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Statistical Model for Predicting Pesticide Penetration in Woven Fabrics Used for Chemical Protective Clothing

X. Zhang, M. Raheel

Department of Natural Resources and Environmental Sciences, University of Illinois at Urbana-Champaign, 905 South Goodwin Avenue, Urbana, IL 61801, USA

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Occupational exposure of skin to pesticides is a major health hazard among agriculturists. Workers commonly wear conventional work clothing (long sleeved shirts and jeans or work pants) when applying pesticides. Much of the research in pesticide protective clothing has centered on the barrier effectiveness of protective clothing by examining the influence of fabric characteristics. However, variations in barrier properties were also shown to be pesticide-specific. No one fabric has been identified that offers 100% protection against all pesticides in various formulations and concentrations. In general, fabric penetration studies have shown that fabric characteristics, liquid characteristics, and the combination of both are critical for understanding pesticide solution penetration of porous materials. (Hsieh, 1995; Miller and Schwertz, 2000; Raheel, 1988 and 2000) Although a fabric-by-pesticide matrix that would summarize the research findings is highly desirable, however, with numerous fabric variations compounded by hundreds of pesticide chemicals and formulation variations, and different methodologies used for assessing barrier properties, it is difficult to make appropriate recommendations regarding protective clothing.

Thus, there is a need for predictive models to estimate protective clothing material performance and eventually provide recommendations for the types of materials for dermal protection from chemicals, as well as thermal comfort. The model should be simple to use; be applicable to a wide range of pesticide mixture combinations; be truly predictive, that is, applicable to new fabrics/chemicals; and not require data other than those readily available or measured by simple reproducible tests (Goydan et al., 1988).

A predictive model has been developed for non-woven fabrics (Lee and Obendorf, 2001), but since workers commonly wear conventional clothing made of woven fabrics when applying pesticides, it is reasonable to develop a predictive statistical model for commonly used woven fabrics.

MATERIALS AND METHODS

According to the USDA Agricultural chemical usage field crops summary (1998), atrazine, (2-chloro-4-ethylamine-6-isopropylamino-s-triazine and pendimethalin

Correspondence to: M. Raheel

(N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine) are two of the most widely used pesticides. We selected atrazine as flowable liquid (Aatrex® 4L) and water dispersible powder (Atrazine 90W), and pendimethalin as an emulsibiable concentrate (Prowl® 3.3) formulation. Survey of work clothing store catalogs showed that cotton and cotton/polyester fabrics are commonly used for work clothing. As a result, cotton and cotton/polyester plain and twill weave fabrics were selected to represent the population of commonly used fabrics. Pesticide and fabric characteristics are given in Tables 1 and 2.

Table 1. Physical and chemical properties of the pesticides.

Trade Name	Active Ingredient	% Active Ingredient	Type of Formulation	Mixing Rates		Solubility in water mg/L
				Formula-tion	H_2O	
Aatrex 4L	Atrazine	43.0	Flowable Liquid	14.73 g	100 mL	33
Atrazine 90	Atrazine	85.5	Water Dispersible Powder	1.02 g	100 mL	33
Prowl 3.3	Pendimeth -alin	37.4	Emulsifiable Concentrate	50 mL	50 mL	0.275

Table 2. Fabric characteristics.

Fabric Code	Fabrics	Thick -ness mm	Weight g/m^2	Fiber Density g/cm^3	Solid Volume Fraction	Air Permeability $cm^3/cm^2.sec$
419	Cotton broad cloth	0.215	115	1.52	0.352	36.69
423	Cotton twill	0.495	295.1	1.52	0.392	8.11
7402	PET/Cott 65/35 poplin	0.274	180	1.4355	0.458	10.83
4	PET/Cott 65/35 twill	0.451	257	1.4355	0.397	10.66

Data for fabric surface energy were obtained from literature (Mark, 1996). Air permeability of each fabric was measured according to ASTM D 757-75 (2001), at 21^0C and 65% RH. Water vapor transmission rate was measured using the water method specified in ASTM E 96-95 (2001). Pesticide solutions or emulsions were prepared in different mixing rates at the recommended field rates of each pesticide. Pesticide characteristics including viscosity and surface tension were measured for each pesticide solution. Kinematic viscosity of pesticide solutions was measured according to ASTM D 445-93 (2001), the dynamic viscosity was obtained by multiplying the measured kinematic viscosity by the density of the liquid. Surface tension of the pesticide solutions was measured according to ASTM D1331-89 (2001).

