Bull. Environ. Contam. Toxicol. (1991) 46:343–350

Environmental Contamination and Toxicology

Chlorpyrifos Exposure of Workers Entering Sweet Corn after Chemigation

U. E. Brady,[1] R. Tippins,[1] J. Perry,[1] J. R. Young,[2] and R. D. Wauchope[3]

[1]University of Georgia, Department of Entomology, Athens, Georgia 30602, USA; [2]Insect Biology and Population Management Laboratory and [3]Nematodes, Weeds and Crops Research Unit, Agricultural Research Service—U.S. Department of Agriculture, University of Georgia Coastal Plain Experiment Station, Tifton, Georgia 31793, USA

Exposure of agricultural workers to insecticides is a safety hazard that has received much attention but is difficult to assess. Matsumura and Madhukar (1980) provided a thorough review of the subject with consideration of dermal and respiratory routes of direct exposure.

To our knowledge, no quantitative studies have been reported on exposure of workers following application of an insecticide through an overhead irrigation system. This method of applying insecticides is commonly called chemigation or insectigation and is a rapidly growing practice in this country. Chlorpyrifos in vegetable oil applied to corn in this way effectively controls the corn earworm and the fall armyworm in sweet and field corn (Young, 1981; Chalfant and Young, 1982; Wauchope RD, Young JR, Chalfant RB, Marti LR, and Sumner HR, Deposition, mobility and persistence of sprinkler-irrigation-applied chlorpyrifos on corn foliage and in soil; submitted to Pesticide Science).

The purpose of this study was three-fold: (1) to estimate the degree of dermal and respiratory exposure of workers entering a corn field at selected stages of plant growth and after receiving multiple applications of chlorpyrifos by chemigation; (2) to correlate levels of dislodgable residues of chlorpyrifos on corn foliage with levels determined from dermal and respiratory exposure of workers upon re-entry into treated fields at maturing stages of growth; (3) To determine the distribution of chlorpyrifos in target areas and the drift of chlorpyrifos into non-target areas.

MATERIALS AND METHODS

Experiments were carried out in 1983 at Gopher Ridge, Coastal Plain Experiment Station, Tifton, Ga. Multiple applications of chlorpyrifos by chemigation (Young, 1981) were made at recommended rates to corn

Send reprint requests to R. D. Wauchope at the above address

Table 1. Quantitative distribution of chlorpyrifos applied through a center pivot irrigation system to a field of corn: total chlorpyrifos amounts and volumes collected[a]

Date	July 12			July 26			August 9			Average		
Site	A	B	C	A	B	C	A	B	C	A	B	C
Chlorpyrifos amounts (μg/100 cm^2 collector area)												
μg	234	159	205	382	289	350	368	233	372	328	227	309
s.d.	±24	±14	±24	±66	±22	±27	±67	±32	±67	±52	±23	±36
Volumes Collected (mL/100 cm^2 collector area)												
mL[b]	26	21	24	27	22	26	25	16	29	26	20	26
s.d.	±3	±3	±2	±5	±2	±2	±5	±2	±8	±4	±2	±4

[a]Collection locations A,B, and C were placed 1/4, 1/2 and 3/4 of the radius of the pivot system. Methods are described in text.

[b]mL of spray collected per 100 cm^2 of collector funnel (diameter at top of funnel collector was 10 cm or 78 cm^2 area

(Table 1). At weekly intervals from July 12 through September 6, 1983, 0.5 lbs. of technical chlorpyrifos in 1.3 pints of peanut oil was applied per acre in 0.1 inch of surface water (2715 gallons/acre) to a four acre plot. The initial treatment was made at nine days after planting.

Worker exposure was estimated following selected treatments indicated in Tables 2 and 3. After each chemigation treatment, three workers wearing protective clothing and respirators entered the field 4 hours after treatment to sample foliage for residue analyses and 48 hours after treatment to determine pest control efficacy. Each exposure period was approximately 1/2 hr.

Dislodgable residues of chlorpyrifos on corn were determined by the method of Iwata et al. (1977), in which foliage is washed with an aqueous surfactant ("sur-ten") solution, which is then extracted. The accuracy of the method in our laboratory was determined with ^{14}C radiolabeled chlorpyrifos applied to corn foliage. Recovery was measured up to 3 days after treatment to simulate the time between foliage sampling and determination of dislodgable residue. Foliage samples collected at 4 hr and 48 hr after treatment were held without solvent in extraction jars on ice for 3 days and 1 day, respectively, prior to extraction. Foliage used in ^{14}C studies mentioned above was treated similarly. Discs treated with ^{14}C chlorpyrifos were oxidized (Harvey Instruments Oxidizer) following washing

Table 2. Estimation of dermal exposure of non-applicator workers to chlorpyrifos on corn at 4 and 48 hr after treatment with a center pivot irrigation system.[a]

