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Methods for Assessing Fieldworker Hand Exposure to Pesticides during Peach Harvesting

R. A. Fenske, S. G. Birnbaum, M. M. Methner, and R. Soto

Department of Environmental Science, Cook College, Rutgers University, New Brunswick, New Jersey 08903, USA

Occupational exposure measurements are a critical component of quantitative risk assessments conducted by regulatory agencies to determine pesticide registration status in the United States and Canada (Franklin 1985; Maddy et al 1985). Exposure estimates from field studies exhibit high variability in part due to a lack of standardized and validated assessment methods. Hand exposure measurements are particularly critical in the evaluation of occupational exposure during field harvesting, since exposure to the hands normally represents a major fraction of total dermal exposure (Popendorf et al. 1979; Zweig et al. 1983; Winterlin et al. 1984). Although hand washing and glove monitoring have been conducted routinely over the past twenty years, the validity of these methods remains largely unknown (Durham and Wolfe 1962; Davis 1980; Noel et al. 1983; Zweig et al. 1983).

Cotton glove monitors are simple and inexpensive media for measuring hand exposure, but may overestimate exposure if cotton is more absorbent than skin. Hand washing measures residues which are easily removed from the skin, but necessarily underestimates exposure since some fraction of the pesticide deposited is retained by skin. Only one study has examined these methods systematically (Davis et al. 1983), demonstrating that glove monitors produced significantly higher azinphosmethyl exposure estimates than did handwashing during apple thinning. The experimental design of this study did not investigate the effect of sampling time on exposure estimates, nor did it include the measurement of residues reaching the hands beneath the gloves. The present study was designed to directly compare the glove monitor and handwash methods, and to determine field conditions under which these sampling methods will produce accurate exposure estimates.

Send reprint requests to R. Fenske at the above address.

MATERIALS AND METHODS

Studies were conducted in southern New Jersey during July and August at the Rutgers University Cream Ridge Agricultural Field Station. Captan [N-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide] was selected for study due to its common use as a fungicide on fruits and due to concerns regarding its toxicity. Captan 50W was applied with airblast equipment at a rate of 4.45 kg/ha (2 lb A.I./acre) to peach orchards. Label requirements were followed for worker reentry (<24 hr). Four field harvesters were recruited from the Field Station staff for each of the two study days. Harvesting was conducted at ground level since all trees were dwarf varieties (<2 m in height).

The hands of workers were pre-washed prior to all sample collection according to the handwash procedure described below. Each worker was then outfitted with one lightweight (11.6 mg/cm^2) 100% knit cotton glove commonly used in photographic darkrooms (Coast Inc., Mt. Vernon, NY). The other hand was left bare. Previous studies have demonstrated that most fruit pickers do not exhibit preferential handedness during harvesting (Zweig et al., 1983). However, to minimize potential confounding effects, the gloved hand was randomized between left and right hands within the study group. Workers conducted normal harvesting activities and glove and hand wash samples were collected at specified time intervals; i.e., after 0.5, 1.0, 1.5 or 3.0 hr of picking.

Gloves were removed by field staff wearing disposable latex gloves and placed immediately into a glass jar for storage in an ice chest. The hand beneath the glove was washed in addition to the bare hand. Each hand was washed in a polyethylene bag containing 250 ml of a 10% isopropanol/distilled water solution. The subject's hand was inserted into the bag and vigorously agitated in the solution for 30 sec. The solution was transferred to a 1 liter mason jar, the procedure repeated and the second wash combined with the first. Approximately 100 ml of the sample was transferred immediately into a glass jar for storage in an ice chest.

Foliar residue samples were collected throughout each study using the standard leaf punch method of Iwata et al. (1977). Fifty leaf punches were collected from eight trees located diagonally through the orchard. Temperature and humidity were recorded every hour during each study day. Picking rates were recorded by counting the number of peach buckets collected during the sampling periods (approx 50 peaches/bucket). All samples were transported in an ice-chest from the field to the laboratory on the study day, and were stored at -23^{o}C freezer until analysis.

Glove samples were thawed to room temperature and extracted in 90 ml toluene on a reciprocating shaker table set on high (100 cpm) for 30 min. Hand wash samples were thawed to room temperature and mixed to ensure homogeneity. Two ml of sample were added to 12 ml toluene and 2 ml saturated NaCl. The salt increased the initially low extraction efficiency of the captan in toluene (48.8%) to 97.0%. This solution was placed on the shaker table for 90 min. After a separation time of 5 min, a 1.5 ml aliquot of the toluene extract was removed and analyzed. Leaf punches were surface extracted (Iwata et al. 1977) in a distilled water/surfactant solution for 20 min on the shaker table. The plant material was separated from the liquid phase and the rinse was repeated two times. The three rinses were combined and 2.0 ml of this solution were extracted according to the method described above for handwash samples.

