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Fluorescent Tracer and Pesticide Penetration through Selected Protective Clothing

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The use of a Video Imaging Technique for Assessing Exposure (VITAE) was first described by Fenske *et al.* (1986a, 1986b). This technique employs the use of a fluorescent tracer which, when exposed to longwave ultraviolet light (320-400 nm), emits light in the visible spectrum (450 nm). The VITAE system makes use of a computer-based image processing system, interfaced with a television camera to quantify tracer deposition on skin (Archibald *et al.*, 1993a). Improvements in micro-computer image processing (Fenske *et al.*, 1993) and techniques for quantification of dermal tracer deposition using the VITAE system (Archibald *et al.*, 1993a) supports the value of using the VITAE system as a full-body dosimetry technique for assessing dermal exposure.

The use of protective clothing as a means of reducing dermal exposure has become common in the agriculture workplace (Fenske, 1988b). In a survey of greenhouse chrysanthemum producers, 100 % of all respondents reported using coveralls, gloves and boots when applying pesticides (Archibald *et al.*, 1993b). In recent years there has been increased interest in evaluation of protective clothing. The objectives of many of these studies have been to determine the effectiveness of these materials as a barrier between the pesticide and the applicator.

The ability to assess penetration rates of pesticides during application in field studies is complicated by a number of factors. The first is that exposure often takes place over the entire body region. In most cases the applicator will be wearing several types of protective clothing and under garments. This necessitates a study on the extent of penetration for each type of material. In addition, dermal exposure can result from direct passage of pesticide through the fabric, as well as through gaps, seams or openings in the clothing.

The most common technique used to evaluate the ability of various types of protective clothing to protect against pesticide exposure has been the use of dermal patches, with one attached outside the protective clothing and one beneath (Davis, 1980). A second approach employs protective clothing being placed over a gauze patch which is then placed outside the protective clothing of a pesticide applicator (Maddy *et al.*, 1983). A third approach, used by the U.S. Environmental Protection Agency, is to measure deposition rates of pesticides on outer patches and then use penetration ratios generated in laboratory studies to predict exposure (EPA, 1986).

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Fluorescent tracers have proven to be useful in quantifying exposure beneath clothed areas. Franklin *et al* (1981) examined workers under ultraviolet light following application of azinphos-methyl and a fluorescent tracer and found tracer beneath the protective and ordinary clothing, confirming qualitative penetration of the tracer and suggesting penetration of the pesticide as well. Similar studies by Fenske (1988b, 1990) have also confirmed penetration of tracer and pesticide beneath the protective clothing of applicators.

With improvements to the VITAE system (Fenske *et al. 1991, personal communication*; Archibald *et al.*, 1993a) it was felt that the value of using fluorescent tracers in evaluating the performance of various types of protective clothing should be re-examined. The objectives of this study were to determine the permeability and penetration of selected pesticides combined with tracer to various types of protective clothing and determine if tracer and pesticide penetration ratios remain consistent for pesticides with low to moderate water solubility.

MATERIALS AND METHODS

The fluorescent tracer, 4-methyl-7-diethyaminocoumarin, a commercial whitening agent, was chosen for this study. The insecticides, deltamethrin, endosulfan and pirimicarb, were chosen because of their relatively low water solubility and their widespread use in chrysanthemum production. The tracer was dissolved in Assist® (BASF) oil concentrate at a rate of 1 g tracer plus 10 mL Assist® and added to either 25 mg deltamethrin, or 500 mg endosulfan, or 500 mg pirimicarb active ingredient per litre of deionized water.

The following five types of clothing materials were chosen for a penetration study; rubber, tyvek, cotton, a cotton/polyester blend (50:50) and nylon. The cotton, cotton/polyester and nylon materials were prewashed prior to use. While nylon was expected to offer only minimum protection, it was evaluated as a potential glove material since in a preliminary study, workers had found nylon gloves to be light and comfortable to wear.

