

Health & Safety *Report*

Worker Health and Safety Branch

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GREENHOUSE PESTICIDE MIXER/LOADER/APPLICATOR EXPOSURE STUDY

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Summary

Forty-three greenhouse applications of six pesticides were monitored to investigate the relationship between dermal and inhalation exposure and amount of active ingredient. Within each pesticide, average worker exposure estimates were calculated. The protective value of both rainsuits and normal work clothing during greenhouse application activities was also evaluated. Three exposure scenarios were investigated: outside the rainsuit, beneath a cloth layer, and beneath the rainsuit. Patch dosimetry was used to evaluate exposure outside the rainsuit and beneath a single cloth layer. Patch dosimetry and hand washes were used to evaluate exposure beneath the rainsuit. Inhalation exposure was also evaluated. Exposure estimates varied widely within each pesticide, but were generally greater for pesticides applied at higher rates. Overall mean exposure measured outside the rainsuits was 281 mg, while potential inhalation exposure averaged 0.12 mg. Exposure under a cloth layer averaged 110 mg and exposure beneath the rainsuit averaged 3.4 mg. Residues found outside the rainsuits were predominantly to the lower body, while residues beneath the rainsuits were predominantly to the hands and forearms. Residue penetration through the rainsuits averaged 1% across pesticides. In examining the relationship between each exposure scenario vs. g pesticide applied, a significant relationship was found only for captan exposure beneath the rainsuit ($r = 0.82$). These data may be incorporated into risk assessment documents and used in making regulatory decisions concerning worker protection.

Introduction

Applications of pesticides in greenhouses differ substantially from those made in outdoor field environments. Pesticides may be applied to greenhouse crops year-round, often on a three-day schedule, rather than seasonally, and often at higher application rates than to field crops (See Ref. 1 and 2 for review). Greenhouse pesticide applications are labor-intensive and are often not amenable to the types of engineering exposure mitigation controls available for field use, such as enclosed cabs. Hand-held application equipment places the applicator in closer contact with the sprayed material, in both liquid and aerosol form, and the enclosed space slows the settling and dissipation of residues. Cultivation of greenhouse crops is also labor-intensive, requiring the worker to maintain sustained physical contact with treated foliage. These factors contribute to potentially higher exposure levels for greenhouse workers as compared to field workers. Data on greenhouse applicator exposure is limited (3). In 1987, the Department of Pesticide Regulation (DPR), Worker Health and Safety Branch (WH&S), conducted dermal and inhalation monitoring of 43 greenhouse applications of six pesticides to measure exposure under standard greenhouse conditions and to examine whether exposure and amount of active ingredient applied, independent of pesticide, were linearly related (See Ref. 4 and 5 for other WH&S reports related to this study). The data from this study may be used in preparing estimates of risk to greenhouse mixer/loader/applicators (M/L/As) and in worker protection regulatory decision-making.

Materials and Methods

Field Portion

The study was conducted in San Diego, Santa Cruz, San Mateo, Orange, and Monterey Counties between March and November, 1987. The applications took place in either fully or semi-enclosed greenhouses. All treatments delivered the pesticide via a hand-held spray wand. The following pesticides were selected to represent the typical 100-fold range in greenhouse pesticide application rates: abamectin, acephate, benomyl, captan, chlorothalonil, and fluvalinate. Application rates ranged from 0.009 - 1.13 pounds active ingredient (a.i.) per 100 gallons spray mix. The majority of the spray mixes contained a single target pesticide, with no other pesticides present. For mixes containing more than one target pesticide, residue analysis was restricted to a single target pesticide. The treated crops were alstroemeria, carnations, chrysanthemums, lilies, roses, and various house plants. Application information is presented in Table I.

Forty-three male workers, experienced in greenhouse pesticide applications, were monitored from 1 to 4 hours each (mean = 2.2 h). Several applications involved two monitored workers, performing similar M/L/A tasks simultaneously. Cumulative exposure was monitored over the full time period required to complete mixing, loading and application operations. Each study participant wore the following protective

Table I. Greenhouse Application (App.) Information

Pesticide	Formulation	n	App. Rate (lb a.i./100 gal) Range	Total Applied (g/app.) Range and mean	Commodity
abamectin	emulsifiable concentrate	8	0.009 - 0.01	4 - 12 mean = 2.6	carnation chrysanthemum roses
acephate	soluble powder	10	0.375 - 0.750	104 - 454 mean = 366.8	alstroemeria carnation chrysanthemum lilies
benomyl	wettable powder	1	0.250	227	carnation
captan	wettable powder	8	0.5 - 1.0	141 - 1815 mean = 828.8	carnation house plants roses
chlorothalonil	flowable; wettable powder	9	0.25 - 1.13	236 - 767 mean = 453.6	carnation lilies roses
fluvalinate	flowable	7	0.063 - 0.250	57 - 340 mean = 207.3	chrysanthemum roses
Total		43			