Captan was analyzed by gas-liquid chromatography (Hewlett-Packard 5890A) with an electron capture detector. The glass column (4 mm i.d.) was packed with 1.95% SP-2401 on Supelcoport 100/120. Chromatographic conditions were as follows: nitrogen carrier gas=96.6 ml/min; column temp=195 ^{o}C; detector temp=300^{o}C; injection port temp=200^{o}C. External captan standards were utilized for quantitation. The analytical limit of detection was 0.1 ug/ml. Limits of detection for gloves, handwash solutions and dislodgeable residues were 9, 300 and 180 ug/sample, respectively.

Recovery efficiencies were determined for the glove and handwash procedures by fortifying samples with formulated captan. Mean recoveries and standard deviations for gloves and handwashes were 95.8% +/- 7.8 and 97.0% +/- 1.4, respectively. Blank samples had no detectable captan. Eight samples of each media were fortified with captan formulation in the field to assess transportation and storage effects. Field fortification recoveries for gloves and handwashes were 103.2% +/- 5.0 and 18.4% +/- 11.6, respectively.

The low recoveries from handwash samples fortified in the field prompted a laboratory study simulating field storage conditions. Six sets of triplicate samples were prepared from a fortified handwash solution (2 ug/ml captan). One set was extracted and analyzed immediately, while the others were stored in a refrigerator (4^{o}C) for 1,2,4,8 or 24 hr. An additional set was immediately frozen for 24 hr. Captan recovery from refrigerated samples decreased linearly with time (R^2=.97) at a rate of 1.6%/hr. Loss from the frozen sample was negligible. Similar losses of captan were noted by the California Department of Food and Agriculture (J. Ross; personal communication). These results demonstrate that captan

losses in aqueous solutions are dependent on temperature and time. The temperature of the field samples stored in ice-chests may have become elevated due to high temperatures in the field (28-32^{o}C), resulting in significant degradation prior to frozen storage. Data for handwash samples have been adjusted for storage losses.

Exposure measurements appeared to be normally distributed, with very high or low values occurring infrequently and mean and median values most often similar. Thus, parametric statistics have been employed, including analysis of variance (ANOVA) with repeated measures and the Student-Neuman-Keuls Test (SNK) for multiple comparisons.

RESULTS AND DISCUSSION

Average dislodgeable foliar residues of captan were virtually identical for the two study days, indicating that potential exposure for workers was equivalent (Table 1). The average picking rate (buckets/hr) in July was nearly three times lower than the rate in August (ANOVA; $p<.01$), due both to the greater availability of peaches in August and the experience of the work crew (Table 2). When individual workers were grouped according to their picking rates the mean values of 5, 10 and 20 buckets/hr differed significantly (ANOVA;SNK $p<.05$). Hand and glove exposure measurements were more highly correlated with worker picking rates (R^2 =.58-.69) than with time worked (R^2=.41-.48).

Table 1. Dislodgeable residue levels (ug/cm^2)

Study	N	Mean	Median	Range	Std Dev
July	5	6.41	5.8	4.4 - 10.7	2.6
August	6	6.34	5.6	3.3 - 11.2	3.1

Table 2. Picking rate variability by study and worker

	N	Mean	Median (buckets/hr)	Range	Std Dev
Study					
July	16	6.9*	7.3	2 - 12	2.5
August	16	18.3*	19.7	10 - 24	4.6
Workers					
High rate	12	20.5+	20.5	16 - 24	2.6
Medium rate	12	9.7+	9.1	7 - 13	2.1
Low rate	8	5.2+	5.4	2 - 8	1.9

* sig diff (ANOVA $p<.01$) + sig diff (ANOVA:SNK $p<.05$)

Captan levels recovered from gloves were divided by the sampling interval to yield exposure rates (Table 3). Glove exposure was dependent on sampling time, with the 0.5 hr estimate significantly higher than the 1.5 and 3 hr estimates (ANOVA:SNK; $p<.05$). These results indicate that the absorptive capacity of the glove was greater at the outset of exposure and that the glove rates did not become constant until sampling was extended beyond 1.0 hr. Handwash exposure rates did not exhibit dependence on sampling time (Table 3). The slight decrease observed in rates over time was not statistically significant (ANOVA; $p>.05$). Handwash exposure rates were significantly lower than glove rates for the 0.5 hr and 1.0 hr sampling intervals (ANOVA:SNK; $p<.05$), but were not significantly different for the 1.5 and 3 hr intervals.

