°C for column, injector, and detector. The column was 90 cm x 2 mm, packed with 3% OV 101 on 80/100 mesh Chromosorb W-HP with nitrogen flow of 40 mL/min.

The statistical analyses were computed based on residue remaining, and expressed as percent residue remaining. General Linear Model (GLM) analyses were calculated at $p \leq 0.05$ level of significance for both amount and percent residue remaining after laundering. Orthogonal contrast comparisons were performed along with LS Means for the examination of interactions. Inferences were made between these four experiments.

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[1]Use of this product does not imply endorsement or recommendation.

RESULTS AND DISCUSSION

At the initial contamination, the fabric specimens contained 1.7, 1.8, 1.8 and 2.3 $\mu g/cm^2$ for the cyfluthrin EC, cyfluthrin WP, cypermethrin EC and cypermethrin WP, respectively. Across all specimens, as much as 90 percent, or an average of 1.1 ng/cm^2 of pesticide remained after laundering. Although laundering made a difference in pyrethroid residue, it was not particularly successful. The amount of residue remaining after laundering was 1.1 $ng/cm^2 \pm 1.1$, 0.3 $ng/cm^2 \pm 0.3$, 0.3 $ng/cm^2 \pm 0.1$, and 0.4 $ng/cm^2 \pm 0.9$ for cyfluthrin EC, cyfluthrin WP, cypermethrin EC, and cypermethrin WP, respectively. The residue remaining after laundering was very small; however, the initial contamination was very limited, with a concentration of only 0.1% active ingredient solution. Apparent differences in residues remaining after laundering were noted due to pesticide factors, fabric factors and laundry factors; therefore, GLM analyses were performed for each experiment.

Across the four experiments, the only consistently significant factor was a main effect of fabric finish (cyfluthrin EC: $F=27.72$, d.f.=1,94, $p \leq 0.05$ (for amount) and $F=35.28$, d.f.=1,94, $p \leq 0.05$ (for percent); cyfluthrin WP: $F=18.12$, d.f.=1,94, $p \leq 0.05$ (for percent only); cypermethrin EC: $F=8.31$, d.f.=1,94 $p \leq 0.05$ (for amount) and $F=13.67$, d.f.=1,94, $p \leq 0.05$ (for percent); cypermethrin WP: $F=6.58$, d.f.=1,94, $p \leq 0.05$). All significant interactions included fabric finish except for two (cyfluthrin WP: $F=2.90$, d.f.=3,94, $p \leq 0.05$ and cypermethrin EC: $F=3.03$, d.f.=3,94, $p \leq 0.05$ both for the interaction of fabric weight x detergent concentration).

The effects of fabric finish (Table 1) was so overwhelming that the potential was recognized for other effects to be obscured. The pesticide solution had not been completely absorbed by the finished fabrics at initial contamination, while the unfinished fabrics absorbed all of the pesticide solution. Even with these differences at initial contamination, the unfinished fabrics tended to have lower amounts of after-laundering residue than did the finished fabrics. The functional finish limited pesticide absorption at initial contamination; but this did not mean that pesticide residues after laundering were lower. In fact, the finished fabrics had as much as three times the amount of pesticide residue remaining after laundering than did the unfinished fabrics.

Table 1. Contribution of fabric finish to pyrethroid residues remaining after laundering.

	Unfinished Specimens		Repellent Specimens	
	$\bar{x}$ ng/cm^2	%	$\bar{x}$ ng/cm^2	%
Cyfluthrin				
EC	0.48	22	1.67	100
WP	0.23	7	0.27	63
Cypermethrin				
EC	0.39	16	0.29	26
WP	0.28	10	0.57	67

EC=Emulsifiable Concentrate Formulation.
WP=Wettable Powder Formulation.

Since previous research in our laboratory resulted in recommendations for selecting detergent type per formulation, we paid close attention to the results for detergent type for each of

the four experiments (Table 2). With cyfluthrin EC, we saw that the HDL detergent removed twice as much pesticide as the PHOS ($F=17.34$, d.f.=1,94, $p \leq 0.05$). When the experiment was repeated with cyfluthrin WP, the PHOS detergent was more effective ($F=7.45$, d.f.=1,94, $p \leq 0.05$) on the unfinished fabric, while the HDL was more effective on the SR fabric. This held true when we completed the fourth experiment (cypermethrin WP); PHOS was more effective with a particulate wettable powder, but the detergent differences were not apparent for the cypermethrin EC experiment.

Table 2. Contribution of detergent type to pyrethroid residue remaining after laundering.

	HDL		PHOS	
	$\bar{x}$ ng/cm^2	%	$\bar{x}$ ng/cm^2	%
Cyfluthrin				
EC	0.62	54	1.56	100
WP	0.24	27	0.25	43
Cypermethrin				
EC	0.38	23	0.30	19
WP	0.34	30	0.51	47
Partitioned for unfinished fabric specimens only.				
Cyfluthrin				
EC	0.30	13	0.68	32
WP	0.31	10	0.15	5
Cypermethrin				
EC	0.43	18	0.35	14
WP	0.19	7	0.37	14

EC=Emulsifiable Concentrate Formulation.
WP=Wettable Powder Formulation.
HDL=Heavy Duty Liquid Detergent.
PHOS=Phosphate Powdered Detergent.

