WORKER EXPOSURE TO CHLOROTHALONIL RESIDUES DURING THE HARVEST OF FRESH MARKET POLE TOMATOES

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SUMMARY

Sixteen workers harvesting fresh market pole tomatoes were monitored for hand, arm, torso, thigh, and "total" dermal exposure to chlorothalonil (tetrachlorisophthalonitrile) during a pilot worker exposure study in October 1987. A full-scale exposure study monitoring harvesters over three work days was performed in November. Twenty-one to twenty-five harvesters were assigned to one of three treatment groups on each study day. Treatment groups consisted of workers wearing their "normal attire", or long-sleeved overshirts provided by the researchers with either new nylon knit gloves or latex gloves. The normal attire group wore their own long or short-sleeved shirts and worked either bare-handed or with used nylon knit or latex gloves. Exposure data were sorted by shirt and glove type rather than by treatment groups for analysis purposes. The average "total" exposure for workers wearing normal attire, and provided long-sleeved shirts with new nylon or latex gloves was 1898.1, 1122.8, and 602.8 micrograms chlorothalonil per hour, respectively. Residue penetration through provided long-sleeved shirts was estimated at thirty percent, comparing data from overshirts with corresponding undershirt dosimeters. Latex gloves provided the greatest hand protection when compared with new or used nylon gloves.

However, data indicated that the use of any type of glove along with long-sleeved shirts provided the same protection in regard to overall "total" exposure.

INTRODUCTION

Chlorothalonil (tetrachloroisophthalonitrile) is a broad spectrum fungicide used on ornamental, field and horticultural crops as well as in wood preservatives and paints for the control of numerous plant pathogens, including wood rotting organisms and mildews. Major agricultural crops include pole and bush tomatoes which account for 39 percent of the reported chlorothalonil sales (1). Fungicides are applied to tomatoes throughout the year, but more frequently during the fall planting season when morning dew and rain are prevalent. Wet environmental conditions, such as those encountered during the fall season, promote the growth and spread of Botrytis causing "gray mold" fungus on tomatoes. Growers prefer to use chlorothalonil over other fungicides to control Botrytis because of the long residual activity. Additionally, disease resistance to chlorothalonil has not developed as it has with other fungicides used for Botrytis control. Production of fresh market tomatoes grown on poles requires intensive use of hand labor. Pole tomato workers are exposed to chlorothalonil residues while involved in harvesting and cultural activities such as tying vines, pruning, and suckering. Cultural activities account for a small portion of the year-long work when compared to the time spent harvesting tomatoes. For example, when plants are in full production, workers harvest tomatoes six days per week for eight to ten hours per day. Therefore, workers are potentially exposed to chlorothalonil residues for 48-60 hours per week when plants are at maximum production. Workers could feasibly be harvesting pole grown tomatoes up to nine months during the year depending on the growing region and planting schedules.

Preliminary estimates based on predictive models of harvester exposure to chlorothalonil residues indicate that there may be an unacceptable level of risk to these workers. Potential adverse effects due to chlorothalonil exposure have been identified in the areas of oncogenicity, chronic toxicity and genetic toxicity (2). If, in fact, harvesters are exposed to unacceptable residue levels under actual field conditions, mitigation measures must be applied to reduce their potential exposure. Potential mitigation measures could include the required use of gloves and long-sleeved shirts to reduce potential dermal exposure. This exposure study was conducted to characterize potential exposure to chlorothalonil residues during harvesting activities and examine the protective value of latex gloves, new and used nylon knit gloves, and long-sleeved shirts. .pa

MATERIALS AND METHODS

Staff from the San Diego County Agricultural Commissioner's office and the California Fresh Market Tomato Advisory Board assisted in contacting and arranging cooperation with pole tomato growers. Picking crews that were harvesting late season, mature plants treated with chlorothalonil (Bravo® W-75) one to seven days prior to harvest were selected for monitoring purposes. Mature plants were selected because they would have been treated with chlorothalonil on several occasions prior to and during harvest. Therefore, these plants might contain the highest dislodgeable residues found during the growing season. Subsequently, workers could potentially receive the most exposure to chlorothalonil residues while harvesting mature tomato plants.

Workers were observed during harvesting activities to identify body areas that might be exposed to dislodgeable chlorothalonil residues. The front thigh area, hands, arms, and torso became considerably soiled with tomato sap and field dust after a short period of harvesting. In addition, the head (hats) and shoulders of small stature individuals also became soiled. These individuals were observed reaching with their entire upper body into the canopy in pursuit of ripe tomatoes. Therefore, potential dermal exposure to the upper body, (including head) and front thigh regions was monitored using several types of dosimeters.

Pilot Study:

One picking crew of 16 male workers was monitored for one full workday. Dermal dosimeters were worn the entire workday which included the lunch break (7.7 hours work plus 0.5 hour lunch break). Crew members were assigned to one of the following four treatment groups:

A. bare hands
B. new nylon knit picking gloves provided by the investigators
C. latex gloves
D. used nylon knit picking gloves provided by the workers; presumed to be clean because workers find it difficult to harvest while wearing gloves stiff with tomato sap, and the grower requires the use of clean gloves.

Each worker was provided with a half-sleeved, 100 percent cotton tee-shirt (long-sleeved shirts with the sleeves trimmed to elbow length) to monitor dermal exposure to the torso and upper arm. The tee-shirt was worn under the workers normal attire. Thirteen workers wore long-sleeved button up overshirts, and three workers wore short-sleeved tee-shirts as overshirts; three of the 16 crew members wore their overshirts for only a portion of the work day. At the end of the workday the undershirts were collected, placed in Ziploc^R storage bags, and packed on dry ice (solid carbon dioxide).

