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Effect of Herbicide Formulation on Atrazine Residue Removal from Chemical Plant Workers' Protective Clothing

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Unlike farm workers who may be exposed to pesticide primarily during application, pesticide manufacturing plant workers can be exposed to their product chemicals continuously during their work hours. If the pesticide residues are allowed to remain on the protective clothing, the chance of the pesticide coming in contact with the skin and then being absorbed into the body increases (Wolfe et al. 1967). This may cause skin irritation and other more serious health hazards. To minimize the problem, pesticide contaminated protective clothing needs to be decontaminated before reuse. Laundering has been found to be an effective method of decontamination.

Researchers suggested that pesticide formulation may be a primary contributing factor in the efficiency of residue removal (Easter and DeJonge 1985). Research showed that methyl parathion in emulsifiable concentrate formulation is more difficult to remove than encapsulated and wettable powder formulations (Laughlin et al. 1981). Flowable liquid atrazine was reported to be removable by only one laundering (Raheel and Gitz 1985). However, no published research reported a comparison of different atrazine formulations with respect to their residue removal efficacy from contaminated protective clothing under a common refurbishing protocol.

Atrazine is an effective herbicide widely used for corn and sorghum. Ciba-Geigy Corporation produces herbicide atrazine in three different formulations--water dispersible granule, wettable powder, and flowable liquid. For water dispersible granule and wettable powder atrazine, the most probable mechanism of contamination in a manufacturing plant is by accumulation of air-borne particles of the chemical on the protective clothing. These particles are likely to deposit in the fabric structure, especially in the crenuled areas of fiber, yarn, and fabric surfaces of the protective clothing

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(Obendorf et al. 1983; Kim and Kim 1988). For the liquid formulations such as flowable liquid the contamination is more likely through wetting the fabric by spillage.

The specific objective of this research is to determine the effect of formulation of herbicide atrazine on its removal from protective clothing of atrazine manufacturing plant workers. Because atrazine is not produced in an emulsifiable concentrate (EC) formulation, the results of atrazine formulations were compared with those of EC formulation metolachlor. The transfer of residue to other laundries that are not contaminated or to other parts of the same laundry is a concern for commercial as well as family laundering. An ancillary objective is to determine the transferability of the contaminant chemical to an uncontaminated fabric in a concomitant laundering in each pesticide formulation.

MATERIALS AND METHODS

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) was used in three formulations: water dispersible granule (WDG), wettable powder (WP), and flowable liquid (FL). For emulsifiable concentrate (EC) formulation, metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide), an herbicide for corn, sorghum, and peanuts, was used. The chemical concentrations as produced in the manufacturing plant, not the application concentrations, were used.

A 100% cotton, heavyweight (303.8 g/m^2) twill fabric purchased from Testfabrics, Inc. was used. The fabric is similar in fabric constructional characteristics and weight to the protective clothing fabric currently worn by Ciba-Geigy manufacturing plant workers. Swatches of the fabric, 8 x 8 cm in size, were prepared for contamination, refurbishing, and residue analysis.

The differences in contamination mechanism among the formulations may cause differences in how long the formulations remain with the fabric swatch during the initial stages of laundering. For example, granules when applied on a flat swatch roll off easily, whereas liquids remain in the fabric until the fabric is soaked with wash water. In order to provide a relatively equal amount of time for the formulations to remain with the fabric swatch during the initial stages of laundering, the 8 x 8 cm flat swatch was folded in half to form a 4 x 8 cm rectangular pocket by stitching the two sides. The pocket was contaminated with 1 g of the formulation; therefore, the amount of active ingredient (a.i.) in each formulation was different. The research design was based on equal amounts of formulation (contamination), not on equal amounts of a.i. The pocket opening was closed by hand stitching.

To determine the transferability of the contaminant chemical to a concomitantly laundered cloth, a flat 8 x 8 cm uncontaminated swatch was put in a launderometer canister, a stainless steel cylindrical jar of 3.5 inch diameter and 8 inch height, with the contaminated pocket. Twenty stainless steel balls were added to each canister to provide the agitation needed in laundering. Five pockets and five flat swatches per formulation were used as replications. They were refurbished using a common regimen of laundering and drying (American Association of Textile Chemists and Colorists 1988). A 12 min cycle at 60°C wash water temperature was run. The wash water in a canister was 300 Ml distilled water with 0.38 Ml (0.13% of the liquid volume) commercial heavy duty liquid detergent. Two rinses, each with 300 mL distilled water at 49°C, followed: one for 5 min and the other 3 min.

The laundered pockets and flat transfer swatches were dried at the high temperature setting for 45 min in a household dryer. The tumbling belt of the dryer was disconnected to prevent cross-contamination of the swatches by tumbling. The swatches were pinned onto a metal-mesh rack placed horizontally across the drying chamber to keep them from flying away by the air suction during the drying cycle.

After drying, the pockets were opened by removing the stitches. For residue extraction, each pocket or flat transfer swatch was put in a 250 mL bottle with 75 mL methylene chloride as solvent and shaken for 30 minutes in an Eberbach® shaker. This extraction procedure was repeated once. The combined aliquot of atrazine extraction was concentrated by evaporation using a Büchi® rotary evaporator down to a 2 mL extract. It was not necessary to further concentrate the metolachlor extract. The recovery rate of extraction was 93.5% for atrazine and 103.3% for metolachlor.

