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Granular Terbufos Exposure and Cleanup of Glove Materials

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Midwestern farmers rely on granular insecticides to control crop pests. Although highly toxic, these pesticides are incorporated into the soil, are shaken off fabrics easily, and are considered comparatively safe to use. More than 10.2 million pounds of the active ingredient of granular terbufos were applied to over 74.1 million corn acres in 1990. It is a "Danger" label corn rootworm insecticide, and the precautionary statements indicate it is fatal if swallowed, inhaled, or absorbed through the skin.

Chemically resistant gloves usually are specified on labels of granular insecticides to reduce exposure that might occur during handling of these pesticides. Standard test methods have been developed for liquid and gas permeation and penetration of protective clothing materials (ASTM 1996). A considerable body of knowledge has been accumulated about glove resistance to chemical liquids used as solvents for pesticides (Entholt et al. 1988; Swope et al. 1992).

Little research was identified that documents the result of exposure of textile or glove materials to granular pesticides. Laughlin et al. (1986) compared fabric contamination with emulsifiable concentrate, wettable powder, and encapsulated methyl parathion; they found less contamination from the encapsulated product, based on a method that converted the granules to dilute solution for use in contamination.

Bratten (1988) studied transfer of aldecarb from Timek® granular pesticides to fabric, focusing on the effect of sebum soiling and perspiration. She found that as time of contact increased, the level of contamination increased, and that it dissipated when exposed to air.

In a case study of coveralls worn in a farming operation, Stone and Stahr (1989) demonstrated that terbufos residues remained in the coverall denim for two years, although the garment was washed with every wearing. A subsequent study of clothing worn under the coveralls revealed that trace amounts of terbufos could be found in four out of five shirt and one out of six jean specimens (Stone et al. 1992). Gloves were not examined in these studies.

Stone et al. (1992) described various laboratory methods for granular contamination of fabric specimens and reported that cotton denim was easily contaminated with dry terbufos granules. Contamination was

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found to be a function of contamination amount, exposure time, time delay before extraction, and moisture content of the specimen. Contamination was present after 96 hours of ventilation, following 24 hours of exposure.

No research was identified that documents the contamination of chemically resistant glove materials with granular pesticides. Furthermore, no research was identified that documents the effect of cleanup methods commonly advocated in educational materials about pesticide safety.

The purpose of this study was to determine 1) whether glove materials differed in their performance with relation to a limited exposure to granular terbufos (Counter 15G) and 2) whether washing with detergent and water would reduce measurable contamination.

MATERIALS AND METHODS

Three types of chemically resistant gloves were obtained directly from the manufacturers. They were barrier laminate I, 0.003 gauge, 4H® from Ansell Edmont; neoprene, 28-mil flock-lined, embossed, #723 from Best Manufacturing Co.; and nitrile, 0.022. gauge thick, A-15 Stansolv® from Mapa Pioneer. A fourth glove (barrier laminate II, Silver-Shield™, 0.004 gauge, from Ansell-Edmont) was obtained by mail order and was used only in the petri-dish method test. The terbufos used in this study was obtained from the university farms from a lock and load container of Counter 15G.

Two methods of contamination were tried. These will be referred to as the glove-finger method and the petri-dish method. With the glove-finger method, glove fingers were cut off, fitted over test tubes, and then pushed into a beaker of granules for exposure. With the petri-dish method, flat specimens were taped to gauze and held in covered petri-dishes for exposure.

With the glove-finger method, it was necessary to calculate the surface area of the glove finger exposed during contamination. To measure the surface area, glove fingers (thumb, index, middle, ring, and small) were marked 5 cm below the finger tip and cut open to lie flat. The flat, irregularly shaped areas were scanned by using Macintosh graphic software Photoshop 2.5- 1 and saved as TIFF files. NIH Images 1.54, a public domain image processing and analysis program, was used to measure the defined regions of interest: the measurements were analyzed and reported as sq cm. We assumed that all fingers of the same description (for example, nitrile, index, size 9) from the same manufacturer would have the same surface area. Thumbs were used as controls in the chemical extraction process.

