Bull. Environm. Contam. Toxicol. 27, 101-108 (1981)

Methyl Parathion Removal from Denim Fabrics by Selected Laundry Procedures

C. B. Easley[1], J. M. Laughlin[1], R. E. Gold[2], D. R. Tupy[3]

[1]*Department of Textiles, Clothing and Design,* [2]*Department of Entomology,* [3]*Department of Agronomy, University of Nebraska, Lincoln, NB 68583*

Safety is essential for persons working with pesticides because of the potential of health-endangering exposure. Reduction in pesticide-related accidents among these individuals requires knowledge of pesticide use, toxicology, and proper pesticide handling. WOLFE et al. (1967) established that the principal route of pesticide absorption into the body among agricultural workers was through the skin and not the respiratory system.

Studies investigating potential effects of pesticide-contaminated clothing are limited. FINLEY & ROGILLIO (1969) reported that clothing worn by agricultural workers became contaminated with methyl parathion (MeP) insecticide following cotton field spraying. Laundering of contaminated fabrics with uncontaminated fabrics resulted in a transference of insecticide residue. Bioassays with Drosophila melanagaster Meigen (fruit flies) of the "transfer" fabrics have shown these fabrics to contain enough residue to be biologically active and toxic (METCALFE (1972), FINLEY et al. (1974)). Recommendations were made that contaminated clothing not be washed with regular family laundry since the possibility exists for pesticide transference to uncontaminated clothing. One hot water washing was 75% to 95% effective in removing MeP residue from fabric (FINLEY et al. 1979). There exists a point of conflict in Finley's studies (1969, 1974, 1977, 1979) concerning whether cotton or cotton-polyester fabric is "safer" to wear; the results of these studies to determine relative protection afforded by cotton and cotton-polyester fabrics are not definitive.

News releases from the Cooperative Extension Service recommended the use of ammonia or chlorine bleach as a laundry additive for laundering heavily-contaminated clothing. Although commercial pesticide applicators use an ammonia-water solution to decontaminate spray equipment, the efficacy of ammonia or bleach in removing insecticide contamination from clothing had not been determined.

Previous pesticide/launderability studies had worked only with technical grade material or emulsifiable concentrate formulation. Since agricultural workers use a variety of pesticide formulations, there existed the need to investigate common

0007-4861/81/0027-0101 $01.40

formulations for the effectiveness of various laundry procedures in their removal. The purpose of the present research was to determine the effects of fiber composition, MeP formulations, and selected laundry procedures on removing MeP residues from contaminated fabrics.

METHODS AND MATERIALS

Chemicals

Three formulations of MeP were used to contaminate the fabrics: 1) emulsifiable concentrate (EC); 2) encapsulated (ENC); 3) wettable powder (WP). The active ingredient (a.i.) present in the three formulations was analyzed to insure that actual percent a.i. agreed with label specifications. Analyses of the a.i. in each formulation were 95% to 120% of the labeled amounts. Based on these analyses a 1.25% concentration solution of MeP, a common concentration for agricultural application, was prepared from each formulation by adding distilled water.

Fabrics

Denim fabrics of 100% cotton and 50/50 cotton-polyester were contaminated. Both fabrics were a 2/1 twill, similar in construction and weight. Fabric swatches (8 x 8 cm) were immersed two at a time in 1.25% MeP formulations, which were placed on a magnetic stirrer to provide uniform agitation and to keep the WP and ENC formulations in suspension during the contaminating process. The swatches were stirred until saturated, removed, and air dried.

Laundry Procedures

Four laundry procedures were examined for efficacy of MeP removal from fabric:

1) Pre-rinse: Each contaminated swatch was pre-rinsed for two minutes in warm water at 49°C, then laundered in a 12 minute hot water (60°C) phosphate detergent wash, and two warm water rinses (49°C), three minutes and five minutes respectively. The phosphate detergent selected was AATCC Standard Detergent 124, a 12% phosphate detergent used for textile research.

2) Phosphate detergent wash (Det.): This procedure was the same as described for the pre-rinse, with the omission of the pre-rinse cycle.

