Applied Occupational and Environmental Hygiene

ISSN: 1047-322X (Print) 1521-0898 (Online) Journal homepage: https://www.tandfonline.com/loi/uaoh20

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To cite this article: Richard A. Fenske , Nancy J. Simcox , Janice E. Camp & Cynthia J. Hines (1999) Comparison of Three Methods for Assessment of Hand Exposure to Azinphos-Methyl (Guthion) During Apple Thinning, Applied Occupational and Environmental Hygiene, 14:9, 618-623, DOI: 10.1080/104732299302422

To link to this article: https://doi.org/10.1080/104732299302422

Published online: 30 Nov 2010.

Applied Occupational and Environmental Hygiene
Volume 14(9): 618–623, 1999

1047-322X/99 $12.00 + .00

Comparison of Three Methods for Assessment of Hand Exposure to Azinphos-Methyl (Guthion) During Apple Thinning

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Hand exposures of apple thinners to the pesticide azinphos-methyl (Guthion) were measured using three methods (glove, handwash, and wipe). Hand exposure sampling for each method was conducted following apple thinning work for a period of two hours for six to eight workers. Foliar residue samples were collected on each day of hand exposure sampling in the same orchard blocks that were thinned; foliar residues are considered to have been constant during the four-day study, which took place, on average, six days after pesticide application. Hand exposure estimates derived from each of the three methods differed significantly (ANOVA: $p < 0.001$). Mean measured exposure rates for the glove, handwash, and wipe methods were 6.48, 1.83, and 0.28 mg/hr, respectively. A corrected estimate of hand exposure, 2.7 mg/hr, was calculated from the handwash measurements and the handwash removal efficiency factor from a laboratory study. Comparison with this hand exposure estimate suggests that the glove method produced a 2.4-fold overestimate of exposure, whereas the wipe method produced a 10-fold underestimate. Studies that measure hand exposure to pesticides should include a careful description of sampling methods and should recognize the potential for measurement bias. Furthermore, the standardization and validation of dermal exposure assessment methods are critical to developing more comparable and more accurate pesticide exposure estimates.

Keywords Azinphos-Methyl, Pesticides, Agricultural Workers, Apple Thinners, Exposure Assessment, Dermal Route, Glove, Handwash, Wipe

It has been recognized for more than 40 years that dermal absorption can contribute significantly to workers' total exposure to pesticides and that hand exposures in some work activities contribute the largest proportion of total dermal exposures.[1,2] The accurate and reproducible measurement of hand exposures is therefore an important part of appropriately monitoring workers' exposures, as well as an important element in setting exposure control guidelines and policies. Two previous studies have directly compared glove monitors and handwashing during field labor activities, and both found that gloves produced higher estimates of exposure.[3,4] However, neither study was able to demonstrate the accuracy of either of these techniques. Although it can be argued that gloves probably overestimate exposure due to their adsorptive quality, handwashing most likely underestimates exposure, because some fraction of the residue deposited on the hand is not removed by handwash procedures. Thus, no validated method for hand exposure measurement during field reentry activity has been established, nor is there a standard way to compare measured exposures among the different methods in common use.

The primary purpose of this study was to compare the magnitude and variability of exposure measurements derived from (1) glove, (2) handwash, and (3) hand wipe techniques by field measurement of hand exposure to azinphos-methyl during apple thinning. The present study was nested within a season-long evaluation of apple thinner exposure at multiple work sites.[5] Apple thinning was the focus of this study due to the frequent use of, and exposure to, organophosphorus insecticides during the thinning season, and the substantial contact with treated foliage experienced by workers while thinning. The results reported here provide quantitative comparison of the three methods sufficient for the calculation of rough adjustment factors across the methods. When these results are combined with information from laboratory experiments of removable levels of pesticides from hands,[6,7] a more accurate estimate can be made of hand exposure.

