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Photochemical Reaction of Chlorothalonil in Organic Solvents

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Pesticides are presently a necessary component of cotton pest management systems. For the most part, frequent applications of a variety of chemicals are the only means of suppressing pest populations that exceed economic injury thresholds. Contact with pesticide residues on cotton plants may be hazardous to workers entering treated fields. The Environmental Protection Agency has recognized this problem and responded to it by establishing reentry intervals for the more toxic insecticides.

However the potential danger of these chemicals in contaminated clothing has received little attention. For instance, the only published data on removal of pesticides from clothing by laundering are those reported from the laboratory of the senior author of this paper (FINLEY AND ROGILLIO (1969), FINLEY et al. (1974), and FINLEY et al. (1977)). Furthermore, there is a paucity of information on the quantity of residues accumulated by various clothing fabrics worn in treated cotton fields. FINLEY and ROGILLIO (1969) reported that DDT and methyl parathion residues were collected on trousers worn by insect scouts for 8 hr in treated fields and that 30.4 and 2.6%, respectively, of these residues remained after 1 washing. QUINBY et al.(1958) found that cotton scouts working in fields treated with methyl parathion collected on all garments an average of 3 mg /hr in the 1st hr. after spraying and less than 1 mg /hr 4 hr after spraying. Similar data to that of QUINBY et al. (1958) were published by WARE et al. (1973).

The primary objectives of the research reported herein were (1) to determine the amount of methyl parathion residues accumulated by clothing worn in treated cotton fields, and (2) to develop an efficient laundering method for removing methyl parathion residues from clothing. Methyl parathion was selected because it is used extensively for control of cotton insect pests and is generally representative of the organophosphate group of insecticides.

METHODS AND MATERIALS

Field Phase. The quantity of methyl parathion residues collected by clothing worn in treated fields was determined in 2 ways. The 1st method utilized 6 cotton insect scouts who volunteered to wear suits of clothing (pants and long sleeve shirts provided by the authors) at designated times for 1 full day while

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performing their normal task of estimating pest insect populations. The schedule for wearing suits was (1) during June prior to routine foliar applications of insecticides, (2) during late June or early July after initial insecticide applications, and (3) in late July or August after several applications. No effort was made to determine what insecticides were sprayed on the fields scouted by each volunteer. However methyl parathion was generally used in all cotton fields during 1975 when this phase of the study was done

Matched sets of pants and shirts in work type garments were purchased to fit each man's individual measurements. The khaki colored garments were made of 50/50 cotton-polyester blend fabrics in 170-226 g weight, twill weave. The new suits were washed 1 time by a standard laboratory procedure (AATCC 1975) before they were issued for field wear. The garments were coded for identification by man, wear period, and area of garment to be subsampled for chemical analysis in the laboratory after field wear. Each pants leg was marked at mid-thigh position. The shirt was marked at mid-front and mid-back (combination of mid-front and mid-back areas constitued shirt sample) and each sleeve between the elbow and cuff. These areas on each suit were selected to check concentration of methyl parathion residue accumulated in the fabrics by contact of the cotton insect scouts with cotton plants during the course of routine field inspection for monitoring pest populations. Each suit was divided into 2 equal parts by cutting pants and shirts lengthwise. One part of a shirt and pants was subsampled for chemical analysis and biological assay with Drosophila before washing. The remaining half of each garment was reserved for similar analyses after washing. The samples for pre-wash analyses were cut in 12.7 x 12.7 cm dimensions from the pre-marked area of each garment.

Each set of garments was packaged in a bag made of heavy aluminum foil with an explanation sheet included about the study. A field supervisor was responsible for coordinating, distributing and collecting packages at the field sites and shipping the materials back to the Textiles Laboratory on the day of collection. Suits were stored in the aluminum foil containers in laboratory freezers at $0^{\circ}C$ or lower pending analysis.

The 2nd method for determining the quantity of methyl parathion collected on clothing worn in treated fields was accomplished by having 4 volunteers simulate the monitoring of pest insect populations for 6 hr. on the 1st, 2nd, and 4th day following a single application of methyl parathion. Precision was increased by having each person walk a total distance of 5610 m on each day. Fabric swatches (30.5 x 50.8 cm), rather than entire suits, pinned around each pants leg above the knee, were used to measure residue accumulation. Double layers of fabric (hand stitched together) were employed to ascertain if residues on the under layer were significantly less than on the outer layer.

