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Permeability of Two Types of Cotton Fabric Used in Personal Protective Clothing to the Insecticide Methamidophos

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The use of personal protective equipment (PPE) has been recommended in Brazil as the only safety measure for work with pesticides. However, if available, the use of PPE is unbearable under field conditions because it results in great discomfort to the worker due to retention of humidity and heat on the body surface (Bull and Hathaway 1986).

The materials used for the confection of PPE worn by workers exposed to pesticides are impermeable or water-repellent. Sets of PPE produced with water-repellent cotton fabrics treated with Teflon™ have been officially approved and are commercialized for the protection of workers exposed to pesticides, with no assays evaluating the protective efficacy and lifetime of the PPE being available. So far, few studies have evaluated the protective capacity of some of these water-repellent sets of PPE only under field conditions and using new, not previously washed fabrics. Under conditions of field application with high exposures, such as manual application of pesticides to potato cultures, a new set of PPE consisting of a light cotton fabric treated with a water-repellent substance has shown satisfactory protection (Oliveira and Machado-Neto 2003). The objective of the present study was to determine under laboratory conditions the permeability of two types of cotton fabric (Jeans and AZR treated with Teflon™) to the insecticide methamidophos with and without laundering.

MATERIALS AND METHODS

The permeability of the fabrics to methamidophos was evaluated by spraying a solution containing the insecticide in a Potter Precision Laboratory Spray Tower (Burkard Manufacturing Co. Ltd.). The amount of insecticide applied to the fabrics was collected on pure cotton pads placed above and under the fabric. Commercial rectangular pads (Sussex Indústria e Comércio Ltda) measuring 5 x 6 x 0.5 cm with a mean retention capacity of up to 21.43 mL water were used.

The fabric samples were placed on a Petri dish positioned on the tray of the Potter Precision Laboratory Spray Tower and treated with methamidophos-containing solutions (Figure 1).

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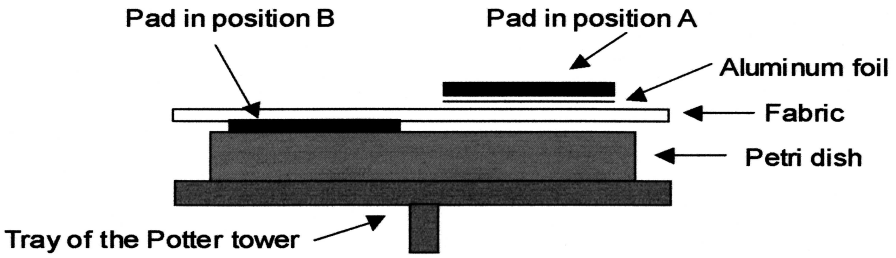

Figure 1. Scheme of spray solution application for evaluation of the permeability of the fabrics to the insecticide methamidophos showing the position of the cotton pads above (A) and under (B) the fabric on the Petri dish situated on the tray of the Potter Precision Laboratory Spray Tower.

Permeability was determined based on the difference between the amount of methamidophos collected on the cotton pads at positions A (above the fabric) and B (under the fabric). Aluminum foil was placed under the pad at position A to prevent passage and loss of the spray applied to the cotton pad.

Two initial experiments were performed to standardize the analyses and the method of methamidophos extraction from the cotton pads. The first experiment was conducted to determine the calibration curve of the analytical standard (methamidophos) injected at different concentrations into a Varian CP-3800 gas chromatograph (GC) with a termohionic specific detector (TSD), equipped with a CP-8400 autosampler. The second experiment was carried out to determine the percent recovery of methamidophos from the cotton pads fortified with the spray solution containing increasing concentrations of methamidophos.

Calibration curve of the analytical standard was analyzed by injecting test solutions containing variable concentrations of methamidophos in ethyl acetate (0.01 to 100.0 $mg.L^{-1}$) into the GC, with 5 repetitions. Malathion at a concentration of 1.0 $mg.L^{-1}$ was added to these samples as internal standard and 1 µL of the sample was injected into the GC. Chromatographic analysis was carried out according to the method of Pavarini (2002). The results were analyzed separately at three concentration ranges of methamidophos 0.01 to 0.50 $mg.L^{-1}$, 1.0 to 5.0 $mg.L^{-1}$, and 6.0 to 100.0 $mg.L^{-1}$. Limit of quantification and detection of the method were calculated as proposed by Anvisa (2002).

Methamidophos was recovered from the cotton pads by extraction of the insecticide with ethyl acetate from pads previously contaminated with the insecticide at concentrations ranging from 0.05 to 5.0 $mg.L^{-1}$. For extraction, 80 mL ethyl acetate and 10 g sodium sulfate were added to the flasks containing the pads. The flasks were shaken and heated in a water bath to 40°C for 40 min, and centrifuged for 5 min at 2500 rpm. The extracting solutions were filtered through a qualitative cellulose filter, 2 mL aliquots of the filtrate were transferred to a 100 mL round flask, and 1 $mg.L^{-1}$ of the internal standard malathion was added. The solvent was evaporated under a compressed air stream, and the samples were resuspended in 2 mL ethyl acetate, shaken for 30 s in a test tube shaker and stored

in vials. The vials were then placed in the vial holders of the CP-8400 autosampler, and 1 μL was injected into the GC.