MATERIALS AND METHODS

Three exposure assessment techniques were used within a four-day period in a single apple orchard which had been sprayed with a 50 percent wettable powder (WP) Guthion formulation at 2 lb a.i./acre. Guthion contains the organophosphorus insecticide, azinphos-methyl [O,O-dimethyl S-(3,4-dihydro-4-keto-1,2,3-benzotriazinyl-3-methyl) dithiophosphate] as its active ingredient.

The orchard selected for the study was located in the Wenatchee region of central Washington. Orchard selection was based on the following criteria:

1. The orchard manager conducted conventional spray applications of organophosphorus insecticides;
2. Six or more apple thinners were employed at the site; and
3. The primary language of the workers was either English or Spanish.

Workers who performed apple thinning at the site were contacted through their employer, asked to participate in the study, and given a small monetary incentive. This study was approved by the University of Washington Human Subjects Review Committee, and participants provided informed consent. Each participant was asked about recent work history, demographics, and pesticide use in a brief screening interview. None of the workers was involved in pesticide application. Eight workers were recruited in all, and six to eight participated on each of the four consecutive study days.

The orchard blocks studied had been sprayed four to nine days prior to field sampling activities. Dislodgeable foliar residues were measured prior to work activities each day to establish that foliar levels were comparable over the four days of hand exposure assessment sampling. Collection of foliar samples that could be matched to each worker (i.e., samples of the actual trees they were to thin during the exposure sampling period) proved to be impractical, because workers often worked as teams, moved from one row of trees to another without clear notice, and thinned at varying rates. Thus, leaf samples represented the dislodgeable residues on the trees that were thinned by the whole crew during each day of the study period. All sampling was conducted during the period June 13–16, 1994.

Participants were asked either to (1) wear cotton gloves during thinning, (2) wash their hands in a polyethylene bag containing a surfactant/distilled water solution at the end of the exposure period, or (3) wipe their hands with a surfactant/distilled water solution at the end of the exposure period. For all hand exposure assessment samples, workers washed their hands with a surfactant-distilled water solution immediately prior to thinning activities to minimize pre-exposure contamination. A two-hour exposure period was used, long enough to avoid confounding by brief breaks in work activities by individuals, but short enough to evaluate worker exposures between regularly scheduled breaks.

For the glove exposure assessment method, each worker was supplied with two 100 percent cotton knit gloves (Photoco) commonly used in photographic darkrooms (weight = 21.7 mg/cm^2). Researchers wearing clean latex gloves pulled the cotton gloves off workers' hands at the end of the sampled period. Each glove was placed in a separate 16-oz. sample jar and stored on ice. For analysis, the left and right gloves were combined into one sample. For the handwash exposure assessment method, hands were washed in a polyethylene bag containing 250 ml of distilled water containing 1% Sur-Ten (sodium diocytyl sulfosuccinate), a surfactant. The worker's hand was inserted into the bag and vigorously agitated in the solution by a staff person for 60 shakes in 30 seconds, with the bag held tightly at the worker's wrist to prevent leakage. The washing procedure was conducted twice for each of the worker's hands, and the combined solution from all four washes was transferred to a clean 3.75 liter mason jar.

Approximately 100 ml of the total 1000 ml sample was transferred immediately into an 8-oz. glass sample jar for storage on ice. For the hand wipe exposure assessment method, a researcher used three $3'' \times 3''$ 12-ply cotton surgical gauze pads sprayed lightly with the surfactant wash solution to wipe each hand: one pad was used for the palm, one for the back of the hand, and one for the fingers and thumb. These pads were placed in a clean 9-oz. glass jar for storage on ice. For analysis, the wipes of the left and right hands were combined into one sample. All hand exposure samples were transported daily for storage at $-23°C$ in a laboratory freezer in Wenatchee.