Two types of dermal patches were used to assess potential exposure to the front thigh and head regions. The first type of patch, which was used to monitor the front thigh area, was constructed of an outer layer of cloth (7-ounce 65% dacron polyester, 35 percent cotton twill) backed with a layer of 12-ply cotton gauze and food grade aluminum foil. Each patch was housed in a foil-backed patch holder which exposed 23.76 square centimeters (cm^2) of sampling media. One patch was attached to each of the worker's front thigh pant legs. At the end of the monitoring period, the cloth layers were separated from the gauze and foil layer, and treated as separate samples for analysis purposes.

The second type of patch, which was used to monitor the head, was constructed of a 12-ply gauze layer backed with aluminum foil housed in a patch holder. One gauze patch was attached to the front and rear sections of a clean baseball type hat. At the end of the workday, head and thigh patches were collected then placed in separate 4-ounce glass jars, sealed with foil, capped, and stored with dry ice.

Handwash samples were collected prior to the start of the workday, before morning and lunch breaks, and at the end of workday. For each handwash, the worker was instructed to clean both hands for one minute in a bag containing approximately 400 mL of surfactant solution (0.1% dioctyl sodium sulfosuccinate in distilled water). Rinse water was transferred to an amber 500 mL Nalgene bottle and stored on dry ice. This procedure was repeated twice at the "end of the workday" sampling interval. In addition, the lower arm was washed, then wiped with gauze pads moistened with surfactant solution. These pads were included in the second rinse sample bottle.

Foliage samples were collected from the field immediately prior to and after harvest using methods similar to those described by Iwata et al. (3). Ten adjacent rows were selected and marked with flagging tape. Two leaf discs were collected from each side of the ten rows using a Birkestrand 2.54 cm diameter leaf punch. A total of 40 leaf discs was collected from the sampling area; three sub-samples were collected at each sampling interval. After sample collection, jars were sealed with aluminum foil, capped, and stored on ice until analysis. Samples were analyzed for dislodgeable chlorothalonil residues using the methods described in Appendix I.

<u>Full Scale Tomato Harvester Study</u>:

After completion of the pilot study and upon review of the resulting data, problems were identified and changes were made in the protocol for the full-scale exposure monitoring study. Potential dermal exposure was monitored using slightly different methods than those utilized in the pilot study. In addition, the workers were placed in treatment groups by type of shirt and hand protection. Workers were assigned to one of three treatment groups for each of the three monitoring periods or study days.

One picking crew was monitored for three days within a five day period during November 1987. The same set of five fields were harvested each study day. These fields were treated with chlorothalonil three days prior to harvest. Therefore, the application was three, six, and seven days prior to harvest on study days one through three, respectively. Chlorothalonil was applied by aircraft at the rate of 2.25 pounds active ingredient per acre. The crew was monitored for the entire workday (8.5 hours or 9 hours including lunch) on study days one and two. On study day three, workers were monitored during harvesting activities which occured 4.5 hours in the morning. Twenty-five workers (20 males, five females) participated on day one, 23 workers (18 males, five females) on day two, and 21 workers (17 males, four females) on day three of the study. All crew members were assigned a "Worker Number" for use throughout the study. Workers were assigned to three harvesting groups; individuals designated as workers one through nine were Group A; 10 through 17 were Group B, and 19 through 26 were Group C. Harvesting groups were assigned to one of three treatment groups on each study day. The three treatments were as follows:

Treatment I: Latex gloves and clean, long-sleeved button-up overshirts (provided). Overshirts were constructed from 60 percent polyester, 40 percent cotton fabric laundered prior to use to ensure removal of sizing.

Treatment II. New nylon knit picking gloves and clean, long-sleeved overshirts (provided).

Treatment III. Workers own normal work attire which included long or short-sleeved shirts with their own latex or knit gloves, if gloves were worn.

On study day one, harvester Groups A, B, and C were assigned to treatment groups I, II, and II, respectively. On day two, treatments were alternated between groups, with Group A, B, and C assigned to treatments III, I, and II, respectively. Observations from study days one and two indicated that the required use of latex gloves would not be practical because many of the subjects in this group were non-compliant. Although several workers in treatment group II would not comply with wearing nylon knit gloves, the percentage was low. Therefore, on study day three, the latex glove treatment group (Treatment I) was eliminated. On study Day 3, the picking crew was divided into two groups: one group wore new knit gloves and long-sleeved shirts (Treatment II) and the second group wore their normal work attire (Treatment III). The treatment per worker per day is presented in tabular form in Appendix II.

Potential exposure to the torso and arms was monitored using long-sleeved 100 percent cotton tee-shirts as dermal dosimeters. Long-sleeved tee-shirts were used as dosimeters rather than the half-sleeved tee-shirts that were used in the pilot study because arm washes were not performed in the full scale study. Tee-shirt dosimeters were worn under the provided long-sleeved shirt or the worker's own overshirt for the entire work day. Sleeves were were removed from the torso at the shoulder seam, then placed in two individual Ziploc^R plastic bags and treated as separate samples for analysis.

On study day three, provided long-sleeved overshirts were collected in addition to tee-shirt dosimeters. Overshirt sleeves were separated from the torso, placed in individual Ziploc^R plastic bags, and treated as two samples for analysis. Residue data collected from overshirt samples were used to estimate the protective value of long-sleeved shirts.

A cloth-gauze patch was affixed to the pant legs of each workers' front right and left thigh. Thigh patches were constructed in the same manner as the cloth and gauze patches used in the pilot study. Patches were separated into individual layers for analysis purposes after collection. Head patches were not used in the full scale study.

Handwash samples were collected before harvesting began, at morning break, before lunch, and at the end of the workday. Handwashes were performed in the same manner as in the pilot study except the lower arm was not washed. Samples collected at the pre-work and pre-break sampling intervals consisted of one handwash. The handwash procedures were repeated twice at the pre-lunch and post-work sampling intervals.