Alpha-cellulose (ITT Rayonier Inc., Stamford, CT.) was cut into 10 cm × 10 cm patches and aluminium foil was placed on the back of each patch. The patch was then placed on a wooden block and a 15 cm × 15 cm section of the protective materials which was stretched tightly over the alpha-cellulose patch. Staples were placed into the wood in the periphery of each section to hold it securely and maximize the opportunity for the chemical which is adsorbed onto the surface of the protective clothing to diffuse through the clothing and onto the alpha-cellulose patch (Figure 1). Test blocks were then placed in a custom spray cabinet equipped with and single flat-fan nozzle (Spraying Systems 8004E) operating at 250 kPa (37.5 psi) and sprayed with one of the three tracer/pesticide mixtures at one of three rates; 10, 30 or 50 μL per 1 cm × 1 cm. These rates were equivalent to 1000, 3000 or 5000 L of spray solution per ha and represented 1×, 3× and 5× the tracer/pesticide rates per unit area. Each cloth, tracer/pesticide and rate combination sprayed was replicated four times. Uncovered alpha-cellulose patches were sprayed to assess the ratios of tracer:pesticide deposition. After spraying, blocks were allowed to stand for 1 hour to facilitate diffusion of the pesticide and tracer through the clothing materials. Blocks were then removed, the protective material lifted off and the patches were placed into a 150-mL Erlenmeyer flasks with 50 mL methanol and tracer and pesticide extracted (Archibald *et al.*, 1993a). Two patches were spiked with known

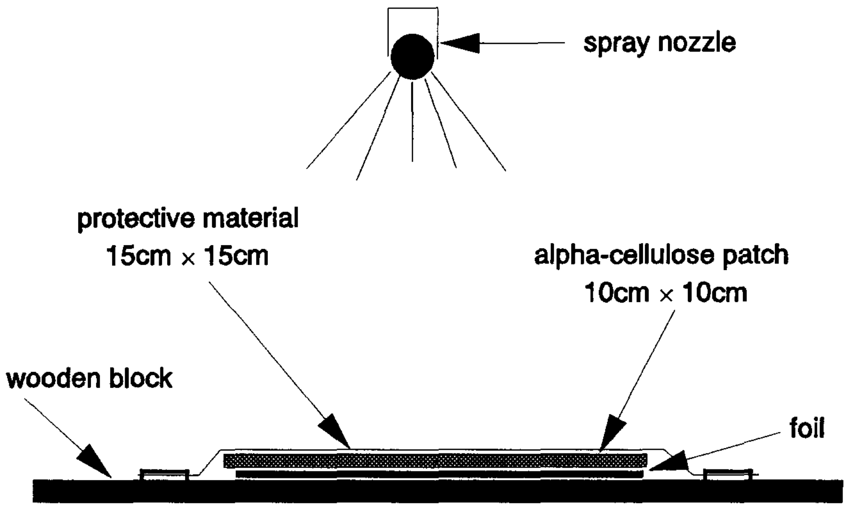

Figure 1. Configuration of protective material and alpha-cellulose patch in penetration study

concentrations of tracer and pesticide to serve as recovery checks.

Flasks containing patches were placed on a customized flat-top shaker table and agitated for 1 hour. Methanol and patches were filtered under vacuum through 5.5 cm ashless Whatman filter paper. The Erlenmeyer flask and filter paper were each rinsed with an additional 5 mL of methanol. The solvent was then divided into two equivalent portions for separate analyses of tracer and pesticide.

The tracer portion of the extract was detected using a SPF-125 Spectrophotofluorometer (Travenol Lab. Inc., MD) and quantified using reference standards. The pesticide portion of the extract was placed in a boiling flask and evaporated to near dryness in a Buchi RE111 Rotavapor at 55°C. Boiling flasks were then rinsed 3 times with small quantities of iso-octane and rinses transferred to volumetric flasks, brought up to 5 mL with iso-octane prior to transfer into glass test tubes and capped prior to analysis by gas chromatography.