Pesticide repellency, retention and penetration were measured according to ASTM F2130-01(2001), Standard Test Method to Measure Penetration of Liquid Pesticides through Protective Clothing Materials, using a layered fabric assembly. The top layer was the test specimen, the bottom layer was an absorbent collector layer (Benchkot Plus). Two methods of analysis were used for assessing pesticide penetration, gas chromatographic (GC) and gravimetric analyses. Only penetration data are reported here. For GC analysis percentage pesticide penetration was calculated using the following equation:

$$\text{Percent Penetration} = M_p \times 100/M_t \qquad [1]$$

Where,
M_t = total known mass of pesticide applied to the test specimen
M_p = mass of pesticide extracted from the collector layer
Mass of pesticide for M_p was calculated by measuring the concentration of pesticide active ingredient in the collector layer extract by gas chromatography.

For gravimetric method, percent pesticide penetration was calculated using the following equation:

$$\text{Percent Penetration} = M_p \times 100/M_t \qquad [2]$$

Where,
M_t = total known mass of pesticide applied to the test specimen
M_p = weight change of the collector layer after contamination of test specimen

Statistical analyses were performed on textile and pesticide mixture parameters and penetration data, using the SAS system. Multiple linear and multiple polynomial regression analyses were performed. Surface tension difference (γ_{diff}), viscosity of pesticide solutions (η), thickness of fabrics (t) and solid volume fraction of the fabrics (v) were used as independent variables. Percentage penetration obtained from GC analysis (P1) and gravimetric analysis (P2) were used as dependent variables. Stepwise selection method was used to select the optimum subsets from the independent variables.

RESULTS AND DISCUSSION

Critical surface tension of polyester, cellulose, and 65/35 cotton –polyester blend were 43, 44, and 43.35 mN/m respectively (Mark, 1996). The surface tension difference was calculated using the following equation:

$$\gamma_{diff} = \gamma_S - \gamma_L \qquad [3]$$

Where,
γ_{diff} = the surface tension difference (mN/m)
γ_S = the critical surface tension of a given solid (mN/m)
γ_L = the surface tension of pesticide solution (mN/m)
The values of each fabric- pesticide pair are shown in Table 3.

Table 3. Surface tension difference.

Fabric	Pesticide	γ_S (mN/m)	γ_L (mN/m)	γ_{diff} (mN/m)
419	F1, Aatrex 4L	44	29.12	14.88
419	F2, Atrazine 90	44	41.45	2.55
419	F3, Prowl 3.3	44	23.39	20.61
423	F1, Aatrex 4L	44	29.12	14.88
423	F2, Atrazine 90	44	41.45	2.55
423	F3, Prowl 3.3	44	23.39	20.61
7402	F1, Aatrex 4L	43.35	29.12	14.23
7402	F2, Atrazine 90	43.35	41.45	1.9
7402	F3, Prowl 3.3	43.35	23.39	19.96
4	F1, Aatrex 4L	43.35	29.12	14.23
4	F2, Atrazine 90	43.35	41.45	1.9
4	F3, Prowl 3.3	43.35	23.39	19.96

Table 4. Fabric/ pesticide parameters and penetration (%) of pesticide solution.