To expose the glove fingers to granular insecticide, 150 mL of terbufos granules were measured into a 200 mL beaker. Glove fingers were benchmarked 5 cm from the tip of the finger and cut off where the finger joined the hand. Each finger was mounted over a clean Pyrex test-tube, was held with a test-tube clamp, and then was pushed carefully by hand into a beaker of granules to the bench mark. Each

finger was exposed separately to the granules for three minutes under a hood. At least six fingers of each material were exposed.

Half the specimens of each material were not washed after exposure. The other half were washed while still on the test tube, by using a spring clamp to hold them during stirring in a beaker of 150 mL distilled water. Liquid Tide® was used in the proportion recommended for a regular load of household laundry. The wash solution did not contact the inside of the glove finger.

After exposure, four extracts per finger were prepared for analysis: 1) sterile cotton gauze pads were used to wipe fingers, which we then immersed in 30 mL ethyl acetate, 2) fingers were rinsed in 75 mL ethyl acetate for 20 seconds, 3) fingers were soaked in 50 mL ethyl acetate for 72 hours, and 4) the test tubes that held the fingers were rinsed with 50 mL ethyl acetate for 20 seconds.

A Bendix 2500 gas chromatograph with an NFPD (Rubidium Chloride Bead) detector with a column temperature of 195°C and a temperature of 250°C was used for both injection and detection. Two injections per each specimen extract (ethyl acetate) were made and the terbufos contamination was calculated from the peak height.

Because gloves were different sizes, the measured contamination was divided by the surface area of each finger specimen calculated as described previously to give comparable data on exposure per square centimeter.

With the petri-dish method, 6 sq cm glove specimens taken from the palm or back of the hand were cut and marked to show a 4 sq cm contamination area. Specimens were taped to gauze at the edges and placed in petri dishes. Terbufos granules (0.05 g) were measured into foil weighing boats, and were then sprinkled over the contamination area of the glove specimen. Specimens were allowed to stand in a covered petri dish for 30 min. After exposure, glove specimens were lifted with tweezers and, if necessary, tapped with a spatula to remove granules from the surface. Specimens were trimmed with scissors to the 4 sq cm marks and the edges discarded. Half the specimens were washed; half were not. Three specimens of each glove material were examined for each treatment; the sequence of contamination was randomized.

Washed glove material specimens were separated from the gauze backing, held with tweezers, and stirred for three minutes in a beaker of 150 mL distilled water with detergent in the same proportion as would be used for household laundry. After washing, the specimens were dried in ambient air under the hood for 30 minutes. The dry specimens were placed in 30 mL of ethyl acetate in labeled test tubes, capped, and refrigerated.

The petri-dish specimens that were not washed and all the gauze specimens were placed directly into labeled test tubes containing 30 mL ethyl acetate, capped, and refrigerated. All specimens were extracted

for at least 16 hours. Pesticide residues were determined by using gas chromatography using the procedures previously reported (Stahr 1992).

For the glove-finger specimens, the sum of residues from the wipe, rinse, and soak were determined with the GLM procedure in SAS; any results having $p < 0.05$ were treated as statistically significant. For the petri-dish specimens, the total contamination for the specimen was the basis for the statistical analysis with $p < 0.05$ (Bower-man and O'Conner 1990).

RESULTS AND DISCUSSION

Considering all specimens, both not washed and washed, a significant difference among materials was found by using both methods of contamination, as shown in Table 1. The glove-finger contamination method resulted in higher contamination levels per sq cm than was obtained through the petri-dish method, as defined. In both methods, the barrier laminates showed the least contamination and the neoprene the most. The standard deviations were greater for the neoprene and nitrile in both methods.

Forcing the finger into the granules had some frictional effects that were not measured and could have increased contact between granules and the materials. Visual inspection showed that granules slid off the surface of the barrier laminate I, but tended to be snagged and held by the fused seams. The neoprene, a more elastic material, may have increased in surface area as it was forced into the granules, causing higher contamination levels per sq cm. The greater amount of dust visible on the surface of the neoprene fingers after contamination was confirmed by the chemical analysis.

Table 1. Terbufos contamination of glove materials by exposure method.

