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Removal of Paraquat from Contaminated Fabrics

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Paraquat, 1,1'-dimethyl-4,4'-bipyridinium dichloride, is one of the more toxic of the herbicides. It is used in agriculture usually as a water-soluble concentrate. Agricultural pesticide applicators are a group most likely to be contaminated by this compound, either by direct contact with the skin (Gunn and Stevens 1976) or through contaminated clothing (Johnson and Byers 1979; Wolfe et al. 1967). The work reported here concerns methods for removal of paraquat formulation from fabrics which are often worn by agricultural workers.

MATERIALS AND METHODS

Test fabrics included a 3 oz, 65/35 polyester-cotton, plainweave; an 8 oz, 100% cotton twill weave and a 14 oz, 100% cotton denim. Sizing was removed by American Association of Textile Chemists and Colorists (AATCC) method 124-1984 with modifications which included a fabric softener in the final rinse for samples tested for this variable.

Analytical standard of paraquat dichloride was obtained from the U.S. EPA Standards Repository. Paraquat dichloride[methyl-^{14}C], 7.91 mCi/mmole, was obtained from Amersham Corp. Radiochemical purity was checked by paper and thin-layer chromatography.

Two solutions were prepared for the contamination of the test fabrics. They were of the same chemical composition, but one contained 4.5 µCi/mL of ^{14}C-labeled paraquat. The solutions contained 2.0 mL of Ortho paraquat (29% a.i.) and 0.25 mL Ortho X77 surfactant diluted to 100 mL with water.

Test swatches were treated with 50 µL of contaminating solution and dried at 22 °C and 65% relative humidity for 24 h prior to the laundering or test procedures.

The AATCC test method 61-1980 as modified by Easley, et al.(1982), was used in the laundering studies. An Atlas Launder-Ometer model B5 was used for washing and rinsing steps with 500-mL canisters.

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A New Brunswick G-2 gyrotary shaker with 250-mL flasks was employed for the prerinse. For 8 x 8 cm swatches, 150-mL volumes were used for the prerinse, wash and rinse steps. The prerinse studies with 29 x 29 cm swatches employed 4-L flasks and 2 L of solution.

A number of laundering regimens were tested. For the prerinses, a water temperature of 49°C was used and the solutions tested were distilled and tap water, with and without 0.5% NaCl. Two temperatures were tested in the wash step, 49°C and 60°C. Four detergents were tested: a carbonate (Tide), a phosphate (Tide, 6.1%P), a heavy-duty liquid (Era) and AATCC standardized detergent 124 (12.4%P). For the washing step, 1.8 g/L of solid detergent or 2.6 mL/L of liquid detergent were used. In the rinse step, distilled water was used at either 41° or 49°C.

The extraction and colorimetric analyses were carried out as follows: Place the swatch (8 x 8 cm) in a 1.5 x 9 cm tube with a constriction at the lower end so that the fabric is tightly packed. Pass 15 mL of 4M ammonium chloride through the column so that the flow rate is 2-3 mL/min. Dilute the eluate to 15 mL with the same solvent and remove an aliquot for colorimetric analysis by the method of Calderbank and Yuen(1965). Elute denim swatches in the same manner, but use 25 mL of the 4M salt solution. Dilute the eluate to 25 mL before assay of an aliquot. The limit of quantitation was 1-2 μg/swatch with the 3- and 8-oz fabrics and 4-5 μg/swatch with 12-oz denim.

Determination of ^{14}C in the swatches was done as follows: Cut the 3 and 8-oz swatches into 2 x 4 cm sections and place each section in a counting vial with 1.0 mL of water and 15 mL of scintillation solvent. The solvent contained 10g PPO and 1.0g of dimethylPOPOP per L of toluene-Triton x-100 (67:33,v/v). A 50 μL aliquot of the ^{14}C-labeled contaminating solution gave the same counting efficiency when dispersed in this scintillation solvent system alone or on a 2 x 4 cm section of the 3- or 8-oz fabric. Counting efficiency was determined with standard [^{14}C]toluene (New England Nuclear Corp.).

