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Laundry Factors Influencing Methyl Parathion Removal from Contaminated Denim Fabric*

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Some pesticide residues are readily absorbed into the body through the skin (WOLFE et al. 1967), yet different parts of the body absorb various pesticides at unequal rates (BAKER and BRADSHAW 1979; BRANSON and HENRY 1981). Curtailing dermal exposure has led to wide spread recommendations for protective clothing. As a result, two different approaches to protective clothing systems have recently been taken. One recommendation includes covering exposed body surfaces with worker apparel (i.e., wearing long-sleeved shirts and full-length trousers), while the other proposes wearing non-moisture absorbant coverings over regular clothing. However, professional pesticide applicators indicated the discomfort associated with supplemental coverings outweighed the protection offered (TWETEN 1982).

An Occupational Safety and Health Administration (OSHA) Standard 1910.267a has stated that protective clothing consist of a "washable fabric," however, recommendations for laundering such fabric are not included in the standard. Laundering pesticide contaminated clothing therefore remains a problem for the pesticide user. Efforts to reduce dermal exposure and reduce pesticide residue levels in contaminated clothing items through effective laundering procedures continue to demand attention. This paper presents a series of studies which address the decontamination of clothing through laundry. The variables studied included: 1) pesticide concentration levels; 2) effects of multiple launderings and 3) household sudsy ammonia pre-soak concentrations.

MATERIALS AND METHODS

A 100% cotton 2/1 twill denim was purchased from a local retail outlet (weight=321.4 g/m^2; thread count=69 x 42ypi).

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The fabric was stripped of manufacturer-applied warp sizing and softeners through a series of five washings, using the AATCC 135-1978 laundry procedures. Following pre-conditioning, the fabric was cut into 8 x 8 cm swatches for contamination.

Chemical

Methyl parathion [0,0-dimethyl O-p-nitrophenyl phosphorothioate (MeP)] pesticide solutions used in this study were made up from 54% active ingredient (a.i.) emulsifiable concentrate (EC) formulation. The selected MeP EC was manufactured by the Chevron Chemical Company. Specific concentrations are delineated in the description of each experiment.

Contamination of Fabric

Denim fabric swatches were contaminated by pipetting one ml of MeP solution onto the fabric. During the contamination process, a magnetic stirrer provided uniform agitation of the solution. Swatches were suspended from a drying rack while the solution was pipetted, and remained suspended to air dry.

Laundry Process

Fabric swatches were individually laundered in stainless steel canisters of an Atlas Launder-Ometer (model B5), using a modified AATCC test method 61-1980 (AATCC 1981). A heavy duty liquid detergent (Dynamo®) was used in these studies, as previous work by EASLEY et al. (1982) had shown this detergent type to excel in MeP EC removal at 49°C (warm) and 60°C (hot) water temperatures. Manufacturer recommendations of a 0.13% detergent wash solution was prepared on a volume of 150 ml distilled water per fabric swatch. The laundering included a 12 minute wash cycle and five- and three-minute rinse cycles. After air drying, the fabric swatches were held in glass bottles for solvent extraction.

Extraction Process

Contaminated unlaundered swatches (controls) and laundered swatches were extracted with two 150 ml aliquots of reagent grade acetone. Mechanical shaking for three hours at 120 rpm on a Precision Scientific® Shaker Bath (model 50) facilitated extraction. Extracts were held at 5°C until chromatographic analysis.

Gas Chromatograph Process

The extracts were concentrated with N_2 stream evaporation or acetone diluted, so that samples contained between 0.02 and 15 ng/µl MeP. A one ml aliquot of the adjusted extract was mixed with 9 ml of toluene and an internal standard of ethyl parathion (0.378 or 0378 ng/µl).

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[1]Tradenames use does not represent product endorsement.

One µl aliquots were analyzed with a Varian 3700 gas chromatograph with a CDS 111C data system using an electron capture detector. Separation was achieved on a 2 m x 2 mm glass column packed with 1.5% OV-17 and 1.95% OV-210 on 80/100 mesh chromasorb WHP. Injection, detector and oven temperature were 220 °C, 270°C, and 190°C respectively. Nitrogen flow was 30 ml/min.

Statistical Analysis

Differences in the amounts of MeP ($\mu g/cm^2$) between the control and laundered swatches were expressed in percentages of insecticide removed. Statistical differences were tested with ANOVA with indication of significance at the $p < 0.05$ level. All work was replicated three times.

I. Pesticide Concentration Levels

Pesticide-applicator clothing is most likely to become contaminated by full-strength concentrates and dilute pesticide solutions during mixing, handling, and application of chemicals. The effect that different pesticide concentrations have on the ease or difficulty of removing such residues from clothing by laundering has received limited study (LILLIE et al. 1981).

