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Handgun Applicator Exposure to Ethion in Florida Citrus

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Freezing weather in 1981, 1982, 1983, and 1985 resulted in extensive damage to Florida citrus. Florida's citrus acreage was reduced from 847,856 acres in 1982 to 624,492 acres in 1986 (Parsons 1987). To put some perspective on these losses, the loss to Florida citrus acreage in these years would be the same as destroying the entire apple acreage in Washington State. Florida's citrus acreage has rebounded to an estimated 697,929 acres in 1988 and the process has accelerated due to a stable market, relatively good weather, and more intensive production practices (Parsons 1987, Parsons et al. 1986).

There are no good estimates on the number of handgunners in Florida citrus. In solid plantings of young trees, the handgunner has been replaced by specialized young tree application equipment. However, for two to four years after planting, pesticides may be applied to young trees by handgun, particularly in groves with surviving larger trees. A typical handgun crew consists of a driver and two applicators. The applicators walk behind a tank truck with 50 ft hoses and apply pesticides to each tree with an adjustable handgun. In some cases, applicators ride on the rear of the tank truck. All three men assist with loading and mixing the pesticide.

For loading, a liquid pesticide is drained from a 55 or 30 gal steel drum into a plastic bucket to a predetermined mark. Wettable powders are weighed into a plastic bucket using a hanging scale. One of the men then climbs onto a catwalk and pours the measured material into the tank. The tank is filled with water from an overhead standpipe or from a nearby lake or canal prior to adding the pesticide.

There is one report in the literature concerning 2,4-D handgunners for aquatic vegetation and one for greenhouse handgun applicators (Nigg and Stamper 1983; Stamper et al. 1989a). In contrast to 2,4-D aquatic handgunners or greenhouse handgunners, citrus handgunners work in the open and their exposure to pesticides is subject to the full impact of the wind.

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Additionally, both applicators spray simultaneously, sometimes from the opposite sides of a tree. By observation, citrus handgun pesticide applicators appeared to be exposed to high quantities of the pesticide mixture. This report details our examination of handgunner exposure to ethion in Florida citrus.

MATERIALS AND METHODS

Three male subjects (handgun crews are usually male) participated in the study. Subject no. 1 was a driver-mixer: height 5'11" and weight 204 lb. Subject no. 2 was a sprayer-mixer: height 5'9" and weight 160 lb. Subject no. 3 was a sprayer-mixer: height 5'11" and weight 155 lb. Each was experienced in handgun work practices and was instructed to continue his normal work routine. Subjects wore identical long-sleeved shirts and pants made of 65% cotton/35% polyester made by Dickies, Inc. These were purchased locally and issued to each worker. Workers also wore rubber knee boots and dust masks which covered the nose and mouth area. They did not wear gloves. Their total body surface areas were estimated from height and weight according to the Gehan and George (1970) formula.

All applications were by handgun and were made in groves containing young trees and a few surviving 8-12 ft mature trees. The hand-held, adjustable spray guns were Boss Sprayer guns (Gun-jet No. 2, Spraying System Company) attached to 50' x 1/2" ID hoses. The spray mixture was 2 qt ethion 4EC, 4 gal oil, 1 lb Benlate, in 700 gal water. The spray mixture was applied at 800 psi as a fine spray but was occasionally adjusted to a coarse spray in order to reach the tops of mature surviving trees.

Exposure dosimeters were 10.16 cm x 10.16 cm (4 x 4 in.) alpha-cellulose pads with a glassine weighing paper backing. The pads were placed outside of clothing as follows: one on the hat facing frontward; one on the upper middle of the back; one on the chest near the pectoral region; one on each shoulder, facing frontward; one on each forearm, slightly below the elbow and facing outward; and one on each thigh, midway between hip and knee and facing frontward. During pad removal, samplers handled pads by their outside perimeters only. Pads were wrapped individually in foil and placed on ice in Gott™ coolers. Subjects' handwashes were collected by separately rinsing each hand in a baggie containing 250 mL of 95% ethanol. Each hand was rinsed three times. Rinses were kept separate and were transported to the laboratory in pint Mason jars. Upon reaching the laboratory, all samples were stored in a freezer at -20°C until extraction. Each subject was monitored six times. One applied tank mix equaled one monitoring period.