3) Phosphate detergent wash plus ammonia laundry additive (Det. + NH_3): This treatment was identical to that of the phosphate detergent wash with the addition of ammonia laundry additive (3.5%-4% ammonia concentration) in the wash cycle.

4) Phosphate detergent wash plus bleach laundry additive (Det. + NaOCl): This treatment was the same as described for the phosphate detergent wash with the addition of liquid chlorine bleach (5.25% sodium hypochlorite) laundry additive in the wash cycle.

Laundry solutions were prepared on a volume of 150 ml wash water per fabric swatch. Detergent weight and laundry additive volumes were proportional to the 150 ml wash water. All volumes were proportionally calculated from a 45 liter wash load to duplicate the home laundering situation.

Contaminated swatches that were pre-rinsed were placed individually in 500-ml glass jars with distilled water and shaken on an Eberbach mechanical shaker to simulate the pre-rinsing cycle of an automatic washing machine. A modified AATCC test method 61-1975 (AATCC 1979) was implemented for laundering procedures, using an Atlas Launder-Ometer to duplicate home laundering for the wash cycle and two rinsing cycles. Individual Launder-Ometer canisters allowed for isloated laundering of swatches and steel balls added to each canister simulated laundry agitation. Constant temperature of the Launder-Ometer water bath was maintained. At the end of each cycle, water was decanted from the canisters by magnetizing the steel balls to the canister bottom. Additional water of the specified temperature was then added for the subsequent cycle. Following completion of the laundry process, the fabric swatches were air dried and then retained in glass jars for extraction procedures.

Extraction Procedures

To extract the MeP, 150 ml glass-distilled acetone was added to each jar containing a laundered swatch. The jar was shaken for one hour at 170 revolutions per minute, 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 were combined.

Gas Chromatographic Procedures

A solution of acetone extract: toluene (2:18) 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. The separation column was 1.83 m x 3 mm I.D. packed with 3% OV-25 on 100-120 mesh Chromosorb W HP. The column temperature was 213°C, that of the inlet was 217°C, and the detector was 300°C. Nitrogen carrier gas flow was 21.5 cc/minute, air flow was 50 cc/minute and hydrogen was 3 cc/minute. Replicated injections of 1.06 ul were made from each sample. Standard solutions of MeP (technical grade 99.9% purity), from the Environmental Protection Agency Health Effects Research Laboratory, were injected after every fourth sample solution for calibration.

Contamination of the Fabric Before and After Laundry

Estimating the extent to which fabrics had been initially contaminated was necessary for comparison with post-laundry residue levels (Table 1). Contaminated control fabric swatches for each fabric and formulation were used an an indicator of

TABLE 1

MEAN mg/cm^2 OF MeP IN TWO FABRICS BEFORE AND AFTER LAUNDERING WITH FOUR LAUNDRY PROCEDURES[a]

Treatment	Before Laundering $\bar{X}$ mg/cm^2	After Laundering $\bar{X}$ mg/cm^2	Treatment	Before Laundering $\bar{X}$ mg/cm^2	After Laundering $\bar{X}$ mg/cm^2
EC[b]-C[c]			EC-C/P[e]		
Control[d]	0.616		Control	0.585	
Pre-rinse		0.076	Pre-rinse		0.018
Det.		0.090	Det.		0.071
Det + NH_3		0.056	Det. + NH_3		0.029
Det. + NaOCl		0.076	Det. + NaOCl		0.071
ENC[f]-C			ENC-C/P		
Control	0.587		Control	0.558	
Pre-rinse		0.003	Pre-rinse		0.003
Det.		0.019	Det.		0.009
Det. + NH_3		0.018	Det. + NH_3		0.011
Det. + NaOCl		0.035	Det. + NaOCl		0.015
WP[g]-C			WP-C/P		
Control	0.660		Control	0.839	
Pre-rinse		0.004	Pre-rinse		0.011
Det.		0.054	Det.		0.078
Det. + NH_3		0.048	Det. + NH_3		0.060
Det. + NaOCl		0.041	Det. + NaOCl		0.062

[a] Calculations based on 3 replications

[b] Emulsifiable concentrate

[c] Cotton

[d] Control (contaminated fabric with no treatment)

[e] Cotton/polyester (50:50)

[f] Encapsulated

[g] Wettable powder

initial contamination and as a baseline (100%) for percentage removal calculations. Analysis of variance (ANOVA) comparing the degree of contamination between fabrics and formulations showed no significant difference ($F=1.601$, d.f.=5,12), indicating that both fabrics initially retained like amounts of MeP. Comparisons of fabric contamination after laundry were calculated to ascertain the amounts of MeP removed by the laundry process.