The purpose of this experiment was to determine the completeness of residue removal during laundering when a range of concentration levels had been used to contaminate denim fabric. Five concentrations of MeP EC were prepared as contaminants: 0.25%, 0.5%, 1%, 2%, and 54% (undiluted). Fabric swatches were laundered through one cycle which included a 60°C (hot) wash and two 49°C (warm) rinses. All procedures were performed as previously descibed.

Results and Discussion

As anticipated, a linear relationship was found between the initial MeP concentrations and the amounts of residue remaining following laundry (Table 1). The doubling of concentrations (i.e. 0.25% to 0.5%, 0.5% to 1%, and 1% to 2%) generally caused decreasing rates of removal.

TABLE 1
IMPACT OF LAUNDERING ON REMOVING VARIED CONCENTRATIONS OF MeP EC FROM CONTAMINATED DENIM FABRIC

MeP Concentration	ng/cm^2 Remaining*	% Removed
0.25%	1.43 ± .48	95.6
0.50%	2.84 ± .46	95.8
1.0%	10.90 ± 2.09	91.7
2.0%	65.64 ± 6.48	74.7
54.0%	5025.00 ± 1179.35	19.5

*ng/cm^2 remaining after a single laundry cycle.

These findings emphasize the difficulty in removing MeP residues from fabric as the concentration level increases. While lower-level concentrations were more readily removed, the full strength or undiluted concentration was particularly difficult to remove. The actuality that less than 20% of the concentrated pesticide was removed by one laundry cycle indicates that pesticide applicators need to use extreme caution when working with full-strength chemicals.

II. Multiple Launderings

One laundry cycle does not totally remove pesticide residues from contaminated fabrics (EASLEY et al. 1982, 1981; FINLEY et al. 1979, 1977, 1974; KIM et al. 1982; LILLIE et al. 1981), and remaining residues may be biologically active (EASLEY et al. 1982; LAUGHLIN et al. 1981; METCALFE 1972). Two questions then arise: 1) How many washings are needed to thoroughly remove residues from contaminated fabrics? 2) At what point are laundered contaminated fabrics decontaminated and/or are they no longer biologically toxic? This phase of the study addressed these aspects.

Fabric swatches were contaminated with 1.25% a.i. (field strength) or 54% a.i. (undiluted) MeP EC. Contaminated swatches were individually laundered one through ten complete laundry cycles. A 49°C (warm) wash and rinse water temperature were used as this combination is most frequently selected by consumers (LOVEDAY 1979). Other procedures were as earlier described.

Biological activity of the laundered contaminated denim fabrics was measured via bioassays with Blattella germanica (L.); (German cockroaches) biotype: Orlando normal. Procedures coincided with those reported by LAUGHLIN et al. (1981) and EASLEY et al. (1982).

Results and Discussion

Distinct differences can be noted between the two concentration levels used in this experiment (Table 2). Although the amount of MeP removed generally increased over ten launderings, the dissimilarity between 1.25% a.i. and 54% a.i. concentrations emphasized the difficulty in residue removal with increased pesticide concentration.

The 1.25% concentrate was more completely removed during laundering. Significant differences ($p \leq .05$) were found between subsequent wash cycles up to, and including, the third laundry cycle. After the third cycle, the amount of MeP removed was consistently in excess of 99%. But the undiluted 54% concentate was almost impossible to remove due to retention of MeP in the fabric. Even after ten cycles, only 66.7% of the full-strength (54% a.i.) MeP residue had been removed, and the detected residue on the fabric was $2{,}435 \pm 406.8$ g/cm^2. MeP residues in this range on laundered fabric have been reported as contributing to the death of an adult man (SOUTHWICK et al. 1974).

TABLE 2
EFFECTS OF MULTIPLE LAUNDERINGS ON REMOVAL OF MeP EC FROM CONTAMINATED DENIM FABRIC

Laundry Cycle	1.25%		54%	
	ng/cm_2	% Removed	ng/cm_2	% Removed
1	29.26 ± 7.31	81.69*	6153 ± 1029.8	15.79*
2	6.36 ± 3.48	96.02*	4780 ± 336.8	34.58*
3	0.93 ± 0.23	99.42*	4355 ± 483.2	40.40*
4	0.56 ± 0.11	99.65	3746 ± 244.0	48.73*
5	0.47 ± 0.04	99.70	3634 ± 216.4	50.27*
6	0.48 ± 0.04	99.70	3326 ± 434.5	54.48*
7	0.43 ± 0.14	99.73	3617 ± 933.1	50.50*
8	0.40 ± 0.12	99.75	2789 ± 344.7	61.83*
9	0.44 ± 0.08	99.73	2608 ± 442.6	64.31*
10	0.59 ± 0.28	99.63	2435 ± 406.8	66.68*

*Bioassays with Blattella germanica (L.); (German cockroaches) biotype: Orlano normal were performed on these fabrics and were found to be toxic within 24 hours.