Foliar residue samples were collected using the standard leaf punch method of Iwata et al.,[8] using a leaf punch sampler with a stroke-activated counter. Prior to field sampling, each 4-oz. collection bottle was washed and dried and its tare weight recorded. The block of trees to be thinned was identified, and 10 trees were sampled prior to thinning. The leaf punch die was cleaned with an alcohol-soaked swab, and a labeled sampling jar was attached to the leaf punch sampler. Leaf punches were collected from each of four quadrants of each of the 10 trees (40 leaf punches per sample). Jars were capped, stored on ice, and transported each day to the field laboratory freezer for storage ($-23°C$). All samples were later transported on dry ice to the University of Washington for analysis.

Information was obtained from the grower on orchard block sizes, block locations, tree types, azinphos-methyl spray date, application rate, tractor speed, application techniques and uniformity, and any malfunctions and/or repeated areas in the spraying process. Data on irrigation and weather conditions were also obtained. No precipitation occurred on any of the sampling days.

The sampling that was conducted is shown in Table I. For the glove dermal exposure assessment method, eight workers were recruited on day 1 (June 13), of whom seven also participated on day 4 (June 16). Different blocks within the orchard were thinned on the two days of glove sampling. The block for day 1 was sprayed with azinphos-methyl four days prior to sampling (on June 9). The block for day 4 was sprayed nine days prior to sampling (on June 7). Sampling was conducted in the afternoon on day 1 and in the morning on day 4. For the wash and wipe

dermal exposure assessment methods, six of the eight workers participated on each of two days (June 14 and 15). On day 3 (June 15), participants were five of the six workers who had participated on day 2, plus one worker who had not. Sampling on days 2 and 3 was conducted in two different orchard blocks within the same site sampled on day 1 (June 13); both were sprayed with azinphos-methyl five and six days prior to sampling (on June 9). Three wash and three wipe samples were taken each morning and afternoon on each of the two days, for a total of 12 dermal exposure assessment samples using each of these two methods.

A total of 23 glove samples, 22 handwashes, and 23 hand wipe samples were collected. Samples from workers included 15 glove samples, 12 handwash samples, and 12 hand wipe samples. Field blanks, spiked samples, and duplicate handwash aliquots were concurrently collected and analyzed as a part of quality assurance and control (data not presented). Two glove, two wash, and two wipe blank samples were collected; six gloves, six washes, and nine wipes were spiked with known amounts of azinphos-methyl formulation in the field laboratory on the sample days. With two of the handwash exposure samples on June 15, duplicate 100-ml aliquots were taken from the 1000 ml of handwash solution. In all, 23 foliar residue samples were collected during the hand exposure assessment study. In addition, a replicate field sample, a field blank, and a fortified sample were submitted with each day's foliar residue samples.

Sample extraction and analysis was conducted at the University of Washington's Environmental Health Laboratory. For glove samples, 150 ml of ethyl acetate was added to sample jars, which were placed on a shaker table at 100 cycles per minute (cpm) for 30 minutes. After gloves were squeezed out with tweezers and removed, 15 ml of the extract was transferred to a 40-ml vial; 0.95 ml of the solution was transferred to a gas chromatography (GC) vial, and 50 μl of triphenyl phosphate (TPP) (at 5 μg/ml) was added as an internal standard. For wash samples, 2 ml of the wash solution was transferred to glass culture tubes; each tube was spiked with 10 μl of tributyl phosphate (TBP) at 959 ng/ml in acetone; 2 ml of ethyl acetate and approximately 1.2 g NaCl were added to each sample. Capped tubes were vortexed for four minutes and centrifuged for five minutes at 2500 cpm; 0.95 ml of the upper layer was transferred to a GC vial; 50 μl of TPP at 5 μg/ml was added.