RESULTS AND DISCUSSION

Percentages of MeP Removed

The laundry process removed a mean of 80% to 99% MeP (Table 2). Mean percentages removed were higher for encapsulated (ENC) and wettable powder (WP) formulations, with ranges of 93% to 99% MeP removed. Emulsifiable concentrate (EC) MeP removal was lower, ranging from 80% to 88%, indicating that EC formulation apparently was more difficult to remove.

TABLE 2

MEAN % MeP REMOVED BY LAUNDERING

Treatment	Pre-rinse	Det.	Det. + NH_3	Det. + NaOCl
EC-C	87.8	84.5	80.6	88.8
EC-C/P	88.2	84.6	83.7	86.3
ENC-C	98.4	98.1	97.9	97.8
ENC-C/P	98.9	96.8	97.5	97.9
WP-C	99.1	93.3	93.6	93.8
WP-C/P	99.9	95.7	96.3	96.3

Pre-rinsing proved to be effective when fabric and formulation were considered. Percentages of total MeP removed by pre-rinsing were generally higher than for the other laundry procedures. Immersion of contaminated fabrics in the pre-rinse cycle of the pre-rinse laundry procedure resulted in removal of substantial amounts of MeP (Table 3), but pre-rinse removal of ENC and WP was significantly greater ($P \leq .05$) than that of the EC (EC, 25%-34%; ENC, 65%-67%; WP, 61-79%). MeP removed when the wash cycle was the first aqueous solution was significantly greater ($P \leq .05$) than when the pre-rinse cycle was the initial aqueous solution. This significant finding could have resulted from assistance of detergent or detergent plus additive. MeP removal during the washing cycle may be partially attributed to the alkalinity (pH 9.7) of the phosphate detergent since MeP is hydrolyzed to 4-nitrophenol in an alkaline medium.

Differences Attributable to Fabric, Formulation, and Laundry Procedures

Fabric. Although it was observed that the EC formulation was more difficult to remove from both fabrics than the ENC or WP formulations, fiber content of fabrics made no difference in the efficacy of MeP removal. It was initially suspected that since EC formulations are oil-based, there might be an affinity for oleophilic polyester fibers, although no significant difference between fiber content was shown based on gas chromatographic analysis.

TABLE 3

MeP REMOVED BY PRE-RINSE CYCLE VS. WASH CYCLE

Treatment	$\bar{X}$ Cum %[a] Pre-rinse	Det.	Det. + NH_3	Det. + NaOCl
EC-C	34.2[b]			
	71.5[c]	59.3	59.0	62.3
EC-C/P	25.3			
	70.3	61.5	68.4	52.7
ENC-C	67.2			
	90.1	82.1	81.5	85.1
ENC-C/P	65.2			
	94.1	70.6	84.3	77.1
WP-C	61.8			
	94.3	79.5	79.5	77.8
WP-C/P	79.6			
	95.5	80.4	75.5	81.3

[a] Cumulative % is step or step plus previous step removal

[b] Pre-rinse cycle of pre-rinse laundry procedure

[c] Wash cycle of detergent and detergent + additive laundry procedure

Previous work had raised the question of whether cotton or cotton-poylester fabric is "safer" to wear. These data indicated no difference, and the fabric of either fiber content are similiar in their relative "safety."

Formulation. Significant differences ($P \leq .01$) in the completeness of MeP removed were found among the three formulations; therefore, statistical partitioning was done to identify where specific differences occurred. Partitioning revealed that the cause of differences among formulations was the lower percent of EC removed, indicating difficulty in removal. The ENC formulation was most consistently and effectively removed. The WP formulation was also easily removed but with more variability.

