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Methyl Parathion Redeposition during Laundering of Functionally Finished Protective Apparel Fabrics

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Fabrics commonly used for work clothing, cotton and/or polyester, will continue to be used for clothing of pesticide applicators. On these fiber contents, pesticide spills onto the fabric may wet the area of original spill, and remain in that position, or may migrate to adjacent areas increasing the potential for accidental exposure. Previous and current research has identified the best recommendation for laundering clothing soiled with some pesticides (Laughlin and Gold 1987); however, no work to date has shown how to completely remove residues from laundered fabric. Work is needed on minimizing soiling and soil redeposition while enhancing pesticide soil removal in laundering.

The mechanisms of enhanced soiling and therefore difficulty in soil removal include penetration of the soil (dependent upon surface tension of soil and fiber, viscosity of the soil, and distance between fibers and interstices between yarns), entrapment in the structure of the fiber and/or in spaces of fibers fractured by the mechanical wear of laundering or during use, and the chemical reaction of soil with fiber and finish. Obendorf and Klemash (1982) have established through scanning electron micrographs and x-ray diffraction analysis, the presence of oily soil in the lumen, crenulations and convolutions of cotton and in the capillary spaces between polyester fibers. Obendorf and Solbrig (1986) noted the parallel between oily soil and pesticide soil, with documentation of methyl parathion on the surfaces of cotton and polyester fibers and in the lumen of cotton fibers.

Soiling occurs not only when the textile is used; the textile may become soiled during laundering. Wet soiling during laundering involves transfer of soil from the textile via the washing solution to another fabric, or generalized redeposition by removal from the site of soiling, transfer into the washing medium and thus to all areas of the fabric. Furthermore, during the laundering process, pesticide residue in the fabric from contamination can be re-solubilized and dispersed throughout the

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fabric by the washing medium. Crone had observed that when heavily soiled materials were washed in the same load with light soiled materials, an equilibrium was approached for all material in the load due to soil redeposition.

Finley et al. (1977) and Easley et al. (1983) have documented transfer of pesticide soil from contaminated fabric to clean fabric during concomitant washing, with the amount of pesticide transferred in the range of 0-2% of residues in the initial soiled fabric. Laughlin et al. (1981) found that pesticide soil transferred from laundering equipment to clean fabric laundered in the equipment immediately following washing of methyl parathion soiled fabric; however, the amounts transferred were less than 0.01% of the initial contamination of the pesticide-soiled fabric.

Although several studies have examined the pesticide residue in fabric specimens after laundering, few studies have explored spread or movement of pesticide through a large specimen fabric from the original site of contamination, and whether that movement from the original site of contamination is enhanced by the presence of water as a solvent in the washing operation.

MATERIALS AND METHODS

A factorial random block design for ascertaining the effectiveness of laundering in removal of MeP residues was designed with four factors: fabric finishes (3); pesticide formulations (2); detergents (2); and wash temperature (2).

The second factorial experiment assessed the movement of pesticide through a large specimen of fabric upon soiling and during laundering was designed with four factors: fabric finishes (3); pesticide formulations (3); sampling ring (10); and laundered/unlaundered (2). All work was replicated a minimum of three times.

Three finishes on 50% cotton/50% polyester bottom weight poplin fabrics obtained from Testfabrics, Inc. were studied. The finishes included: unfinished (UN), durable press (DP) finish, and UN with fluorocarbon soil repellent (SR) finish.

Methyl Parathion (0,0-dimethyl 0-p nitrophenyl phosphorothioate [LD_{50} (mg/kg) oral=14, dermal=67]) (MeP) dilutions were prepared at 1.25% active ingredient (AI) field strength concentration from emulsifiable concentrate formulation (EC), wettable powder (WP), and encapsulated formulations (ENC). Solutions were held in suspension during the contamination process by placing them on a magnetic stirrer. Two-tenths ml were pipetted onto the center of the specimen using a MicroLab P programmable micropipette. Contaminated specimens were allowed to air dry. Specimens were laundered or were evaluated unlaundered. A 0.2 ml aliquot of the 1.25% AI MeP was placed in glass for each replication for each formulation, allowed to air dry, and prepared in acetone as a baseline for determining recovery rate.

