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Effect of Exposure Time on the Sorption of Pesticide Emulsifiable Concentrates through Microporous Fabrics

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The use of protective clothing for pesticide applications and handlers has been a topic of concern for over two decades. Research conducted by Maibach (1971) indicates that dermal sorption could account for up to 87% of the total sorption by the human body. Although researchers have proved that use of protective clothing can reduce dermal exposure, there is still a need for clothing that provides comfort, protection, and can be satisfactorily laundered (Langhlin 1986). Most previous studies conducted on Goretex fabrics used field strength pesticide solutions or emulsions (Branson et al. 1986, Easter 1983, Orlando et al. 1981) and some suggest that the above fabric type could provide adequate protection against a limited number of pesticides.

A study by Branson et al. (1988) was conducted on three-layer Goretex fabric with an outer layer of nylon rip stop and an inner layer of nylon tricot fabric. An emulsifiable concentrate was pipetted onto fabric specimens, and the samples were dried for 15 hours. Sunlight exposure tests, and the laundry tests were conducted on dried contaminated samples. The above procedure does not allow for excess pesticide to be removed to simulate rolling off of pesticide from the surface of a water-repellent fabric. Raheel (1988) studied pesticide penetration in fabrics, including water-repellent fabrics. Excess field strength pesticide solution or emulsion was rolled off from water-repellent fabrics after 20 minutes contact time, and the contaminated sample was then allowed to air dry for 12 - 14 hours. According to the procedure used by Kerschall et al. (1986) the excess field strength pesticide was rolled off after 10 seconds and the fabric were then allowed to air dry. The

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surfactant and solvent present in an emulsifiable formulation increase the wettability of a fabric by reducing the surface tension of the fabric and the pesticide solution (Langhlin et al. 1986). Use of emulsifiable concentrate, and the time for which the water-repellent samples are in contact with the pesticide concentrate could have a significant effect on the percentage of a pesticide sorbed by the fabric. For this study, to simulate accidental spills while mixing, pesticide concentrate was rolled off the fabric and the contaminated sample was then air dried, extracted and analysed. The objective of this research was to study the sorption of pesticide at different exposure times (contact time) from a method validation perspective. The exposure time for this study is defined as the "contact time" between the application of pesticide and removal of excess pesticide to simulate rolling off of pesticide concentrate from a water-repellent fabric.

MATERIALS AND METHODS

A three-factorial design was used for the study. The three factors were: a) two pesticides; b) four exposure times; and c) four fabrics.

Table 1. Physical characteristics of fabrics used for the study.

Fabric Code	Fabric Weight gm/m^2	Outer fabric characteristics		
		Fiber Content	Weave	Yarn Count yarns/cm
Polyester	178.0	Polyester	Plain	22 x 22
Nylon	226.8	Nylon	Plain	17 x 13
Acrylic	214.5	Acrylic	Plain	16 x 13
Commercial	251.0	Polyester	Plain	32 x 19

Ten yards each of acrylic, polyester, and nylon fabrics, were purchased from Testfabrics, Inc. The fabrics were laminated to polytetrafluoroethelyene membrane (PTFE), and then the outer fabric was treated with a water-repellent finish by W.L. Gore Co. The PTFE membrane had an oleophobic finish on the side that was not laminated to the fabric. In addition to the fabrics mentioned above, a commercial three-layer Gore Tex^{R} fabric was acquired having an outer layer of polyester taffeta and an inner layer of nylon tricot.

The commercial fabric also had a water-repellent

finish on the outer surface. The characteristics of the fabrics are given in Table 1.

Commercially available emulsifiable concentrates of Diazinon [0,0-diethyl-0-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate], 47.5% active ingredient, and chlorpyrifos [0,0-diethyl-0-(3, 5, 6-trichloro-2-pyridyl) phosphorothioate], 44.4% active ingredient, were used for the study. The label concentrations of active ingredient were checked and verified by gas chromatography.

One yard of each fabric was cut, after discarding the first and the last yard from each roll. Twenty centimeter strips along the selvedge were cut and discarded, and the remaining fabric was cut into 8x8 cm squares. The squares were then randomly selected for different exposure times and pesticides and coded according to each combination.