1983 Date	Time[b] (hr)	Chlorpyrifos ($\mu g/100cm^2/hr$) on Area of Body							
		Head (hat)	Shoulder	Forearm	Chest mid	Thigh (front)	Ankle	Hands R	Hands L
7-26	4	7.8 ±2.8	6.6 ±1.1	5.2 ±1.1	5.6 ±0.5	5.5 ±0.7	8.7 ±1.8		
7-28	48	3.0 ±2.3	3.3 ±1.7	6.2 ±3.0	2.8 ±2.1	4.3 ±3.0	4.6 ±2.0		
8-9	4	10 ±3.6	21 ±10	41 ±12	13 ±5.9	17 ±4	27 ±8.8	48 ±28	38 ±7
8-11	48	16.6 ±3.0	13.3 ±1.8	11.7 ±3.7	12.4 ±2.6	11.4 ±4.6	13.3 ±5.1		
8-23	4	21.0 ±5.0	18.0 ±6.0	39.0 ±28.4	10.0 ±2.3	18.0 ±2.2	30.5 ±7.1	44 ±5	38 ±12
8-25	48	-[c]	9.0 ±3.5	9.7 ±6.8	-[c]	6.9[d]	13 ±4.3	20 ±5.6	15[d]
9-6	4	46.1 ±8.9	39.1 ±10.3	112 ±78.0	9.0 ±0.6	24 ±4.3	29 ±14	129[d]	80[d]
9-8	48	10.4 ±0.5	11.2 ±3.2	17.3 ±9.2	6.7 ±2.8	8.2 ±3.2	7.4 ±1.6		

[a]Each figure ±1s.d. is the average of results obtained with three workers.

[b]Hours after treatment.

[c]Samples were contaminated and were not included in analyses.

[d]Samples were from only two workers.

in sur-ten solution.

The methods of Durham and Wolfe (1962) and Davis (1980) were used with one modification to collect samples for estimation of dermal and respiratory exposure. Polyurethane foam (6 mm thick) was employed in place of alpha-cellulose pads. Polyurethane foam has been used to recover organochlorine insecticides and PCBs from water (Gesser et al., 1971; Musty and Nickless, 1974). Foam was prewashed in 2 exchanges of ethyl acetate to remove any material that would interfere with GLC analyses.

Table 3. Estimation of respiratory exposure of non-applicator workers to chlorpyrifos on corn at the indicated times after treatment with a center pivot irrigation system[a].

1983 Date	Hr. After Treatment	μg Chlorpyrifos/100 cm^2 Respirator Filter/0.5 hr			
		L-O[b]	L-I	R-O	R-I
July 26	4	<0.4	<0.4	<0.4	<0.4
July 28	48	<0.4	<0.4	<0.4	<0.4
August 9	4	0.7	<0.4	0.9	<0.4
August 11	48	<0.4	<0.4	<0.4	<0.4
August 23	4	1.3±0.4	<0.4	1.6±0.6	<0.4
August 25	48	<0.4	<0.4	0.4	<0.4
Sept. 23	4	1.8±0.6	<0.4	1.7±0.7	<0.4
Sept. 24	48	<0.4	<0.4	<0.4	<0.4

[a]Each figure ±1 s.d. is the average of results obtained with three workers.

[b]L = left, R = right, O = outer, I = inner filter

Polyurethane foam (100 cm^2 surface area) was fastened to protective clothing with Velcro strips at each of the body sites indicated in Table 2. Cotton gloves were worn during each exposure period. Two stacked foam pads were placed in each side of a face mask respirator (Comfo, MSA A) on the outer side of the commercial filter of the same diameter. Distribution of chlorpyrifos to different areas of the plot was estimated as follows: A group of four spray collecting devices (a glass funnel with the stem in a glass tube) was positioned just above the canopy at three locations; 0.25, 0.5, and 0.75 the radius of the pivot. Chlorpyrifos was sampled on foam collectors in nontarget areas. The insecticide in drift spray was collected on 30 x 30 cm polyurethane foam pads stationed at selected sites outside the designated treatment area.

Each foam patch from exposed workers was submerged in 20 ml of GLC grade ethyl acetate immediately after workers completed duties in the plot. Gloves were similarly extracted in an appropriate amount of ethyl

Table 4. Recovery of dislodgable residues of ^{14}C chlorpyrifos on corn foliage[a]

Time after applic.	% of applied dose in indicated fractions			
	Hexane extract[a]	Water after hexane extract.	Oxidized leaves after sur-ten/ water extract.	Total % of applied dose
	4 ppm[b] = 0.04 $\mu g/cm^2$			
5 min.	68.7±4.7	5.4±0.4	28.1±1.8	102.2±2.8
1 day	62.0±3.0	5.7±0.2	30.6±3.9	98.3±2.3
3 days	43.3±5.4	5.7±0.2	47.8±4.5	96.7±2.5
	15 ppm[c] = 0.15 $\mu g/cm^2$			
5 min.	69.5±7.1	9.6±2.5	20.9±3.6	99.9±5.1
1 day	52.1±4.8	7.9±3.0	41.4±0.3	101.4±4.0
3 days	44.8±5.3	13.4±0.5	42.4±5.8	100.6±4.6

[a]Dislodgable residue is based on combining two extracts of each of three washes of leaf discs in sur-ten/water.