Bioassays performed on the 54% a.i. contaminated unlaundered controls and fabric laundered through ten laundry cycles caused 100% mortality to test German cockroaches within 24 hours. The 1.25% MeP contaminated laundered fabrics, however, were found to be biologically inactive after the third washing. From these results, discarding clothing contaminated with highly concentrated pesticides would be a well-advised recommendation; for clothing contaminated with lesser concentrations, a minimum of three launderings may be suggested.

III. Household Ammonia Pre-Soak

The use of laundry additives as an contributing factor in pesticide residue removal needs to be more completely studied. EASLEY et al. (1981) investigated the effects of sudsy household ammonia (NH_3) and bleach (NaOCl) as laundry additives and found that, at a ratio of 250 ml NH_3 or NaOCl: 45 l water, the presence of either additive diminished residue removal. This ratio results in an extremely weak ammonia-water solution and it was believed that stronger solutions such as those used by pesticide handlers to clean application equipment, may have practical application in laundry situations.

Fabric swatches were contaminated with a 1.25% MeP EC and then pre-soaked in one the following four NH_3 concentrations prior to laundering: 1) full-strength sudsy household NH_3; 2) 1 (NH_3)/4(H_2O); 3) 1 (NH_3)/32 (H_2O); 4) 1 (NH_3)/256 (H_2O)--equivalent to 250 ml (1 cup) NH_3 per 45 l (12 gal) wash load. Two pre-soaking procedures were used for each concentration

level: A) fabric swatches were pre-soaked in the NH_3 solution for seven minutes in Launder-Ometer canisters. They were then removed and placed in a clean laundering canister with 150 ml detergent solution: B) swatches were NH_3 pre-soaked for seven minutes in Launder-Ometer canisters, after which detergent was added to the same canister, i.e., pre-soaking and laundering occurred in the same canister with no replacement of liquid solution. Temperature remained constant at 49°C (120°F) throughout the laundry process for the pre-soak and rinse cycles.

Results and Discussion

Ammonia pre-soak removed 80% to 96% of the MeP (Table 3). No significant differences were found between the two pre-soak

TABLE 3
INFLUENCE OF VARIED AMMONIA (NH_3) PRE-SOAK CONCENTRATIONS ON THE REMOVAL OF MeP EC FROM CONTAMINATED DENIM FABRIC

NH_3: H_2 Concentrations	A		B	
	ng/cm^2	% Removed	ng/cm^2	% Removed
1:0	16.99 ± 16.34	89.81	6.33 ± 2.35	96.20
1:4	20.85 ± 10.34	87.20	13.38 ± 2.44	91.66
1:32	29.36 ± 12.48	81.80	25.34 ± 7.93	84.29
1:256	31.13 ± 9.04	80.23	29.46 ± 3.81	81.30

procedures although procedure "B," in which pre-soak and laundry occurred in the same canister, resulted in slightly higher removal. Based on these findings recommendations might be made to pre-rinse contaminated pesticide applicator clothing in sudsy household ammonia; however this procedure would necessitate, at minimum, four gallons of ammonia per wash load. Thus, the benefit of this method hardly seems justified when one considers that other laundering procedures are equally effective.

An earlier study by EASLEY et al. (1981), in which similar variables were investigated (1.25% MeP EC concentration, 0.4% NH_3 concentration, 100% cotton fabric), found that a warm water pre-rinse followed by a complete laundry cycle removed approximately 88% MeP. NH_3 when used as a laundry additive in the wash cycle, removed an average of 82% MeP and actually inhibited the effectiveness of detergent. Since these amounts fall within the range of that removed by an NH_3 pre-soak at all four concentration levels, the overall effectiveness of an NH_3

laundry additive must be questioned; pre-rinsing in water appears to be as effective as an NH_3 pre-soak.

CONCLUSIONS

The level of MeP concentration is inversely related to the amount of residue removed through laundry. As a result, higher pesticide concentrations or undiluted chemicals require utmost care in handling. Even following ten multiple launderings, residues of an undiluted MeP contaminant can be readily detected in fabrics, as well as cause mortality to German cockroaches within 24 h. It is recommended therefore, that clothing contaminated with high pesticide concentrations be disposed of by burning or burial, as the fabric remains unsafe to the wearer. Fabrics contaminated with lesser MeP concentrations (i.e. field strength) require a minimum of three launderings before biological activity reaches a harmless level. In addition, sudsy household ammonia as a laundry additive does not practically contribute to pesticide residue removal as the cost and amount of ammonia required to fill a washing machine is not feasible. Other laundry procedures, such as pre-rinsing and/or multiple washing, appear to be more effective.

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