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Nitrile Butyl Rubber Glove Permeation of Pesticide Formulations Containing 2,4-D-Amine, DDT, DEET, and Diazinon

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Chemical protective gloves are in common use for minimizing occupational exposure to pesticides; however, few reports have documented the permeability of these gloves, especially to pesticides applied in the field as formulations (Moody and Ritter, 1990; Schwope et al., 1992). The formulants (emulsifiers, etc.) used as pesticide vehicles comprise a wide variety of compounds that may affect the integrity and hence the barrier properties of the glove matrix to pesticides. The present study was designed to determine the effect of pesticide formulation on glove permeability by comparing the permeation of pesticides applied in an acetone vehicle *versus* formulated products of the herbicide 2,4-D-DMA, the organophosphorous insecticide Diazinon, the organochlorine insecticide DDT, and the insect repellent DEET. As well as testing two widely-used commercial pesticide formulations (2,4-D-DMA in Killex[R] and Diazinon in Green Cross Diazinon Fruit Tree Spray), DDT was tested dissolved in a common petroleum oil since it had been used extensively in early Canadian forestry spray programs for spruce budworm control (Yule & Tomlin, 1971). DEET dissolved in a commercial cream insect repellent was tested since DEET may contaminate chemical protective clothing and has recently been reported to have an effect on the surface ultrastructure of glove material (Moody and Nadeau, 1992).

We have previously reported an automated *in-vitro* diffusion analysis (AIDA) method for quantifying the permeability of gloves to pesticides and that the method has several advantages (e.g. HPLC analysis, temperature control) to the standard ASTM test method for chemical protective clothing (Moody and Ritter, 1990). The AIDA procedure was used in the present study to measure the permeability of Sol-Vex (nitrile butyl rubber) gloves to pesticides.

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MATERIALS AND METHODS

^{14}C-ring-labelled pesticides were employed. Radiochemical purity > 95% and chemical authenticity were confirmed by Radio-TLC and GLC/MS, respectively. ^{14}C-2,4-D-DMA (2,4-D-dichlorophenoxyacetic acid dimethylamine) (SA 16.6 mCi/mM) and ^{14}C-DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane) (SA 12 mCi/mM) were obtained from Sigma Chemical Co., St. Louis, MO. ^{14}C-DEET (diethyl-m-toluamide) (SA 4.4 mCi/mM) and ^{14}C-Diazinon (O,O-diethyl O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate) (SA 16.7 mCi/mM) were obtained from Du Pont New England Nuclear, Boston, MA. Pesticide formulations included Killex^{R} containing 11.8% 2,4-D-DMA (Green Cross Products, Ciba-Geigy Canada Ltd., Toronto, ON); 3-IN-ONE^{R} Household oil, Boyle-Midway Canada Ltd., Toronto, ON (to which 10.0% DDT (Sigma Chemicals Co., St. Louis, MO) was added); Skintastic^{R} cream containing 6.7% DEET (S.C. Johnson & Son, Ltd., Brantford, ON); and Green Cross Diazinon Garden and Fruit Tree Spray containing 12.0% Diazinon (Fisons Horticulture Inc., Mississauga, ON). Ringer's saline was used to mimic human sweat at the glove/skin interface and was employed as a receiver solution for the pesticide permeating the glove. The pH of Ringer's saline solution was adjusted to 5.5 with 0.1 N HCL and was pumped at a flow rate of 40 μL/min under the glove surface with the glove specimen mounted in an AIDA cell chamber as described previously for skin absorption tests (Moody and Martineau 1990; Moody and Ritter, 1992).

The AIDA cell chamber (Moody and Martineau, 1990) was machined from aluminum and was heated on a Reacti-Therm III (Pierce, Rockland, Il) to maintain the glove specimens at 37 $\pm$ 0.5°C. Rectangular strips (ca. 1 cm X 5 cm) were cut from the palmar surface of Sol-Vex nitrile butyl rubber gloves (#37-175) purchased from Becton-Dickinson Canada, Inc., Cowansville, PQ. For each AIDA test, a glove strip from one glove specimen was placed over the 4 permeation cells in the AIDA cell chamber with the inner glove surface facing the receiver solution. For treatment, 0.1 μCi of ^{14}C-labelled pesticide dissolved in either 250 μL acetone or 250 μL formulation was applied to each glove specimen (0.2 cm^2). The receiver solution was harvested every 2 hr for 24 hr in a fraction collector and the fractions were analyzed by liquid scintillation counting (LSC) and the % of the applied ^{14}C-radiolabel dose permeating the glove was calculated by electronic spreadsheet (Moody and Martineau, 1990). At the end of each 24 hr test, the treated glove surface was rinsed with 5 mL of a 50% aqueous dilution of Radiac soap (Atomic Products, Shirley, NY) followed by 5 mL of distilled water. The glove strip was then cut into the four cell sections which were extracted separately in 5 mL of methanol for ca. 12 hr. The percentage of the applied dose persisting in the glove surface washes and glove extracts was determined by LSC.