Exposed pads were center cut into a 40.32 cm^2 (2.5 x 2.5 in.) square and the square was quartered on a cutting board. The blade and cutting edge were washed with acetone and methanol after each pad had been cut. The quarters were placed into a 225 mL jar with 50 mL of a 30% acetone-70% hexane mixture and shaken on a flat rack shaker (New Brunswick Scientific, Model R-2) for 5 min at 350 RPM. This process was repeated once. Extractions from the two steps were combined, one drop of light paraffin was added, and the entire mixture was placed on a rotary evaporator (Brinkman Instruments, Model RE-120) at 40°C. The sample was taken to dryness and transferred into 10 mL hexane with three, approximately 3 mL rinses. After the third rinse, the 10 mL volumetric flask was brought to the mark with hexane. Samples were placed into 20 mL scintillation vials, sealed with opaque tape, and stored at -20°C until the sample was analyzed by GLC. Quality assurance pads were fortified with 10 µg ethion; recovery from these pads was 95.6 ± 9.9% (mean ± SD, n = 76). Quality assurance pads were included with each trial set of pads.

Handwash samples were transferred to a 500 mL separatory funnel and 100 mL deionized water was added. 50 mL hexane was added to this mixture and the separatory funnel was shaken for 2 min, venting frequently. The hexane fraction was removed to a boiling flask containing one drop of light paraffin oil. This process was repeated once, resulting in a total hexane extract of 100 mL. This volume was evaporated to dryness on a rotary evaporator and transferred into 10 mL of hexane. Samples were stored as described above. Recovery from 10 µg ethion handwash fortifications was 97.4 ± 5.4% (mean ± SD, n = 8).

All analyses were by gas chromatography using Ni^{63} electron capture detection. The gas chromatograph was a Perkin-Elmer Model 8320, Norwalk, CT. The column was 10 m x 0.25 mm (ID) DB-1 (0.5 µ film thickness) fused silica. Helium was the carrier gas with a 1 mL/min flow rate. Temperatures were: oven 175°C, injector 185°C, and detector 300°C. Injection was splitless. The lower quantitative limit of the GLC, defined as 10 times the baseline noise level for the instrument, was 100 ng per 10 mL (10 ppb).

During an analytical run, standards were introduced no less often than every fifth sample. A standard curve, consisting of at least four different known standard concentrations and their peak areas, was constructed and a regression analysis was used to quantify samples of unknown concentrations. For quantitative purposes, ethion (Lot MRU470, 95% purity) was obtained from FMC Corp., Agricultural Chemical Group, Middleport, NY 14105.

RESULTS AND DISCUSSION

Table 1 presents the percent of the total body exposure per body area. There were no statistically significant right vs. left differences in exposure (t-tests, $p < 0.05$). The applicators received a significantly greater percent exposure to the legs, and less percent exposure to the hands, than the driver (Subj. no. 1). The leg and hand exposure accounted for 78% and 73% of the applicators' exposure and 67% of the driver's exposure. On the average, the driver had a greater percentage of head-neck exposure than the applicators, although driver and applicator head-neck exposure data are inseparable statistically (t-test, $p < 0.05$).

Table 1. Percent exposure allocation of the total body exposure (including hands) (mean ± SE, n = 6)

	Subj. 1 driver-mixer	Subj. 2 applicator-mixer	Subj. 3 applicator-mixer
Head-neck (8)[a]	13 ± 10	5 ± 1	5 ± 1
Chest (17)	5 ± 2	6 ± 1	5 ± 1
Back (17)	4 ± 1	8 ± 2	4 ± 1
R. arm (7)	3 ± 1[b]	5 ± 2	4 ± 1[b]
L. arm (7)	8 ± 4	3 ± 0[b]	5 ± 1
R. hand (3)	22 ± 6[b]	10 ± 3	5 ± 1[b]
L. hand (3)	17 ± 6	10 ± 3[b]	4 ± 1
R. leg (19)	16 ± 7	24 ± 5	34 ± 4
L. leg (19)	12 ± 4	29 ± 6	35 ± 4

[a]Percent of total body area from height and weight according to Gehan and George (1970). [b]Hand-arm preference.

The mean ± S.E. estimated total body accumulation rate (ETBAR) in mg/hr, including hands, for six replications for each subject were: driver = 22.6 ± 4.1 mg/hr; applicator no. 1 = 116.6 ± 26.0 mg/hr; and applicator no. 2 = 169.7 ± 28.8 mg/hr. Applicator's no. 1 and no. 2 ETBAR's are statistically the same. The driver received about one-fifth the ETBAR of the applicators, a statistically significant reduction (t-test, $p < 0.05$).

Mean ± S.E. handwash accumulation rates in mg/hr for the six replications were: driver = 9.8 ± 4.0 mg/hr; applicator no. 1 = 27.4 ± 14.0 mg/hr; and applicator no. 2 = 15.9 ± 5.1 mg/hr. According to t-tests, no right vs. left differences in handwashes could be confirmed, even at $p < 0.10$.