A second ethyl acetate extraction was conducted, like the first, by adding 2 ml of ethyl acetate to the tubes. For wipe samples, 100 ml of ethyl acetate was added to sample jars, and all other analysis steps were the same as for the glove samples. Leaf punch samples were surface extracted in a distilled water/surfactant solution for 20 minutes on a shaker table. The plant material was separated from the liquid phase and the extraction repeated twice. The three extracts were combined and 2 ml of the combined extraction solution were added to 12 ml ethyl acetate. This solution was placed on the shaker table for 90 min at 100 cpm. After 5 min, a 1.5 ml aliquot of the ethyl acetate layer was removed and analyzed.[8] All ethyl acetate extracts were analyzed by capillary gas chromatography on a Hewlett Packard HP5890A series II gas chromatograph, with a flame photometric detector operating in the phosphorus mode.

Laboratory recovery studies for each dermal exposure assessment method were conducted prior to sample analysis to ensure that target compounds could be removed from sampling matrices with high efficiency and reproducibility. As indicated previously, to test recovery efficiency in the field, each dermal exposure assessment medium was spiked and then handled, transported, and analyzed with the field samples.

All exposure (and exposure rate) values are reported as total exposure (or exposure rate) to two hands. Exposure rates were

TABLE I
Study design: sampling conducted

Day	Time of day	Leaf samples	Hand exposure sampling: thinners[A]		
			Glove	Wash	Wipe
1	p.m.	7	A, B, C, D, E, F, G, H	—	—
2	a.m.	2	—	B, D, G	A, C, F
	p.m.	2	—	A, C, F	B, D, G
3	a.m.	2	—	A, D, G	B, C, H
	p.m.	2	—	B, C, H	A, D, G
4	a.m.	8	A, B, C, D, F, G, H	—	—
Field exposure samples		23	15	12	12
QA/QC samples[B]		12	8	10	11
Total samples		35	23	22	23

[A]Individual workers are represented by uppercase letters.
[B]Includes field spike, field blank, and duplicate samples.

TABLE II
Mean azinphos-methyl recovery efficiency for the extraction of spiked samples for each of the dermal media (glove, wash, and wipe)

	Laboratory spiked samples[A]			Field spiked samples[B]	
Method	*N*	Recovery (%)	CV (%)	*N*	Recovery (%)	CV (%)
Glove	12	99.8	3.6	6	110.4	4.7
Wash	12	97.9	4.2	6	82.2	6.1
Wipe	10	101.9	4.8	9	93.0	6.2

[A]Spiking levels (in mg) for laboratory spiked samples were as follows: 1 ($N = 6$) and 3.9 ($N = 6$) for gloves; 3.2 for washes; and 0.1 ($N = 5$) and 2.1 ($N = 5$) for wipes.
[B]The spiking level (in mg) for field spiked samples was 5 mg per sample for all three media.

determined by dividing the exposure mass by the sampling time (2 hours). All data analysis was conducted using SPSS 6.1.1 for Macintosh.

RESULTS

The results of the laboratory and field recovery efficiency study are shown in Table II. Laboratory recovery efficiencies from the dermal sampling media were nearly 100 percent. Recoveries from field spikes for the gloves and wipes were also nearly 100 percent. Some loss was observed for the field spiked handwash samples, probably due to the aqueous matrix. Exposure data reported here were not adjusted for either laboratory or field recovery values.

Table III shows the dislodgeable foliar residue results for each day and the two-day mean foliar residue levels. Daily means ranged from 1 to 1.5 $\mu g/cm^2$. A one-way ANOVA of foliar residue by day showed that differences among the four means were not significant ($p = 0.10$). Mean residue levels for days 1 and 4, as compared to days 2 and 3 using an independent samples t-test, were not different. Thus, exposure potential, measured as dislodgeable foliar residues, can be considered to be constant for the purposes of comparing results from the hand exposure sampling media.

Glove, wash, and wipe methods showed substantially different exposure results. As shown in Table IV and in Figure 1, the glove exposure rate (6.48 mg/hr) was 3.5-fold higher than the wash rate (1.83 mg/hr); and the wash estimate was 6.4-fold higher than the wipe rate (0.28 mg/hr).