When we studied cypermethrin EC and WP, we saw a main effect of detergent concentration. As detergent concentration increased, residue decreased until residue remaining leveled, between the 1.0× and 1.5× detergent concentrations (Table 3), illustrating the quadratic relationship revealed through orthogonal contrasts for both formulations of cypermethrin. We found no contribution of detergent concentration when experiments used cyfluthrin EC and WP.

An interaction of fabric weight with detergent concentration was present for cyfluthrin WP ($F=2.90$, d.f.=3,94, $p \leq 0.05$) but there was no main effect for cyfluthrin EC (Table 4). The 10.5 oz/yd^2 fabric retained much less residue than the 14 oz/yd^2 fabric; but at 1.5× detergent concentration, there was a marked increase in residue retention in the less heavy fabric. Increased suds may have inhibited removal. The fabric weight with detergent concentration interaction was present for cypermethrin EC ($F=11.62$, d.f.=3,94, $p \leq 0.05$) and for cypermethrin WP ($F=4.58$, d.f.=3,94, $p \leq 0.05$). As fabric weight increased, residue increased. SR fabric specimens returned more residue than did UN specimens.

Both pesticides were removed by laundering. The cypermethrin in either EC or WP formulation, was more easily removed by laundering than the cyfluthrin. The cyfluthrin EC formulation proved to be the most difficult to remove. This is because EC formulations

contain an oily medium as carrier for the active ingredient; thus, the EC formulations have the same soil removal problems as other soils of an oily nature. Oily soils penetrate into the cotton fiber and become entrapped in the crenulations and lumen where detergents are less successful in soil dislodgement. WP formulations, containing clay or talc as a carrier for the active ingredient, are more effectively removed by the presence of a builder in phosphate detergents. Thus, type of detergent was an important contribution to completeness in residue removal in laundering.

Table 3. Mean amounts and percentages with significant differences due to detergent concentration in pyrethroid residues after laundering.

	Detergent Concentration							
	0×		0.5×		1.0×		1.5×	
	ng/cm²	%	ng/cm²	%	ng/cm²	%	ng/cm²	%
Cyfluthrin								
EC	0.93	75	1.37	100	0.99	84	1.05	100
WP	0.25	31	0.27	41	0.20	28	0.28	40
Cypermethrin								
EC	0.53	30	0.28	19	0.27	19	0.27	17
WP	0.20	12	0.42	33	0.55	56	0.53	52
Partitioned for unfinished fabric specimens only.								
Cyfluthrin								
EC	0.59	27	0.53	24	0.53	24	0.31	13
sig dif[1]	———		———		———		———	
WP	0.29	10	0.26	9	0.18	6	0.18	6
sig dif[1]	———		———		———		———	
Cypermethrin EC	0.71	29	0.30	12	0.25	10	0.25	10
sig dif[1]	———		———		———		———	
WP	0.25	10	0.21	8	0.13	5	0.52	19
sig dif[1]	———		———		———		———	

[1]Means underscored by the same line are not significantly different ($p \leq 0.05$).

The HDL detergents are noted for their ability to remove oily soil; the HDL detergent should be better at removing the EC formulation residues. The HDL detergent was more effective in removing the EC formulation and, the PHOS detergent for the WP formulation residues. Based on these findings, we recommend the launderer of clothing contaminated with cyfluthrin or cypermethrin select a detergent for formulation: HDL detergent for EC formulations and PHOS detergent for WP formulations.

The MedH fabric retained less residue after laundering, but more research is needed before conclusive recommendations about fabric weight are made. The question needs to be asked: how well does a light weight fabric prevent penetration of pesticide to dermal surfaces. Increasing detergent concentration is helpful in removing pesticide residues. More vigorous laundry procedures should be investigated relative to heavy weight fabrics.

Table 4. Mean amount and percentages due to fabric weight in pyrethroid residues after laundering.

	10.5 oz/yd^2		14 oz/yd^2	
	$\bar{x}$ ng/cm^2	%	$\bar{x}$ ng/cm^2	%
Cyfluthrin				
EC	0.98	81	1.19	100
WP	0.22	28	0.28	42
Cypermethrin				
EC	0.25	19	0.43	22
WP	0.49	38	0.36	38
Partitioned for unfinished fabric specimens only.				
Cyfluthrin				
EC	0.37	18	0.60	26
WP	0.15	5	0.31	10
Cypermethrin				
EC	0.25	10	0.53	23
WP	0.33	12	0.23	9

EC=Emulsifiable Concentrate Formulation.
WP=Wettable Powder Formulation.

Acknowledgments. The research was funded in part by the Nebraska Agricultural Research Division Project 94-014 and contributes to the Southern Regional Research Project S-208 "Textile Fiber Systems for Performance, Protection and Comfort." Published as Journal Series Number 9464, Agricultural Research Division, University of Nebraska.

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Received February 23, 1991; Accepted April 5, 1991.