A second method for measuring ^{14}C on the swatches was necessary because of the color in the denim: Cut the denim swatch into sections of 150-200 mg and oxidize the sections in a biological oxidizer (Harvey Instrument Co. Princeton, NJ). Collect the carbon dioxide in 20 mL of scintillation solvent. This solvent contained 10 g PPO and 1.1 g dimethylPOPOP per L of toluene/2-methoxyethanol/2-ethanolamine (50:35:15, v/v/v). Calibrate for oxidation and counting efficiency by oxidizing 10-20 mg of standard [^{14}C]benzoic acid (NEN) with about 150 mg of fabric.

RESULTS AND DISCUSSION

Optimal conditions for removal of paraquat from the test fabrics were established with the nonradioactive formulation and colorimetric determination, and then confirmed with the ^{14}C-labeled formulation. The use of a radioactive label greatly facilitated and improved the quantification. The technique has been used before in studies on the removal of soiling material from fabric (Gordon, 1968).

Essentially no differences were observed in the efficacy of the two temperatures in the wash and rinse steps. The carbonate and phosphate (Tide) detergents were the most effective in paraquat removal while the liquid detergent was least effective. The use of fabric softener did not affect paraquat removal when a prerinse was used. An optimal laundering procedure, within the parameters tested, is presented in Table 1.

Table 1. Paraquat remaining on contaminated swatches after prerinses and optimal laundering regimen, and paraquat transferred to uncontaminated fabric.[a]

	Paraquat on swatch (μg)		
	8 oz	14 oz	3 oz
Prerinse only[b]			
a. Distilled water	95.9 ± 7.7	124.9 ± 12.5	42.0 ± 5.5
b. Tap water	24.3 ± 7.3	73.5 ± 17.6	11.8 ± 2.8
c. Distilled + 0.5% NaCl	14.5 ± 5.6	32.2 ± 6.4	8.8 ± 1.1
d. Tap water + 0.5% NaCl	14.5 ± 3.0	29.2 ± 7.6	9.2 ± 1.1
Optimal laundry regimen[c]	3.3-3.7	10.8-11.5	1.6-1.7
Transfer to uncontaminated swatch during laundry[c]	0.5-0.6	1.8-2.4	0.1-0.2

[a] All swatches received 330 μg of paraquat.

[b] Colorimetrically determined from 9-12 replicates each. The mean and standard deviation are reported.

[c] Paraquat[^{14}C] was used. The optimal laundering regimen includes: a 2 min prerinse at 49°C in 0.5% NaCl; 9 min wash with 1.8 g/L of detergent at 49°C; and two rinses at 41°C for 3 and 2 min respectively. A range from three replicates is reported.

The prerinse removed most of the pesticide and was the most effective individual step. The efficacy of a simple water extraction in the removal of pesticides from fabrics has been observed by other investigators using different pesticides(Easley et al. 1981, 1983; Kim et al. 1982). The addition of 0.5% NaCl to the prerinse solution improved paraquat removal (Table 1). The salt may reduce the ionic interaction of the paraquat cation with the negative charges found on the fabric surface (Bogle 1977). The detergent wash and rinses removed some of the paraquat remaining after the prerinse. However, 1-3% of the pesticide remained regardless of the method of removal. Studies in other laboratories with methyl parathion, alachlor, DDT and additional pesticides have also found that there is an incomplete removal of pesticide with similar laundering regimens (Easley et al. 1981, 1983; Finley et al. 1974; Metcalfe, 1972; Kim et al. 1982). Paraquat contrasts with most pesticides in that it is very water soluble and rather insoluble in most organic solvents. Easley et al. (1983), found that although the water-soluble amine salt of 2,4-dichlorophenoxyacetic acid (2,4-D) was readily removed from textile fabrics with just water, very small amounts remained. The water-insoluble ester of 2,4-D was not efficiently extracted from textiles with water alone.