Pesticides were analyzed using a Hewlett-Packard 5880 gas chromatography with dual capillary injection system and automatic liquid sampler. A ^{63}Ni electron capture detector was used for detection of deltamethrin and endosulfan and a nitrogen-phosphorus thermionic detector for pirimicarb analyses. The column was a J&W fused silica capillary, 15 m X 0.247 mm, with 0.25 μm coating of SE-30 (Chromatographic Specialties Ltd., Brockville, Canada). Injector temperature was 250°C, and the detector 300°C. The column oven was programmed for an initial 1 min hold at 90°C, followed by 20°/min to 150°C, and 5°/min to 250°C. Helium carrier gas with argon-methane make-up gas was used for the electron capture detector. Helium carrier gas was used for the nitrogen-phosphorus detector. One μL of extract was auto-injected, with capillary inlet system configured in splitless mode with bypass valve open for 0.5-1.0 min. Stock solutions of analytical reference standards were prepared in iso-octane.

Laboratory procedures used to analyze tracer from alpha-cellulose patches are similar to those previously described (Archibald *et al.*, 1993a). The limit of detection for the tracer was 1 μg/L and the limit of quantification was 3.2 μg/L. Analytical recovery of the tracer was 98 $\pm$ 2 %. The detection limit for deltamethrin and endosulfan was 1 μg/L and the limit of quantification 10 μg/L. Analytical recovery of deltamethrin and endosulfan ranged from 74-91 %. Results were not corrected for recovery. The detection limit for pirimicarb in alpha-cellulose patches was 25 μg/L, with a limit of quantification of 50 μg/L. Analytical recovery of pirimicarb was 85-98%. Reported results were not adjusted for recovery.

RESULTS AND DISCUSSION

Tracer/pesticide solution ratios remained relatively constant on outer patches (Table 1). The data confirmed earlier findings that dissolving the tracer in an oil emulsifier prior to mixing with water and pesticide results in constant deposition ratios relative to initial tank mixtures. For all tracer/pesticide combinations, the 50 μL spray solution/cm^2 application rate did not always provide five times the quantity of the 10 μL spray solution/cm^2 application rate. This may have been due to run-off of the spray solution before it could be totally adsorbed by the patch.

Despite applying as much as 50 μL per cm^2 (5000 L/ha) of spray solution, there was no pesticide or tracer found in any of the patches placed below the rubber or tyvek protective clothing (data not presented). Trace levels (5 μg/kg) were found on 4 tyvek patches treated with the deltamethrin/tracer spray solution and 1 tyvek patch treated with endosulfan/tracer at the 50 μL per cm^2 rate. These results suggest that these materials do not permit penetration of the pesticide even at very high application volumes, thus providing excellent protection.

Table 1. Mean (Standard Deviation) deposition quantities (μg per cm^2) of pesticide/tracer spray solutions on alpha-cellulose patches (N = 4)

	Initial mixture mg active ingredient/L water	Application of spray solution per cm^2 10 μL	30 μL	50 μL
Deltamethrin	25	0.3 (0.1)	0.8 (0.2)	0.91 (0.19)
Tracer	500	5.4 (1.7)	16.4 (1.2)	22.1 (1.7)
Ratio	1:20	1:19.3	1:20.5	1:24.3
Endosulfan/	500	5.4 (0.1)	16.4 (1.8)	22.2 (4.1)
Tracer	500	5.3 (0.1)	18.3 (0.9)	27.2 (2.6)
Ratio	1:1	1:1	1:1.2	1:1.2
Pirimicarb/	500	5.5 (0.2)	14.4 (1.2)	28.7 (2.5)
Tracer	500	5.3 (0.1)	14.2 (0.7)	34.3 (2.2)
Ratio	1:1	1:1	1:1	1:1.2