The fabrics tested were AZR (water-repellent) and Jeans, including new not previously used fabric and fabric submitted to 10, 20 and 30 manual or mechanical washes without and with washing soap. AZR was a beige 0.25 mm thick cotton plain weave weighing 153.49 $g.m^{-2}$ previously treated with Teflon™ to make the fabric water-repellent. Jeans was a pure cotton denim 0.75 mm thick cotton fabric weighing 458.66 $g.m^{-2}$.

The fabric samples were cut into 20 x 20 cm squares with 1 cm folded borders and sown to prevent fraying. Manual washing of the fabric samples consisted of scrubbing for 30 s in a conventional washtub and rinsing in 4 L clean water for 60 s in a plastic bucket. Mechanical washing was carried out in a semiautomatic Colormaq washing machine. The fabric samples were submitted to a 5 min wash cycle in 32 L water in the washtub of the machine. Liquid Omo Multiação™, manufactured by Unilever, was used as washing soap at a dose of 3.75 mL per liter water.

The solution sprayed on the samples was prepared with 6.2 mL of commercial Metafós™ plus 993.8 mL water. This product is an emulsifiable concentrate manufactured by Milênia Agro Ciência S.A. and contains 600 $g.L^{-1}$ methamidophos. A Potter Precision Laboratory Spray Tower calibrated at a pressure of 5 $lbf.pol^{-2}$ was used as the spraying equipment. A volume of 12 mL per fabric sample was applied. Immediately after spraying, the cotton pads were removed and stored in a glass flask for methamidophos extraction and quantification.

A completely random experimental design with 5 repetitions was used, with the treatments arranged and analyzed statistically in two factorial schemes. The first scheme consisted of factor A = type of fabric and number of washes (8 levels), factor B = washing method (2 levels), and factor C = washing soap (2 levels). The levels of the factors were: A = type of fabric (AZR with 0, 10, 20 and 30 washes; Jeans with 0, 10, 20 and 30 washes), B = washing method (manual and mechanical), and C = washing soap (without and with). The second scheme consisted of factor A = type of fabric and washing method (4 levels), factor B = washing soap (2 levels), and factor C = number of washes (4 levels). The levels of the factors were: A = type of fabric (AZR washed manually, AZR washed mechanically, Jeans washed manually, and Jeans washed mechanically), B = washing soap (without and with), and C = number of washes (0, 10, 20 and 30 washes). For statistical analysis, the data obtained for the quantification of the insecticide methamidophos were transformed to log (x + 1.0).

RESULTS AND DISCUSSION

The calibration curve methamidophos concentrations for concentration intervals ranging from 0.01 to 0.50 $mg.L^{-1}$, 1.0 to 5.0 $mg.L^{-1}$ and 6.0 to 100.0 $mg.L^{-1}$ were calculated using the following equations, respectively: $Y = 0.6173X - 0.0074$ (R^2

= 0.9904); Y = 0.8501X – 0.3788 (R^2 = 0.9962), and Y = 1.0341X – 0.18 (R^2 = 0.9985). The y values were replaced with the means of the chromatogram areas obtained for each expected concentration value. Table 1 shows that the lowest concentration value with a calculated coefficient of variation below 10% was reached for a concentration of 0.05 $mg.L^{-1}$.

Table 1. Methamidophos concentrations, mean areas obtained, standard deviation (SD), coefficient of variation (CV) of the test solutions with concentrations ranging from 0.01 to 0.50 $mg.L^{-1}$, 1.0 to 5.0 $mg.L^{-1}$ and 6.0 to 100.0 $mg.L^{-1}$, and the calculated limit of quantification and detection.

Concentrations ($mg.L^{-1}$)	Area methamidophos/Area malathion		
	Mean (counts)	SD	CV (%)
0.01	0.0012	0.0029	245.0
0.03	0.0159	0.0024	15.1
0.05	0.0251	0.0024	9.6
0.07	0.0363	0.0035	9.7
0.10	0.0552	0.0024	4.4
0.30	0.1549	0.0069	4.4
0.50	0.3144	0.0313	10.0
1.00	0.5381	0.0187	3.5
2.00	1.3244	0.0376	2.8
3.00	2.0392	0.0582	2.9
4.00	3.0094	0.1656	5.5
5.00	3.9460	0.0960	2.4
6.00	5.4208	0.0953	1.8
8.00	9.1753	0.2707	3.0
10.00	10.3343	0.1734	1.7
25.00	26.5175	0.9004	3.4
50.00	52.5246	1.6732	3.2
75.00	79.0654	1.1389	1.4
100.00	101.3509	2.3928	2.4

LOQ = limit of quantification = 0.039 $mg.L^{-1}$
LOD = limit of detection = 0.01329 $mg.L^{-1}$

The concentration values recovered from the samplers (Table 2) were obtained with the three equations fitted in the previous test, replacing the y values with the mean areas obtained for each expected concentration value. The recovery of methamidophos from the cotton pads (89.90 to 119.38 %) and the recovered concentrations were above the limit of quantification and detection, remaining within acceptable limits (Anvisa 2002).