Fabric samples were placed on 10cm x 10cm foil covered tiles and 0.1 mL of the pesticide concentrate was applied by a constant-volume-micropipetter. The fabric samples were then allowed to remain in contact with the pesticide for 0, 10, 20, or 30 minutes after which the excess pesticide that was not sorbed by the fabric was removed with a disposable pipette. The pesticide stain was then dabbed twice with kimwipes.® In previous studies, excess field strength aqueous emulsions were rolled off (Raheel 1988 and Kerchall et al. 1986) from water-repellent fabric before the contaminated samples were allowed to air dry. In the preliminary tests, we observed that while rolling off excess pesticide, varying amount of pesticide concentrates adhered to the fabric. So, in order to reduce experimental variability, the disposable pipette method was used before the contaminated samples were air dried at room temperature for 12 to 24 hours. The above procedure was used to simulate accidential spill while mixing the pesticide in which the pesticide would roll-off from the surface of the water-repellent fabric. The 12 to 24 hours drying time was used to simulate pesticide drying on the garment before it was cleaned.

Each sample was then placed in a screw-top erlenmeyer flask and 50 mL of acetone was added by pipette. The flasks were placed in an orbital mechanical shaker for 45 minutes at 280 rpm. The extraction procedure was then repeated twice. A Hewlett-Packard 5890A gas chromatograph (GC) equipped with an N/P thermionic detector, a 7673A automatic sampler, and a series

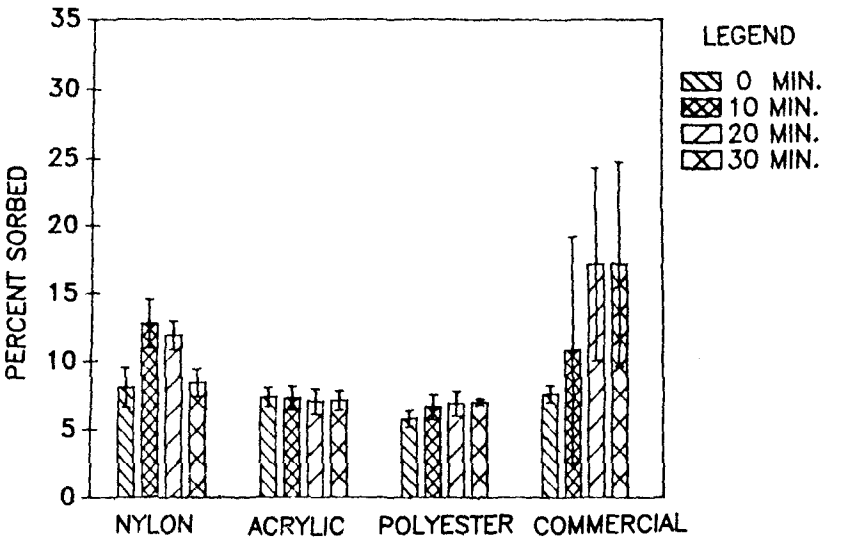

Figure 1. Mean and standard deviation of percent diazinon sorbed by water-repellent microporus fabrics at four exposure times.

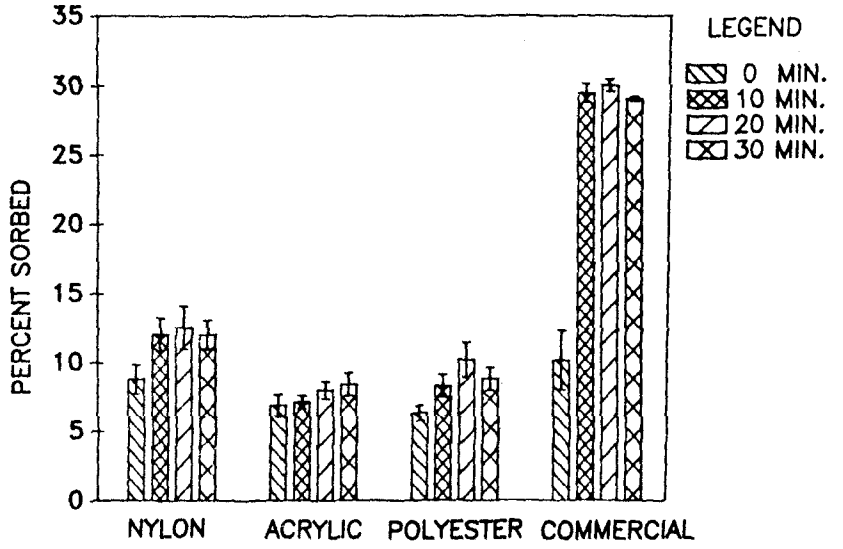

Figure 2. Mean and standard deviation of percent chlorpyrifos sorbed by water-repellent microporus fabrics at four exposure times.