Penetration and deposition data for the tracer and pesticides applied to the cotton, cotton/polyester and nylon are shown in Table 2, 3 and 4. Even at high rates of application, there was no detectable deltamethrin residue found beneath the cotton material and only small quantities beneath the blended material (25 ng) and nylon (66 ng) (Table 2). The penetration ratio of deltamethrin and tracer remained relatively constant for the blended material. The quantity of tracer which penetrated the protective clothing was much greater then the initial pesticide/endosulfan ratio. However, with the exception of the high rate, the ratio remained relatively consistent within each protective material category (Table 3). When pirimicarb was applied with the tracer, the penetration ratios were inconsistent. The quantity of tracer which passed through all three materials was much lower than when applied in combination with deltamethrin or endosulfan, suggesting that less of the pirimicarb was less adsorbed to the fabric.

Results from this study did not support the initial hypothesis that penetration ratios of pesticide and tracer would remain consistent within different types of protective clothing. While the fact that residues could not be detected below the rubber and tyvek patches does indicate that these materials are effective at preventing exposure, it could not provide data on the penetration rates for the pesticide/tracer combinations evaluated.

Table 2. Mean (Standard Deviation) deltamethrin and tracer penetration quantities through selected protective materials (N = 4)

Protective material	μL spray solution applied per cm^2	ng deltamethrin per cm^2 of inner patch	ng tracer per cm^2 of inner patch	Ratio of pesticide to tracer[A]
Cotton	10	ND	85 (18)	NA
	30	ND	135 (21)	NA
	50	ND	150 (35)	NA
Blend	10	ND	30 (11)	NA
	30	5 (4)	40 (18)	1:7.7
	50	25 (15)	202 (56)	1:8.3
Nylon	10	ND	900 (125)	NA
	30	12 (10)	1775 (188)	1:100
	50	66 (42)	2275 (148)	1:33

[A]Initial ratio 1:20

Table 3. Mean (Standard Deviation) endosulfan and tracer penetration quantities through selected protective materials (N = 4)

Protective material	μL spray solution applied per cm^2	ng endosulfan per cm^2 of inner patch	ng tracer per cm^2 of inner patch	Ratio of pesticide to tracer[A]
Cotton	10	10 (3)	50 (4)	1:5
	30	13 (4)	70 (3)	1:26
	50	15 (1)	75 (4)	1:5
Blend	10	3 (2)	70 (12)	1:25
	30	12 (4)	250 (23)	1:20
	50	59 (29)	500 (111)	1:9
Nylon	10	15 (5)	1300 (130)	1:100
	30	24 (12)	1770 (128)	1:100
	50	88 (56)	2900 (194)	1:33

[A]Initial ratio 1:1

Table 4. Mean (Standard Deviation) pirimicarb and tracer penetration quantities through selected protective materials (N = 4)

Protective material	μL spray solution applied per cm²	ng pirimicarb per cm² of inner patch	ng tracer per cm² of inner patch	Ratio of pesticide to tracer[A]
Cotton	10	7 (2)	2 (1)	1:0.28
	30	57 (4)	4 (1)	1:0.07
	50	116 (11)	5 (2)	1:0.04
Blend	10	18 (3)	3 (1)	1:0.17
	30	31 (4)	4 (1)	1:0.13
	50	116 (17)	6 (2)	1:0.05
Nylon	10	120 (55)	250 (112)	1:2.1
	30	250 (65)	330 (86)	1:1.3
	50	565 (112)	400 (88)	1:0.7

[A]Initial ratio 1:1

Deltamethrin and endosulfan are hydrophobic pesticides and may have been more readily adsorbed to the fabric than the tracer which resulted in low penetration rates of these pesticides. Pirimicarb had greater penetration rates in the cotton and blended materials, suggesting that it was less readily adsorbed to the fabric than the tracer. The results do support the need to use dermal patches beneath protective clothing to establish penetration factors for specific pesticide/tracer combinations when employing video imaging as a technique for assessing exposure.

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