Fabric	Pesti-cide	γ_{diff} mN/m	Viscosity η mPa·s	SolidVolume Fraction, v	Thick-ness,t mm	Penetration GC P1	Penetration Gravimetric P2
419	F1	14.88	2.18	0.352	0.215	64.285	64.45
419	F2	2.55	1.31	0.352	0.215	46.239	66.883
419	F3	20.61	12.88	0.352	0.215	74.166	63.27
423	F1	14.88	2.18	0.392	0.495	13.327	11.8
423	F2	2.55	1.31	0.392	0.495	14.465	37.69
423	F3	20.61	12.88	0.392	0.495	33.854	35.845
7402	F1	14.23	2.18	0.458	0.274	11.302	28.743
7402	F2	1.9	1.31	0.458	0.274	24.384	59.58
7402	F3	19.96	12.88	0.458	0.274	33.899	44.893
4	F1	14.23	2.18	0.397	0.451	8.256	24.793
4	F2	1.9	1.31	0.397	0.451	34.899	65.883
4	F3	19.96	12.88	0.397	0.451	3.486	15.197

Penetration (%) of liquid pesticides through protective clothing materials obtained for each set of fabric/pesticide parameters tested are presented in Table 4.

Regression model: To determine the characteristics for each parameter that significantly influenced the penetration phenomena, regression analyses were performed using the established categories (Table 4). Percent penetration (P1 and P2) were the dependent variables. Stepwise selection procedure was used in the multiple linear regression model to select a most useful subset of the independent variables. Since the plot of percent penetration versus each variable suggested a linear model might be insufficient to describe the model, quadratic terms of each variable also were included when applicable.

Model for Gas Chromatographic Analysis, P1: In selection step 1, variable thickness (t) was entered, and the following regression equation resulted in an R-Square value of 0.4287 :

$$P1 = -119.8\,t + 73.2 \qquad [4]$$

In step 2, variable solid volume fraction (ν) was added to the model which increased the R-Square to 0.7080. All variables left in the model are significant at P< 0.15 level, no other variable met the P< 0.15 significance level for entry into the model. So, the final model selected for P1 is as follows :

$$P1 = -116.5\,t - 299.4\,\nu + 191.7 \qquad [\text{Model } 1]$$

The regression analysis indicates that fabric thickness and solid volume fraction are parameters significantly influencing pesticide penetration phenomenon. It also shows that fabric thickness is the most influential. Both fabric thickness and solid volume fraction are negatively related with pesticide penetration. The R-Square is 0.7080, which indicates that model 1 is fairly good. The viscosity of the pesticide solution and surface tension difference were insignificant at the P< 0.15. This indicates that probably the viscosity range of pesticide mixtures was not wide enough, and the fabric/pesticide critical surface tension difference was not reached in this study.

Model for Gravimetric Analysis, P2: In selection step 1, variable thickness (t) was entered, and the following regression equation resulted in an R-Square of 0.4211:

$$P2 = -108.5\,t + 82.2 \qquad [5]$$

In step 2, variable surface tension difference (γ_{diff}) was added into the model which increased the R-Square value to 0.6100.

$$P2 = -108.6\,t - 1.1\,\gamma + 96.1 \qquad [6]$$

In step 3, the square of variable surface tension difference ($\gamma_{diff}^{\,2}$) was entered which brought R-Square to 0.7361.

$$P2 = -108.5\,t - 5.7\,\gamma + 0.2\,\gamma^2 + 108.2 \qquad [7]$$

In the final step, variable Viscosity (η) was entered which increased R-Square to 0.8369. All variables left in the model were significant at the P< 0.15; no other variable met the $P< 0.15$ significance level for entry into the model, so the final model for P2 is:

$$P2 = -107.7\,t - 23\,\gamma + 1.3\,\gamma^2 - 11.2\,\eta + 155.4 \qquad [\text{ Model 2 }]$$

The regression analysis indicates that the linear terms of fabric thickness, viscosity of pesticide solution, and surface tension difference, are the parameters significantly influencing pesticide penetration phenomenon. It also shows that fabric thickness is the most influential, followed by the linear and quadratic term of surface tension difference, and viscosity of pesticide solution. The linear terms of fabric thickness, viscosity of pesticide solution, and surface tension difference are negatively related with pesticide penetration. The quadratic term of surface tension difference has negative relationship with penetration. The solid volume fraction is insignificant at the $P< 0.15$. Since we used only limited fiber types, and fabric geometries, the data might be insufficient to show the significance of solid volume fraction on pesticide penetration. However, the model has R-Square value of 0.8369, showing that it is a good model.