clothing and equipment over work clothes for the duration of each exposure monitoring interval: mid-calf-length rubber boots, rainsuit, (bib overall pants and hip-length jacket), mid-forearm-length, chemical resistant, waterproof gloves, goggles or face shield, the rainsuit hood and/or a hard hat, and a half-face dual cartridge respirator equipped with organic vapor cartridges. While representing greater protection than required by product labeling, this protective clothing and equipment is worn as standard practice by California greenhouse applicators. Rainsuit cuffs were tucked into the gloves to minimize exposure to spray materials. Study staff provided new rainsuits and gloves to each worker prior to each monitored exposure period.

Dermal Exposure Dermal exposure was measured by the use of modified Durham and Wolfe patches, knit glove liners, and hand washes (6).

Dermal Patches Two types of patch dosimeters were used, an outer patch composed of three layers and an inner patch composed of two layers. All layers measured 7.6 x 7.6 cm. Outer patches were constructed of an outer layer of 7-ounce, 65% Dacron polyester/35% cotton twill, a middle layer of 12-ply, 100% cotton gauze, and an inner layer of food grade aluminum foil. Outer patches constituted two samples, the twill layer, and the gauze/foil layers combined. Inner patches were constructed of the gauze and foil layers only and, combined, constituted one sample. Patch layers were stapled into a foil-backed patch holder that exposed 23.75 cm² of sampling media. Prior to the exposure period, paired left and right patches were taped to the outside of the rainsuit in the following locations: chest, upper arm, front and

back forearm, front and back thigh, and front and back shin. Similarly, paired upper and lower back patches were taped in place. Inner patches were taped under the rainsuit to the outside of workers' clothing and placed to correspond to the outer patch body regions without obstruction by the outer patches. At the end of the exposure period, the patch holders were removed and paired left and right patches (and upper and lower back patches) were combined to provide three samples for each body region (27 patch samples per worker). Head patches, consisting of only the gauze and foil layers, were taped to the outside front and back of the outermost head covering, either the hood or hard hat, and combined to provide one sample for this region. Each patch sample was placed in a four-ounce glass jar, the jar then sealed with aluminum foil, capped, and stored frozen until extraction. Inside shin patches were protected by both the rainsuit and rubber boots. All other inside patches were protected by only the rainsuit. This strategy allowed the evaluation of exposure at three levels of dermal protection: unprotected (outer cloth patches and the head patches), protected by a cloth layer (outer gauze/foil patches), and protected by a rainsuit (inner gauze/foil patches). Comparisons of residues captured at each of these levels evaluated the relative residue penetration through cloth and rainsuits, and thus the relative protection offered by each layer. Regional exposure distribution was also investigated.

Gloves Knit gloves of either 100% cotton (for abamectin applications; pre-washed to remove fabric and finish interferences), or 100% nylon (for all other pesticide applications; pre-washing not indicated) were worn as liners under the waterproof gloves for the duration of the monitoring interval (Table II). Glove liners were collected at breaks and at the end of the day, prior to collecting hand washes. New glove liners were distributed after a break. Left and right gloves were combined as a single sample, sealed in a one-gallon Zip-Loc[®] bag and stored frozen until extraction.

Handwashes One hand wash was collected prior to the exposure period and two sequential washes were collected prior to breaks and at the end of the exposure period. Each consisted of a one-minute wash in 800 mL of a 1% sodium dioctyl sulfosuccinate solution, contained in a one-gallon polyethylene bag. The sample was placed in a 1.0-L Nalgene[®] bottle, the bottle capped, then stored frozen until extraction.

Inhalation Exposure Airborne concentrations of pesticides were measured using a personal air sampling pump attached to the worker's belt. The pump was connected to a sampling train consisting of a plastic filter cassette, loaded with appropriate glass fiber filter and mounted in the worker's breathing zone, backed by the appropriate sorbent tube, if indicated (Table II). A Kurz Model 540S mass flow meter was used to set the pump flow rate to 1.0 liter of air per minute (1 L/min) at the start of the monitoring period and to assess the flow rate at the end of the monitoring period. Pumps were turned off for any break longer than five minutes. Final pump flow rate and elapsed time were recorded for each monitoring interval. Cassettes and sorbent tubes were capped, then placed in jars. The jars were then capped and stored frozen until extraction.

Quality Control All quality control samples, as specified in the following descriptions, were handled, stored, shipped, and analyzed in the same manner as field samples. Formulated product and spray tank samples were stored separately from exposure samples.