The handwash data for wash no. 1 were combined for the three workers; wash no. 2 and no. 3 data were similarly combined. The various handwash results, expressed as a percentage of the first handwash, are (n = 36): handwash no. 1 = 100%; no. 2 = 20.6 ± 1.7%; and no. 3 = 6.8 ± 0.6%. We propose a model based on the assumption that each handwash removes a fraction (α) of the pesticide present before that wash. This is a standard first-order model that will yield an exponential decline in the pesticide remaining on hands. Expressed in terms of the amount initially present, M_o, the amount remaining after the first wash would be $M_o(1 - \alpha)$, after the second wash $M_o(1 - \alpha)^2$, after the third wash $M_o(1 - \alpha)^3$, etc. The amount removed by the first wash is $M_o\alpha$, by the second wash $M_o\alpha(1 - \alpha)$, by the third wash $M_o\alpha(1 - \alpha)^2$, etc. Expressed as a percent of the first wash, the second wash removed 100% $(1 - \alpha)$, the third 100% $(1 - \alpha)^2$, etc., or generally, the n-th wash removed W_n = 100% $(1 - \alpha)$ n - 1. Hence, $\ln(W_n) = \text{constant} + (n - 1)\ln(1 - \alpha)$. Regression of $\ln(W_n)$ on $(n - 1)$ yields $\alpha = 0.74 \pm 0.04$, with an R^2 of 0.99.

Table 2. Comparison of estimated total body accumulation rate (ETBAR) of this study with other studies where subjects wore no gloves

Crop location	Work activity	Pesticidal compound	ETBAR, including hand exposure (mg/hr)	Literature reference
Citrus	airblast applicator	dicofol	12 ± 2	Nigg et al., 1986
Citrus	airblast applicator	dicofol	26 ± 3	Nigg et al., 1986
Citrus	airblast mixer-loader	dicofol	4 ± 1	Nigg, et al., 1986
Citrus	airblast mixer-loader	dicofol	8 ± 1	Nigg et al., 1986
Greenhouse	boom tractor driver	fluvalinate	0.3	Stamper et al., 1989b
Greenhouse	boom tractor driver	chlorpyrifos	4.5	Stamper et al., 1989b
Greenhouse	boom tractor driver	captan	2.8	Stamper et al., 1989b
Greenhouse	boom tractor driver	chlorothalonil	5.1	Stamper et al., 1989b
Airboat	handgun applicator	2,4-D	16 ± 4	Nigg & Stamper, 1983
Airboat aq. weeds	handgun applicator	2,4-D	10 ± 2	Nigg & Stamper, 1983
Airboat aq. weeds	handgun applicator	2,4-D	17 ± 4	Nigg & Stamper, 1983
Airboat aq. weeds	handgun applicator	2,4-D	18 ± 5	Nigg & Stamper, 1983
Citrus	handgun appl.-mixer	ethion	117 ± 26	Present study
Citrus	handgun appl.-mixer	ethion	170 ± 29	Present study
Citrus	driver-mixer	ethion	23 ± 4	Present study

To summarize, the pesticide left on the hands after n washes, expressed as a fraction of that initially present, is $F = (1 - \alpha)^n$. Including the error term in α results in:

$$F = (1 - \alpha)^n \left[1 \pm \frac{n \, \Delta\alpha}{1 - \alpha} \right]$$

For example: what percent of the original ethion would be left on the hands after 5 washes in 95% ethanol?

$$F = (1 - 0.74)^5 \left[1 \pm \frac{5(0.04)}{1 - 0.74} \right]$$

$$= 0.12\% \pm 0.09\% \text{ of the original amount.}$$

The model's agreement with the field data can be calculated.

Expressed as a percent of the first wash, the second wash, according to the model, removes 100% $(1 - \alpha) = 26 \pm 4\%$, compared to the observed $21 \pm 2\%$; the third wash removes 100% $(1 - \alpha)^2 = 7 \pm 2\%$, compared to the observed $7 \pm 1\%$.

A similar model may be constructed for different compounds, wash solvents, and recovery techniques. However, the analytical form of this model may not hold for all handwash procedures. Certainly the specific values obtained for α and $\Delta\alpha$ will vary with procedure.

In comparing the ETBAR values in Table 2 with the ETBAR values of this study, the driver-loader of the handgun tank truck had a pesticide exposure comparable to an airblast applicator while the citrus handgun applicators had a pesticide exposure 5-10 times greater than with other application work practices. Based on these data, Florida citrus handgun pesticide workers are the most heavily exposed work group of any application technique we have examined.

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