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Effects of Laundering upon the Removal of Atrazine and Metolachlor from Cotton, Cotton/Polyester, and Polyester Fabrics Treated with Fluorochemical Finishes

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The health and safety of pesticide applicators can be enhanced by the use of appropriate protective clothing while applying pesticides. Numerous studies have been conducted in the last three decades to study the performance of protective clothing materials in reducing pesticide exposure (Laughlin and Gold, 1988; Leonas et al., 1989; Raheel 1988a; Raheel, 1988b). As laundering is commonly used to decontaminate reusable clothing, laboratory studies are typically conducted to determine the effectiveness of the decontamination process in the removal of pesticide retained in the fabric. The laundering studies are also used to determine the durability of the finish after repeated laundering for textile materials treated with water and oil repellent finishes. These studies are particularly important for evaluating the performance of finished fabrics after simulated "wear". In the 1980s and early 1990s, woven fabrics treated with commercially available fluorochemical finishes such as Quarpel® and Zepel® were evaluated as potential materials for protective clothing garments (Leonas and DeJonge, 1986; Keaschall et al., 1986; Uyenco and Obendorf, 1984). These studies showed that the fluorochemical finishes reduced the penetration of the pesticides through textile materials. The level to which the penetration of pesticides was reduced was dependent on the finish that was applied. The performance of the fabrics after repeated launderings varied considerably. This could be due to factors such as type and method of application of finish and the pesticide used to contaminate the material.

Reported here is the performance of fabrics finished with Zonyl® (fluoroalkyl methacrylate polymer), as evaluated at the University of Maryland Eastern Shore. No research to the best knowledge of authors has been conducted to study the performance of fabrics finished with Zonyl® against liquid pesticides. Recently "wear studies" were conducted to evaluate the performance of these finished fabrics exposed to simulated abrasion and sunlight and the results have been reported elsewhere (Shaw et al., 1996; Shaw et al., 1997). This study focuses on the performance of the treated fabrics after repeated contamination and laundering cycles. The amount of pesticide accumulation was used to determine the effectiveness of the laundering process in removing pesticide. The performance of the finished fabric after repeated launderings was measured by determining the amount of penetration of the pesticide through the material.

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MATERIALS AND METHODS

A 2 x 3 x 3 factorial design was used for the study. The three factors were pesticide, test fabric, and number of launderings, respectively. Atrazine (41% a.i. flowable liquid) and metolachlor (68.5 % a.i. emulsifiable concentrate) were the pesticides used for this study. Concentrated pesticides were used to simulate the worst case scenario. The fiber contents of the fabrics selected in this study were cotton and cotton/polyester fabrics that are commonly used for worker apparel (Laughlin and Gold, 1988). A 100% woven polyester fabric was tested. The physical characteristics of three fabrics are given in Table 1. Zonyl®, a water and also oil repellent finish, was commercially applied to all the fabrics according to manufacturer's specifications.

Table 1. Physical characteristics of test fabrics.

Fiber Content	Weight (g/m^2)	Weave	Yarn Count (/cm)	Thickness (mm)
Cotton (100%)	187.5	Plain	41x21	0.35
Cot/Poly (65/35%)	190.9	Plain	46x26	0.32
Polyester	212.2	Plain	17x16	0.52

For pesticide application, a three-layer assembly was prepared which consisted of a top layer (test fabric) and collector layers (knit fabric and aluminum foil). The test assembly was placed horizontally and a fixed-volume pipettor was used to apply 0.1 mL of pesticide solution to the center of the 8 x 8 cm fabric specimens. After 10 min, the excess pesticide was removed from the surface of the fabric using a disposable pipette (Shaw and Hill, 1991). The three-layer fabric assembly was allowed to air dry overnight. The top layer was separated from the collector layer, laundered, and subsequently extracted to measure pesticide accumulation. The collector layers were discarded for all cycles except the last one for each level of laundering. The last collector layers (knit and foil together) were extracted to measure penetration. Three replicates were tested for each combination.
To determine the effect of laundering, the contaminated fabric specimen was laundered 1, 10, and 20 times respectively. The method, 61-IIA, of the American Association of Textile Chemists and Colorists was modified for this study. Each fabric specimen was laundered in a steel can with 200 ml of soap solution at 49° C for 10 min using a launder-o-meter. After laundering, specimens were rinsed twice with distilled water and then allowed to air dry at room temperature (200 mL each). Contamination and laundering constituted one cycle. The pesticide application described above was performed prior to each laundering cycle until the desired number of launderings was achieved.