Formulated Product Samples: An aliquot of approximately one ounce of the target formulated product was collected prior to each monitoring interval. Each aliquot was placed in a four-ounce glass jar, which was sealed with aluminum foil, capped, sealed into a Zip-lo[®] bag, then placed immediately on dry ice and kept frozen until extraction. These samples were used for laboratory quality control fortifications.

Spray Tank Samples: For each exposure period, approximately 16 ounces of tank mixture was collected and divided evenly into a 16-ounce Nalgene[®] bottle and a 16-ounce glass jar. Both containers were capped, the Nalgene[®] bottle stored frozen until extraction and the glass jar stored chilled to approximately 34 - 40 °F until extraction. Approximately one ounce of tank mixture was collected in a four-ounce glass jar for use in sample media fortification. Tank mix remaining in the sample collection jar after media fortification was retained for analysis. The jar was sealed with aluminum foil, capped, and stored frozen until extraction.

Sample Fortification: Two sets of dermal media were fortified with diluted tank mixture at 2, 5, and 20 times the minimum detection level (MDL) for the respective pesticide. Each set consisted of two replicates at each rate. A single replicate at each fortification rate consisted of the following: one cloth and one foil patch, combined; one gauze and one foil patch, combined; one patch cut from the appropriate glove fabric (nylon or cotton), and one 400-mL aliquot of hand wash solution. All patches measured 7.6 x 7.6 cm. One set of fortified media was stored on dry ice when the pesticide application began. The second set was stored on dry ice at the end of the monitoring period. Two sets of air sampling media, identical to the media used for the worker monitoring, were fortified with tank mix solution diluted to two times the MDL. Each set was connected in train to a pump calibrated to an air flow of 1 L/min. The pumps drew air through the fortified media for one hour. The final pump flow rate was recorded.

Field Background: Air samples were collected for one hour pre-application. Each sampling interval included two pumps drawing air through clean filtration media. Each sample consisted of a sampling train identical to that used for the worker monitoring, with the pump calibrated to a flow rate of 1 L/min. Final pump flow rates were recorded.

Field Blanks: One set of sample blanks was submitted for analysis with each set of field samples. Each set consisted of the following: one three-layer patch (cloth/gauze/foil), one two-layer patch (gauze/foil), a nylon or cotton glove fabric square (depending on the pesticide being monitored), a 400-mL aliquot of hand wash solution, and a set of inhalation media appropriate for the pesticide under evaluation. Field blanks were briefly exposed to greenhouse conditions in an area away from the treatment site, then handled in the same manner as exposure samples.

Laboratory Portion

Sample Extraction and Analysis All extractions and analyses were conducted by the California Department of Food and Agriculture, Center for Analytical Chemistry. Exposure samples and associated field quality control samples were analyzed in the same manner. Tank mix and formulated product samples were brought to room temperature and mixed thoroughly in the sample container before sub-sampling for extraction, then diluted to 2, 5, and 20 times the MDL for analysis.

Residues of acephate, captan, chlorothalonil, and fluvalinate were extracted from cloth and gauze patches, gloves and glove fabric patches, sorbent tubes, and air filters with ethyl acetate. Residues of captan, chlorothalonil, and fluvalinate in hand wash, tank mix and formulated product samples were extracted with ethyl acetate and dried with sodium sulfate. Acephate residues were extracted from hand wash, tank mix, and formulated product samples by blending an aliquot with ethyl acetate and sodium sulfate, then evaporating to the desired volume.

Abamectin extraction and analysis was conducted according to a modification of Method 5004 of Merck, Sharp and Dohme Research Laboratories (7). Residues on cloth and gauze patches, and gloves and glove fabric patches, were extracted with methanol. Residues on sorbent tubes and air filters were extracted with toluene-acetonitrile. For hand washes, tank mix, and formulated product samples, sodium chloride was added to an aliquot and residues were extracted with ethyl acetate followed by drying with sodium sulfate. Extracts were derivatized with acetic anhydride in N,N-dimethylformamide with 1-methylimidazole as a catalyst. The reaction mixture was dissolved in chloroform and passed through a Sep-pak[®] silica cartridge. The eluant was evaporated to dryness and re-dissolved in methanol.

For benomyl, residues on cloth and gauze patches, gloves, sorbent tubes, and air filters were extracted with methanol. Hand washes, tank mix, and formulated product samples were extracted with dichloromethane, evaporated, then extracted with methanol.

Frozen storage recovery was conducted using tank mixture diluted to 1, 5 and 20 times the MDL and frozen for 8 weeks. Each week, sub-samples were brought to room temperature, mixed thoroughly, and analyzed. Analyses for acephate, captan, chlorothalonil, and fluvalinate were conducted by gas chromatography, using nitrogen as the carrier gas.