The amount of paraquat remaining on the fabric appears to be a function of the fabric weight (Table 1). This relationship between fabric weight and pesticide retention has been observed with other pesticides (Kim et al. 1982; Finley et al. 1974).

Contamination of the laundering apparatus with pesticide has been observed with methyl parathion contaminated fabric(Laughlin et al. 1981). Similar contamination was not observed in this study with ^{14}C-labeled paraquat. This may be due to the very water-soluble nature of this organic salt.

Redeposition of paraquat from contaminated swatch to uncontaminated swatch was observed (Tables 1 and 2). The amount of pesticide absorbed by the uncontaminated fabric was a function of the fabric weight. Redeposition of the paraquat was found to occur primarily in the prerinse step where the greatest amount of pesticide was in solution. Redeposition has been observed with pesticides (Laughlin et al., 1981), lipids and detergents (Gordon, 1968) and appears to be a general phenomenon of organic compounds with textile fabrics.

A series of experiments were carried out to determine which parameters could be changed to improve the efficacy of paraquat removal during prerinse (Table 3). Increasing the time of the prerinse had essentially no effect; however, increasing the volume or using two sequential prerinses was more effective in paraquat removal than the standard prerinse alone. Two prerinses gave results similar to the optimal laundry regimen, although the use of detergent would be advantageous in the removal of other soiling material.

A series of prerinses using two levels of paraquat contamination were tested for efficiency of pesticide removal (Table 4). After six prerinse steps, the level of residual paraquat reached a constant level, although the amount remaining on the swatches was greater on the swatches with the greater initial contamination.

When the paraquat-contamination solution was applied to the 8- and 14-oz fabrics, the 50 µL of liquid was confined to an area of 1-3 cm in diameter. During the laundering experiments, it was found that the residual paraquat was redeposited over the entire swatch. The redeposition was found to occur primarily in the prerinse step and the amount redeposited appears to be proportional to the fabric weight.

Table 2. Transfer of paraquat to uncontaminated swatches during prerinse.

Contaminated swatches[a]		Uncontaminated swatches	
Fabric	Paraquat remaining(μg)	Fabric	Paraquat remaining(μg)
3 oz plain	2.0-2.2	3 oz plain	1.3-1.5
3 oz plain	2.0-2.1	8 oz twill	3.5-3.7
8 oz twill	3.8-4.2	8 oz twill	3.1-3.6
8 oz twill	3.8-4.2	3 oz plain	1.3-1.5

[a] The contaminated fabric was treated with 330 μg of ^{14}C-labeled paraquat. The prerinse regimen is that described for the control in Table 3.

Table 3. Efficacy of paraquat removal by changing prerinse parameters.

Variable(s) altered	Paraquat remaining(μg)[a]	
	8 oz twill	3 oz plain
Control[b]	4.5-4.9	2.4-2.6
10 minute	4.7-5.0	2.3-2.4
300mL	2.8-3.1	1.4-1.7
10 min, 300mL	2.9-3.0	1.3-1.5
Two prerinses	1.6-1.7	1.1-1.2

[a] Each swatch was treated with 330 μg ^{14}C-labeled paraquat dichloride. The data represent the range from three replicates.

[b] The control was a single prerinse for 2 min in 150 mL of 0.5% NaCl at 49°C.

Table 4. Effect of a series of prerinses in the removal of paraquat[^{14}C] from an 8-oz twill.

Number of prerinse[a]	Paraquat remaining (μg)	
	130 μg applied	1300 μg applied
1	10.8	66.3
2	7.5	20.8
3	2.5	14.3
4	3.6	11.7
5	3.6	10.5
6	3.4	10.1

[a] Each prerinse was for 2 min in 150 mL of 0.5% NaCl at 49°C.