Comparison of Gas Chromatographic Analysis and Gravimetric Analysis:
Gravimetric analysis is considered as a substitute for gas chromatographic analysis because it is easy to implement and a less expensive method. However, the results of the two methods are not well correlated. Gravimetric analyses generally showed higher percentage penetration values than gas chromatographic analyses (Table 4). Since gravimetric analysis calculates percentage penetration of the weight of the pesticide solution, while gas chromatographic analysis calculates the percentage penetration of the weight of the active ingredient only, it suggests that the penetrated pesticide solution has lower concentration than that of the pesticide solution applied. That is, the test fabric (top layer) acts as a filter and retains the active ingredient. Thus the gravimetric analysis overestimates the actual pesticide penetration.

Thermal Comfort Property and Fabric Protection Performance:
Percentage protection of each fabric against pesticide penetration as well as air - permeability and rate of water vapor transmission data are given in Table 5. The protection property was calculated as follows:

$$\text{Protection (\%)} = 100 - \text{Percentage penetration (\%)} \qquad [\ 8\ ]$$

Correlation between air permeability and water vapor transmission of fabrics and % protection is given in Table 6. The comfort performance of fabrics is related to transport properties of fabrics, which include total thermal resistance, vapor evaporation, and air permeability, and it is evaluated fundamentally by a combination of these properties. Air permeability is responsible for ventilation functions of materials. The air permeability of fabrics depends predominantly on their structure, (Sun, G. et al., 2000). In general, a negative relationship between

Table 5. Air permeability , water vapor transmission, and % protection of fabrics.

Fabric code	Fabric Air-permeability $cm^3/cm^2.sec$	Fabric Water -vapor transmission $g/h.m^2$	Pesticide	Percentage protection GC	Percentage protection Gravimetric
419	36.69	25.0	F1	43.185	35.55
			F2	53.760	33.12
			F3	60.692	36.73
423	8.11	24.56	F1	88.225	88.20
			F2	85.533	62.31
			F3	82.058	64.15
7402	10.83	42.97	F1	90.011	71.26
			F2	75.614	40.42
			F3	82.033	55.11
4	10.66	58.74	F1	92.703	75.20
			F2	65.103	34.12
			F3	98.153	84.80

Table 6. Correlation coefficients between protection performance and thermal comfort parameters for untreated fabrics.

Thermal comfort parameters	Correlation coefficient	
	%Protecion, GC	%Protection, Gravimetric
Air permeability	-0.84369	-0.65722
Water vapor transmission	0.43868	0.21727

fabric protection performance and air permeability (R^2, -0.84) was found, that is, barrier performance dropped with increased air permeability of fabric. This result is consistent with previous research (Wadsworth et al., 1988). Under conditions of heat stress, vapor permeability of clothing also is important since it allows evaporation of perspiration, thus providing cooling. As indicated in Table 6, a weak positive correlation (R^2, 0.44; 0.22) exists between water vapor transmission and protection performance of the fabrics in this study. As shown earlier, pesticide penetration also is largely dependent on fabric thickness and solid volume fraction, which are dominant components in fabric structure. Therefore, the high correlation between air permeability attributed to the structural features and protection can be used to predict barrier function of non-repellent finished woven fabrics. On the other hand, vapor transmission of materials is affected not only by fabric structure, but also fiber chemistry. Thus, it is reasonable to explain that vapor transmission and protection performance exhibited less correlation than air permeability with protection performance.

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