RESULTS AND DISCUSSION

In comparison with the pesticides applied in acetone, the % glove permeation was much reduced in all cases for the formulated products (Table 1). For example 58.2 $\pm$16.7% permeation of DEET applied in acetone was observed whereas only 0.1 $\pm$0.02 % DEET permeation was observed for the Skintastic^R formulation. As shown in Fig. 1, the % permeation of DEET applied in acetone reached a maximum at 4 hr post-application and then decreased rapidly until achieving a steady low rate of permeation after ca. 18 hr post-application. Since the % permeation was calculated solely on the basis of ^{14}C-activity, the observed reduction in permeation was probably due to a diluting or even a saturating effect of the unlabelled pesticide present in the formulated pesticide tests. The amount of pesticide applied to the glove surface ranged from 103 to 183 mg/cm^2 in the formulation tests but was only 6 to 18 μg/cm^2 for the ^{14}C-pesticides applied in acetone.
The high standard deviation (SD) in some of the mean % permeation data reported in Table 1 was attributed to 'microholes' resulting from manufacturing defects in the glove membrane. It is notable, however, that the glove test strip in the Diazinon formulation test appeared crenulated in all four test cells at 24 hr post-treatment and that visible surface cracks were observed in test cell #4, a cell that had 0.9% permeation in comparison with a mean of 0.1 $\pm$.01% permeation for the other 3 replicates. This corrosive effect was observed in a further test (n = 4) with the formulated product. "The presence of xylene in the Diazinon product tested may explain the observed corrosive effect of the Diazinon formulation on the glove material and the resultant enhanced permeability," Personal Communication, H. Kenney, Fisons Horticulture Inc., Mississauga, ON). This is an important observation since the present data suggest that pesticide formulations containing xylene may alter the protective efficacy of nitrile butyl rubber chemical protective clothing.

Table 2 demonstrates for pesticides applied in acetone that a large reservoir of pesticide resided in the glove membrane at 24 hr post-application that was not removed by a surface wash of soapy water. This methanol extractable reservoir ranged from 22% to 33% of the applied dose (Table 2). This reservoir would explain the continued permeation of the pesticides at a constant rate

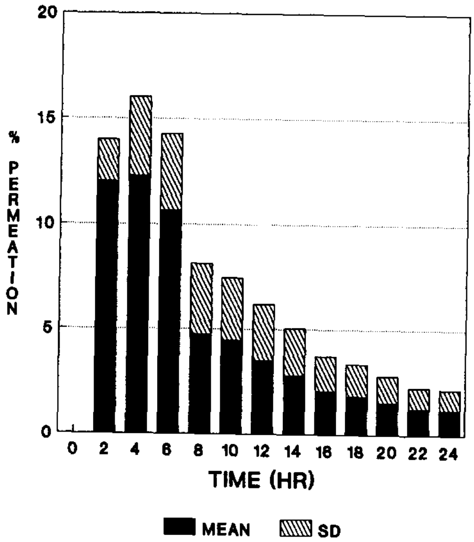

Figure 1. Glove % permeation of ^{14}C-DEET applied in acetone to Sol-Vex gloves *versus* time. Mean ±SD (n = 4).

Table 1. Mean ±SD (n = 4) % permeation of acetone and formulated ^{14}C-radiolabelled pesticides applied to Sol-Vex nitrile butyl rubber gloves for 24 hr.

Pesticide	Acetone[a]	Formulated[b]
2,4-D-DMA	0.8 ±0.72	0.0 ±0.00
DDT	3.1 ±3.91	0.0 ±0.00
DEET	58.2 ±16.7	0.1 ±0.02
Diazinon	10.2 ±10.6	0.3 ±0.39

Data are shown for pesticides applied either in acetone[a] or in formulation[b] (2,4-D-DMA in Killex[R]; DDT in 3 IN-ONE[R] oil; DEET in Skintastic[R]; Diazinon in Green Cross Diazinon Garden and Fruit Tree Spray).

at later sampling times as mentioned previously for the data for DEET in Fig. 1. In contrast with the acetone data (Table 2), the reservoir effect was not evident for the formulated products, however, this probably resulting from a dilution of the ^{14}C-activity by the unlabelled pesticide in the glove matrix and the gloves would still contain appreciable amounts of pesticide. For example for the 2,4-D-DMA formulation test, the 5.1% reservoir (Table

Table 2. Mean ±SD (n = 4) % recovery of ^{14}C-radiolabelled pesticides from soapy water surface washes and methanol extracts of the glove material 24 hr post-treatment.

Pesticide		Wash(W)	Extract(E)	W+E
2,4-D-DMA	acet[a]	4.8 ±1.15	22.0 ±3.17	26.8 ±2.99
	form[b]	4.7 ±1.08	0.4 ±0.08	5.1 ±1.01
DDT	acet[a]	7.2 ±4.99	32.8 ±15.13	40.1 ±20.05
	form[b]	0.8 ±0.36	2.2 ±0.88	3.0 ±1.24
DEET	acet[a]	8.2 ±1.37	26.1 ±0.89	34.3 ±1.61
	form[b]	2.5 ±1.34	1.7 ±1.06	4.1 ±2.39
Diazinon	acet[a]	5.6 ±1.86	24.8 ±8.57	30.5 ±10.40
	form[b]	1.4 ±0.47	3.6 ±0.92	5.0 ±1.20

Data are shown for pesticides applied either in acetone[a] or in formulation[b]. Total mass balance % recovery (% glove washes + % extracts + % permeation + % in AIDA cell chamber washes) was ≥ 92 % in all cases.

2) would have contained 9 mg/cm^2 of glove (5.1% of 182 mg/cm^2 applied dose). We stress this point since the dataindicate that pesticide workers may receive long term exposure from pesticide reservoirs in contaminated gloves even following glove rinsing with soapy water. It is recommended that further studies be conducted to elucidate this glove pesticide reservoir effect.

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