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Loss of Pirimicarb Residues from Contaminated Fabrics

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Pirimicarb is widely used in Alberta greenhouses as an insecticide to control aphids in cereals, fruit, ornamentals, and vegetables. Its toxicity is high with an LD_{50} of 147 mg/kg for rats (Worthing and Walker, 1983). With the intensive use of pesticides such as pirimicarb, much attention has been paid to their impact on the environment and on human health and safety. The use of pirimicarb in greenhouses presents a particular hazard because space is limited and conditions are hot and humid. These conditions enhance direct or indirect dermal absorption and inhalation of pirimicarb; therefore, the greenhouse workers face potential health problems if their work clothing contaminated with pirimicarb is not properly decontaminated before re-use.

Much research has been done regarding the relationship between pesticides and human health and safety, as well as various methods to remove pesticide residues from clothing. Some analytical research has been done on pirimicarb. Cabras, Spandedda, Tuberoso, and Gennari (1989) used HPLC to separate pirimicarb and its major metabolites. No decontamination studies, however, have been found to date on work clothing contaminated with pirimicarb. This paper was part of a study to investigate the removal of pirimicarb residues from fabrics through laundering (Zhou, 1993). It was noted during the experiment that much pirimicarb was lost after initial contamination of fabrics and 24-hours of air drying in a fumehood. As pirimicarb is a highly toxic insecticide in wettable powder formulation, the purpose of this paper is to determine how much pirimicarb was lost after contaminated fabrics were exposed to air and to investigate the mechanism of the loss of pirimicarb. If the insecticide "dusted off" the fabrics, greenhouse workers could be at risk through inhalation of the powder.

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MATERIALS AND METHODS

The two fabrics used in this study were a bleached, mercerized 100% cotton purchased from Testfabrics, Inc. (style # 423) and 65/35 polyester/ cotton obtained from a U.S mill. These fabrics are similar in fiber content, fabric construction and mass to fabrics commonly found in the work clothing worn by pesticide applicators. The 100% cotton was a 3 x 1 twill weave with 45 x 23 yarns/cm, mass of 305 g/m^2 and thickness of 0.8 mm. The 65/35 polyester/cotton fabric was a 2 x 1 twill weave with 34 x 19 yarns/cm, mass of 270 g/m^2 and thickness of 0.7 mm (CAN/CGSB-4.2 No.5.1-M90; CAN/CGSB-4.2 No.37-M87; CAN/CGSB-4.2 No.6-M89 (IS0 7211/2-1984), Method C). The two fabrics were cut into specimens 8 cm square on the bias to prevent ravelling in laundering. Before contamination with pirimicarb, specimens were conditioned overnight in a standard atmosphere of 20 + 2°C and 65 + 2% relative humidity.

The insecticide pirimicarb, 2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyl dimethylcarbamate, (commercial Pirimor* 50WP produced by Chipman Inc.) was a wettable powder with 50.7% active ingredient measured by high performance liquid chromatography (HPLC). The powder has a vapor pressure of 4mPA at 30°C. Pirimicarb was applied to the fabrics at the dilutions recommended for field use, 0.5 mg/mL (0.025% active ingredient). The pirimicarb suspension was poured into a beaker and magnetically stirred during the contamination procedure.

The following procedure was used to contaminate fabrics with pesticide (Rigakis et al., 1987). Fifteen conditioned specimens of each fabric type (cotton or 65/35 polyester/cotton) were held horizontally on foil covered wires in a fumehood. Using a digital Eppendorf micropipette, 0.5 mL of diluted pirimicarb was deposited in the center of each fabric specimen. In order to determine the accuracy of the dilution and to calculate extraction efficiency, the pesticide mixture (0.5 mL) was also pipetted into each of three empty 500 mL Erlenmyer flasks. In addition, three specimens each of cotton and polyester/cotton were placed individually into 500 mL Erlenmyer flasks and contaminated with 0.5 mL diluted pirimicarb on the spiked-in-erlenmyer (SE) specimens relative to the mass of pesticide only (P) deposited in three empty flasks:

Extraction Efficiency (%) = 100 (SE/P)