The operating conditions were as follows:

Fluvalinate: Hewlett-Packard 5880 A, 5% phenyl methyl silicone capillary column, 25 m by 0.20 mm ID; 15 p.s.i., split vent at 50 mL/min, septum purge at 2 mL/min, ECD make-up at 30 mL/min, injector 275 °C, oven 270 °C, detector 300 °C.

Chlorothalonil: Hewlett-Packard 5880 A, 5% phenyl methyl silicone capillary column, 25 m by 0.20 mm ID; 15 p.s.i., split vent at 50 mL/min, septum purge at 2 mL/min, ECD make-up at 30 mL/min, NPD make-up at 20 mL/min, injector 275 °C, oven 270 °C, detector 300 °C.

Captan: Hewlett-Packard 5880 A, 5% phenyl methyl silicone capillary column, 12.5 m by 0.20 mm ID; 15 p.s.i., split vent at 50 mL/min, septum purge at 2 mL/min, ECD make-up at 30 mL/min, injector 225 °C, oven 195 °C, detector 350 °C.

Acephate: Hewlett-Packard 5880 A, SE 54 fused silica capillary column, 25 m by 0.20 mm ID; 15 p.s.i., helium make-up at 25 mL/min, split vent at 50 mL/min, septum purge at 2 mL/min, NPD make-up at 30 mL/min, injector 225 °C, oven 120 °C, detector 250 °C.

Analyses for abamectin and benomyl were conducted by HPLC. The operating conditions were as follows:

Abamectin: Perkin Elmer series 4, Altex Ultrasphere ODS, 5 µm column, 150 mm by 4.6 mm ID, mobile phase 93% methanol, 7% water, 1.5 mL/min, oven 35 °C, fluorescence detector: excitation, 364 nm, emission, 480 nm.

Benomyl: Perkin Elmer series 4, Altex Ultrasphere ODS, 5.5 µm column, 150 mm by 4.6 mm ID, mobile phase 50% methanol, 50% (NH₄)₂HPO₄ (0.01 M), 1.5 mL/min flow rate, oven 35 °C, UV detector, 282 nm.

The MDL was defined as three times the baseline noise level. MDLs for each sampling medium and pesticide are presented in Table II. Sub-samples of the prepared extracts were analyzed to determine the range of expected residues. Standard curves of at least three different concentrations in this range

Table II. Minimum Detection Limits for Sampling Media (µg/sample)

Compound	Gauze	Cloth	Glove	Air filter	Sorbent tube	Hand wash ^{/1}
Abamectin	0.25	0.25	1.25 C	0.10 \a	0.02 \b	2.0
Acephate	0.25	0.25	1.25 N	0.10 \a	N I	2.0
Benomyl	0.50	0.50	2.50	0.20 \a	0.04 \d	4.00
Captan	0.12	0.12	0.62 N	0.05 \a	N I	1.0
Chlorothalonil	0.12	0.12	0.62 N	0.05 \c	0.01 \d	1.0
Fluvalinate	0.25	0.25	1.25 N	0.20 \a	0.02 \b	2.0

/1 400 mL of hand wash solution

C Cotton gloves

N Nylon gloves

N I Not Indicated

\a Glass fiber filter, type AE

\b Type Chromosorb 102

\c Glass fiber filter, type A

\d XAD-4 resin

were run with the exposed samples. Standards were introduced no less often than every 15 exposed samples. Standards were obtained from the U. S. Environmental Protection Agency, Pesticide and Industrial Chemical Repository, Research Triangle Park, NC 27711.

Data Analysis Uncontrolled variables for most exposure intervals included time worked, type of greenhouse, crop and maturity, ventilation system, temperature, humidity, time of day, brand of sprayer,

nozzle type, bench height, and aisle width, among others. Some exposures were replicated, consisting of two workers performing similar tasks simultaneously, using the same tank mix and working for approximately equal time periods. Data were grouped to allow general observations about greenhouse exposures. Non-detected residues were reported at the MDL. Exposure was calculated by extrapolating patch residues to the corresponding body surface area(s), using EPA Subdivision U guidelines (8). Exposure estimates for outer, inner, and dermal exposure, given below, were then developed from the adjusted patch residues. Regional exposure distribution (%) was calculated by comparing total summed residues for each anatomical region (range of n = 37 to 43). Pre-exposure hand wash residues were reported but not included in exposure estimates. Exposed hand wash and knit glove residues were summed for dermal exposure to the hands. Inhalation exposure was calculated by summing filter and sorbent tube residues, then adjusting for a 36.75 L/min breathing rate for moderately heavy work in high heat conditions (8,9). Four exposure scenarios were investigated: mean outer, cloth, inner, and dermal exposures were calculated across pesticide, for workers with complete exposure residue data sets (n = 37). Head patch residues were included only in the calculation of outer exposure.