Three aliquots of acetone (50 mL) were used to extract the pesticides from each test fabric and collector layer. The contaminated layers (top and collector) were extracted separately using an orbital shaker set at 200 rpm for 45 min. The three aliquots were combined and analyzed using Hewlett Packard 5890 gas chromatograph equipped with a nitrogen/phosphorus detector and 30 m x 0.32 mm ID fused silica capillary column. The temperature program was: 40° C (1 min), ramped to 260° C at 40° C/min, and held at 260° C for 2 min.
Pesticide accumulation results were expressed as means and standard deviations of the amount (mg) of the active ingredient accumulated in the laundered fabric and the percentage of the active ingredient remaining in the material. The formula used to calculate the % accumulation is given below:

$$\%\ \text{Accumulation} = \frac{\text{amount (mg) of active ing. in the laundered specimen x 100}}{\text{amount (mg) of active ing. per application x no. of application}}$$

Pesticide penetration through the fabric was expressed as the means and standard deviation of the amount of active ingredient (mg) in the collector layer and the percentage of pesticide that penetrated through the material.

$$\%\ \text{Penetration} = \frac{\text{amount (mg) of active ingredient in the collector layer x 100}}{\text{amount (mg) of active ingredient per applications}}$$

RESULTS AND DISCUSSION

As seen in Table 2, atrazine accumulation after 1, 10, and 20 cycles was very low for all the fabrics. The maximum amount of buildup was 0.22 mg. This indicates that laundering was very effective in removing atrazine that was applied as a concentrate. Atrazine is extremely soluble in water and thus easily removed. As the formulation used was flowable liquid, it did not have any oil-based additives that would adversely impact the removal process. Although the accumulation of metolachlor in the fabric was higher than that of atrazine, highest mean value was less than 3.5%. The mean value for metolachlor accumulation in the cotton fabric after 10 launderings was 24.45 mg (3.23% of the amount applied) and after 20 launderings was 26.85 mg (1.77% of the amount applied). Although the amount of metolachlor increased by 2.4 mg between the 10 and 20 launderings, the percent remaining in the fabric was lower (3.23% vs. 1.77%).

The amount of pesticide that penetrated through the fabric was measured by extracting the collector layer after 1, 10, and 20 contaminations. For atrazine, the cotton and cotton/polyester fabrics had less than 0.05% penetration at all three levels of contamination. This indicates that the cotton and cotton/polyester finished fabrics were effective in preventing the atrazine concentrate from penetrating even after 20 launderings. However, one of the polyester fabrics had 4.75 mg (10.44%) penetration. For fabrics with fluorochemical finishes, the

Table 2. Atrazine accumulation in treated fabrics after different laundering cycles

	Number of Launderings											
	1				10				20			
	Amount (mg)		Percent (%)		Amount (mg)		Percent (%)		Amount (mg)		Percent (%)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Cotton	0.01	0.00	0.03	0.01	0.17	0.02	0.04	0.00	0.12	0.01	0.01	0.00
Cotton/Polyester	0.04	0.00	0.08	0.01	0.16	0.03	0.04	0.01	0.10	0.01	0.01	0.00
Polyester	0.01	0.00	0.02	0.00	0.06	0.04	0.01	0.01	0.22	0.17	0.02	0.02

Table 3. Metolachlor accumulation in treated fabrics after different laundering cycles

	Number of Launderings											
	1				10				20			
	Amount (mg)		Percent (%)		Amount (mg)		Percent (%)		Amount (mg)		Percent (%)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Cotton	0.02	0.03	0.03	0.04	24.45	5.63	3.23	0.74	26.85	3.97	1.77	0.26
Cotton/Polyester	0.09	0.03	0.12	0.04	8.10	2.60	1.07	0.34	48.45	3.90	3.20	0.26
Polyester	0.03	0.04	0.03	0.05	23.40	7.17	3.08	0.95	28.35	4.32	1.88	0.29

Table 4. Penetration of atrazine to the collector layer after different laundering cycles

	Number of Launderings											
	1				10				20			
	Amount (mg)		Percent (%)		Amount (mg)		Percent (%)		Amount (mg)		Percent (%)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Cotton	0.01	0.00	0.02	0.00	0.02	0.01	0.04	0.02	0.01	0.00	0.02	0.00
Cotton/Polyester	0.01	0.00	0.02	0.00	0.05	0.04	0.11	0.08	0.01	0.00	0.02	0.00
Polyester	0.01	0.00	0.02	0.00	0.17	0.17	0.36	0.38	4.75	6.53	10.44	14.36

Table 5. Penetration of Metolachlor to the collector layer after different laundering cycles