The amount of atrazine or metolachlor residue was determined by using a Tracor® 540 gas chromatograph (GC). The GC was equipped with a flame ionization detector and a glass column packed with 4% SE-30 and 6% OV-210, Support Chrom WHP 80/100 mesh. The column and detector temperatures were 200°C with helium as the carrier gas. A 4 μL volume of extract was injected. The peak area was calculated by a Spectra-Physics® 4290 integrator interfaced with the GC. Three replicated injections were made for each 2 mL vial for each contaminated or transfer fabric swatch. To determine the effect of herbicide formulation on residue removal, statistical procedures of analysis of variance (ANOVA) and Duncan's multiple range test were performed.

RESULTS AND DISCUSSION

The GC data on pocket swatch residues ($\mu g/cm^2$) remaining after the refurbishing process for each of the three atrazine formulations and for EC metolachlor are shown in Table 1. The mean percentage residue in the table is based on the active ingredient (a.i.) amount of the initial 1 g contamination of each formulation. The a.i. amounts of the formulations are 90% for water dispersible granule (WDG), 76% for wettable powder (WP), 41% for flowable liquid (FL), and 86.4% for emulsifiable concentrate (EC) formulations.

Table 1. Herbicide residue amounts in the refurbished protective clothing fabrics[a]

	Herbicide and Formulation			
	Atrazine			Metolachlor
	WDG	WP	FL	EC
	6.4	7.5	5.7	1417.2
	8.7	6.1	7.7	1461.3
	7.9	9.7	5.5	1395.3
	9.9	9.2	5.6	1287.5
	8.2	8.8	6.1	1259.4
$\bar{X}$ =	8.2	8.3	6.1	1392.5
	(<0.1%)	(<0.1%)	(<0.1%)	(10.0%)

[a]Residue amount ($\mu g/cm^2$) remaining in the contaminated pocket swatch

The results of the ANOVA test indicate that residue amounts remaining in the pocket swatches do not differ significantly by atrazine formulation--WDG, WP, and FL. Regardless of its formulation, atrazine was effectively removed by the refurbishing treatment. More than 99% of the a.i. of the 1 g applied formulation was removed for all the formulations of atrazine.

When the EC formulation of metolachlor was considered with atrazine formulations, the effect of formulation was significant ($p<.0001$) due to the large residue amounts of EC metolachlor (Table 1). The mean percentage residue of EC formulation metolachlor is 10% of the initially applied a.i. amount. This increased residue retention of EC formulation metolachlor may be partly due to the chemical difference between atrazine and metolachlor. However, metolachlor has a much higher water solubility (530 ppm at 20°C) than atrazine (33 ppm at 20°C); therefore, metolachlor should be removable by washing more easily than atrazine. However, the emulsifier used in the EC formulation seems to prevent the metolachlor a.i. from dissolving in water, thus making the formulation more difficult to remove by washing. This result agrees with the findings of Easter and DeJonge (1985) and Laughlin et al. (1981).

Table 2 shows the GC data on flat swatch residues ($\mu g/cm^2$) that transferred from the contaminated pocket swatch during the refurbishing process. The mean percentage residue in the table is based on the remaining residue amount of the contaminated pocket swatch, not the initially applied a.i. amount.

Table 2. Transfer residue amounts in the refurbished protective clothing fabrics[a]

	Herbicide and Formulation			
	Atrazine			Metolachlor
	WDG	WP	FL	EC
	1.3	3.6	0.7	1.7
	1.1	2.5	0.8	2.2
	2.6	2.6	0.9	3.3
	2.4	6.3	0.9	5.0
	1.4	5.8	0.7	2.8
$\bar{X}$ =	1.8	4.2	0.8	3.0
	(22.0%)	(50.6%)	(13.1%)	(0.2%)

[a]Residue amount ($\mu g/cm^2$) transferred to the flat uncontaminated swatch

For all four formulations, the transfer residue amounts are small compared with the applied a.i. amounts to the pocket swatches. However, the percentage ratios of transfer amounts to pocket residue amounts, ranging from 13.1% to 50.6% (Table 2), are high except for EC metolachlor (0.2%). The mechanism of residue transfer is most likely through absorption of the applied and dispersed a.i. by the flat transfer swatch. For atrazine, the majority of the residues remained in the contaminated pocket fabric for the WDG and FL formulations; however, the a.i. in the WP formulation transferred to the initially uncontaminated flat swatch more easily. The percentage ratio of transfer amounts to pocket residue amounts is 50.6% (Table 2) for the WP formulation.

Overall, the FL formulation of atrazine shows the lowest amounts of pocket residues (Table 1) and transfer residues (Table 2) in terms of the a.i. quantity. The formulation seems to wash out easily from the contaminated fabric; this agrees with the results of Raheel and Gitz (1985). It also does not transfer much to other materials that are washed together. The EC formulation metolachlor shows an extremely low percentage of transfer (Table 2), compared with the high pocket residue amounts (Table 1). This can be explained, as in the pocket swatch residue removal, by the effect of emulsifier in the formulation that prevents the a.i. from dissolving in the water and thus from transferring to other materials in the same wash. How to remove EC formulation metolachlor more completely remains to be a topic for further research.

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