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Prediction of Pesticide Dermal Exposure and Urinary Metabolite Level of Tree Crop Harvesters from Field Residues*

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The establishment of a rational harvester reentry time into a pesticide-treated field requires estimation of the transfer coefficient (cm^2/hr) between foliar residue levels ($\mu g/cm^2$) and the accumlation rate on the body of the harvester (μg/hr). Our laboratory undertook an experiment in 1982 (Nigg et al. 1984) investigating the transfer of chlorobenzilate leaf residues to the body of Florida citrus harvesters in an effort to determine whether this coefficient might be regionally invariant, given the same compound and same crop. Dermal exposure was not estimated specifically in this study because some exposure pads were placed outside regular work clothing and some inside. The transfer coefficient to the outside of clothing was in agreement with that obtained in previous studies on the same crop in California (Popendorf and Leffingwell 1982), suggesting that regional differences may not greatly affect the magnitude of the transfer coefficient.

The present study was undertaken for these purposes: (1) to confirm this previous result, (2) to determine whether soil residues also correlate with body exposure, and (3) to obtain a transfer coefficient between field surface residues and residues penetrating normal work clothing, so that a better estimate of dermal exposure could be made from field conditions.

MATERIALS AND METHODS

Chlorobenzilate (ethyl 4,4'-dichlorobenzilate CAS No 510-15-6) was professionally applied with 'airblast' equipment to a mature block of 'Valencia' orange trees during April 16-18, 1983. The rate was 2 lb AI in 250 gal of water per acre. Another professional crew consisting of one foreman and 10 workers began harvesting the grove on April 25, 1983. Harvesters wore long-sleeved cotton shirts and cotton workpants. Exposure pads were pinned inside the shirt on the back, chest, both shoulders, both upperarms, and both forearms; they were also pinned inside the pants on both shins. Pads consisted of 4 x 4 in. glassine

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weighing paper backing, a 4 x 4 in. alpha-cellulose center, and a 16-ply 4 x 4 in. surgical gauze sponge outer dust collection medium. The alpha-cellulose center and the surgical gauze required a cleanup procedure prior to use in order to remove compounds which otherwise would have interfered with chlorobenzilate during gas chromatography (Nigg and Stamper 1983). Hand exposures were determined with 95% ethanol rinses. Untimed urine samples were collected at noon each sampling day. One replication of sampled leaves and fruit consisted of 40 one-inch-diameter leaf punches and 10 fruit, respectively. Soil samples were taken midway between trees by vacuuming surface soil upward through a 40-mesh screen. These sampling methods have been described in detail (Iwata et al. 1977, Gunther et al. 1977). Eight leaf sample replicates, four fruit replicates, and eight soil replicates were taken randomly within the harvesting area each sampling day. All samples were immediately placed in an ice chest and transported to the laboratory. Leaf samples were extracted immediately and the extracts stored at -20°C. All other samples were stored for 7-10 days at -20°C prior to analyses.

Chlorobenzilate was dislodged from leaf and fruit surfaces with a mild soap solution, extracted, and analyzed by gas chromatography. Chlorobenzilate was removed from the soil by sonication with methanol. The urinary metabolite of chlorobenzilate, 4,4'dichlorobenzilic acid, was oxidized to dichlorobenzophenone for gas chromatographic analysis and the chlorobenzilate equivalent calculated. Details for these procedures appear elsewhere (Nigg and Stamper 1983).

Analytical standards of chlorobenzilate (99.6% pure), 4,4' dichlorobenzilic acid(75%), and 4,4'-dichlorobenzophenone (92%) were supplied by Ciba-Geigy Corp., Greensboro, NC 27409.

RESULTS AND DISCUSSION

Recovery from six gauze pads fortified with 10 μg of chlorobenzilate was 97 ± 3%, and from 18 urines fortified at 100 ppb was 58 ± 4% (two outlying results of 1% and 7% could not be accounted for). Recovery analyses were not conducted on leaves, fruit, or soil as previously developed procedures were followed (Nigg et al. 1984).

Sampling data are presented in Table 1. Daily mean values are reported, together with the standard error of the mean and number of replications. Individual participating subjects constitute the daily replicates for exposure pads, handwash rinses, total body exposure estimates, urinary metabolite level, and number of boxes picked. Total body exposure was estimated from individual pads after the method of Wojeck et al. (1982).

