

## Detergents and Water Temperature as Factors in Methyl Parathion Removal from Denim Fabrics<sup>1</sup>

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Clothing worn by pesticide workers is subject to contamination during mixing and loading operations, application, disposal, clean-up, and storage. Recent investigations have demonstrated that once contaminated, textiles are difficult to decontaminate through common home laundering practices (EASLEY et al. 1981, FINLEY et al. 1977, 1979). Determining effective laundering procedures for clothing decontamination has become imperative for those who work with pesticides, including commercial applicators and home gardeners.

Interdepartmental research at the University of Nebraska has studied the effectiveness of laundering procedures in removing pesticides from contaminated fabrics. Contributions have been made toward understanding the extent to which pesticides can contaminate clothing, and the removal of such contamination by laundry procedures.

Recent work by EASLEY et al. (1981) indicated varying success in the removal of methyl parathion (MeP) from fabrics in laundry. MeP emulsifiable concentrate was more difficult to remove from cotton and cotton/polyester denim fabrics than were encapsulated or wettable powder formulations. Fiber content was not a contributing factor in removal of the MeP regardless of formulation. Of the laundry procedures investigated, more complete removal was found for a pre-rinse followed by a wash and two rinses. The use of ammonia or bleach as laundry additives caused no appreciable changes in amount of MeP removed. Additionally, LAUGHLIN et al. (1981) discovered the washing equipment was susceptible to MeP retention, with possible transference to subsequent laundry.

Commercial detergents available on today's market include three classifications: phosphate, carbonate, and heavy duty liquid detergents. Initial pesticide laundry studies at Nebraska have used the high phosphate American Association of Textile Chemists and Colorists (AATCC) Standard Detergent 124. However, such high phosphate detergents are not generally available, and the use of these detergents is restricted in certain areas of the United States. FINLEY et al. (1977) used a heavy duty carbonate detergent for laundering MeP contaminated clothing. Heavy duty liquid detergents, which are increasing in popularity, merit investigation in pesticide removal in laundry. These detergents are specifically noted for oily soil removal from synthetic fabrics.

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In general, pesticide studies have used hot water temperatures; however, there are several reasons to investigate lowered temperature ranges. In profiling the practices of the Nebraska textile consumer in a Standard Metropolitan Statistical Area, LOVEDAY (1979) found a warm wash/warm rinse combination to be the most frequently used appliance setting for general washing procedures. The second most commonly used appliance setting was a warm wash/cold rinse temperature combination. Although hot water laundering was once a common family practice, current concern for energy conservation has caused reduction in temperatures of hot water heaters. Appliance manufacturers have also eliminated options for rinse water temperatures, creating a mandatory cold water rinse. In addition, synthetic fabrics now constitute a measurable portion of the family laundry. These fibers are heat sensitive and it is recommended they be laundered at lowered temperatures.

The purpose of this study was to determine whether commercially available detergents were efficacious in pesticide removal when used in washing procedures of different water temperatures. Emphasis was also given to the relationship between fiber content and pesticide retention. The important and unique contribution of this study was the close duplication of in-home laundry procedures, with commercially available detergents and common laundering temperatures.

## MATERIALS AND METHODS

The materials and methods in this study were similar to those used by EASLEY et al. (1981) and LAUGHLIN et al. (1981).

### Fabrics

Two denim fabrics of 100% cotton and 50/50 cotton-polyester were used. A catalogue survey showed these fiber contents to be common in men's work clothing. Both fabrics were a 2/1 left-hand twill weave. The cotton and cotton-polyester fabrics had a thread count of 69 x 42 and 65 x 47, respectively. Average weight of both fabrics was 321.4 g/m<sup>2</sup>.

### Chemical

An emulsifiable concentrate formulation of methyl parathion (Ortho\* Methyl Parathion 5 Emulsive, 54.0% a.i.; manufactured by Chevron Chemical Company) (MeP) was used to contaminate the fabrics. The active ingredient (a.i.) present in the formulation was analyzed using procedures outlined by the Association of Official and Analytical Chemists (1980). Based on this analysis a 1.25% concentration, a solution commonly used in agricultural applications, was prepared.

### Fabric Contamination

Fabric swatches (8 x 16 cm) were immersed in 1.25% MeP concentration and placed on a magnetic stirrer to provide uniform agitation during the contamination process. The swatches were stirred until saturated, removed and air dried. Swatches were

then cut into two 8 x 8 cm squares for paired comparisons, with one half a laundered sample and the other half a compared control.