Foliage samples were collected on the same schedule and in the same manner as in the pilot study. Samples for dislodgeable residues were collected each study day, but samples from Study Day 3 were inadvertently destroyed.

Handwash, patch, tee-shirt, and overshirt dosimeters were stored with dry ice, where as foliage samples were stored with ice. All samples were packed in coolers and shipped to the California Department of Food and Agriculture, Chemistry Laboratory Services in Sacramento for analysis. Foliage samples were extracted within 24 hours. Dermal monitoring samples were placed in frozen storage ($\leq 10^{o}F$) until analysis. Complete analytical methods are presented in Appendix I.

The following information was recorded for each day:

- Treatment history for each field.
- Field conditions including ambient temperatures.
- Condition of plants in each field which included age, height, and variety.
- Worker's name, age, and physical appearance.
- Clothing worn by each worker on each day of the study.
- Observations of each worker's activities during the monitoring period.

A summary of this information is presented in Appendix III.

Dermal Estimates and Statistical Methods:

Hand exposure was determined by summing the residue levels detected in all handwashes collected after the start of the work day. Arm and torso exposure was determined using tee-shirt sleeve and torso residue data, respectively. Chlorothalonil residue data collected from the gauze and foil layer of cloth-gauze patches were extrapolated to estimate potential exposure to front thighs using one-half of the total thigh surface area or 1710 cm^2 (4). Data were converted to micrograms residue per square centimeter patch surface area, then multiplied by the front thigh surface area to estimate potential exposure. Each workers' "total" dermal exposure was calculated by summing hand, arm, torso, and extrapolated thigh residue data. All exposure data were normalized to an hourly exposure rate.

Although workers were assigned to specific treatment groups, several workers were non-compliant, particularly those in the treatment group wearing latex gloves. In addition, several workers wore their own shirts (short and long sleeves) rather than the provided shirts. Workers assigned to the "normal attire" group worked either bare-handed or with a variety of glove "types" (latex, new or used nylon knit). Therefore, for analyses purposes data were grouped by glove type, shirt type, and study day rather than by treatment group and treated as individual experimental units (Appendix IV). If an individual changed their glove or shirt type during the workday, their exposure data were not included in the final analyses.

The resulting treatment groups were unbalanced in size, therefore the General-Linear Models (GLM) procedure was used to develop analysis of variance tables. The GLM procedure handles unbalanced data using the method of least squares to fit general linear models (5). The effects of glove type, shirt type, and study day in relation to hand, arm, and "total" exposure were examined. Duncan's Multiple Range Test was employed to compare mean values (5). In several cases, the data were placed into subsets to eliminate data that may bias the analysis results. Data subsets were compiled for the following analyses:

A. Hand exposure data from individuals wearing new nylon knit gloves (excluding data from day 3) were compared with data from individuals wearing latex gloves (provided gloves).

B. Hand, arm, and "total" exposure data for individuals wearing new nylon knit or latex gloves, and new long-sleeved shirts (provided) were compared to the group wearing their own nylon gloves (used) and their own long-sleeved shirts (used).

C. "Total" exposure data for workers not wearing gloves were compared with "total" exposure data for those individuals wearing latex and nylon knit gloves (the workers own gloves and provided gloves). Data from those workers wearing short-sleeved shirts and gloves were eliminated since this subset did not exist in for workers not wearing gloves.

RESULTS

Pilot Study:

Observations and results from the one-day pilot study were compiled to identify problems and necessary revisions in the protocol for the full scale study. Preliminary analyses of data estimated potential hand and forearm, and "Total" (hand, arm, and extrapolated thigh data) exposure for each treatment group (Table I). Review of data identified study design problems that were corrected for the full-scale study.

Full Scale Study:

Exposure data collected from each individual during the three study days are presented as micrograms chlorothalonil per sample in Appendix V. Normalized exposure data for individuals complying with their treatment group assignments for the entire monitoring period are presented in Appendix VI. Mean hand, arm, and "total" dermal exposures are summarized by glove type, shirt type, and study day in Table II. The "total" dermal exposure was determined by summing hand, arm, torso, and front thigh (protected by pants) exposure estimates.

DISCUSSION

Harvester exposure data were analyzed as though they were collected from a completely randomized factorial study. Therefore, day cross-over effects were not addressed in the analyses.

Several of the workers participated in both pilot and full-scale harvester exposure studies. Dermal exposures for individuals who had prior experience in worker exposure studies were compared with dermal exposures from individuals with no prior experience. T-test results indicate that there were no significant differences in dermal exposure between the two groups ($P < 0.05$)[1/]

1/ All tests performed on the data were considered significant if probability was less than 0.05.

Hand and Arm Exposure:

Hand exposure was affected by the type of glove worn (if any) and the work day. As expected, hand exposure was greater when no glove was worn. Latex gloves provided more hand protection than new nylon knit gloves when data for these two treatments were compared (study day 1 and 2 data only). There was no significant difference in hand exposure when new or used by nylon knit gloves were worn (Table III). Both nylon glove types were found to provide the same level of protection. The similar dermal exposures found between the two groups also indicated that the used gloves did not retain chlorothalonil residues acquired from previous workdays. The workers gloves were presumed to be clean each day because gloves were not wearable after they were contaminated with dried tomato sap. Additionally, growers required workers to clean and disinfect their gloves daily to prevent transmission of plant pathogens.

Comparison of handwash data collected from workers not wearing gloves with those workers wearing nylon gloves (new and used) indicated that the use of nylon gloves provided approximately 90 percent protection to dislodgeable chlorothalonil residues. Poppendorf et al. (6) also found that knitted nylon gloves provided 90-95 percent hand protection to "contact" phosalone residues during peach harvesting activities.