Table 3. Glove and handwash exposure rates by sampling time interval (N=8 for each time and sampling medium)

Time	**Glove exposure rate**			**Hand exposure rate**			G/H
(hr)	Mean (mg/hr)	Median	Std Dev	Mean (mg/hr)	Median	Std Dev	Ratio
0.5	43.6[a]	43	28	18.0	17	9	2.4*
1.0	32.5	31	18	15.5	15	8	2.1*
1.5	23.2[b]	25	8	16.6	16	8	1.4
3.0	21.0[b]	19	9	14.7	13	9	1.4

a,b glove rate at 0.5 hr sig diff than 1.5, 3.0 hr rates (ANOVA:SNK $p<.05$)

* glove rates sig diff than hand rates (ANOVA:SNK $p<.05$)

The relationship between glove exposure rates and sampling time was further investigated by grouping data according to the three picking rate categories (Figure 1). Statistical analysis was not appropriate due to small sample sizes (3,3 and 2, respectively), but the trends illustrate important relationships among the variables under study. The dependence of glove exposure rates on sampling time (Table 3) was accentuated for the High picking group: the 0.5 hr rate (60 mg/hr) fell to 45 mg/hr for the 1.0 hr sample, and to 23-28 mg/hr for the 1.5 and 3 hr samples. Exposure rates for the Medium picking group also decreased consistently, although rates were lower and the differences smaller than in the High group. Finally, rates of the Low picking group showed no evidence of time dependence.

These patterns are best explained by considering glove loading (i.e., total mass of captan deposited on glove) as an indicator of absorptive capacity. Decrease in absorptive capacity may be due to collection of moisture, soil and/or sweat, together with captan resi-

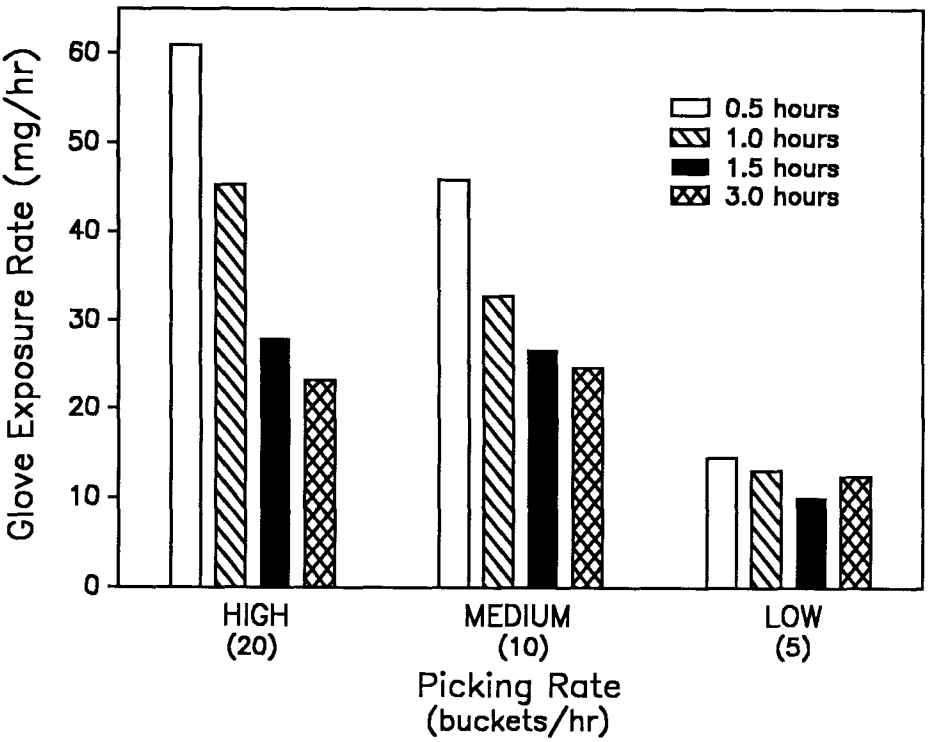

Figure 1. Glove exposure rates by picking rate category

dues. The Low picking group accumulated an average of 37 mg over the 3 hr sampling interval, whereas the High picking group accumulated an average of 30 mg in 0.5 hr, with an increase in loading of only 50% (45 mg) when sampling time was doubled. Thus, under the conditions of this study it appears that loading of 30-50 mg modified the absorptive capacity of the glove. Bare hand exposure rates remained constant over time within each picking rate category, although average rates differed significantly among the picking categories (22.5, 16.4 and 6.4 mg/hr for High, Medium and Low groups, respectively; ANOVA:SNK, $p<.05$).