For the first phase, eight by eight cm specimens of UN, DP and SR finished fabrics were contaminated with EC or ENC formulations of MeP. Contaminated specimens were Launder-Ometer laundered at 60°C (140°F) wash and 49°C (120°F) rinse or at 49°F (120°F) wash and rinse with one of two detergent formulations [heavy duty liquid nonionic detergent (HDL) at 0.13% or AATCC Standard Detergent 124 at 0.2%].

For the second experiment, EC, ENC, or WP formulations of MeP at 1.25% AI were pipetted (0.2 ml) into the center of one square meter fabric specimen. Contaminated specimens were placed on a nylon surface one meter square during contamination and allowed to air dry.

The contaminated specimens were laundered in an automatic home washing machine for a 12 minute wash, a spray rinse cycle (3 min) and a deep rinse cycle (5 min). Laundering was done in a full (12 gal) water volume at 49°C with 34 ml (1/4 cup) heavy duty liquid nonionic detergent. This detergent and water temperature combination had been shown to be effective in MeP removal under laboratory conditions (Laughlin et al. 1985). Since there was concern about contamination of the washing equipment, and transference to fabrics, the washing machine was cleaned by operating through 5 complete washing cycles at 49°C with 12% phosphate detergent. In the fifth decontamination cycle, an 80 x 80 cotton "check" fabric was included to determine if MeP residues were present that might affect subsequent results. MeP in the range of 0.001 $\mu g/cm^2$ were found under each condition.

Sampling from each specimen of the one meter square of fabric was done from the center, the original site of contamination, and from nine concentric rings. Since movement of moisture-carried soil follows warp and filling yarns, the 1.91 cm dots of fabric were punched out in mobius strips, such that each sampling was off-set from the previous sampling of the adjacent ring by 15°. Thus, the center "ring" was comprised of one 1.91 cm die cut specimen, the first concentric ring included four 1.91 cm die-cut specimens and the second through tenth concentric rings included eight 1.91 cm die cut specimens. (See Figure 1).

A template with scribed concentric rings on mobius strips was used to insure that sampling occurred in similar ways across replications. A cork borer and mallet were used to die-cut specimens. Specimens were individually extracted in 100 ml reagent-grade acetone on a mechanical shaker for 1.5 hour at 120 rpm. Extract was decanted and replaced by an additional 100 ml acetone for a second shaking. At the end of the 3 hour shaking time, the fabric specimen was removed, discarded and the two extracts combined. Recovery rates were 97.1+% of the AI pipetted onto the specimen, and recovery rate was used to calculate residues.

The extracts were concentrated with a rotary evaporator and nitrogen stream evaporator. One μl aliquots were analyzed with a Varian Vista 6000 gas chromatograph with 4270 data system using an electron capture detector using an external standard (99.7% MeP). Separation was achieved on a 2m x 2mm glass column packed with 10% OV-101 on 80/100 mesh Chromasorb W-HP with a nitrogen flow of 30 ml/min. Injection, detector, and oven temperature respectively were 250°C, 270°C, and 220°C.

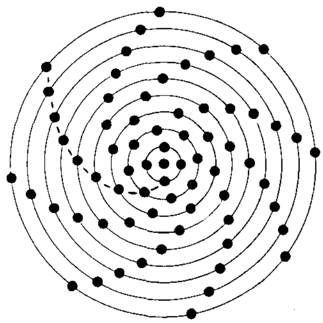

Figure 1. Sampling diagram.

Baseline contaminations of pre-laundered specimens were used to calculate percent residue remaining after laundering. Statistical differences among the finishes, the sampling site, and/or the unlaundered/laundered specimens were calculated using a General Linear Model Analysis with an indication of significance at the $p \leq 0.05$ level. Separation of means was achieved with Least Significant Means.