	Laminate I		Laminate II		Neoprene		Nitrile	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Glove finger								
µg/sq cm	6.1	1.6	n.t.	n.t.	14.0	3.3	9.1	5.4
Petri dish								
µg/4 sq cm	39.8	7.5	29.8	5.6	62.6	16.7	39.6	14.4
µg/sq cm	2.5		1.9		3.9		2.5	

n.t. = not tested SD = standard deviation

Table 2 compares level of contamination found on not-washed and washed glove fingers, with each material considered separately. The three-minute washing process significantly reduced contamination for the neoprene and nitrile glove fingers. After laundering, contamination was 67% lower for nitrile and 31% lower for neoprene, but not significantly lower for barrier laminate.

In no instance, however, was contamination of materials entirely eliminated. The test tubes "protected" by the glove fingers did not show

pesticide contamination for any of the glove types following the three-minute granular exposure. Glove fingers not laundered showed contamination of the gauze, a larger amount in the ethyl acetate rinse solution, and measurable contamination after the soak period.

Table 2. Terbufos residue in µg/sq cm in not-washed and washed glove fingers.

	Gauze Wipe	Rinse	Soak	Total	SD	Pr >F
Barrier laminate						
Not washed	1.3	2.0	2.2	5.5	1.52	
Washed	1.1	3.1	2.7	6.9	1.46	0.197
Neoprene						
Not washed	1.4	15.0	0.7	17.1	2.74	
Washed	n.d.	10.9	0.9	11.8	1.18	0.016
Nitrile						
Not washed	3.6	9.9	0.2	13.7	2.95	
Washed	0.4	4.0	0.1	4.5	0.77	0.006

n.d. = not detected SD = standard deviation

Contamination of the gauze is important because it confirms that residues are transferred easily from contaminated gloves to other apparel textiles, even in the dry state. The results of the 20-second rinse in ethyl acetate suggest that pesticide was either on or close to the surface and was attacked easily by the extraction solvent. The comparatively small amounts obtained after the extended soak in the solvent confirm that notion.

No detectable contamination was found in controls or in rinse solutions from test tubes used under the gloves. This indicates that hands would have been protected for 3 minutes of granular exposure, assuming no breaks or tears in the glove materials.

Table 3 summarizes results of the petri-dish contamination method and clean-up of four glove materials. In this instance, the neoprene again showed higher residue levels and the barrier laminates least. Both barrier laminates showed less variance among specimens than did the neoprene and nitrile materials. In no instance was contamination of the gauze detected, so all of the glove materials “protected” the gauze for the 30 minutes that the 0.05g of granules were scattered on them.

The disturbing finding in the petri-dish exposure and cleanup approach is that there were no significant decreases in the contamination levels as a result of washing. An obvious explanation might be that the longer exposure time gave more opportunity for penetration into the material. Another obvious explanation is that the washing process itself was flawed. By immersing the whole specimen (inside and out) into the wash solution, the pesticide contamination washed off the outside of the

specimen had opportunity to redeposit on the inside of the glove material. From the inside surface it would be easily extracted when immersed in solvent.

Table 3. Terbufos residue in not-washed and washed 4 sq cm specimens.

	Mean	SD	Pr > F	µg/sq cm
Barrier laminate I				
Not washed	45.2	7.2		2.8
Washed	34.4	1.2		2.2
			0.06	
Barrier laminate II				
Not washed	32.9	3.5		2.1
Washed	26.7	6.3		1.7
			0.20	
Neoprene				
Not washed	71.4	13.9		4.5
Washed	52.9	15.7		3.3
			0.20	
Nitrile				
Not washed	43.7	15.7		2.7
Washed	35.4	14.8		2.2
			0.54	

SD = standard deviation

In practical terms, the glove-finger and petri-dish experiments with granular terbufos show that advice given pesticide applicators about washing off their gloves while still on their hands is well taken. These experiments also demonstrate the need for further research to establish standard protocols for granular contamination and decontamination. Neither the glove-finger nor the petri-dish method is recognized by standards organizations, but each suggests an approach that might be considered for further evaluation by standards committees.

Further research on gloves also should consider examination of variables such as the effects of longer granular exposure times and the effects of other cleanup protocols that might enhance results. A contamination protocol with granular products should have round-robin testing to create a standard method.

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