DISCUSSION

The hypothesis that handwash measurements can serve as valid estimates of hand exposure to pesticides has gained some support within the research and regulatory communities. The popularity of the handwash approach finds its origin in the seminal paper by Durham and Wolfe[2] which reported a 95 percent efficiency for an ethanol rinse procedure. This value is misleading, however, as it was determined by rinsing the hands twice, and assuming that the total removed by the two rinses represented 100 percent of the pesticide on the hands. No attempt was made to measure the amount of pesticide actually deposited on the hand. Thus, the 95 percent value was simply the amount removed by the first wash compared to that removed by two washes. Perhaps due to human subjects concerns, no further research to determine the accuracy of these procedures was conducted for approximately 30 years.

TABLE III
Mean dislodgeable foliar azinphos-methyl residues in field study orchards

Sampling day(s)	Days post-application	*N*	Mean foliar residue ($\mu g/cm^2$)	CV (%)	Hand sampling method
Day 1	4	7	1.05	26	glove
Day 2	5	4	0.98	21	wash, wipe
Day 3	6	4	1.48	43	wash, wipe
Day 4	9	8	1.38	22	glove
1 and 4	—	15	1.22[A]	27	glove
2 and 3	—	8	1.23[A]	42	wash, wipe

[A]Mean foliar residues for days 1 and 4, compared using a t-test to days 2 and 3, were not different.

TABLE IV
Mean measured exposure rate for each exposure assessment method (mg/hr), with comparison to estimated true exposure level

Method	*N*	Mean measured exposure rate (mg/hr)[A]	CV (%)	Percent of estimated true exposure rate[B]
Glove	15	6.48	28	240
Wash	12	1.83	27	68
Wipe	12	0.28	33	10

[A]Reported as total hourly exposure to two hands. Means were compared using ANOVA, and all are significantly different from each other ($p < 0.001$).
[B]Based on an exposure rate of 2.7 mg/hr, determined by adjusting the handwash exposure rate for handwash removal efficiency of 68 percent (see Discussion).[7]

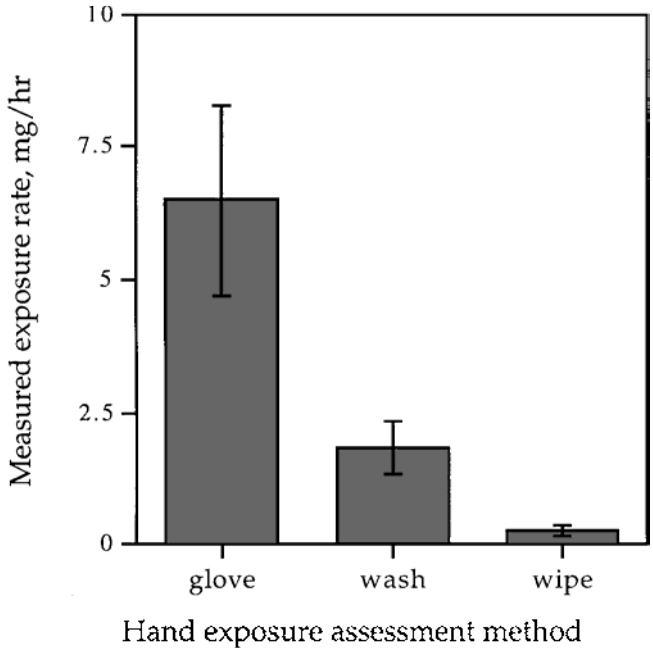

FIGURE 1
Comparison of hand azinphos-methyl exposure measured using glove, wash, and wipe methods (mean ± standard deviation).

The U.S. Environmental Protection Agency (EPA) "Subdivision K" guidance document for agricultural worker reentry exposure recommends that cotton gloves be used to measure hand exposure; handwashing is not presented as an option.[9] This recommendation is in keeping with an implicit recognition that handwashing will not remove lipophilic compounds from the skin completely, and will thus tend to underestimate exposure. In a similar guidance document for pesticide handler exposure assessment, the "Subdivision U" guidelines, the EPA recommends both the cotton glove monitors and the handwash, but not the hand wipe.[10] This approach seems reasonable in the context of pesticide handling, because this work may involve contact with concentrated liquids, and gloves may well absorb an unrealistically high amount of material during splashes or spills. Nonetheless, the handwash method measures only what can be removed from the skin following exposure, and thus may underestimate true hand exposure.

