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Barrier Efficacy of Woven and Nonwoven Fabrics Used for Protective Clothing: Predictive Models

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Exposure of skin to pesticides is a major health hazard among agricultural workers. The Environment Protection Agency (EPA) estimates that in the farm sector alone, some 560,000 sites such as farms, forests, and greenhouses have workers who come in contact with pesticides during their workday (US EPA, 1992). Workers commonly wear conventional clothing (long sleeved shirts and jeans or work pants) and occasionally, use disposable protective clothing made of non-woven fabrics when applying pesticides. In general, fabric penetration studies have shown that fabric characteristics, liquid characteristics, and the combination of both are critical for understanding pesticide solution penetration in porous materials (Miller and Schwertz 2000; Raheel 1988, 2000; Lee and Obendorf 2001). Due to the variety and complexity of pesticide formulations and mixtures, as well as the variety of fabrics, there is a need for predictive models to estimate protective clothing materials' performance for screening purposes. Such information may be used to provide recommendations for the types of materials for chemical protective clothing. Previous work done in our laboratory reported a predictive model for woven fabrics only (Xhang and Raheel 2003). This research expands upon the previous work and includes a wider range of woven fabrics, a variety of non-woven fabrics, as well as a range of pesticide variables, in an attempt to develop statistical predictive models. Additionally, the predictive models are validated with actual laboratory data.

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 (N- (1-ethylpropyl)-3,4-dimethryl-2, 6-dinitrobenzenamine) are widely used for control of broadleaf and grassy weeds in many crops. We selected atrazine in flowable liquid formulation (Aatrex ® 4L) and pendimethalin as an emulsifiable concentrate (Prowl® 3.3). Aatrex 4L, from Syngenta Crop Protection Inc., Greensboro, NC contained 43.0% atrazine active ingredient. Prowl® 3.3 EC, from BASF, Princeton, NJ. contained 37.4 % pendimethalin active ingredient. Pesticide characteristics are listed in Table 1. Pesticide solutions were prepared in different mixing rates at the recommended field rate of each pesticide. Adjuvants were used to modify surface tension and viscosity of solutions as shown in Table 2.

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Triton X100®, a non-ionic surfactant from Rohm and Haas was used to modify the surface tension of pesticide solutions. Acrysol®, a commonly used thickener in textile finishes, also from Rohm and Haas, was used to modify the viscosity of pesticide solutions as suggested by previous work (Xhang and Raheel, 2003). Pesticide characteristics including viscosity and surface tension were measured according to the standard methods of the American Society for Testing and Materials (ASTM, 2001). The viscosity and surface tension of pesticide solutions is shown in Table 2.

Table 1. Characteristics of pesticides.

Trade Name	Active Ingredient	Mixture Code	Mixing Rates			
			Pesticide	Distilled Water	TritonX 100	Acrysol
Prowl 3.3 (P1)	Pendime-thalin 37.4 %	P1L1	50ml	50ml	0.0 ml	0.0 ml
		P1L2	50ml	50ml	2.0 ml	0.0 ml
		P1L3	50ml	50ml	2.0 ml	1.0 ml
Aatrex 4L (P2)	Atrazine 43.0 %	P2L1	14.79g	100ml	0.0 ml	0.0 ml
		P2L2	14.73g	100ml	2.0 ml	0.0 ml
		P2L3	14.73g	100ml	2.0 ml	1.0 ml

Table 2. Viscosity and surface tension of pesticide solutions.

Pesticide	Kinematic Viscosity mm^2/s	Density g/cm^3	Dynamic Viscosity mPa.s	Surface Tension mN/m
Prowl 3.3 P1L1	7.96	1.01	8.03	24.02
Prowl 3.3 P1L2	12.14	1.01	12.26	24.61
Prowl 3.3P1L3	46.09	1.01	46.55	30.39
Aatrex 4L P2L1	1.43	1.12	1.60	26.71
Aatrex 4L P2L2	1.86	1.12	2.08	29.10
Aatrex 4L P2L3	12.04	1.12	13.48	29.20

Survey of work clothing store catalogs revealed that cotton and cotton/polyester fabrics were commonly sold for work clothing. Also, a wide range of non-woven disposable garments, made of different fiber types is available. Consequently, we selected eight cotton and cotton/polyester plain, and twill weave fabrics, and eight different types of non-woven fabrics to represent the population of commonly used fabrics. Fabric parameters including fabric thickness, weight, solid volume fraction, surface energy, air permeability, and water vapor transmission rate were characterized using standard methods of the American Society for Testing and Materials (ASTM, 2001). Fabric parameters are summarized in Table 3.