9000, Model 300 data system was used for the analysis of all extracts. The GC was fitted with a J&W DB-608 large-bore capillary column (0.53 mm I.D. x 30m) maintained at 190°C for both pesticides. The injection port temperature was set to 210°C for diazinon and 220°C for chlorpyrifos. The detector was maintained at 250°C for all runs. Helium carrier gas was used at a flow rate of 20 mL/min at a head pressure of 210 kPa. Flowrates for the detector gases were set according to the manufacturers recommendations - 3.5 mL/min (H_2) and 120 mL/min (air) which is essential for proper operation of the detector. The detector bead-heating current was adjusted to obtain a baseline signal of 20 units on the display panel. Under these conditions, the retention times were 3.2 minutes for diazinon and 6.9 minutes for chlorpyrifos.

For each determination, a 1 mL aliquot of the acetone extract was transferred to a 2 mL crimp-sealed auto-injector vial with the injector syringe set for 2 uL. Quantitation was normally obtained by software comparison of sample peak areas with the peak area of an external standard (99.8% pure, EPA, RTP; 10 ng/uL in acetone) contained in a previously prepared calibration table which was updated prior to each series of sample runs. Measured pesticide concentrations in ng/uL were first converted to total mg recovered and then to percent of applied amounts after correcting for the weight percent of active ingredient and liquid density in each emulsifiable concentrate.

RESULTS AND DISCUSSION

As seen in Figs. 1 and 2, there was very litte difference between pesticide sorbed by acrylic and nylon at various exposure times. The standard deviation for 10, 20, 30 min exposure times for the commercial fabric was very high (Fig. 1). This was due to one or two extremely low readings for each of the three exposure times. During the application of pesticide to the fabric, visual observations were made and any variation in the drop sorption was recorded. When chlorpyrifos was applied to commercial fabric, it was noted that there was a variation in the sorption rate of pesticide within the same treatment. This variation could be due to inconsistency in the water-repellent finish on the fabric.

The percent of pesticide sorbed was least when excess pesticide was removed immediately after application (Table 4). In all fabrics except commercial

Table 2. Analysis of variance of percent pesticide sorbed by four fabrics with four exposure time.

Source of Variation	d.f.	F-Value	Prob > F
Fabric	3	181.81[a]	0.0001
Pesticide	1	83.34[a]	0.0001
Exposure Time	3	35.77[a]	0.0001
Fabric*Pesticide	3	41.80[a]	0.0001
Fabric*Exposure Time	9	14.79[a]	0.0001
Pesticide*Exposure Time	3	5.67[a]	0.0001
Fabric*Pesticide *Exposure Time	9	4.45[a]	0.0001

[a]Indicates significance at 0.01 level

Table 3. Student-Newman-Keuls multiple range test between exposure time of four different fabrics.

Polyester				
Exposure Time (Minutes)	20	30	10	0
Mean Percent Values	8.53	7.88	7.43	6.03
Acrylic				
Exposure Time (Minutes)	30	20	10	0
Mean Percent Values	7.72	7.50	7.17	7.08
Nylon				
Exposure Time (Minutes)	10	20	30	0
Mean Percent Values	12.42	12.23	10.22	8.44
Commercial Polyester				
Exposure Time (Minutes)	20	30	10	0
Mean Percent Values	23.61	23.15	10.16	8.87

Note: There was no signficant difference between values underlined by the same line.

polyester, there was no signficant difference between the other three exposure times (Table 3). The acrylic and polyester fabrics used for the study seem to be most consistent.

As seen in Figs 1 and 2, the percent chlorpyrifos sorbed by the commercial fabric is higher than the percent diazinon. The mean values for the amount of diazinon sorbed by fabrics were significantly different from those of the amount of chlorpyrifos sorbed (Table 4). The significant difference between pesticides could be due to the inert ingredients (e.g. surfactants used) or due to the differences in electrostatic attraction between fabrics and pesticides.

Table 4. Student-Newman-Keuls multiple range test results.

Between fabrics				
Fabric	Acrylic	Polyester	Nylon	Commercial
Mean Percent Values	7.37	7.47	10.83	18.95
Between exposure time				
Exposure Time (Minutes)	20	30	10	0
Mean Percent Values	12.97	12.24	11.79	7.61
Between pesticide				
Pesticide		Diazinon		Chlorpyrifos
Mean Percent Value		12.99		9.31

Note: There was no significant difference between values underlined by the same line.

Based on the results of the study, 10 minutes exposure time is recommended for pipette drop method of applying pesticide on water-repellent fabrics.

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