A laboratory study of the handwash removal efficiency of the fungicide captan found 78 percent removal upon immediate handwashing and 68 percent removal after one hour.[6] The protocols used in the captan study were first reported in a study of chlorpyrifos removal efficiency.[7] Although no similar study has been reported for azinphos-methyl, the captan value for one-hour exposure can be considered an appropriate surrogate for azinphos-methyl and the two-hour sampling period in this study, with the caveat that temporal characteristics of the field exposure somewhat compromise the confidence with which this direct comparison can be made. The comparable log octanol:water partition coefficients of azinphos-methyl and captan (azinphos-methyl log K_{ow} = 2.75; captan log K_{ow} = 2.35) support the assumption that azinphos-methyl is at least as sorptive to skin as captan.[11] It is important to note that matching on pesticide characteristics including partition coefficient, pesticide formulation, and handwash protocol is critical to making appropriate comparisons of handwash removal efficiencies.

In contrast to captan and azinphos-methyl, chlorpyrifos (log K_{ow} = 4.96) is typically formulated as a liquid concentrate, and the other two pesticides are formulated as wettable powders.[11] Table V presents relevant parameters for captan, azinphos-methyl, and chlorpyrifos. The use of surrogate data is widely accepted in pesticide exposure and risk analysis, but further research is needed to determine handwash removal efficiencies for various classes of pesticides and the formulations in which they are used.

The 68 percent one-hour captan removal efficiency value, which may overestimate azinphos-methyl removal, can be used in conjunction with the handwash measurements for apple thinners in this study to generate a hand exposure rate estimate of 2.7 mg/hr. The last column of Table IV indicates that the glove, handwash, and wipe exposure assessment methods result in hand exposure rate estimates of 240 percent, 68 percent (by definition), and 10 percent, respectively, of this estimated true hand exposure rate. Thus, estimates derived from different hand exposure assessment methods must be reported and used with care, taking into consideration the widely different results these methods produce. Even though it is unlikely that these particular relative values hold true for the entire class of organophosphorus pesticides, it is probably the case that the basic inequalities hold true, with the glove estimate higher than the handwash

TABLE V
Comparison of parameters relevant to handwash removal for chlorpyrifos, captan, and azinphos-methyl

Compound	Log octanol: water partition coefficient[11] (log K_{ow})	Formulation type	Removal efficiency at 1 hour
Captan	2.35	Wettable powder	68%[7]
Azinphos-methyl	2.75	Wettable powder	Unknown
Chlorpyrifos	4.96	Liquid concentrate	22%[10]

estimate, and the handwash estimate, in turn, higher than the wipe estimate.

This study illustrates the problems of comparability and validity inherent in the use of hand exposure assessment techniques. It is important that hand exposures be reported with recognition of potential measurement bias. Standardization is important in improving comparability across methods. Additional studies of validity are needed to improve the scientific accuracy of hand exposure assessment values used for the purposes of exposure evaluation, biomonitoring and health outcome studies, and for establishing policies and regulations regarding dermal exposures to pesticides.

ACKNOWLEDGMENTS

The technical assistance of David Kalman, I-Chwen Lee, Garland Bellamy, Arlene Stebbins, and Brian McDonald was greatly appreciated. Special thanks to Emily Allen for her help in developing this manuscript. The authors also wish to gratefully acknowledge all the participants in this study. This investigation was supported by the National Institute for Occupational Safety and Health (Contract No. 9438155), the University of Washington's Field Research and Consultation Group, and the Pacific Northwest Agricultural Safety and Health Center (NIOSH Cooperative Agreement No. U07/CCU012926-02).

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