The foreman was not included in these mean values as his work activity differed markedly from the other subjects. He received

38 ± 16% of the mean handwash exposure of the other combined subjects, 47 ± 5% of the mean total body exposure, but only 11 ± 4% of the mean urinary metabolite level of the other subjects. That a 53% reduction in mean body exposure should result in an 89% reduction in mean urinary concentration may seem surprising. However, a strict comparison of such long term means is probably not justified because of the complicated kinetics of urinary excretion (Goldstein et al. 1969).

Linear correlation coefficients, calculated between a number of variables paired on a daily basis, appear in Table 2, followed in parentheses by the number of pairs. The significance level of the correlation is also given, as well as selected regression line slopes and intercepts. The major relationships sought in this experiment were between worker body exposure and foliar, fruit, or soil residues; urinary concentration and worker body exposure; and urinary concentration and foliar, fruit, or soil residues.

The only linear relationships from the first group clearly validated by the data analysis were between soil surface residues and both total body and hand exposures. These relationships were established at a 99% significance level with correspondingly low standard errors in regression line slopes. We are not proposing, however, on the basis of this single experiment, that soil residue levels are a better predictive index of worker exposure than foliar residues. The possibility is interesting, but no published studies on soil residues versus worker exposure are available for comparison. More than the correlation coefficient, it is a well-defined regression line slope which is critical to any predictive model. Two recent models for the prediction of total body exposure from foliar residues for tree crop harvesters are in rather good agreement (Nigg et al. 1984; Popendorf and Leffingwell 1982). In the present study, no reliable linear relationship was established between foliar residues and exposure. A regression line slope of 2061 ± 2948 cm^2/hr did, however, result. A slope of 10652 ± 2392 cm^2/hr was obtained for the same compound one year earlier (Nigg et al. 1984). The two slopes (transfer coefficients), however, cannot be directly compared because they reflect different experimental designs. In our earlier study, the exposure to the lower body was estimated from pads placed outside the workpants on both thighs and shins. In the present study, shin pads were placed inside the workpants while inside thigh pads were categorically refused by our subjects. In order to compare the two coefficients, it is necessary to estimate what total body exposures would have been in our earlier study had thigh pads not been worn and had shin pads been placed inside the workpants. Fortunately, this can be done. The protective value of disposable coveralls was 96% in a study (Nigg and Stamper 1983) on chlorobenzilate; a more recent study by the authors on dicofol gives a protective value of 91% for a cotton workshirt and 97% for the same disposable coveralls. It would seem reasonable to re-estimate lower body exposure from

Table 1. Mean ± S.E.M. (No. replications) daily chlorobenzilate residues on leaf, fruit, and soil surfaces; fluxes onto harvester exposure pads; hands and estimated total body accumulation rates; urinary metabolite level; boxes of fruit picked

Date (1983)	4/25	4/26	4/27	4/28	4/29
Leaf ($\mu g/cm^2$)	.399 ± .030 (8)	.437 ± .040 (8)	.545 ± .019 (8)	.748 ± .047 (8)	.582 ± .043 (7)
Fruit ($\mu g/cm^2$)	.202 ± .036 (4)	.139 ± .013 (4)	.244 ± .016 (4)	.218 ± .023 (4)	.195 ± .031 (4)
Soil (ppm)	no sample taken	0.83 ± 0.16 (8)	10.86 ± 0.93 (8)	7.90 ± 0.67 (8)	6.85 ± 0.39 (8)
Flux ($\mu g/cm^2 hr$) on various pads					
Back		.012 ± .002 (8)	.053 ± .011 (9)	.026 ± .005 (10)	.047 ± .008 (9)
Chest		.013 ± .002 (6)	.104 ± .015 (9)	.059 ± .016 (10)	.054 ± .013 (9)
Shoulder		.024 ± .015 (8)	.050 ± .007 (9)	.039 ± .009 (10)	.053 ± .018 (8)
Upperarm		.017 ± .001 (7)	.198 ± .026 (9)	.092 ± .011 (10)	.111 ± .017 (9)
Forearm		.039 ± .006 (7)	.448 ± .075 (8)	.199 ± .040 (10)	.207 ± .019 (9)
Shin		.011 ± .007 (6)	.056 ± .011 (9)	.032 ± .004 (10)	.021 ± .004 (9)
Accumulation rate ($\mu g/hr$)					
Hands		30 ± 12 (8)	113 ± 58 (9)	107 ± 72 (10)	105 ± 46 (9)
Estimated total body		277 ± 51 (7)	2085 ± 151 (9)	1077 ± 160 (10)	1102 ± 141 (9)
Urine (ppb)	2.6 ± 0.5 (9)	5.9 ± 1.2 (8)	13.9 ± 3.0 (9)	57.7 ± 12.0 (10)	100.7 ± 27.9 (9)
Boxes picked	69 ± 4 (9)	79 ± 7 (8)	53 ± 2 (8)	88 ± 6 (10)	49 ± 4 (9)