Outside Rainsuit

Outer (O):

$$O = \text{outer cloth patches} + \text{head patches}$$

Cloth (C): Exposure under a cloth layer

$$C = (\text{outer gauze} + \text{foil patches})$$

Outside Rainsuit Exposure = $O + C$ = Exposure to an unprotected worker

Inside Rainsuit

Inner (I): Exposure under protective clothing

$$I = (\text{inner gauze} + \text{foil patches}) + \text{hand exposure}$$

Dermal (D): Residues available for percutaneous absorption, using an estimate of 10% residue penetration through clothing (i.e., 10% of inner patch residues) (10):

$$D = 0.10[I - \text{hand exposure}] + \text{hand exposure}$$

Cloth and rainsuit penetration were calculated as follows:

$$\% \text{ cloth penetration} = [\text{cloth exposure} / (\text{outer} + \text{cloth exposure})] \times 100$$

$$\% \text{ rainsuit penetration} = [\text{inner exposure} / (\text{outer} + \text{cloth} + \text{inner exposure})] \times 100$$

Linear correlation analysis was conducted on the following: outside rainsuit exposure (outer + cloth residues) vs. g a.i. applied, inner exposure vs. g a.i. applied, and inner exposure by pesticide vs. g a.i. applied. A 0.05 level of statistical significance was selected.

Results

Recovery data are presented in Appendix 1. Tank mix and formulated product recoveries were 95%, with the exception of captan. This compound is readily hydrolyzed and had very poor recoveries for both

formulated product and tank mix spikes from handwash solutions (37 - 38%). As expected, captan also demonstrated poorer recoveries for tank mix spikes compared to recoveries of formulated product. Where conducted, storage recovery results were $\geq 90\%$, with the exception of benomyl (53%), which is highly insoluble in aqueous media. The high MDL for benomyl is related to both insolubility and hydrolysis, as are poor recoveries for hand wash and tank mix samples with benomyl present at levels less than 2 X the MDL. Blank samples had no detectable residues. Ninety-eight percent of all field samples were analyzed within 8 weeks. None of the study results were adjusted for recoveries. Individual worker exposures are given in Appendix 2, available on request, and include raw residue data for inhalation, patch and hand exposure, regional exposure extrapolation, and calculation of outer (O), cloth (C) and inner (I) exposure.

Worker exposure means are presented in Table III, for workers with complete exposure residue data sets (n = 37). Inhalation exposure averaged 0.12 mg. This represents a "worst case" estimate of potential inhalation exposure as 96% of these data were extrapolated from the MDL. The half-face respirators worn by all workers provided 90% protection from ambient inhalation exposure (11). Thus, actual inhalation exposure is estimated at 0.01 mg.

Table III. Mean Worker Exposure (mg) to Six Pesticides (n = 37) For Five Exposure Scenarios

	Outside Rainsuit			Inside Rainsuit	
	Inhalation	Outer	Cloth	Inner	Dermal
Exposure Potential	0.12	281	110	3.4	0.8
% Penetration			28% of outer residues	1% of outside rainsuit residues	19% of inner residues, 0.2% of outside rainsuit residues

Potential Inhalation = ambient pesticide residues adjusted for 36.75 L/min breathing rate (Ref. 9)

Outer = outside cloth patches, extrapolated to body region

Cloth = outside gauze and foil patches, extrapolated to body region

Inner = inside gauze and foil patches, extrapolated to body region, + hand exposure

Dermal = 10% of inner patch residues + 100% hand exposure

Estimates of outer, cloth, and inner exposure are also somewhat conservative with 4%, 15%, and 3%, respectively, deriving from extrapolations using the MDL for dermal matrices. Non-detected values for outer exposure were too few to be characterized. Non-detected residues for cloth and inner exposure were generally associated with low overall exposure for that worker, rather than with a pattern of non-detected residues for specific body regions. Overall, outer exposure was about 2.5 times greater than cloth exposure and about 80 times greater than inner exposure. Cloth exposure was about 30 times greater than inner exposure. Mean residue penetration through the outer patch cloth layer was 28% and through the rainsuit, 1% (n = 37).

Inner Exposure Exposure beneath protective clothing (inner exposure), normalized for spray rate, was examined for each pesticide. Results for workers with complete residue data sets (n = 37) are presented in Table IV. Inner exposure represents patch residues potentially available for dermal absorption,

subsequent to penetration through a clothing layer, and hand residues immediately available for percutaneous absorption. In general, pesticides applied at higher rates had correspondingly higher inner exposures. The exception was captan, with the highest mean amount applied (828.8 g) and the second lowest exposure (2.7 µg/g a.i. applied, n = 7). Each pesticide gave a wide range of exposures, with the mean weighted by several very high values. Thus, the median exposure is generally less than the mean; for chlorothalonil, the mean exposure is about 14 times the median.