Ideally, workers should wear latex gloves to provide maximum hand protection during harvesting activities. Realistically, workers do not like to wear latex gloves because they are uncomfortable and restrict hand movement. Additionally, workers find that wet or dew laden tomatoes are difficult to grasp with latex gloves. Workers may also be exposed to chlorothalonil residues during other activities such as tying vines and pruning. Latex gloves can not be worn while handling very young plants because bruising will result. Therefore, requiring the use of latex gloves during harvesting and other cultural activities would probably result in a high degree of non-compliance.

As expected, analyses indicated that workers wearing short-sleeved shirts had greater arm exposure than those workers wearing long sleeved shirts. The workers own long-sleeved shirts provided the same protection as the provided long-sleeved shirts (Table IV).

Both hand and arm exposures were significantly different between study days. Hand exposure was greater on study day one when compared with days two or three. Whereas, arm exposure was less on study day one when compared with days two and three (Tables III and IV). A significant day effect still existed when data collected from workers wearing short-sleeved shirts were not included in the analyses. After the short-sleeved worker group was removed, comparisons indicated, arm exposure from day one was less than exposure from day three, but the arm exposure on day two was not significantly less than day three nor significantly greater than day one (Table V).

Ritcey et al. (9) found that captan residues on harvesters' clothing, particularly gloves, were slightly greater when strawberry plants were wet with dew. On study day two, the harvesters arms and hands became considerably wet with dew during the morning harvest activities. This factor could account for some variability in our data, however, hand and arm exposures do not appear to be greater on study day two.

The inverse relationship between hand and arm exposure over the three day study period may be due to the nature of harvesting activities. The same fields were harvested on each day of the study, but the first day of study was also the first picking for these fields in approximately a week. Field observation noted that the distribution and number of ripe tomatoes on each bush differed between study days. On day one, ripe tomatoes were primarily located on the outer canopy thus, they were easily located and picked. As the harvest and study progressed, the availability of ripe tomatoes on the outer canopy was reduced. Workers were forced to search in the canopy for ripe tomatoes on study days two and three. Searching entailed lifting and moving branches and leaves to locate ripe tomatoes which resulted in additional contact and exposure to workers' arms.

Not only were tomatoes more difficult to locate as the study progressed, but there were less tomatoes to harvest. Therefore, it appears the daily trends between hand and arm exposures were due to the nature of the harvest activities in relation to the number and location of tomatoes on or in the canopy. The decrease in hand exposure as the study progressed may have been due to the decrease in actual number of tomatoes available for picking. In contrast, the increase in arm exposures may be due to the necessity of using arms to move foliage to locate any available tomatoes inside the canopy.

Other investigators studied the relationship between worker productivity and potential exposure to pesticide residues. The exposure to residues in relation to work rate (in number of boxes picked) has been determined for some tree fruits (7). A relationship between productivity and tomato harvesters exposure to chlorothalonil has been noted; the investigator found transfer of residues from fruit and foliage was highly correlated with the weight of the harvested fruit (8). Productivity rates were not available for this study, however field observations clearly indicated that less fruit was harvested on each subsequent study day. Similarily, hand exposure decreased as the study progressed.

<u>Total Exposure</u>:

The "total" exposure (hand, arm, torso, and extrapolated thigh exposures was significantly affected by glove type and the shirt type worn, but not by the study day. Additionally, the torso and thigh exposures were not significantly affected by any of the measured variables. Total exposure to workers not wearing gloves was greater when compared with total exposure for workers wearing gloves. There was no difference in total exposure when comparing data from workers wearing their own nylon knit gloves with workers wearing new nylon gloves, or when new nylon gloves were compared with latex gloves. However, when workers wore used nylon gloves the total exposure was higher than if they had worn latex gloves (Table VI). Additional analyses determined that the arm, hand, and total exposures for workers wearing provided nylon gloves and long-sleeved shirts were not significantly different from the respective exposures for workers wearing their own nylon gloves and long-sleeved shirts.

Workers wearing short-sleeved shirts had greater total exposure than those workers wearing provided shirts own long-sleeved shirts' (Table IV). No difference in exposure between the two long-sleeved shirt groups was noted. However, other investigators (10) found that when workers are "fully protected" by a long-sleeved shirt and denim pants, the degree of protection may vary with the actual clothing worn. The type or weave of the fabric, fabric content, fabric finish, and whether the fabric is clean or contaminated may affect the degree of protection. These factors could account for some of the variability observed in exposure data between individuals.

When hand exposure was high, it accounted for the majority of the workers' exposure. Similarily, when arm exposure was very high, it also accounted for the majority of the workers exposure. Several investigators found that hand and forearm exposure accounted for approximately 90 percent of the total dermal exposure (8, 11, 12). If clothing or gear is worn to protect these areas, potential exposure to chlorthalonil residues during harvesting activities can be significantly reduced. Other investigators also found the use of gloves, long-sleeved shirts, long trousers, and caps significantly lowered tomato harvesters potential exposure to chlorothalonil residues (8).

Residue levels found on provided overshirts worn on day three were compared with the residue levels found on corresponding undershirt dosimeters to determine the protective value of long-sleeved shirts. Percent penetration through clothing ranged from 17 to 38 percent with a mean of 29.6 percent. Penetration through the shirt torso region was 8 percent; in contrast penetration through openings in the sleeve or the fabric was 34 percent (Table VII).

<u>Transfer Factor:</u>

Several investigators have calculated ratios for dermal exposure rate with dislodgeable foliar residue levels for workers harvesting or thinning tree and row crops (11, 13). Ratios or transfer factors were calculated using data from the current study to determine the amount of foliage, thus the amount of dislodgeable pesticide residue, a worker may contact during typical tomato harvesting activities. The following formula was used to calculate a transfer factor:

$$\frac{\text{Total Dermal Exposure (ug residue/hr)}}{\text{Dislodgeable Foliar Residues (ug/cm}^2\text{)}} = \begin{array}{c}\text{Transfer Factor} \\ \text{(cm}^2\text{/hour)}\end{array}$$

The mean dislodgeable chlorothalonil residue level of 1.9 ug/cm^2 was calculated using data from study days one and two (Table VIII). The mean total dermal exposures to the upper body were estimated using data collected from overshirt and undershirt dosimeters and handwashes. The mean front thigh exposure for workers wearing pants was calculated using patch dosimeter data collected from all three study days (Appendix IV).