Table 1. Mean ± S.E.M. (No. replications) daily chlorobenzilate residues on leaf, fruit, and soil surfaces; fluxes onto harvester exposure pads; hands and estimated total body accumulation rates; urinary metabolite level; boxes of fruit picked (cont'd)

Date (1983)	5/2	5/3	5/4	5/5	5/6
Leaf ($\mu g/cm^2$)	.516 ± .023 (8)	.554 ± .023 (8)	.195 ± .027 (8)	.483 ± .041 (8)	.766 ± .090 (8)
Fruit ($\mu g/cm^2$)	.195 ± .065 (3)	.312 ± .052 (4)	.082 ± .010 (4)	.178 ± .040 (4)	.062 ± .015 (4)
Soil (ppm)	4.10 ± 0.49 (8)	3.05 ± 0.43 (8)	0.69 ± 0.13 (8)	0.48 ± 0.12 (8)	0.54 ± 0.10 (8)
Flux ($\mu g/cm^2 hr$) on various pads					
Back	.027 ± .004 (10)	.027 ± .006 (9)			
Chest	.040 ± .007 (10)	.032 ± .009 (8)			
Shoulder	.031 ± .007 (10)	.027 ± .007 (9)			
Upperarm	.063 ± .010 (10)	.042 ± .012 (9)			
Forearm	.100 ± .016 (10)	.090 ± .014 (9)			
Shin	.015 ± .003 (10)	.011 ± .001 (9)			
Accumulation rate ($\mu g/hr$)					
Hands	48 ± 15 (10)	31 ± 10 (9)			
Estimated total body	633 ± 90 (10)	535 ± 93 (9)			
Urine (ppb)	14.4 ± 4.5 (10)	56.4 ± 17.8 (9)	62.5 ± 11.6 (10)	30.8 ± 7.4 (10)	32.9 ± 7.3 (9)
Boxes picked	84 ± 6 (10)	69 ± 5 (9)	50 ± 5 (10)	95 ± 10 (10)	67 ± 5 (5)

Table 2. Correlation coefficients , correlation significance levels, and regression lines, Y on X, between various harvester and field variables.

Y	X	Corr. coeff.	Sig. level (%)	Reg. line slope	Reg. line intercept
Mean daily total body exposure (μg/hr)	X_1[a]	+.33 (6)[b]	44	+2061 ± 2948[c] cm^2/hr	-210 ± 1686[c] μg/hr
"	X_2	+.26 (6)	35	+2824 ± 3779 cm^2/hr	+338 ± 843 μg/hr
"	X_3	+.96 (6)	99	+170 ± 25 μg/ppm-hr	+3 ± 161 μg/hr
Mean daily handwash exposure (μg/hr)	X_1	+.64 (6)	81		
"	X_2	+.03 (6)	4		
"	X_3	+.93 (6)	99	+10 ± 2 μg/ppm-hr	+15 ± 154 μg/hr
Mean daily urine conc. (ppb)	X_1	+.14 (10)	29		
"	X_2	+.05 (10)	11		
"	X_3	+.15 (9)	29		
"	X_4	+.05 (6)	7		
"	X_5	+.40 (6)	54		
Mean daily urine conc., next day (ppb)	X_1	+.77 (8)	98	+151 ± 51 ppb-cm^2/μg	-28 ± 26 ppb
"	X_2	+.49 (8)	77	+220 ± 160 ppb-cm^2/μg	+2 ± 33 ppb
"	X_3	+.70 (7)	92	+4.9 ± 2.3 ppb/ppm	+31 ± 12 ppb
"	X_4	+.38 (5)	43	+.017 ± .023 ppb-hr/μg	+43 ± 23 ppb
"	X_5	+.63 (5)	71		
Daily total body exposure (μg/hr)	X_6	-.30 (53)	97		