Table 3. Fabric characteristics.

Fabric Code	Fabrics	Yarn Density (Yarn/cm)		Fabric Weight gm/m^2	Fabric Thick-ness, mm	Fiber Density g/cm^3	Solid Volume Fraction	WVT* $g/h.m^2$	Air-perm-eability $cm^3/cm^2.s$	Surface Energy mN/m
		Warp	Weft							
Woven fabrics										
A	Polypropylene, plain	20	14	188.86	0.46	0.92	0.446	2002.8	25	29
B	Cotton, print cloth	43	27	108.09	0.21	1.52	0.339	1790	67	44
C	Polyester, plain	18	15	174.42	0.36	1.38	0.351	1994.2	105	43
D	Cotton, broadcloth	54	28	121.95	0.21	1.52	0.382	2002.8	35	44
E	Cotton, twill	40	24	245.72	0.41	1.52	0.394	1823	8	44
F	Cotton, poplin	46	26	172.71	0.27	1.52	0.421	2137	14	44
G	Cot/Poly, sheeting	26	23	151.82	0.3	1.43	0.353	1807.6	70	43.35
H	Cot/Poly,broadcloth	54	28	100.99	0.18	1.43	0.391	1942.9	42	43.35
Non-woven fabrics										
I	Polyethylene	-	-	38.36	0.14	0.97	0.282	NA	NA	31
J	Polypropylene	-	-	98.88	0.37	0.92	0.290	1702	NA	29
K	Polypropylene	-	-	78.39	0.29	0.92	0.294	1446.5	NA	29
L	Woodpulp/Polyester	-	-	67.58	0.21	1.38	0.233	2120.2	60	43
M	Polyester	-	-	69.74	0.25	1.38	0.202	2019.9	141	43
N	Polypropylene	-	-	55.82	0.26	0.92	0.233	1856.1	37	29
O	Polypropylene	-	-	58.55	0.24	0.92	0.265	1651.9	NA	29
P	Polypropylene	-	-	62.82	0.21	0.92	0.325	42.79	NA	29

*WVT= Water Vapor Transmission

Pesticide retention and penetration in fabrics were measured according to ASTM method F 2130-01(2001), using a layered fabric assembly as described in our earlier report (Xhang and Raheel 2003). The top layer was the test specimen and the bottom layer was an absorbent collector layer. Pesticide penetration was calculated by gravimetric method from weight change of the collector layer after contamination of the test specimen.

RESULTS AND DISCUSSION

Pesticide penetration data of all 16 fabrics, using Prowl and Aatrex (P1 and P2), pesticides in 3 mixture compositions (L1, L2, and L3) are shown in Table 4.

Table 4. Pesticide penetration (%) in fabrics.

Fabric	Prowl 3.3			Aatrex 4L		
	P1L1	P1L2	P1L3	P2L1	P2L2	P2L3
A	51.79	62.73	63.35	62.67	62.85	54.86
B	71.02	75.09	75.14	81.84	75.81	84.74
C	70.35	71.35	70.84	84.75	68.4	83
D	65.9	74.51	82.06	75.65	76.11	73.8
E	40.58	42.13	46.57	33.12	32.95	26.88
F	69.85	61.86	73.53	71.69	69.68	73.17
G	68.16	69.64	74.96	85.38	78.63	72.71
H	82.99	81.04	84.35	88.86	82.51	83.78
I	35.01	40.64	13.98	5.11	25.19	16.9
J	7.64	5.91	8.22	9.92	8.53	5.69
K	10.13	11.79	9.24	12.23	11.35	12.51
L	64.73	66.65	59.76	64.65	66.36	62.9
M	83.65	82.81	71.43	79.03	83.8	75.88
N	86.48	66.43	72.27	63.18	75.65	78.84
O	1.03	0.72	2.65	4.77	5.59	5.56
P	3.19	2.66	1.24	0.17	0.53	3.23

Regression analyses were performed using the SAS® system (SAS Institute, 2000) to determine the characteristics of fabrics and pesticide solutions that influenced liquid penetration in fabrics. Also, correlation coefficients between % liquid penetration and fabric/ liquid parameters were obtained and are given in Table 5. The data indicated that surface tension difference, water vapor transmission, and air-permeability were significantly correlated with liquid penetration; solid volume fraction and fabric thickness showed lower correlation coefficients.

Regression analyses were performed using the established parameters (Table 5) to determine which parameter significantly influenced liquid penetration. Liquid penetration was the dependent variable. Stepwise selection procedure of the SAS® system (SAS Institute, 2000) was used in the multiple linear regression models to select a most useful subset of independent variables. All variables left in the models were significant at the $p < 0.15$.