The fabric swatches consisted of either all-cotton or 50/50 cotton-polyester blend fabrics, 56-113 g weight, bleached, and

free of special finishes. Fabric swatches were coded to identify man, day of re-entry, right or left leg, and fabric by layer and fiber content. Swatches were packaged in individual bags made of heavy aluminum foil with instructions included for pinning them to the pants just above the knee. Each volunteer wore a double layer of cotton fabric on 1 pants leg and a double layer of 50/50 cotton-polyester blend on the other pants leg. Positioning of the fabric swatches on the pants legs was done in a random manner. The swatches were returned to the laboratory at the end of the day they were worn in the field. The outer and under layers of fabric were separated and each layer was repackaged in a new aluminum foil bag and stored in a freezer at $0^{\circ}C$ or lower.

The cotton field used for this experiment was sprayed on August 9, 1976, with methyl parathion emulsifiable concentrate in water at the rate of 1.12 kg /ha The cotton plants were 90 - 114 cm. high and brushed strongly against the leg as the men walked along the rows inspecting plants for insects and insect damage. No rain occurred in the area during the course of the study.

Extraction and Analysis of Methyl Parathion. Chemicals and procedures used were the same as those reported by FINLEY et al. (1974). The mean recovery of methyl parathion from spiked samples was 60 and 69% for cotton and 50/50 cotton-polyester blend, respectively.

Biological Assay. The biological activity of methyl parathion residues was measured using the techniques reported by FINLEY et al. (1974).

Laundering. The laundering formula recommended by FINLEY et al. (1977) was used in this study.

Retention of Radiolabeled Methyl Parathion. Carbon^{14} labeled methyl parathion was synthesized in the LSU Nuclear Science Center according to the method of FLETCHER et al. (1950). The label occurs in the methoxy groups attached to the phosphorus atom in methyl parathion. The specific activity was about 0.025 μCi/M. Cotton and cotton-polyester (50/50) fabrics measuring 12.7 x 12.7 cm were spiked with the C_{14} methyl parathion at 40 ppm based on fabric weight. After the solvent (methanol) evaporated, radioactive and non-radioactive fabrics of the like fiber content were laundered (1 wash with 2 rinses - see FINLEY et al. (1977)) together in a small automatic agitator type washer. The samples were air dried and C_{14} content measured by liquid scintillation counting.

The Statistical Analyses of Data. Data for the field study with suits were examined with analyses of variance with 6 scouts (replications), 3 wear-periods, 3 areas of suit and 2 washes (wash vs no-wash) as factors.

Similar analyses of variance were performed with data from the field study with fabric swatches with 4 scouts (replications), 2

fabrics, 2 fabric layers and 3 re-entry days as factors.

In both studies methyl parathion residue and Drosophilia mortality (conducted on transformed data [$\sqrt{x+0.5}$]) were the variables.

RESULTS AND DISCUSSION

Field Study with Suits. Only very low concentrations of methyl parathion (less than 0.05 ppm) were detected in suits worn by insect scouts for 1 day in cotton fields prior to insecticide applications. Obviously methyl parathion had been applied in 1 or

TABLE 1

METHYL PARATHION RESIDUES (PPM) EXTRACTED FROM 50/50 COTTON-POLYESTER SUITS WORN FOR 1 DAY BY COTTON INSECT SCOUTS AND THEIR REDUCTION BY LAUNDERING