[a] X_1: Mean daily leaf residue conc. ($\mu g/cm^2$); X_2: Mean daily fruit residue conc. ($\mu g/cm^2$); X_3: Mean daily soil residue conc. (ppm); X_4: Mean daily total body exposure estimate (μg/hr); X_5: Mean daily hand exposure (μg/hr); X_6: Daily boxes picked

[b] Number of data pairs

[c] Standard error

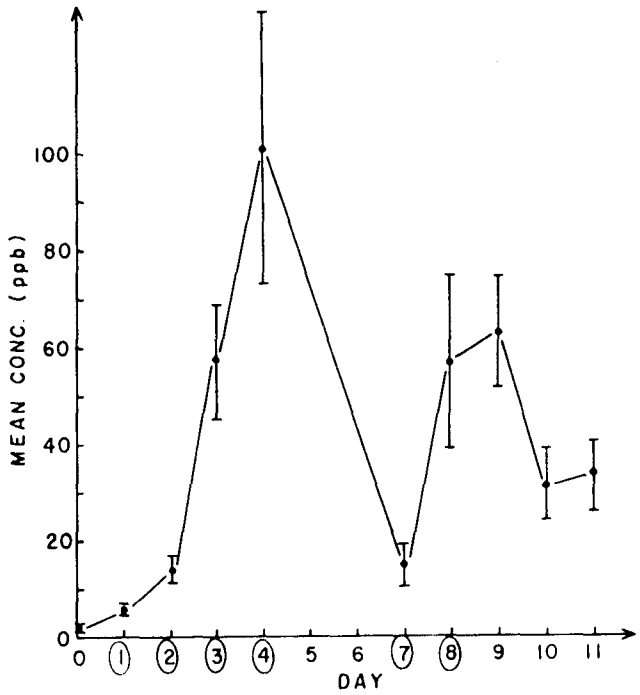

Figure 1. Mean daily urinary chlorobenzilate concentration, all harvesters vs. time. Day 0 = 25 April 1983; circle surrounding day denotes a harvester exposure day.

our earlier (Nigg et el. 1984) data, for purposes of comparison with the present data, by using shin pad contamination only, but reduced by 91%. The resulting re-estimation of total body exposure, inside clothing, for our earlier study then yields a coefficient of 2841 $\pm$ 427 cm^2/hr which compares favorably with the 2061 $\pm$ 2948 cm^2/hr obtained here, even though the latter value lacks precision.

A hindrance toward obtaining valid correlations in this study arose partly from an unavoidable circumstance encountered in the field. Spraying was carried out over several days. Harvesters were usually sent to work in areas of the grove which had been sprayed about the same number of days previously. As a result, the usual decline in field surface residues with time one normally observes does not exist in Table 1. In fact, residues in the field were often at about the same level when worker body exposure was being monitored. If the X-values (field residues) do not distribute themselves at much wider intervals than their standard error (here, about 13%), significant correlations with any other variable cannot be expected.

Urinary concentrations correlated well with field residues sampled the previous day, less well with body exposure from the previous day, and not at all with field residues or body

exposures on the same day. This suggests that the process of dermal absorption and urinary excretion of chlorobenzilate extends over several hours in humans. Figure 1, a plot of mean daily urinary concentration over all harvesters versus time, shows rises in urinary concentration with persistent exposure, followed by declines with approximately a 2-day half-life during unexposed periods.

A two-factor analysis of variance was carried out on the estimated total body exposure of the 10 harvesters (one factor) and the 6 exposure days (other factor). A significant variation among harvesters resulted. This variation, while not extreme, was still valid at about the 95% confidence level and is, of course, unaccounted for by differences in field residues. Variations in body exposure rates among workers nominally performing the same tasks are not uncommon and are usually attributed to differences in work practices among workers. Work practices are difficult to quantify and monitor. Work productivity is easier to quantify (boxes picked per day) but difficult to monitor because the record keeping, performed by the foreman, is in practice often rather creative. For example, a worker's total for the day may be inflated by the foreman at the expense of a second worker in financial debt to the first in order to assure payment of the debt. This may explain why no correlation was obtained between daily boxes picked and total body exposure in the present study since foremen routinely corroborate altered productivity data. Our previous study with workers under the supervision of a more literal forewoman showed a positive correlation with 90% significance.

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