Transfer factors were calculated for an "unprotected worker" (no shirt or gloves) and for workers wearing several types of protective clothing. Mean arm and torso exposure for an unprotected worker was calculated using residue data from overshirts and the corresponding undershirt collected on study day three (Table VII). Mean arm and torso exposure for workers wearing long-sleeved shirts, (provided and workers' own shirt), and mean hand exposures were calculated using residue data collected from each treatment group on study days one to three (Appendix IV).

The estimated upper body exposure and corresponding transfer factor for each worker treatment group are presented in Table IX. These exposure data should be used only as estimates because variations between workers and study days were not addressed in the analyses. Mean front thigh exposure accounted for 2-12% of the monitored exposure depending on the worker treatment group. Since thigh data estimated only partial leg exposures and the resulting data varied considerably between workers, the mean exposure and transfer factor data were presented separately in Table IX. Calculated transfer factors ranged from 429 cm^2/hour to 2842 cm^2/hour depending on the level of protection. As would be expected, the use of gloves and shirts decreased skin contact with foliage, thus reducing potential dermal exposure and the estimated transfer factor.

Dislodgeable Foliar Residues:

There was no significant difference between dislodgeable residue levels found in foliage samples collected before harvest compared with samples collected after harvest. Additionally, no effect on dislodgeable foliar residue levels did not differ significantly between field sampling sites or study days (Table VIII).

CONCLUSIONS

Field observations and monitoring data indicated that the majority of dermal exposure occurred either on the workers hands or arms. Potential dermal exposure to chlorothalonil residues ranged from 480 to 1855 ug/hr for workers protected by long-sleeved shirts and some type of glove. Although latex gloves provided the most protection in regards to hand exposure, this difference was not seen when comparing total dermal exposures for individual wearing latex and nylon gloves. In contrast, the estimated dermal exposure for a worker not protected by a shirt or gloves was 5400 ug/hour. These data clearly demonstrate that the use of long-sleeved shirts and gloves regardless of the type, significantly reduces dermal exposure to chlorothalonil residues during the harvest of pole-grown tomatoes.

TABLE I: Chlorothalonil Residue Exposure Data for Workers Participating in the Pilot Study
(in micrograms per hour)

TREATMENT[1/] GLOVE	N	HANDS AND FOREARM				"TOTAL"[2/]			
		MEAN	STD DEV	MINIMUM	MAXIMUM	MEAN	STD DEV	MINIMUM	MAXIMUM
NONE	2	1533.3	38.8	1505.8	1560.8	4048.2	3060.7	1884.0	6212.4
NEW NYLON	4	913.1	336.7	649.7	1406.4	2358.7	1616.8	1347.3	4773.7
USED NYLON	3	1727.6	1515.4	648.3	3460.0	3185.9	1492.7	1501.5	4344.5
LATEX	4	762.9	236.4	532.7	1082.3	1316.2	421.0	1019.1	1927.0

1/ Shirt type variable not controlled in pilot study.

2/ "TOTAL" represents the total potential dermal exposure to the hands and forearms, torso and upper arms; and from thigh region and front thigh region.

TABLE II: TOMATO HARVESTER CHLOROTHALONIL EXPOSURE RESIDUE DATA (in micrograms per hour)

				HAND				ARM				TOTAL			
GLOVE	SHIRT	DAY	N	MEAN	STD DEV	MINIMUM	MAXIMUM	MEAN	STD DEV	MINIMUM	MAXIMUM	MEAN	STD DEV	MINIMUM	MAXIMUM
Latex	New Long	Day 1	4	20.5	6.0	15.4	28.8	356.9	106.6	216.2	445.4	480.2	117.4	326.0	581.6
		Day 2	2	27.1	21.6	11.9	42.4	682.9	500.4	329.1	1036.7	847.9	551.5	457.9	1237.9
	Used Long	Day 2	2	30.7	14.7	20.3	41.1	506.7	499.6	153.4	860.0	629.2	497.3	277.6	980.8
New Nylon	New Long	Day 1	7	188.5	106.7	63.4	365.9	520.5	331.7	187.6	1033.4	882.1	480.9	372.7	1667.3
		Day 2	10	106.4	42.2	57.8	169.0	732.7	322.0	307.3	1364.0	1046.8	393.3	689.9	1824.2
		Day 3	10	215.2	184.1	88.9	622.2	1040.6	499.7	295.6	1594.2	1367.2	678.0	475.2	2290.9
	Used Long	Day 2	1	238.2	.	238.2	238.2	847.4	.	847.4	847.4	1202.9	.	1202.9	1202.9
		Day 3	1	209.1	.	209.1	209.1	761.1	.	761.1	761.1	1018.9	.	1018.9	1018.9
Used Nylon	New Long	Day 2	1	313.4	.	313.4	313.4	1334.8	.	1334.8	1334.8	1855.3	.	1855.3	1855.3
	Used Long	Day 1	4	321.6	142.3	192.3	488.7	457.9	236.4	209.5	779.3	915.3	292.0	637.9	1287.2
		Day 3	5	103.8	46.3	55.3	159.3	712.5	451.5	226.4	1162.4	853.6	489.8	327.4	1340.9
	Used Short	Day 2	3	311.5	105.7	216.8	425.5	2087.2	988.1	1075.9	3050.4	2554.2	994.9	1571.9	3561.2
		Day 3	1	1267.3	.	1267.3	1267.3	1581.8	.	1581.8	1581.8	2896.2	.	2896.2	2896.2
None	New Long	Day 1	2	2432.3	873.2	1814.8	3049.8	836.4	459.5	511.4	1161.3	3506.0	1352.3	2549.8	4462.2
		Day 3	1	420.9	.	420.9	420.9	1214.9	.	1214.9	1214.9	1725.9	.	1725.9	1725.9
	Used Long	Day 1	3	3833.2	420.2	3348.4	4091.2	673.2	306.0	461.3	1024.0	4681.5	627.6	4040.6	5294.9
		Day 2	1	938.1	.	938.1	938.1	799.2	.	799.2	799.2	2063.4	.	2063.4	2063.4
		Day 3	3	354.4	128.6	239.6	493.3	1049.6	548.6	574.4	1650.0	1492.2	671.6	863.6	2199.9

TABLE III: Hand Exposure to Chlorothalonil Residues in Micrograms per Hour Compared by Glove Type and Study Day.