Table 5. Correlation coefficients between % penetration and fabric/pesticide parameters.

Fabric/Pesticide Parameters	% Penetration	
	Correlation Coefficient	P Value
Surface Tension Difference	0.60831	<0.0001
Viscosity	-0.00819	0.9369
Solid Volume Fraction	0.20818	0.0418
Fabric Thickness	-.04988	0.6294
Water Vapor Transmission	0.65115	<0.0001
Air Permeability	0.48507	<0.0001
SurfaceTension of Pesticide	-0.00016	0.9987

In selection step 1, variable thickness (t) was entered in the model, resulting in the following regression equation with R-square value of 0.3861:

$$P = -95.48\ (t) + 97.05 \qquad \text{[Step 1, Model 1]}$$

In step 2, variable air permeability (a) was added in the model, which resulted in R-square value of 0.5187:

$$P = -83.62\ (t) + 0.12\ (a) + 86.57 \qquad \text{[Step 2, Model 1]}$$

In step 3, solid volume fraction (ν) was added in the model, which increased the R-square value to 0.6022:

$$P = -103.26\ (t) + 0.20\ a + 67.99(\nu) + 64.75 \quad \text{[Step 3, Model 1]}$$

In step 4, surface tension difference (γ_{diff}) was added in the model, which increased the R-square value to 0.7391:

$$P = -138.64\ (t) + 0.26\ (a) + 101.79\ (\nu) - 0.99\ (\gamma_{diff}) + 73.69 \qquad \text{[Step 4, Model 1]}$$

In the final step, surface tension of pesticide (γ_{liq}) was added in the model, which gave R-square value of 0.7571. Therefore, the final model [Step 5, Model 1] is:

$$P = -145.10\ (t) + 0.27\ a + 107.96\ (\nu) - 1.17\ (\gamma_{diff}) - 0.82\ (\gamma_{liq}) + 98.01$$

Regression analyses indicated that linear terms of fabric thickness, surface tension difference and surface tension of pesticide solution were negatively related with pesticide penetration. Whereas, linear terms of fabric solid volume fraction and air permeability were positively related with pesticide penetration.

In order to select the most appropriate model among steps 1-5, we compared the actual laboratory liquid penetration data with the calculated data from the predictive models. The results of one pesticide solution (P1L1) on all 16 fabrics

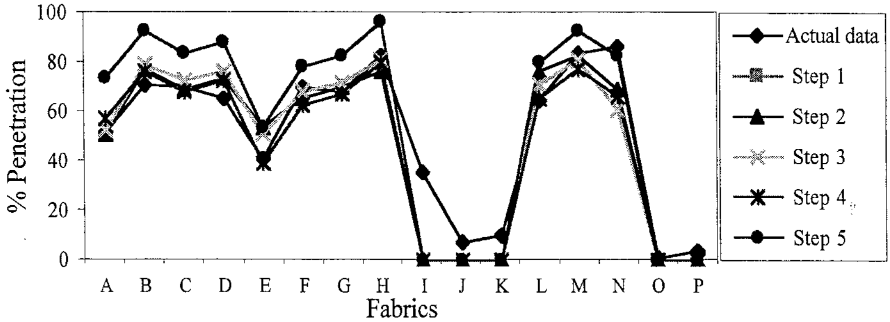

Figure 1. Prowl (P1L1) penetration data and step 1 to 5 SAS calculated data.

Table 6. Prowl (P1L1) penetration data and step 1 to 5 SAS calculated data.

Fabric	Actual % Penetration	SAS Step 1	SAS Step 2	SAS Step 3	SAS Step 4	SAS Step 5
A	51.79	140.97	51.10	52.59	56.91	73.84
B	71.02	117.10	77.04	79.48	76.68	92.28
C	70.35	131.42	69.06	72.44	68.02	83.29
D	65.9	117.10	73.20	76.04	72.78	88.33
E	40.58	13620	53.24	50.82	39.28	53.34
F	69.85	122.83	65.67	68.28	62.95	78.14
G	68.16	125.69	69.88	71.74	67.04	82.29
H	82.99	114.23	76.55	81.13	80.30	96.28
I	35.01	110.41	-	-	-	-
J	7.64	132.38	-	-	-	-
K	10.13	124.74	-	-	-	-
L	64.73	117.10	76.21	70.92	65.12	80.18
M	83.65	120.92	82.58	80.87	77.47	92.89
N	86.48	121.87	69.27	61.17	66.08	83.11
O	1.03	119.96	-	-	-	-
P	3.19	117.10	-	-	-	-