#### Laundering Procedures

Contaminated swatches were laboratory laundered in a 60°C (hot) wash/49°C (warm) rinse; 49°C (warm) wash/49°C (warm) rinse; or 30°C (cold) wash/30°C (cold) rinse water temperature using one of four laundry detergents. Three commercially available detergents were selected to represent principal detergent categories: phosphate<sup>1</sup>, carbonate<sup>2</sup>, and heavy duty liquid<sup>3</sup>. The fourth detergent used in this study was AATCC Standard Detergent 124, a 12% phosphate detergent used for textile research.

A modified AATCC test method 61-1975 (AATCC, 1979) was used for laundering procedures. Wash and rinse solutions were prepared on a volume of 150 ml distilled water per swatch, with volumes proportionally calculated from a 45 liter wash load. The powdered detergents were added at 0.3 g/150 ml, while the heavy duty liquid used was 0.4 ml/150 ml. An Atlas Launder Ometer (model B5) duplicated home laundering procedures for a 12 minute wash and two rinse cycles of five and three minutes, respectively. Following completion of the laundry process, fabric swatches were air dried and retained in glass bottles for extraction procedures.

#### Extraction Procedures

The MeP contaminated unlaundered swatches (controls) and laundered swatches were extracted in 150 ml glass-distilled acetone which was added to each bottle containing a swatch. The bottle was mechanically shaken for one hour, whereupon the acetone extract was decanted and replaced by an additional 150 ml acetone for a second hour of shaking. The fabric swatch was removed at the end of the two hour period, and the two extracts combined.

#### Gas Chromatographic Procedures

A solution of acetone extract and toluene was prepared from each sample to facilitate gas chromatographic analysis. Extracts were analyzed using a Hewlett-Packard gas chromatograph (model 5840A) with a nitrogen-phosphorus thermionic detector. Replicated injections were made from each sample. Standard solutions of 99% pure technical grade MeP were injected after every fourth sample for calibration. The amount of MeP extracted from the unlaundered and laundered swatches was expressed in nanograms (ng)/cm<sup>2</sup>.

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<sup>1</sup>Cheer\*--8.7% phosphate level; manufactured by Proctor & Gamble Co.

<sup>2</sup>Purex\*--carbonate; manufactured by Purex Corporation.

<sup>3</sup>Solo\*--nonionic heavy duty liquid, containing no phosphate; manufactured by Proctor & Gamble Co.

The use of tradenames was for the sole purpose of designating a product and does not signify endorsement over comparable brands.

## Biological Assay

Biological assays with Blattella germanica (L); (German cockroaches) biotype: Orlando normal were performed to assess biological activity. Trials were conducted in environmental chambers at 30°C and 10-20% R.H. Ten adult males were placed on each of the treated fabrics, dorsum up. The cockroach mortality was recorded after 24 and 48 hours.

## Statistical Analysis

The differences in the amounts of MeP ( $\text{ng/cm}^2$ ) between the control and the laundered swatch were expressed in percentages of MeP removed, and then subjected to arc sin transformations to counter heterogeneity of variance. Analysis of variance (ANOVA) and Duncan's multiple range test comparing these percentages were computed, with  $p < 0.05$  as indication of significance.

## RESULTS

### Initial MeP Contamination of Fabric Swatches

Based on gas chromatographic analysis and statistical testing, there were no significant differences between the amount of MeP initially contaminating the paired halves (Mean = 0.243,  $\pm 0.066 \text{ ng/cm}^2$ ) of the originally saturated swatches (8 x 16 cm). Therefore, this was a strong indication that the contamination technique utilized in this study was valid.

A comparison between cotton and cotton-polyester of the MeP retained by the swatches indicated there were no significant differences through four replications ( $F=0.143$ ; d.f.=1.78;  $p=0.7076$ ). This is in agreement with findings of EASLEY et al. (1981) that cotton and cotton-polyester initially retained like amounts of MeP.