Initially, it was noted that the unlaundered 100% cotton specimens contaminated with pirimicarb had only 67% pesticide residue remaining on them after contamination and air drying for 24 hours in the fumehood. It was expected that they would contain close to 100% of the pesticide that was pipetted onto them. Since the loss of 33% of the pesticide during the 24 hour drying period was unexpected and could not be explained, an additional set of experiments was done to determine whether the pesticide loss was due to a breakdown of the pirimicarb or whether the pesticide was lost to the air in the fumehood (the fan was left on during the 24 hour drying period). A second set of 100% cotton and 65/35% polyester/cotton specimens was contaminated with pirimicarb, one specimen per fabric type for each of the following drying conditions. Cotton and polyester/cotton specimens were contaminated in the usual manner while pinned to foil covered wires in the fumehood, then left on the wires with air movement for 1 day and 22 days. One specimen of each fabric type was also placed in an Erlenmyer flask, contaminated with pirimicarb, then closed with a Teflon-lined screw cap. These specimens had no air movement for 1 day and 22 days after contamination.

In order to extract pirimicarb from the specimens, pesticide grade acetone was added to each flask containing a specimen. Details of the extraction and analysis may be found in Zhou, 1993. To determine the pirimicarb residue in each flask, the residue was dissolved in 50:50 acetonitrile: buffer solution for injection into the HPLC instrument. The HPLC system used a SSI 220 B HPLC pump, automatic Rheodyne injection valve, a 25 cm x 2.1 mm ID Supercosil-18-DB analytical column covered with fiberglass and cotton insulation, a guard column, SSI 500 detector of variable UV/Visible light, and a computerized integrator (HP3396A). The conditions for the chromatography of pirimicarb were optimized from the research of Cabras and co-workers (1989). Supelco Canada recommended that 8 mM triethylamine be used in the buffer solution to solve peak tailing problems. Calibration graphs were obtained by using a series of dilutions of pure pirimicarb. The amount of pirimicarb (mg) was measured directly from the area of the peak due to the pesticide, taking the calibration factor into account. The detection limit of the instrument was 2.2×10^{-6} mg/mL for pirimicarb (5.5×10^{-7} mg per specimen). A standard solution was injected before and after duplicate specimen runs to confirm the retention time of pesticide peaks.

RESULTS AND DISCUSSION

The percent pirimicarb residue remaining on fabric specimens is listed in Table 1. After contamination and air drying for 24 hours, the pirimicarb residue in cotton

Table 1. Pirimicarb residue remaining after contaminated fabrics are air dried for 1 day and 22 days in fumehood or closed Erlenmyer flask.

Specimen (n=l)	One Day mg	%	Twenty-two Days mg	%
P[a]	0.1253	/		/
C-C[b]	0.0839	67	0.0631	50
C-SE[c]	0.1254	100	0.1291	100
PC-C[d]	0.0868	69	0.0600	48
PC-SE[e]	0.1262	100	0.1239	99

[a] p = "pesticide only", without fabric in flask.
[b] C-C = Cotton specimen, air dried in fumehood.
[c] C-SE = Cotton "spiked-in-Erlenmyer" specimen.
[d] PC-C = Polyester/cotton specimen, air dried in fumehood.
[e] PC-SE = Polyester/cotton "spiked-in-Erlenmyer" specimen.

and polyester/cotton specimens decreased to 67% and 69%, respectively, whereas the residue in "spiked-in-Erlenmyer" cotton and polyester/cotton specimens was 100%. After 22 days of air drying in the fumehood, 50% and 48% residues were found in cotton and polyester/cotton controls, respectively; however, the percent residue remaining in "spiked-in-Erlenmyer" specimens remained essentially the same, that is almost 100%. Therefore, the pirimicarb residue in specimens must be removed by the circulating air in the fumehood rather than chemical degradation, since the residue in specimens which were dried in closed Erlenmyer flasks did not decrease. This finding implies that pirimicarb residues in work clothing may "dust off" as the applicator works in the greenhouse. Hence, the workers, the worksite, and equipment could be directly and/or indirectly contaminated. In addition to dermal exposure to pirimicarb, greenhouse workers may inhale the pirimicarb residue that dusts off their work clothing. Respiratory protection for greenhouse workers becomes essential as they work in a confined space with less mixing of fresh air than out-of-door workers. Laughlin and Gold (1987) found that storage of methyl parathion contaminated cotton and 50/50 cotton/polyester for six months at 21°C with a constant exchange of air dissipated some 99% of the chemical. In this study, however, variables such as temperature and air exchange velocity were not investigated. No other researchers have reported similar experiments involving dispersion of pesticides to the air.

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