In examining residue penetration through rainsuits by pesticide, the single benomyl application exhibited far greater penetration than did the other pesticides monitored (28.3% for benomyl vs. a mean of <2% for each of five other pesticides). While this observation needs to be replicated to confirm this high value, its magnitude had little effect on the overall calculation of average residue penetration.

Table V presents the mean exposure to each body region for outer, cloth, inner, and dermal exposure scenarios for all workers (n = 37 to 43). The lower body receives the greatest portion of outer and cloth exposure, with 59.4% and 75.3%, respectively. Inner and dermal exposure are primarily to the forearms and hands, with 79% and 88.9%, respectively. No significant correlation was found for total outer, cloth, and inner exposure vs. g a.i. applied. For analyses by pesticide, only captan inner exposure correlated significantly with amount applied ($r = 0.82$, $p < 0.05$).

Discussion

Inhalation Exposure The small contribution of inhalation exposure to total body exposure for greenhouse applicators (<1% of outer exposure) is consistent with observations by other investigators. Previous studies reported respiratory values for greenhouse mixers and applicators of <0.1% - 1.5% of total body exposure (12,13,14). Inhalation exposure in this study, when adjusted for respirator use and compared to all measured exposures beneath the rainsuit, represents just 0.3% of inner, or protected, exposure.

Table IV. Inner Exposure by Pesticide (inside patches + hand exposure)
(Exposure = µg/g a.i. applied)

Pesticide	n	Mean grams applied	Median Exposure	Mean Exposure	SD	% CV	% Rainsuit Penetration
Abamectin	8	2.6	2.0	2.6	2.2	85	0.48
Acephate	8	366.8	6.0	19.6	38.8	198	1.84
Benomyl	1	227	NA	8.6	NA	NA	28.3
Captan	7	828.8	2.1	2.7	2.6	96	0.48
Chlorothalonil	8	453.6	2.8	38.8	79.9	206	1.50
Fluvalinate	5	207.3	7.5	6.5	2.9	45	0.50

SD Standard deviation
CV Coefficient of variation
NA Not Applicable

Table V. Mean Residues and Percent Regional Exposure for Outer, Cloth, Inner and Dermal Exposure

Region	N	Outside Rainsuit				Inside Rainsuit			
		Outer		Cloth		Inner		Dermal	
		mg	%	mg	%	mg	%	mg	%
Head	43	5.30	1.6	NA	NA	NA	NA	NA	NA
Back	43	12.67	3.9	1.23	0.9	0.14	2.8	0.014	1.5
Chest	42	34.12	10.4	9.31	6.7	0.12	2.4	0.012	1.3
Upper Arm	41	51.85	15.8	11.73	8.4	0.15	3	0.015	1.6
Back Forearm	37	16.08	4.9	7.22	5.2	2.86	56.8	0.286	30
Front Forearm	37	13.03	3.9	4.95	3.6	0.62	12.3	0.062	6.5
Hand	40	NA	NA	NA	NA	0.50	9.9	0.5	52.4
Thigh Back	40	22.93	7	9.30	6.7	0.10	2	0.01	1.0
Thigh Front	40	82.20	25	55.53	40	0.30	6	0.03	3.1
Shin Back	41	31.37	9.6	17.46	12.6	0.15	3	0.015	1.6
Shin Front	41	58.27	17.8	22.32	16	0.10	2	0.01	1.0
Total		327.82	99.9	139.05	100.1	5.04	100.2	0.954	100

Inhalation Exposure averaged 0.12 mg (n = 42)

Outer exposure = outside cloth patches

Cloth exposure = exposure through a cloth layer = outside gauze and foil patches

Inner exposure = exposure under protective clothing = inside gauze and foil patches + hand exposure

Dermal exposure = 10% of inner patch residues + 100% of hand exposure

NA = Not Available; no exposure value for this region

Worker Exposure Variations in individual work habits can have a large effect on exposure measurements. When mixing and loading pesticides, patch contamination from a spill or splash will contribute to very high apparent exposures when extrapolated to body region. When applying, the worker is surrounded to some degree by a fine mist of suspended droplets. The spray wand is held at chest height and from this region down, the applicator frequently contacts the spray as well as runoff from the treated plants. The forearm and hand regions are a prime area for contamination as the arm is typically extended and often slightly raised, allowing both spray material and runoff to run down the arm of the protective clothing.