By GLOVE	N	MEAN	DUNCAN GROUPING
NONE	10	1879	A
NYLON (USED)1/	14	309	B
NYLON (NEW)2/	28	172	B
LATEX	8	25	B

By DAY	N	MEAN	DUNCAN GROUPING
1	20	953	A
3	21	268	B
2	20	180	B

TABLE IV: Arm Exposure to Chlorothalonil Residues in Micrograms per Hour Compared by Shirt Type and Study Day.

By SHIRT TYPE	N	MEAN	DUNCAN GROUPING
OLD SHORT1/	4	1961	A
NEW LONG2/	7	767	B
OLD LONG1/	20	699	B

By DAY	N	MEAN	DUNCAN GROUPING
3	21	985	A
2	20	948	A
1	20	530	B

1/ The workers own attire.

2/ Provided shirts and gloves.

TABLE V: **Arm Exposure to Chlorothalonil Residues in Micrograms per Hour; Day of Study Effect on Arm Exposure After Removal of all Values for Workers with Short Sleeve Shirts.**

By DAY	N	MEAN	DUNCAN GROUPING	
3	20	955	A	
2	17	746	A	B
1	20	530		B

TABLE VI: **"TOTAL"1/ Exposure to Chlorothalonil Residues in Micrograms per Hour Compared by Glove Type and Shirt Type.**

By GLOVE	N	MEAN	DUNCAN GROUPING		
NONE	10	2932	A		
NYLON (USED)2/	14	1453		B	
NYLON (NEW) 3/	29	1122		B	C
LATEX	8	609			C

By SHIRT TYPE	N	MEAN	DUNCAN GROUPING	
OLD SHORT2/	4	2640	A	
OLD LONG 2/	20	1600		B
NEW LONG 1/	37	1203		B

1/ "TOTAL" exposure is the sum of hand, arm, torso, and extrapolated thigh data.

2/ The workers own attire.

3/ Provided shirts and gloves.

TABLE VII: **Chlorothalonil Residue Levels Found on Overshirts and Undershirts from One Treatment Group of Tomato Harvester; Study Day Three. (adjusted to micrograms per hour)**

(in micrograms per hour)

WORKER	OVERSHIRT[1/]			UNDERSHIRT[2/]			PERCENT CLOTHING PENETRATION		
Number	Torso	Arm	Total	Torso	Arm	Total	Torso	Arm	Total
1	770.7	2173.8	2944.5	76.7	1506.2	1582.9	9	41	35
2	323.1	2115.6	2438.7	30.9	1349.8	1380.7	9	39	36
3	270.0	1789.3	2059.3	22.0	495.3	517.3	8	22	20
4	380.9	1790.0	2170.9	28.4	1320.4	1348.8	7	42	38
5	582.9	1934.2	2517.1	27.3	878.7	906.0	5	31	26.5
6	614.2	1752.7	2366.9	39.8	1214.9	1254.7	6	41	35
7	1092.9	1815.3	2908.2	58.9	1074.4	1133.3	5	37	28
8	214.0	1364.4	1578.4	24.2	295.6	319.8	10	18	17
9	278.4	2302.0	2580.4	54.4	1594.2	1648.6	16	41	39
10	1035.6	2475.6	3511.2	35.6	1517.1	1552.7	3	38	31
11	221.1	1386.9	1608.0	21.4	374.7	396.1	9	21	20
Mean	525.8	1900.0	2425.8	38.1	1056.5	1094.6	8 ±3%	34 ±9%	30 ±8%

1/ Provided long-sleeved shirts.
2/ Long-sleeved undershirts used as dosimeters.

TABLE VIII: Chlorothalonil Dislodgeable Residues Found on Tomato Foliage Prior to and After Harvest.

(in micrograms per square centimeter)

STUDY DAY[1/]	DAYS AFTER APPLIC	PRE-HARVEST A	PRE-HARVEST B	PRE-HARVEST C	PRE-HARVEST D	POST-HARVEST A	POST-HARVEST B	POST-HARVEST C	POST-HARVEST D
1	3	2.30	2.01	2.50	-	2.24	1.18	-	-
1	3	1.82	1.54	1.22	2.09	1.79	2.83	2.62	3.00
2	6	0.94	1.73	0.92	-	1.30	1.22	1.42	-
2	6	0.99	1.77	1.63	-	3.00	2.29	2.21	-
2	6	2.25	3.56	3.75	-	1.10	0.89	1.44	-

[1/]Residue data not available from samples collected on Study Day 3.

TABLE IX: Estimated Upper Body Dermal Exposure and the Calculated Dermal Transfer Factor (square centimeters of foliage per hour) for Tomato Harvesters.