RESULTS AND DISCUSSION

Contamination before laundering was significantly lower for the SR finished fabric than for the UN fabric or DP finished fabric (F=4.875; df=2,18; $P \leq 0.05$). Contamination of UN and DP specimens was 5 times that of the SR specimen. The SR finish effectively limited pesticide absorption (Table 1).

Laundering significantly reduced MeP levels in specimens. It is important to note that initial contamination of the SR specimen was approximately 20% that of the UN and DP specimens. The fluorocarbon polymer had rendered the fabric more hydrophobic, thus more soil repellent, but also more repellent to the water-plus-surfactant cleaning solutions.

No significant differences were found between detergent type (F=0.248, df=1,83) or washing temperatures (F=0.091, df=1,83), although the removal was slightly greater at the higher temperature (Table 2). Residues after laundering were markedly lower when ENC formulation had been used to contaminate the fabric than when EC was the formulation (F=59.13, df=1,83). These findings are similar to findings of previous studies (Easley et al. 1982).

Laundering variables of temperature and detergent type were not important in differences in pesticide residue after laundering. Differences in MeP residues after laundering were due to formulation of pesticide, with encapsulated formulations more completely removed in laundering (0.25 μg/cm) than the emusifiable concentration formulation (12.36 μg/cm).

Table 1. Levels of initial contamination and after-laundering residues in specimens.

Treatment	Initial Contamination µg/cm	After-Laundering Residue µg/cm	µg/cm
UN	39.08[a]	1.38[c]	3.53[d]
DP	41.13[a]	1.75[c]	4.25[d]
SR	16.36[b]	3.08[d]	18.83[e]

Means with the same letter are not statistically different from each other ($p \leq 0.05$).

Table 2. After-laundering residues of methyl parathion in specimens (Phase I).

Treatment	UN µg/cm	DP µg/cm	SR µg/cm
EC			
49°C			
HDL	1.66	5.72	8.15
PHOS	7.18	5.21	3.38
60°C			
HDL	0.47	1.13	1.17
PHOS	0.76	1.57	1.64
ENC			
49°C			
HDL	0.12	0.13	0.10
PHOS	0.52	0.30	0.06
60°C			
HDL	0.12	0.16	0.04
PHOS	0.23	0.16	0.12

A factorial experiment for assessing the movement of pesticide soil through a large specimen of fabric upon soiling and during laundering was designed with four factors: fabric finishes (three); pesticide formulations (three); sampling ring (ten); and laundered/unlaundered (two). EC, ENC and WP formulations of MeP at 1.25% AI were pipetted (0.2 ml) onto the center of one square meter fabric specimen. After drying, contaminated specimens were laundered or left unlaundered.

Across all variables under study, significant differences in MeP contamination in fabrics were attributable to sampling ring, to fabric finish, and to laundering, with an observed interaction between finish and laundering. To ascertain the impact of laundering, data were further analyzed controlling for laundering.

Significant differences in pesticide contamination attributable to fabric finish of specimens were observed, with greatest amount found in the unfinished fabric (UN) (Table 3), followed by the durable press (DP) finished fabric, and then by soil release (SR) finished fabrics. These findings are consistent with earlier work (Laughlin et al. 1985); since DP and SR finishes increase hydrophobicity, the pesticide soil may have moved to other sites along the yarns rather than being held in the capillary spaces between fibers and within the convolutions and lumen of the cotton fibers for these two functionally finished fabric specimens.

Table 3. Effect of fabric finish on removal and redeposition of methyl parathion during laundering.