While contamination of areas beneath the rainsuit is generally considered attributable to pesticide penetration, the hood, neck, arm, glove, leg, and boot openings, coupled with the pumping, bellows-like action observed for these areas, all provide opportunities for the pesticide to bypass, rather than penetrate, the protective clothing barrier (15). Contamination by processes other than penetration frustrate the investigator attempting to characterize "typical" greenhouse worker exposure, while demonstrating the potential for risk and the importance of mitigation measures. In this study, outside cloth and gauze pads were often observed to be saturated with spray solution. This obfuscates the assumptions inherent in considering gauze pads to reflect cloth penetration, since skin does not exhibit the wicking characteristics of gauze and a cloth layer may not contact the skin as closely as did the patch layers. Nonetheless, the potential for saturation of the outer garment emphasizes the value of waterproof outerwear in protecting workers conducting greenhouse spray operations.

Outer and Cloth Exposure Outer and cloth exposure were primarily to the legs (59.4% and 75.3%, respectively; Table V). Stamper et al. (13) found similarly high outer exposure (84%) to the legs of greenhouse handgunners applying fluvalinate, chlorpyrifos, ethazol, and dicofol. Fenske et al. (12), in evaluating greenhouse M/L/A exposure to the fungicide fosetyl-AI, found the legs and forearms each contributed about 25 - 50% to outer exposure, with mixers accumulating greater exposure to the legs and applicators accumulating greater exposure to the forearms. In this study, forearm residues represent about 10% of both outer and cloth exposure scenarios.

Inner and Dermal Exposure The mean coefficient of variation (CV) for inner exposure was 126%. This is probably related only partly to variation in compounds, subjects, spray rates and work periods since large variations in exposure measurements are common for greenhouse workers, even in studies where spray rate, compound or monitoring period are held constant. Fenske et al. (12) found a mean CV of 84% and 103%, respectively, for outer and inner exposure. Stamper et al. (13) found a mean CV of 40% in total body residue accumulation to greenhouse handgunners. Inner and dermal exposures were primarily to the hands and forearms, in sharp contrast to the exposure distribution observed for outer and cloth exposure. This reflects both the greater degree of arm/hand contact with the sprayed materials, compared to the lower body, and the protection offered to the lower legs by both the rainsuit and the tall boots.

Mean dermal exposure was estimated to be 0.8 mg (Table III), or 0.36 mg/hr (mean exposure period = 2.2 h). Previous WH&S studies have estimated median dermal exposure to 65 M/L/As in agricultural field operations to be about 1.0 mg/h, using hand washes under gloves and bi-layer patches, mounted under cloth coveralls, to simulate penetration through clothing (16). While about one-third of the dermal exposure data in the present study were based on extrapolations from MDLs, greenhouse workers were more highly protected than in the previous WH&S investigations. Yet greenhouse workers' dermal exposures were in the same range as workers in conventional field M/L/A operations. This emphasizes the unique exposure environment present in greenhouses and underscores the need for a more complete understanding of the role of factors influencing exposure.

Head Exposure Workers in this study wore either hard hats, rainsuit hoods, or both, which, coupled with goggles and respirator, protected the majority of the head region. Overall means for this study indicate that the head (5.3 mg, Table V) contributed about 1% to exposure outside the rainsuit. However, if the rainsuit hood were not worn, this same amount would be deposited on the head and would constitute approximately 50% of inner exposure and nearly all of dermal exposure. Other investigators have found significant exposure to the head when protective gear is not worn. Fenske et al. (12) found the exposed face and neck regions accounted for 28 - 38% of exposure, via extrapolations of outside chest, back and shoulder residues. Mestres et al. (14) added 10% of dermal exposure to account for head exposure.

Forearm and Hand Exposure The forearm is the primary inner exposure site (69.1%, Table V), while the hands contributed about 10%. However, inner patches collected only 8% (3.48 mg vs. 41.28 mg) of the forearm residues found outside the rainsuit. The back of the forearm collected several times the front forearm residues, as this area captures most of the runoff to the arm. This pattern of inner residue distribution is similar to that found by other investigators for dermal exposure distribution. Both Fenske and Mestres measured greenhouse M/L/A dermal exposure directly. Fenske et al. (12) found a distribution of dermal exposure to the forearm and hand of 50% and 6%, respectively, using gauze forearm patches beneath work clothing, and hand rinses beneath latex gloves. Mestres et al. (14), monitoring greenhouse applicators using a pneumatic disc harrow to apply dicofol and a vaporizer to apply deltamethrin, found lower total contributions of the hand and forearm (40%, using patches beneath work clothing and glove liners), while finding a similarly greater portion of residues on the forearm compared to the hand (34% and 6%, respectively). Forearm residues in the present study, adjusted for clothing penetration, contribute 36.5% to dermal exposure.