The calculated coefficients of variation were higher than those obtained for the analytical standard, ranging from 10.56 to 50.70 %. However, these values agree with those reported by Leonas et al. (1989), who studied the penetration of captan, dicofol, ethion and methyl parathion in various types of fabrics and obtained calculated coefficients of variation ranging from 2.9 to 235.3 %.

Table 2. Fortifications, mean areas obtained, standard deviation (SD), coefficient of variation (CV), mean recovered concentration ($mg.L^{-1}$), and % recovery of methamidophos from the cotton samplers.

Fortifications ($mg.L^{-1}$)	Area methamidophos/Area malathion)			Recovered concentration ($mg.L^{-1}$)	% Recovery
	Mean (counts)	SD	CV (%)		
0.05	0.0314	0.0065	20.6	0.06	119
0.07	0.0356	0.0077	21.7	0.07	99
0.10	0.0589	0.0146	24.8	0.11	106
0.30	0.1746	0.0254	14.5	0.33	111
0.50	0.2988	0.1515	50.7	0.48	96
1.00	0.6162	0.0651	10.6	1.06	106
2.00	1.1581	0.2132	18.4	1.80	90
3.00	2.0829	0.2955	14.2	3.12	104
4.00	2.9437	0.4977	16.9	4.07	102
5.00	3.6724	0.6502	17.7	4.91	98

As shown in Table 3, the highest permeability to methamidophos was observed for AZR fabric washed 30 times with washing soap. Also, washing soap significantly increased the permeability of the AZR fabric to methamidophos in both washing methods. Probably, washing soap accelerates the reduction of water-repellence of the AZR fabric during washing.

Table 3. Permeability (%) of AZR and Jeans fabrics to methamidophos submitted to different numbers of manual and mechanical washes with and without washing soap.

Fabrics and Number of Washes	Washing Method		Washing Soap	
	Manual	Mechanical	Without	With
AZR – 0	0.00a[1] C[2]	0.00a B	0.00x[1] B	0.00x C
AZR – 10	2.73a BC	0.11 b B	0.18 y B	2.66x BC
AZR – 20	5.05a B	0.60 b B	0.75 y AB	4.91x B
AZR – 30	35.59a A	11.99 b A	0.52 y AB	47.06x A
Jeans – 0	0.00a C	0.00a B	0.00x B	0.00x C
Jeans – 10	1.79a B	0.17 b B	1.81x A	0.15 y C
Jeans – 20	0.21a C	0.00a B	0.10x B	0.12x C
Jeans – 30	0.06a C	0.09a B	0.15x B	0.00x C
SMD (5%)	0.65			
AZR	Manual		0.63x	21.05 y
	Mechanical		0.09x	6.26 y
Jeans	Manual		0.91x	0.12 y
	Mechanical		0.12x	0.01x
SMD (5%)	0.29			

[1] Means followed by the same small letters on the same row and [2] means followed by the same capital letters in the same column did not differ from one another by the Tukey test ($P<0.05$).

In contrast to AZR fabric, the non-utilization of washing soap in Jeans fabric washed 10 times increased permeability. In addition, manual washing increased the permeability of both fabrics to methamidophos.

New AZR and Jeans fabrics were practically impermeable to methamidophos, a result similar to those reported by Leonas et al. (1989) who analyzed the penetration of captan, dicofol, ethion and methyl parathion in various types of new fabrics, including two consisting of 100 % cotton submitted or not to water-repellent treatment. Saleh et al. (1998), studying the penetration of insecticides (chlorpyrifos/allethrins) in different types of new fabrics, including one consisting of 100 % cotton, also obtained results similar to those reported in the present study.

Comparison of the permeability results obtained for the two types of fabric irrespective of the number of washes, washing method and use or not of washing soap showed that the AZR fabric was always more permeable than the Jean fabric. This finding might be explained by the different physical characteristics of the fabrics, especially thickness and weight per square meter. Jean fabric is twice as thick as AZR fabric. Various investigators such as Leonas et al. (1989) and Leonas (1991) have reported different permeabilities as a result of fabric thickness and weight, with thicker and heavier fabric being less permeable to pesticides.

The present results led us to conclude that the method of insecticide spraying on the fabric samples in a Potter Precision Laboratory Spray Tower, and the procedures for the extraction and quantification of methamidophos from the cotton samplers were adequate and efficient for the evaluation of the permeability of water-repellent fabrics to pesticides in liquid medium. New not previously washed fabrics were practically impermeable to the insecticide within the limit of quantification of the analytical method. Manual washing caused a greater increase in permeability to methamidophos than mechanical washing. Washing soap led to a greater increase in permeability in AZR fabric than in Jeans fabric.

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