(in micrograms per hour)

TREATMENT	HANDS mean	HANDS range	ARMS mean	ARMS range	TORSO mean	TORSO range	TOTAL[1/] mean	TRANSFER FACTOR
Unprotected Worker (No shirt or gloves)	1879	240-4091	2957	1660-3993	564	238-1152	5400	2842
Long-sleeved shirt[2/] and no gloves	1879	240-4091	744	12-153	47	14-102	2670	1405
Long-sleeved shirt and nylon gloves[3/]	216	55-1267	744	12-153	47	14-102	1007	530
Long-sleeved shirt and latex gloves	25	12-42	744	12-153	47	14-102	816	429

1/ Estimated mean front thigh exposure of 94 ug/hour (range 6-610 ug/hour) with a corresponding transfer factor of 49 cm^2/hour can be added to these values for a partial exposure estimate for a worker wearing pants.

2/ Includes data from individuals wearing new and used long-sleeved shirts.

3/ Includes data from individuals wearing new and used nylon knit gloves.

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Appendix I

Analytical Methods for Chlorothalonil Residues

Method I

This method is for the determination of chlorothalonil residues on cloth and/or gauze exposure patches.

PRINCIPLE:

Chlorothalonil residues are extracted from the exposure patch material with Ethyl Acetate. The extract is ready for analysis by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Ethyl acetate (EtAc) nanograde. Check for interferences.
2. Analytical standard of chlorothalonil
   a) Stock standard - 1 mg/ml.
   b) Working standards - Dilute stock standard to several working standards covering the linear range of the gas chromatograph and detector used - e.g. 0.1 to 10 ng/ul.
3. A gas chromatograph equipped with either an NP or Ec detector.
4. A 25m x 0.20 mm I.D. capillary column coated with 5% phenyl methyl silicone.
5. A mechanical rotator.

ANALYSIS:

1. Add 50 mls of EtAc to the sample jar containing the patch.
2. Rotate the jar for 30 minutes.
3. Extract is ready for analysis.

EQUIPMENT CONDITIONS:

1. Gas chromatograph - HP 5880A.
   a) Oven temperature - 200 C.
   b) Injector temperature - 200 C.
   c) Detector temperature - 300 C.
   d) For capillary configuration:
      1) Column pressure - 15 PSI
      2) Split vent - 50 mls/min
      3) Septum purge - 2 mls/min
      4) NPD make-up gas flow - 20 mls/min
      5) Ec detector make-up gas flow - 30 mls/min

Using these conditions, chlorothalonil has a retention time of 2.42 minutes.

CALCULATIONS:

Results are reported as micrograms per sample.

Appendix I (Continued)

DISCUSSION:

Recovery: 10 micrograms chlorothalonil - 99%

Method II

This method is for the determination of chlorothalonil residues in handwash samples.

PRINCIPLE:

The handwash samples are first measured for total volume, then extracted with ethyl acetate to remove the chlorothalonil. The ethyl acetate is dried with sodium sulfate and the extract is ready for analysis by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Ethyl acetate, nanograde. Check for interferences.
2. NaCl
3. Glass wool.
4. Na^2SO^4, or use sodium sulfate, anhydrous.
5. Separatory funnels, 500 ml capacity with glass stoppers and teflon stopcocks.
6. Glass filter funnels.
7. Graduated cylinders, 100 ml.
8. Analytical standard of chlorothalonil.
   a) Stock standard - 1 mg/ml.
   b) Working standards - Dilute stock standard to several working standards covering the linear range of the gas chromatograph and detector used - e.g. 0.1 to 10 ng/ul.
9. A gas chromatograph equipped with either an NP or Ec detector.
10. A 25m x 0.20 mm I.D. capillary column, coated with 5% phenyl methyl silicone.

ANALYSIS:

1. Determine the total volume of the handwash sample and record on the sample sheet.
2. Pour the entire sample into a 500 ml sep. funnel.
3. Add 50 grams of NaCl per 100 mls of sample to the sep. funnel and shake to dissolve.
4. Extract aqueous portion with 50 mls of EtAc, draining the solvent through glass wool and Na_2SO_4 into a 100 ml graduated cylinder.
5. Extract the aqueous portion twice more with 25 mls of EtAc, combining all extracts in the cylinder.
6. Bring the volume in the cylinder up to 100 mls with EtAc.
7. Extract is ready for analysis.

Appendix I (Continued)

EQUIPMENT CONDITIONS:

1. Gas chromatograph - HP 5880A.
   a) Oven temperature - 200° C.
   b) Injector temperature - 225° C.
   c) Detector temperature - 300° C.
   d) For capillary configuration:
      1) Column pressure - 15 PSI.
      2) Split vent - 50 mls/min.
      3) Septum purge - 2 mls/min.
      4) NPD make-up gas flow - 20 mls/min.
      5) Ec detector make-up gas flow - 30 mls/min.

Using these conditions, chlorothalonil has a retention time of 2.42 minutes.

CALCULATIONS:

Results are reported as micrograms of chlorothalonil per sample.

DISCUSSION:

Recovery : 10 ugs chlorothalonil - 99%.

METHOD III

This method is for the determination of dislodgeable residues of chlorothalonil from leaf surfaces.

PRINCIPLE:

The surface of leaf punches are rinsed with a distilled water and surfactant solution to remove the pesticide. The aqueous solution is then extracted with ethyl acetate. The EtAc is dried with sodium sulfate and the extract is ready for analysis by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Ethyl acetate, nanograde. Check for interferences.
2. Distilled water.
3. Sur-Ten solution, 2%.
4. NaCl.
5. Glass wool.
6. Na_2SO_4, anhydrous.
7. Separatory funnels, 500 ml capacity with glass stoppers and Teflon stopcocks.
8. Glass filter funnels.
9. Graduated cylinders, 100 ml.

10. Analytical standard of chlorothalonil.
    a) Stock standard - 1 mg/ml
    b) Working standards - Dilute stock standard to several working standards covering the linear range of the gas chromatograph and detector used - e.g. 0.1 to 10 ng/ul.
11. A gas chromatograph equipped with either an NP or Ec detector.
12. A 25 m x 0.20 mm I.D. capillary column coated with 5% phenyl methyl silicone.