Laundry Procedures. Of the laundry procedures investigated, the use of ammonia additive was the least effective in amount of MeP removed (Figure 1). Percentages of MeP removed

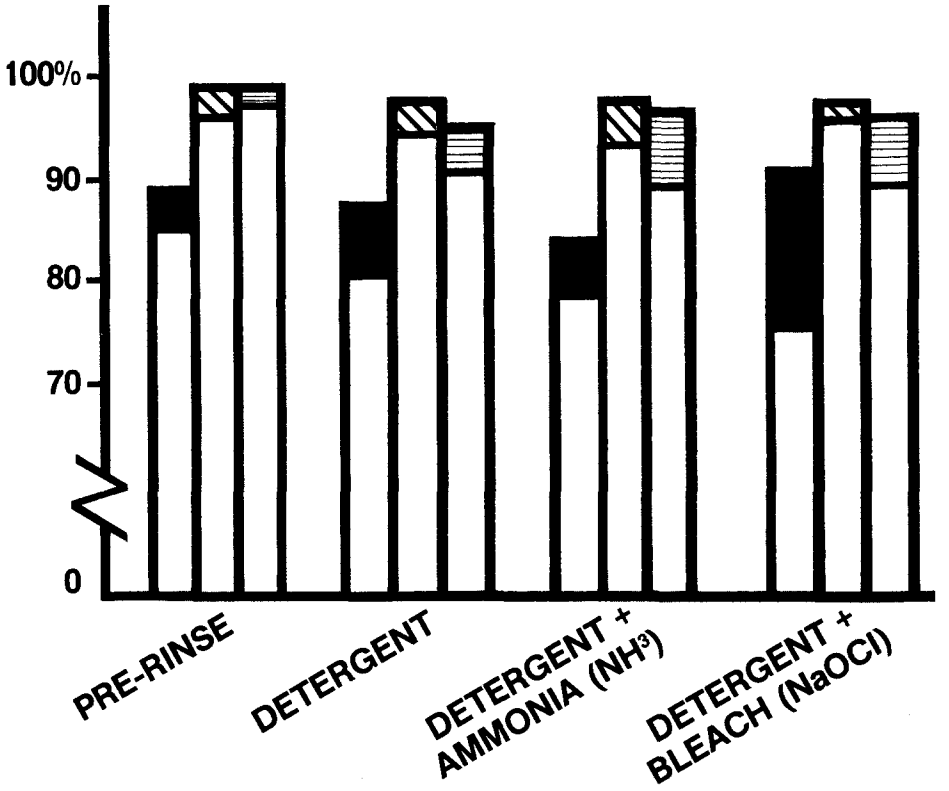

Figure 1. % Range of MeP Removed By Laundry Procedures

by laundering with phosphate detergent plus ammonia additive were significantly lower ($P \leq .01$) than other procedures. Bleach was slightly more effective than ammonia as a laundry additive.

The pre-rinse procedures was the most effective in removing WP MeP residue from both fabrics. Because WP formulations are a combination of technical material (a.i.) and micronized clay or talc, pre-rinsing may have aided in removing such particulate matter. Although the pre-rinse procedure also resulted in higher percentages removed from the EC and ENC formulations, these differences were not statistically significant.

REFERENCES

AATCC Tech. Man., Amer. Assoc. Test. Chem. and Col. 55, 174 (1979).

FINLEY, E.L., and J.R.B. ROGOLLIO: Bull. Environ. Contam. Toxicol. 4, 343 (1969).

FINLEY, E.L., G.I. METCALFE, AND F.G. MCDERMOTT: Bull. Environ. Cont. Toxicol. 12, 268 (1974).

FINLEY, E.L., J.B. GRAVES, T.A. SUMMERS, P.E. SCHILLING and H.F. MORRIS: La. Agr. Expt. Sta. Circ. 104, 7 p. (1977).

FINLEY, E.L., J.B. GRAVES, and F.W. HEWITT: Bull. Environ. Contam. Toxicol. 22, 598 (1979).

METCALFE, G.I.: Master's Thesis. La. St. Univ. (1972).

WOLFE, H.R., W.F. DURHAM and J.F. ARMSTRONG: Arch. Environ. Health. 14 622 (1967).

Accepted May 17, 1981