Sampling Ring Position	Methyl parathion on the specimen (µg/cm^2)					
	Unfinished Fabric		Durable-Press Finish		Soil-Resistant Finish	
	Before Laundry	After Laundry	Before Laundry	After Laundry	Before Laundry	After Laundry
Center	1702.2	9.21	1214.8	20.93	1083.3	13.71
1	174.8	0.34	51.1	0.58	6.7	0.08
2	0.01	0.04	0.1	0.03	0.1	0.01
3	0.00	0.04	0.0	0.02	0.1	0.04
4	0.00	0.03	0.0	0.02	0.0	0.01
5	0.00	0.02	0.0	0.02	0.0	0.01
6	0.00	0.02	0.0	0.02	0.0	0.01
7	0.00	0.01	0.0	0.02	0.0	0.01
8	0.00	0.04	0.0	0.02	0.0	0.01
9	0.00	0.02	0.0	0.01	0.0	0.01

See Figure 1 for sampling-ring diagram.

Significant differences in contamination were due to sampling ring. Levels of pesticide were greatest at the initial site of contamination and in the first concentric ring, a distance of approximately 2 cm from the site of initial contamination. Only trace amounts were found in subsequent rings, and, although above minimum level of detectability (0.1 ppm), should be considered background noise. No interaction of finish and ring was observed.

The greatest amount of after-laundering pesticide soil was located at the initial site of soiling; but there was generalized soiling throughout the fabric. Fabric finish did not cause significant differences in contamination after laundering. These findings are consistent with Phase I of this study. It is important to note that initial contamination of the SR specimen was less than half that of the

UN and DP specimens. Since there was an interaction effect of fabric finish with sampling ring, partitioning was done to elucidate the interaction ($F=14.99$, $df=2,9$, $p \leq 0.05$). Less soil removal was noted at the original soil site for DP and SR finish, as would be anticipated. Pesticide removal is a greater problem on DP and SR finished fabrics, although generalized residues after laundering are in the same range as those residues found in UN fabrics.

Although the variable, sampling ring produced significant differences, with the greatest residues found at the initial site of contamination, and in the first concentric ring, the contamination was an extremely small proportion of the initial contamination. Approximately 99% of the pesticide soil had been removed from the initial site of contamination, and approximately 96% of pesticide soil had been removed from the area immediately adjacent to the site of contamination. Rings 2 through 9 were significantly different from the center and ring 1, and contained small, but measurable amounts of MeP. During laundering, the water/detergent acted as a solvent moving the soil from the fabrics; but also aided in generalized redeposition of the pesticide soil throughout the fabric. When heavily contaminated material was laundered, an equilibrium was approached throughout the whole area of the fabric due to soil redesposition. MeP in those amounts ($\mu g/cm^2$) are not biologically active to German cockroaches [Biotype: Orlando Normal] (Laughlin et al. 1981). The fluorocarbon polymer reduced the surface activity of the fabric, thus making the fabric more soil resistant; but, the finish promoted soil redeposition in laundering and residue removal was a smaller percentage of contamination. Additional work is needed to assess the difficulty in dislodging pesticide residues from DP and SR finished fabrics through study of laundering treatments that optimize pesticide soil removal.

The SR finish afforded protection by limiting sorption of MeP into the specimen. The MeP found on the contaminated, unlaundered SR fabric was less than half that found on unlaundered unfinished fabric. Residues of MeP after laundering were higher (though not significantly) in DP and SR fabrics. Previous work has led to recommendations to use a soil repellent fabric finish, and to avoid durable press finished fabrics. Additional research is needed to confirm whether DP and SR finishes have a retentiveness for pesticides, and to ascertain ways to minimize residue redeposition and to optimize residue removal in laundering.

Generally, very limited distribution over an area greater than five cm from the site of contamination was observed; however generalized redeposition of pesticide soil during laundering was observed. Based on these findings, recommendations are made to vigorously treat the site of soiling before and in laundering. Keaschall et al. (1986) have shown the effectiveness of a laundry pre-treatment for pesticide soils. Redeposited pesticide residue in minute amounts is extremely difficult to remove from most fabrics. Earlier work has shown fabrics soiled with pesticides require a full measure of detergent in full volume of water to maximize removal. Results of this study confirm the importance of laundering daily, in home laundering conditions and cleaning the equipment after each use.

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