\- = Not Measurable

are shown in Figure 1, and Table 6, as an example. Figure 1 shows that the models in steps 2, 3, and 4 are very close to the actual data. Where as, step 1 is off the chart, and step 5 gave values widely different than the actual data. Among the models in steps 2, 3,and 4, the model in step 4 fits the actual data curve most closely. Therefore, we selected step 4 as a general predictive model for woven and non-woven fabrics in this study. The final model is:

$$P = -138.64\ (t) + 0.26\ a + 101.79\ (v) - 0.99\ (\gamma_{diff}) + 73.69 \qquad \text{[Step 4, Model 1]}$$

We observed that some non-woven fabrics of low thickness also showed low level of liquid penetration. This conflicts with the findings of the predictive model in step 4. Since all woven and four of the non-woven fabrics were porous, the main mechanism of penetration in these fabrics is bulk flow of liquid. This mechanism is not applicable to non-woven fabrics that were coated with a monolithic film; permeation (transport at molecular level) may be a more feasible mechanism. Permeation testing was not within the scope of these experiments. Therefore, it is appropriate to analyze the data of woven and non-woven fabrics separately.

For woven fabrics, correlation coefficients between fabric/pesticide parameters and liquid penetration are shown in Table 7. Fabric thickness, air permeability and solid volume fraction showed significant correlation coefficients at $p < 0.15$.

Table 7. Correlation coefficients between % penetration and woven fabric/pesticide parameters.

Fabric/Pesticide Parameters	% Penetration	
	Correlation Coefficient	P Value
Surface Tension Difference	0.14514	0.3250
Viscosity	0.04486	0.7621
Solid Volume Fraction	-0.37710	0.0082
Fabric Thickness	-0.69347	<0.0001
Water Vapor Transmission	0.15331	0.2982
Air Permeability	0.53330	<0.0001
SurfaceTension of pesticide solution	0.10163	0.4919

Regression analyses were performed using the established parameters given in Table 7. Stepwise selection procedure was used as described earlier, to select a most useful subset of independent variables.

In selection step 1, variable fabric thickness (t) was entered, and the following regression equation resulted in an R-square value of 0.4809:

$$P = -106.18\,(t) + 100.88 \qquad \text{[Step 1, Model 2]}$$

In selection step 2, air permeability (a) was entered, and the following regression equation resulted in an R-square value of 0.6707:

$$P = -96.22\,(t) + 0.20\,(a) + 88.31 \qquad \text{[Step 2, Model 2]}$$

In selection step 3, solid volume fraction (v) was entered, and the following regression equation resulted in an R-Square value of 0.8521:

$$P = -134.79(t) + 0.47(a) + 329.56(v) - 39.06 \qquad \text{[Step 3, Model 2]}$$

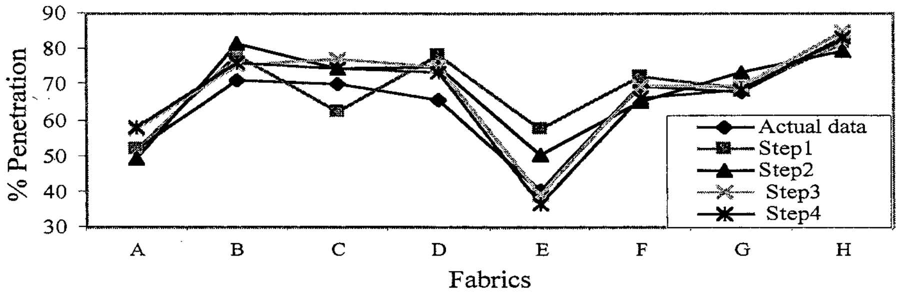

Figure 2. Pesticide P1L1 penetration data and step 1 to 4 SAS calculated data

Table 8. Pesticide P1L1 penetration data and step 1 to 4 SAS calculated data.

Fabric	Actual % Penetration	SAS Step1	SAS Step2	SAS Step3	SAS Step4
A	51.79	52.03	49.04	57.67	58.03
B	71.02	78.58	81.50	75.84	76.38
C	70.35	62.65	74.67	77.44	74.39
D	65.9	78.58	75.10	74.97	73.75
E	40.58	57.34	50.46	39.28	36.74
F	69.85	72.21	65.13	69.87	66.13
G	68.16	69.02	73.44	69.73	68.60
H	82.99	81.76	79.39	85.27	83.62

In selection step 4, surface tension difference (γ_{diff}) was entered, and the following regression equation resulted in an R-square value of 0.8703:

$$P = -143.46\ (t) + 0.42\ (a) + 251.47\ (v) - 0.55\ (\gamma_{diff}) + 4.11 \quad \text{[Step4, Model 2]}$$