Captan residues recovered from the hands beneath gloves indicated that breakthrough occurred within the 0.5 hr sampling interval and increased with sampling time (Figure 2). Gloved hand exposure was equal to bare hand exposure for the 1 hr sampling interval, and exceeded bare hand exposure for longer sampling times. The sum of glove and gloved hand exposure rates was approximately 50 mg/hr for the 0.5, 1.0 and 1.5 hr sampling intervals, falling to 40 mg/hr for the 3 hr interval. Thus, the decrease in glove exposure rates noted earlier was largely due to deposition of residues on the hand

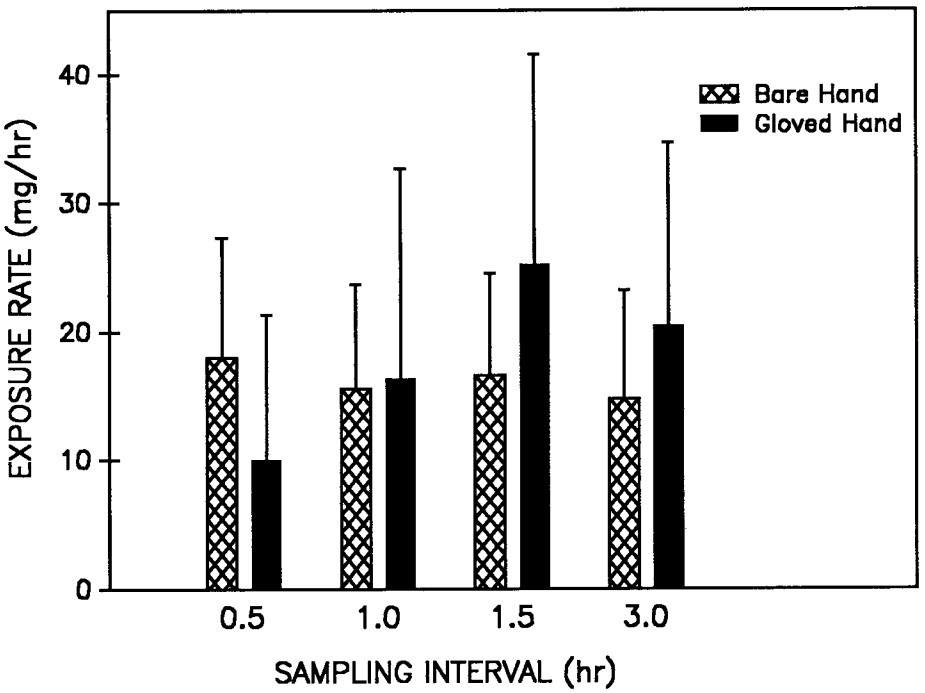

Figure 2. Gloved hand versus bare hand exposure rates (mean + standard deviation; N=8)

beneath the glove. The cotton gloves used in this study cannot be considered protective, since exposure to gloved hands can actually exceed bare hands.

This study indicates that cotton glove monitors produce significantly higher estimates of exposure than hand-washing for short sampling periods only (<1.5 hr). The 1.5 to 2.5-fold difference in exposure rates reported here is much lower than the 5-fold difference found by Davis et al. (1983) during 2 hr of apple thinning. Several differences in sampling procedures may explain this discrepancy. First, the weight of the cotton gloves in the apple thinner study was not specified. Substantially heavier gloves are likely to absorb higher levels of residues. Second, the ethanol handwash used for the apple thinners may have been less efficient in removing azinphosmethyl from the skin than was the iso-proponal/water handwash used in this study for captan. Finally, relative exposure rates may be partially dependent on the properties of the particular chemical and/or formulation under study.

This study highlights the major limitations of current hand exposure assessment methods for field harvesters. First, no standard glove method has been developed.

Both nylon and cotton gloves have been employed in harvester studies with weight or thickness unspecified (Popendorf et al. 1979; Zweig et al. 1983; Winterlin et al. 1984). Weight and thickness are critical variables regarding fabric penetrability (DeJonge and Easter 1987), and presumably affect absorptive capacity. Glove monitors are recommended by the U.S. Environmental Protection Agency, but no specifications are provided (USEPA 1985). Additionally, glove loading is dependent on picking rate and sampling interval length. A standard glove method would thus need to control or characterize all of these variables. Handwash exposure rates are stable relative to sampling time, but are highly dependent on picking rate. Furthermore, a standard solvent such as ethanol may remove different pesticides with varying efficiency, and results from studies in which different solvents have been employed may not be comparable.

The accuracy of these exposure assessment methods remains in question. Studies aimed at determining the relative absorption of pesticides by human skin and cotton gloves could validate the use of glove monitors. Experiments in which known amounts of pesticides are deposited on the skin and subsequently removed could validate the handwash technique. Future exposure assessment studies should control or carefully monitor dislodgeable residue levels, picking rates, and sampling time in an effort to validate the sampling techniques employed.

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