	Number of Launderings											
	1				10				20			
	Amount (mg)		Percent (%)		Amount (mg)		Percent (%)		Amount (mg)		Percent (%)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Cotton	ND*	-	ND	-	66.30	0.86	88.00	1.14	47.40	5.15	63.00	6.80
Cotton/Polyester	ND	-	ND	-	0.08	0.01	0.11	0.01	64.65	2.29	85.00	3.03
Polyester	0.07	0.07	0.09	0.13	72.75	3.92	96.00	5.18	59.40	4.32	78.00	5.70

* Not detected

effects of the fiber content are typically camouflaged by the finish (Raheel 1988a). The penetration through the polyester fabric was most probably due to the fabric construction. Although the polyester fabric was comparatively thicker, it had a more open weave. Thus there was a greater possibility of penetration through the interspaces after repeated laundering.

Pesticide penetration results for metolachor were very high for the cotton and polyester fabrics after 10 and 20 launderings and were high for cotton/polyester fabrics after 20 launderings. The fluorochemical finishes provided repellency by reducing the surface tension of the materials. Pesticide penetration through these fabrics would depend on the fabric characteristic, as well as, the pesticide formulation. The effect of formulation can be clearly seen by comparing the penetration results of the atrazine vs. metolachlor. Atrazine which was a flowable liquid formulation did not, in most cases, penetrate through the fabrics. Whereas, metolachlor which was an emulsifiable concentrate penetrated all of the fabrics after 20 launderings. These fabrics were not effective in providing adequate protection against a 65.5% emulsifiable concentrate after 20 launderings as used here.

Based on these results it can be concluded that the pesticide accumulation in all three treated fabrics was very low for atrazine but not metolachlor. Cotton and cotton/polyester fabrics were effective in preventing the penetration of atrazine through the material after 20 launderings. All three fabrics were not effective in providing protection against metolachlor emulsifiable concentrate. Because the field strength formulation properties are considerably different additional research is needed to assess the performance of finished fabrics with a weave against field strength pesticides.

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REFERENCES

American Association of Textile Chemists and Colorists (1996) Technical manual "Colorfastness to Washing, Domestic; and Laundering, Commercial: Accelerated" Research Triangle Park, North Carolina, vol. 71

Keaschall, JL, Laughlin, JM, Gold RE (1986) Effect of laundering procedures and functional finishes on removal of insecticides selected from three classes. In: RL Barker, GC Coletta (eds) Performance of Protective Clothing, ASTM STP 900, American Society for Testing and Materials, Philadelphia, pp. 162-176

Laughlin J, Gold RE (1988) Cleaning protective apparel to reduce pesticide exposure. Rev Environ Contam Toxicol 101:93-119

Laughlin J, Gold RE (1987) Methyl parathion residue in cotton and polyester functionally finished fabrics after laundering and abrasion. Cloth Textil Res J 5:9-17

Leonas K, DeJonge JO (1986) Effect of functional finish barriers on pesticide penetration, In: RL Barker, GC Coletta (eds) Performance of Protective Clothing, ASTM STP 900, American Society for Testing and Materials, Philadelphia, pp.177-186

Leonas K, Easter EP, DeJonge JO (1989) Effect of fabric characteristics on pesticide penetration through selected apparel fabrics. Bull Environ Contam Toxicol 43:231-238

Raheel M (1988a) Pesticide penetration in fabrics: Fiber chemistry, surface energy, and fabric porosity. Book of Papers, The first international symposium on the impact of pesticides, industrial and consumer chemicals on the near environment. Orlando, FL. February, p127-136

Raheel M (1988b) Dermal Exposure to Pesticides: The barrier effectiveness of protective clothing. J Environ Health 51:82-84

Shaw A, Hill KR (1991) Effect of exposure time on the sorption of pesticide emulsifiable concentrates through microporous fabrics. Bull Environ Contam Toxicol 46:45-52

Shaw A, Lin YJ, Pfeil, E (1996) Effect of abrasion on protective properties of polyester and cotton/polyester blend fabrics. Bull Environ Contam Toxicol 56:935-941

Shaw A, Lin, YJ, Pfeil, E (1997) Qualitative and quantitative analysis of diazinon in fabric exposed to various simulated sunlight and humidity conditions. Bull Environ Contam Toxicol 59:389-395

Uyenco, EFR, Obendorf, SK (1984) Effect of functional finishes on retention of the pesticide malathion on polyester/cotton fabrics. Book of Papers, 1984 International Conference and Exhibition, American Association of Textile Chemist and Colorist 239-247