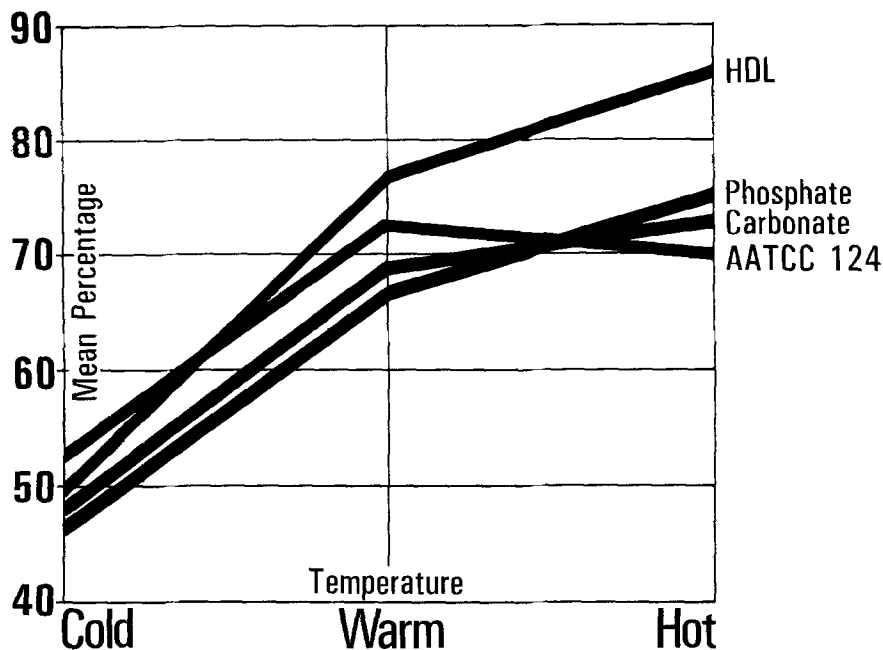
### Effects of Laundry

The mean range of removal of emulsifiable concentrate MeP (1.25%) under the laboratory laundering procedures of one wash and two rinses was 48.5% to 85.1%. Variables of interest in this study were fiber content of fabric, detergent type, and water temperature.

Fiber Content. Fiber content of the contaminated fabric was not a contributing factor in the ease of MeP removal ( $F=0.3719$ ; d.f.=1,74;  $p=0.5509$ ). It was concluded there was no statistical difference between cotton and cotton-polyester in the completeness of removal of MeP contamination, independent of detergents or water temperatures investigated.

Detergents. The four detergents were similar in MeP removal ( $F=0.5919$ ; d.f.=3,72;  $p=0.6263$ ). The AATCC 124 detergent removed 52.7% MeP in 30°C water, 73.4% in 49°C water, with a slight removal decrease noted in 60°C water laundering. The commercially purchased phosphate detergent removed 48.5% to 75.7%. Carbonate detergent encompassed a removal of 48.9% to 72.1%, while the heavy duty liquid (HDL) stretched from 49.9% to 85.1%. Although statistical homogeneity was found

among the four detergents, a definite trend in detergent effectiveness was observed in that the HDL removed higher percentages of MeP at both 49°C and 60°C than did the other detergents tested (Figure 1).



**Figure 1. Water Temperature/Detergent Mean % MeP Removed**

Since emulsifiable concentrate formulations are oil-based and HDL detergents are noted for oil-removing ability, this formulation-detergent combination may have provided for more complete removal.

In an alkaline medium, MeP is hydrolyzed to 4-nitrophenol. It had been theorized that higher detergent alkalinity would produce more pesticide removal during laundry (EASLEY et al. 1981, FINLEY et al. 1974). In this laboratory investigation this was not the case. The pH readings of the detergent solutions varied from 6.4 for HDL detergent to 10.1 for carbonate detergent. Examination of detergents' effectiveness in removing MeP raised question about the alkalinity theory.

Water Temperatures. There was significant evidence of heterogeneity between amounts of MeP removed attributable to water temperature. Mean amounts of MeP removed, inclusive of all four detergents and two fabrics ranged from 76% in 60°C water laundering to 49% in 30°C water washing. 49°C water removed in average of 71% MeP. Statistical contrasts of the data by wash temperature revealed no significant difference between 60°C and

49°C water washing, while 30°C water laundering produced significantly lower removal ( $p < 0.05$ ). This supported, in part, a recent U.S. Air Force study (1980) which noted a tendency for increased residue removal with increased water temperature for diazinon, propoxur, bromacil, and malathion; however, they did not investigate MeP.

### Biological Assays

Bioassays revealed that MeP residues on laundered contaminated denim fabrics were toxic to 100% of the German cockroaches confined on these fabrics. Regardless of water temperature or detergent used all cockroaches died within 24 hours, indicating the fabrics were biologically active and toxic after laundering.

### CONCLUSIONS

Based on the results of this investigation, contaminated denim fabrics should not be laundered in 30°C (85°F) temperature; hotter temperatures are more effective. Although detergents could not be statistically separated, heavy duty liquid detergents appeared to excel in providing higher levels of pesticide removal in water temperatures of 49°C and 60°C. To determine the optimal conditions for pesticide removal by laundering, additional investigations need to be made into the relationships between detergent, pesticide formulation, water temperature, and effects of multiple washings.

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