Table 5 shows the results of an experiment where 50 μL of the herbicide was applied either at the end of 4 x 20 cm swatches or to one corner of 29 x 29 cm swatches. The contamination spot was confined to a 4 x 4 cm area and the spot size was about 2 cm in diameter. After the prerinse, paraquat was found to be uniformly redeposited over the entire swatch. It is likely then that spreading of paraquat from a small area on an article of clothing to the entire article occurs during laundering, although the amount redeposited may be much smaller than the amount applied. The toxicological significance is not known.

Table 5. Effect of swatch size on the redeposition of paraquat[^{14}C] during prerinse.

Swatch size	Paraquat remaining after prerinse		
	Application area	Remaining area	
	(μg)	(ng/cm^2)	Total(μg)
4 x 20 cm[a]	12.2 ± 0.3	691 ± 51	44.2 ± 3.2
29 x 29 cm[b]	5.3 ± 0.3	117 ± 11	96.7 ± 9.1

[a] The prerinse was carried out for 2 min in 150 mL 0.5% NaCl at 49°C. Application area was <16 cm^2. Values are means and standard deviations for three replicates.

[b] The prerinse was carried out for 2 min in 2.0 L 0.5% NaCl at 49°C. Application area was <16 cm^2. Values are means and standard deviations for three replicates.

Several prerinses of paraquat-contaminated clothing in warm water containing table salt appears to be an efficient method for reducing the residues of this pesticide. The prerinse should be done outside of the washing machine with the individual article of clothing alone, thus avoiding possible contamination of the machine or other clothing.

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REFERENCES

AATCC Tech Man (1979) Am Assoc Tex Chem Col 55:174

Bogle M (1977) Textile dyes finishes and auxilliaries, Garland Publishing Inc. New York, NY p 33

Calderbank A, Yuen SH (1965) An ion-exchange method for determining paraquat residues in food crops. Analyst 90:99-106

Easley CF, Laughlin JM, Gold RE, Tupy DR (1981) Methyl parathion removal from denim fabrics by selected laundry procedures. Bull Environ Contam Toxicol 27:101-108

Easley CF, Laughlin JM, Gold RE, Hill RM (1982) Laundry factors influencing methyl parathion removal from contaminated denim fabric. Bull Environ Contam Toxicol 29:461-468

Easley CF, Laughlin JM, Gold RE, Tupy DR (1983) Laundering procedures for removal of 2,4-dichlorophenoxyacetic acid and amine herbicides from contaminated fabrics. Arch Environ Contam Toxicol 12:71-76

Finley EL, Metcalfe GI, McDermott FG (1974) Efficacy of home laundering in removal of DDT, methyl parathion and toxaphene residues from contaminated fabrics. Bull Environ Contam Toxicol 12:268-274

Gordon BE (1968) Radiotracers in fabric-washing studies. J Am Oil Chem Soc 45:367-373

Gunn DL, Stevens JGR (1976) Pesticides and human health. Oxford University Press, Oxford England, 278 pp

Johnson B, Byers T (1979) Agricultural crop pesticide usage in Nebraska-1978. Nebraska Agricultural Experiment Station Report No 100

Kim CJ, Stone JF, Sizer CE (1982) Removal of pesticide residues as affected by laundering variables. Bull Environ Contam Toxicol 29:95-100

Laughlin JM, Easley CB, Gold RE, Tupy DR (1981) Methyl parathion transfer from contaminated fabrics to subsequent laundry and to laundry equipment. Bull Environ Contam Toxicol 27:518-523

Metcalfe GI (1972) The absorption and retention of selected chlorinated hydrocarbons and organic phosphate residue in cotton and cotton-polyester fabrics. Master's Thesis Louisana State University

Wolfe HR, Durham WF, Armstrong JF (1967) Exposure of workers to pesticides. Arch Environ Health 14:622-623

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