The hands, especially when unprotected, have typically been a major route of worker exposure (16, 17). Exposure to the hands contributed 52.4% to calculated dermal exposure in the present study (Table V), representing a five-fold increase over the contribution of the hand to inner exposure (9.9%) and a nearly ten-fold increase when compared to the contribution of the hand to dermal exposure in other studies (6%) (12, 16). In this study, the absolute residue contribution to inner and dermal exposure is identical in both exposure calculations (0.5 mg, Table V). However, when inner patch residues are adjusted for expected

residue penetration through clothing, the hands and the rest of the body contribute approximately equal parts to dermal exposure. The investigators treated all exposure beneath the waterproof glove as dermal exposure to the hand, rather than consider the glove liner residues to be “inner” residues and the handwash residues to be “dermal” residues, because it is not standard greenhouse practice to wear a glove liner. This monitoring strategy emphasizes that measurable penetration occurs beneath waterproof gloves during typical greenhouse applications and that these residues may represent the greatest portion of residues available for percutaneous absorption.

Pesticide Penetration Estimates of penetration of pesticides through work clothing give general values that can be compared to those from other studies. The pesticide residues captured on the outer gauze/foil patches reflect potential pesticide transfer through work clothing. While all study participants wore rainsuits, this may not be standard practice for workers outside California as rainsuits are not often required by pesticide product labeling. Mean cloth penetration was 28%, although saturated outer pads were a confounding factor. Fenske et al. (12) found penetration to pads mounted beneath greenhouse applicators' work clothing to range from 2 - 16%. DPR uses a default clothing penetration value of 10% for applicators, while other WH&S work supports using a 25% clothing penetration value for harvesters (10, 18). Higher penetration values observed for greenhouse applicators may reflect physical activities and a residue environment that are more similar to those of harvesters, where workers may be immersed in the foliage, than to field M/L/As, who typically sit atop a tractor.

Residue penetration through the rainsuit averaged 1% in this study but was markedly greater for the single benomyl application (range = 0.48 - 28.3%, Table IV). Stamper et al. (13) found a similarly large range of 1 - 34% of outer residues penetrating Tyvek® coveralls for four pesticides, with the highest values associated with ethazol applications. Other studies have found Tyvek® to allow an average of only 3% of residues to penetrate (19).

Correlation of Exposure vs. grams a.i.: Exposure was normalized for total amount of active ingredient handled to compare exposures without modifying the data for work rate. Significant correlation between amount handled and exposure, either overall or by pesticide, could validate the use of a generic database for greenhouse M/L/As, simplifying the exposure assessment and risk analysis processes. Ideally, such a database would provide surrogate exposure estimates for pesticides not previously investigated in greenhouse settings. However, in this study, a significant correlation was found only between captan handled vs. residues beneath the rainsuit (inner exposure, $r = 0.82$). Even this apparent correlation for captan may be coincidental, as both the application rate and the exposure rate happened to vary by two-fold. Furthermore, with approximately one-third of all the dermal data extrapolated from the MDL, trends may be obscured by the monitoring method. It appears that exposure is a complex matrix of variables that may not lend itself to modeling in terms of a single physical application parameter. Further clarification of the relative contribution of individual exposure variables could be achieved in future studies by restricting the study to a single active ingredient with a low detection limit, using a single application

setup (crop, equipment, time worked, etc.), and monitoring workers with air pumps, full body dosimeters, hand washes, and face and neck wipes.

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APPENDIX 1

GREENHOUSE MIXER/LOADER/APPLICATOR EXPOSURE STUDY, HS-1455

SAMPLE FORTIFICATION AND STORAGE RECOVERIES

Percent Recovery, means of 15 replicates ; 5 each at 1, 5 and 20 x MDL

Media	Fluvalinate		Chlorothalonil		Captan		Acephate		Abamectin		Benomyl	
	FP	TM	FP	TM	FP	TM	FP	TM	FP	TM	FP	TM
Handwash	100	100	99	96	37	38	105	101	98	97	99	100
Gauze	101	98	98	100	100	64	105	98	100	92	102	99
Cloth	95	100	96	96	96	60	110	105	94	96	101	99
Gloves	101 N	100 N	98 N	98 N	78 N	72 N	118 C	112 C	101 N	109 N	104 N	109 N
Air Filter	102	103	103	98	87	53	108	109	NI	NI	NI	NI
Sorbent Tube	101	99	97	98	82	69	107	115	99	95	97	97
Storage Recovery (8 wk)	NC		97		90		102		NC		53	
Range of MDLs for all matrices (ug/sample)	0.02 - 2.0		0.01 - 1.0		0.05 - 1.0		0.1 - 2.0		0.02 - 2.0		0.04 - 4.0	

FP Formulated Product

TM Tank Mix

N Nylon Gloves

C Cloth Gloves

NI Not Indicated

NC Not Conducted