The regression analyses indicated that the linear terms of fabric thickness, air permeability and solid volume fraction were significant. To validate the models defined in steps 1 to 4, calculated data were compared to the actual laboratory data. Figure 2 and Table 8 compare the actual data of all eight fabrics and one pesticide solution (P1L1) with the calculated data derived from the predictive models as an example. The model defined by step 3 fits best the actual laboratory data, so the final model for woven fabrics is:

$$P = -134.79\ (t) + 0.47\ (a) + 329.56\ (v) - 39.06 \quad \text{[Step 3, Model 2]}$$

For non-woven fabrics, correlation coefficients between pesticide penetration and the fabric/pesticide parameters are given in Table 9. The data showed that fabric solid volume fraction, water vapor transmission, surface tension difference, fabric thickness and air-permeability, were the significant variables influencing liquid

Table 9. Correlation coefficients between % penetration and non-woven fabric/pesticide parameters

Fabric/Pesticide Parameters	% Penetration	
	Correlation Coefficient	P Value
Surface Tension Difference	0.56038	<0.0001
Viscosity	-0.03633	0.8063
Solid Volume Fraction	-0.88922	<0.0001
Fabric Thickness	-0.13083	0.3754
Water Vapor Transmission	0.62059	<0.0001
Air Permeability	0.48172	<0.0429
Surface Tension of Pesticide Solution	-0.04694	0.7514

pesticide penetration. Regression analyses were performed as described for woven fabrics. Stepwise selection procedure was used for non-woven fabrics to select a most useful subset of the independent variables.

In step 1, variable fabric thickness (t) was entered, and the following regression equation resulted in an R-square value of 0.4149:

$$P = 246.60\,(t) + 13.28 \qquad \text{[Step 1, Model 3]}$$

In step 2, surface tension difference (γ_{diff})was entered, and the following regression equation resulted in an R-square value of 0.6086. All variables left in the model were significant at the $p < 0.15$ level. So the final model is:

$$P = 356.90\,(t) + 0.66\,(\gamma_{diff}) - 21.08 \qquad \text{[Step 2, Model 3]}$$

Regression analyses indicated that linear terms of fabric thickness and surface tension difference were positively related with pesticide penetration. We used the models defined in steps 1 and 2 SAS output to compare with actual laboratory data. Figure 3 compares the actual liquid penetration data and the calculated data from the predictive models. Figure 3 indicates that the actual liquid pesticide penetration values of fabrics I, L, M and N are close to the predictive models in steps 1 and 2, these were spun bonded porous fabrics. However, fabric types J, K, O, and P were laminated and showed lower levels of liquid penetration than the predicted values. Therefore, we conclude that the predictive model for non-woven fabrics is applicable only to porous non-woven fabric types.

The regression analyses of all three sets of data (combined data of woven and non-woven fabrics; woven fabrics only; non-woven fabrics only), were analyzed using quadratic terms of the variables as well. No significant differences were found in R-square values. Thus the final models are defined by linear terms of fabrics and pesticide parameters only.

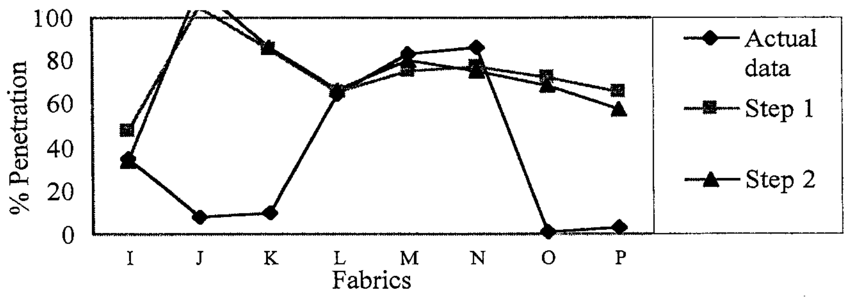

Figure 3. Prowl (P1L1) penetration data and step 1 to 2 SAS calculated data

Thus the final predictive models developed in this study are:

Woven fabrics:	$P = -134.79(t) + 0.47(a) + 329.56(v) - 39.06$	[Model 1]
Non-woven fabrics:	$P = 356.90 (t) + 0.66 (\gamma_{diff}) - 21.08$	[Model 2]

The predictive models suggest that pesticide chemistry is not the most dominant factor in pesticide solution penetration in fabrics. However, the physical characteristics of fabrics and liquid pesticides play a more significant role in predicting barrier efficacy of fabrics.

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