ANALYSIS:

1. To the sample jar containing the leaf punches, add 50 mls of distilled water and 0.2 mls of 2% Sur-ten solution.
2. Rotate the sample jar for 20 minutes.
3. Decant the aqueous portion into a 500 ml separatory funnel.
4. Repeat steps 1-3 twice more.
5. Add 40 grams of NaCl to the separatory funnel and shake to dissolve.
6. Extract aqueous portion with 50 mls of EtAc, draining the solvent through glass wool and Na_2SO_4 into a 100 ml graduated cylinder.
7. Extract the aqueous portion twice more with 25 mls of EtAc, combining all extracts in the cylinder.
8. Bring the volume in the cylinder up to 100 mls with EtAc.
9. Extract is ready for analysis.

EQUIPMENT CONDITIONS:

1. Gas Chromatograph - HP 5880A.
    a) Oven temperature - 200^{o}C.
    b) Injector temperature - 225^{o}C.
    c) Detector temperature - 300^{o}C.
    d) For capillary configuration:
        1) Column pressure - 15 PSI.
        2) Split vent - 50 mls/min.
        3) Septum purge - 2 mls/min.
        4) NPD make-up gas flow - 20 mls/min.
        5) Ec detector make-up gas flow - 30 mls/min.

Using these conditions, chlorothalonil has a retention time of 2.42 minutes.

CALCULATIONS:

Results are reported as micrograms per square centimeter.

DISCUSSION:

Recovery: 10 ugs chlorothalonil - 99%.

Appendix II

Treatments For Each Worker Group on Days One and Two:

Study Day	Worker Group A (#'s 1-9)	Worker Group B (#'s 10-17)	Worker Group C (#'s 19-27)
1	Latex gloves (I)	Nylon gloves (II)	Normal attire (III)
2	Normal attire (III)	Latex gloves (I)	Nylon gloves (II)

Treatment Per Worker on Day Three

Worker Number	Treatment
1-7, 9-12	Nylon gloves (II)
14-15, 19-26	Normal attire (III)

Actual Numbers of Workers Per Treatment Group Per Day

Study Day	Latex Gloves (I)	Nylon Gloves (II)	Normal Attire (III)
1	9	8	8
2	8	9	8
3	None	11	10

APPENDIX III

Summary of Field Observations and Study Conditions

I. Field Site: San Clemente Ranch, Oceanside, CA
"Forth-Field Planting"; 45 acres

Plants were approximately 5-6 months old and were large and bushy ranging in height from 3.5 to 5 feet.

II. Treatment History (October, November 1987)

10/1/87 (ground application):
chlorothalonil
fevalerate
metalaxyl
bacillus thuringiensis
sulfur
sticker-spreader

10/21/87 (ground application):
chlorothalonil
metalaxyl
sulfur
sticker-spreader

11/16/87 (aerial application):
chlorothalonil

III. Monitoring Periods

Study Day 1: 6:45 to 15:45, 9 hours including 0.5 hour lunch
Study Day 2: 6:45 to 15:45, 9 hours including 0.5 hour lunch
Study Day 3: 6:45 to 11:05, 4.33 hours

IV. Personal Data

A. Age: range 18 to 56 years; most individuals were 20-35 years of age.

B. Height: range 4'10" to 5'10"; most individuals were 4'10" to 5'2" in height.

C. Summary of "normal work attire" worn during the study: most workers perferred to wear knitted picking gloves; one male and one female preferred to wear latex gloves; approximately 20 percent of the workers preferred to work bare-handed.

Appendix III (Continued)

Typically, the females wore several layers of clothing on their upper bodies which usually consisted of one or two shires and a sweater. As the air temperature warmed, a layer of clothing was removed.

Most women wore a scarf and hat over their head.

Men were observed wearing several types of shirts: long-sleeved and short-sleeved button-up shirts, and short-sleeved polo and tee-shirts; approximately 66 percent of the men wore long-sleeved shirts. Most men wore base-ball type hats.

Both men and women wore long jean pants or slacks.

Appendix IV

Factors Used to Assign Individuals to Treatment Groups for Data Analyses

GLOVE TYPES:	NO GLOVES CLEAN NYLON KNIT GLOVES (provided by CDFA) USED NYLON KNIT GLOVES (workers own gloves) LATEX GLOVES
SHIRT TYPES: ("SLEEVE")	NO OVERSHIRT LONG-SLEEVED BUTTON-UP OVERSHIRT (provided) LONG-SLEEVED BUTTON-UP OVERSHIRT (workers own shirt) SHORT-SLEEVED SHIRT; TEE-SHIRT AND BUTTON-UP TYPES (workers own shirts)
STUDY PERIOD:	DAY 1 (FULL WORK DAY: 8.5 hours) DAY 2 (FULL WORK DAY: 8.5 hours) DAY 3 (HALF WORK DAY: 4.5 hours)

Appendix V (Continued)

Codes:

Worker= worker identification number
Day = study day

HR1 = number of hours spent wearing a particular gloves or shirt;
HR2 = corresponds with data in G1, G2, S1, and S2 columns.

G1	= glove type worn:	0	no gloves
G2	= glove type worn:	1	provided new nylon knit glove
		2	latex glove
		3	workers own knit glove (presumed clean)

S1	= shirt type worn:	0	no overshirt
		1	provided long-sleeved shirt
		2	workers own long-sleeved shirt
		3	workers own short-sleeved shirt

Pilot = participated in pilot study: 0 no
1 yes

HPRE = pre-work handwash data

HPOST = sum of post-work handwash data

BDY= tee-shirt dosimeter, sleeves

CLOTH= cloth layer of patch dosimeters

GAUZE= gauze and foil layer of patch dosimeters

OB= torso of overshirt dosimeters

OS= sleeves of overshirt dosimeters