		After Initial Application of Insecticides			Following Several Applications of Insecticides		
Scout	Part of Suit	Pre-Wash	1st Wash	2nd Wash	Pre-Wash	1st Wash	2nd Wash
I	Pants	16.74	3.94	2.26	21.50	4.14	1.00
	Shirt	1.88	0.36		11.30	1.16	
	Sleeve	7.80	1.19		5.87	1.77	
II	Pants	1.49	0.26	b/	28.97	7.87	2.02
	Shirt	0.14	0.02		11.96	0.38	
	Sleeve	0.14	0.06		18.48	0.68	
III	Pants	1.36	0.16	b/	7.61	2.95	0.86
	Shirt	0.10	a/		0.59	0.14	
	Sleeve	0.25	a/		0.67	0.21	
IV	Pants	5.10	1.72	b/	7.34	1.30	b/
	Shirt	0.06	a/		1.55	.10	
	Sleeve	0.60	a/		2.20	.28	
V	Pants	15.20	3.30	0.87	15.77	3.03	2.19
	Shirt	2.74	1.98		3.61	0.52	
	Sleeve	5.84	0.69		2.26	0.99	
VI	Pants	1.05	0.21	b/	c/	c/	
	Shirt	0.07	a/				
	Sleeve	0.20	a/				
Mean	Pants	6.82	1.60		16.24	3.86	
	Shirt	0.83	a/		5.80	0.46	
	Sleeve	2.47	a/		5.90	0.79	

a/ Not determined.
b/ Only garments with residues greater than 3 ppm received 2nd wash.
c/ Worker did not participate.

more of the fields entered by the workers since analysis for methyl parathion in control suits not worn in fields was negative. Neither control suits nor suits worn in the field were toxic to Drosophila held on the fabric surface.

Most of the methyl parathion accumulated by garments worn after initial applications of insecticides was present on the pants (Table 1).
Residues extracted from pants ranged from 1.05 to 16.74 ppm with a mean level of 6.82 ppm. The mean residue concentrations in sleeves and the chest area of shirts were 2.47 and 0.83 ppm, respectively. The distribution of residues in the above fashion primarily resulted from cotton plants being relatively small at this time of year.

Much greater concentrations of methyl parathion were extracted from garments exposed later in the year when cotton plants were taller and had received several applications of insecticides (Table 1). The mean residue level for pants(16.24 ppm) was about 3X greater than the value (6.82 ppm) obtained earlier. The mean concentrations of methyl parathion measured in shirts and sleeves of shirts were 5.8 and 5.9 ppm, respectively. The increased residues detected on the chest area of the shirts (7X higher) resulted from cotton plants being higher. The highest residue levels found in pants, sleeves, and shirts were 28.97, 18.48, and 11.96 ppm, respectively.

Differences in residues found in pants, shirts, and sleeves were statistically significant ($P<0.01$) as were differences between wear periods ($P<0.01$).

Field Study with Fabric Swatches. Fabric swatches worn in a cotton field 2 and 4 days after treatment with methyl parathion at 1.12 kg./ha. accumulated approximately 90 and 99% less residues, respectively, than swatches worn the 1st day after application (Table 2).

TABLE 2

MEAN METHYL PARATHION RESIDUE (PPM) EXTRACTED FROM AND % MORTALITY OF DROSOPHILA EXPOSED TO FABRIC SWATCHES WORN IN A COTTON FIELD TREATED WITH 1.12 kg /ha

	Re-entry Interval After Application					
	1 Day		2 Day		4 Day	
Parameter	Cotton	Cotton-Polyester	Cotton	Cotton-Polyester	Cotton	Cotton-Polyester
Fabric Layer						
Outer	30.1	39.5	2.6	3.6	0.23	0.48
Under	13.7	24.6	1.5	3.1	0.19	0.39
Drosophila Bioassay (% Mortality)						
Outer	100	100	40	57	0	2
Under	100	100	32	62	10	7

Only 50-75% as much methyl parathion was extracted from cotton fabric as from cotton-polyester. Furthermore the under layer of either fabric accumulated only 40-80% as much residue as the outer layer. Noteworthy was the fact that the highest residues (30.1-39.5 ppm), which were measured on the fabric swatches worn 1 day after methyl parathion application, were comparable to the highest residue (28.97 ppm) detected in the pants worn by a cotton scout.

Differences in residues for re-entry day, for fabric, and for fabric layer were statistically significant ($P < 0.01$).

Reduction of Methyl Parathion Residues by Laundering. One washing using the laundering procedure developed in the laboratory of the senior author (see FINLEY *et al.* (1977) for specific details) was effective in reducing methyl parathion residues by 75-95% (significant at the $P < 0.05$ levels) (Table 1). Washing seemed to be less effective as the amount of residue in garments increased. Furthermore, a second wash did not remove as much methyl parathion residues (on a % basis) as the initial washing. It must be noted that the suits worn by cotton scouts were exposed to insecticides other than methyl parathion. Laundering effectiveness may have been decreased by the presence of other insecticides (FINLEY *et al.* (1974)).

Biological Activity of Methyl Parathion Residues. Methyl parathion residues accumulated by garments or fabric swatches worn in treated fields were toxic to *Drosophila* confined on these fabrics (Tables 2 and 3). Significantly less ($P < 0.05$) *Drosophila* were killed after exposure to washed suits than to unwashed suits and delayed re-entry significantly ($P < 0.01$) reduced mortality of flies exposed to fabric swatches. Residue levels in excess of 1 ppm on unwashed fabric were usually quite toxic to *Drosophila*. Interestingly, 1 ppm and higher levels detected analytically on washed fabrics were not as toxic as similar residues on unwashed fabric (Tables 1 and 3). Possibly the residues remaining after washing are "bound" in some fashion to the fabric. The fact that less methyl parathion is removed by the 2nd wash in comparison to the 1st wash (on a % basis) tends to support this premise.

As indicated previously, suits worn by cotton scouts were exposed to insecticides other than methyl parathion. Because preliminary laboratory investigations on the toxicity of cotton and cotton-polyester (50/50) fabrics spiked with methyl parathion at dosage levels of 1, 3, 5, and 10 ppm revealed that the approximate LD_{50}'s were 5.5 and 4.1 ppm, respectively, it appears that other insecticides were present on the suits.

Retention of Radiolabeled Methyl Parathion. After cotton and cotton-polyester (50/50) fabrics were spiked with C_{14} methyl parathion and laundered, liquid scintillation counting indicated that 24.3 and 8.8%, respectively, was retained. The difference in amount of C_{14} methyl parathion and/or C_{14} labelled degradation products retained in the 2 types of fabric supports findings in this study as well as those of FINLEY *et al.* (1974) that more methyl parathion is

TABLE 3

PERCENT MORTALITY OF *DROSOPHILA* EXPOSED TO 50/50 COTTON-POLYESTER SUITS WORN FOR 1 DAY BY COTTON INSECT SCOUTS

Scout	Part of Suit	After Initial Application of Insecticides		Following Several Applications of Insecticides	
		Pre-Wash	1st Wash	Pre-wash	1st Wash
I	Pants	100	10	100	100
	Shirt	100	0	100	0
	Sleeve	100	0	100	20
II	Pants	70	0	100	40
	Shirt	0	0	100	0
	Sleeve	0	0	100	0
III	Pants	90	0	100	0
	Shirt	0	a/	0	0
	Sleeve	0	a/	0	0
IV	Pants	100	0	100	0
	Shirt	0	a/	100	0
	Sleeve	10	a/	100	0
V	Pants	100	0	100	80
	Shirt	70	0	100	0
	Sleeve	100	0	100	10
VI	Pants	90	0	100	b/
	Shirt	0	a/	100	b/
	Sleeve	10	a/	100	b/
Mean	Pants	92	2	100	44
	Shirt	28	0	83	0
	Sleeve	37	0	83	6

a/ Not determined.
b/ Worker did not participate.

removed from cotton-polyester fabric than cotton by chemical extraction and washing procedures. Furthermore, clean test fabrics (of the same type) laundered with the C_{14} methyl parathion spiked fabrics were just as radioactive as the spiked fabrics. This verifies the data reported by FINLEY et al. (1974) on transfer of insecticide residues during laundering.

CONCLUSIONS

Substantial residues (up to 40 ppm) of methyl parathion were extracted from clothing worn in a treated cotton field on the 1st day following application. Delaying re-entry until the 2nd or 4th day following application reduced residues by about 90 and 99%, respectively, as compared to the 1st day.

The amount of residue accumulated on clothing increased as the growing season progressed and the number of insecticide applications increased. The areas of clothing covering legs and arms collected the highest amount of residue. Methyl parathion penetrated through an outer layer of fabric onto an under layer. However the residue level on the 2nd layer was only about 50% of that present on the 1st layer. Methyl parathion residues extracted from cotton fabric amounted to only 50-75% of that extracted from cotton-polyester (50/50).

Washing was effective in removing 75-95% of methyl parathion residues from clothing. Washing clean fabrics with those containing methyl parathion residues resulted in contamination of the clean fabrics.

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