[b]7.4 μg (0.042 μCi) ^{14}C-chlorpyrifos + 0.1 μg ^{12}C-chlorpyrifos in 5 μL water (<0.1% benzene) evenly distributed by syringe over one surface of 20 leaf discs (1.97 ±0.07 g): 7.5 $\mu g/203$ cm^2 = 0.037 $\mu g/cm^2$.

[c]10.2 μg (0.058 μCi) ^{14}C-chlorpyrifos + 20 μg ^{12}C-chlorpyrifos in 50 μL methanol (<0.1% benzene) applied as in (b) above: 30.2 $\mu g/203$ cm^2 = 0.15 $\mu g/cm^2$.

acetate. Chlorpyrifos extracted for at least three days from these substrates was analyzed by GLC-FPD (Brady et al., 1980). Chlorpyrifos in irrigation water collected in each of the 12 sampling tubes was quantitatively extracted into 10 ml of hexane immediately following chemigation. Chlorpyrifos in the hexane fraction (dried with sodium sulfate and held at -20°C) was also quantitated by GLC.

RESULTS AND DISCUSSION

Data presented in Table 1 indicates that the amounts of chlorpyrifos deposited by the chemigation were quite consistent between plots and treatments. However, approximately 30% more water spray was consistently collected at the near-pivot (site A) and near-perimeter (C) sites than under the mid-boom (B) sites. The average volume for all sites (24 ml/100 cm^2) was very close to the 25.4 ml expected.

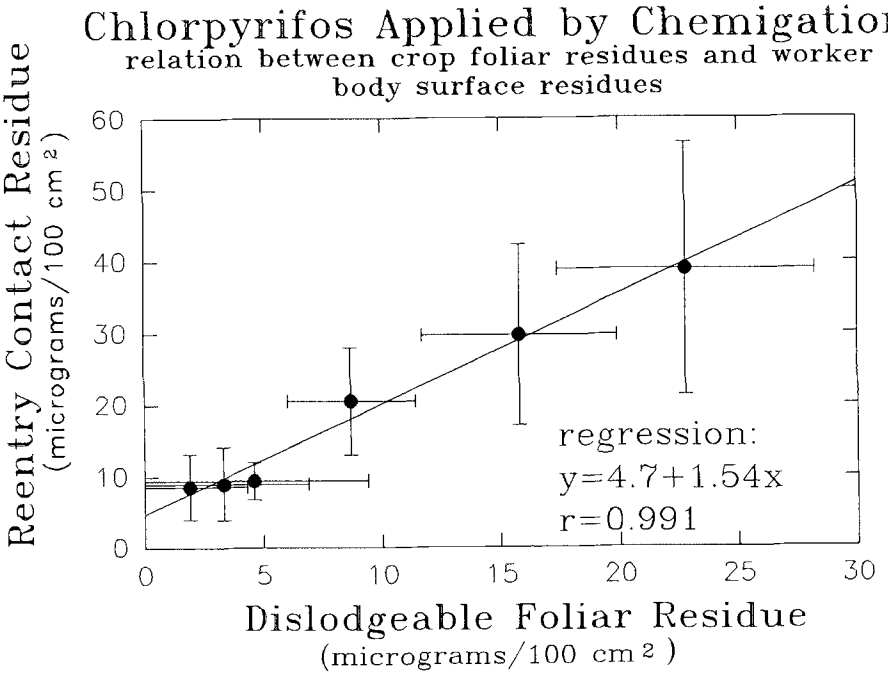

Figure 1. Worker chlorpyrifos residues vs. dislodgable residues: average of all sampled areas (except hands) vs. foliar dislodgeable residues on same date.

However, the average amount of chlorpyrifos obtained from the same traps was only about 290 μg or 51% of the 560 μg/100 cm^2 expected. We cannot explain this poor recovery (especially since volumes were so close to that expected), but the poor chlorpyrifos recovery is consistent with other attempts to quantitate chemigation applications of this compound (Wauchope et al.(1990) see ref. above) .

In exposure tests at 4 hours after treatment, the level of chlorpyrifos on dermal pads varied to some extent with the age of corn treated (Table 2). Re-entry into the field on 7-26 when corn was only 1 m high resulted in relatively low levels of chlorpyrifos on each of the seven dermal test areas. At 4 hours post-treatment on 8-9, 8-23, and 9-23, chlorpyrifos was measured on body areas in the following decreasing order: Arm > shoulder > head > ankle > thigh > chest-back. No differences were found in levels on the back, chest, thigh, or ankle when these three

treatments were compared. With later treatment dates, increasing amounts of chlorpyrifos measured on the head, shoulder, and arm areas reflected increased height of corn plants.

Dermal exposure 48 hours after treatment resulted in chlorpyrifos levels that varied greatly between treatments and between body areas sampled. Although dermal levels at 48 hours generally were low compared with those at 4 hours (Table 2), these data indicate the persistence of chlorpyrifos on corn foliage and continued potential for worker exposure 48 hours after application.

Chlorpyrifos recovered from respirators of workers exposed to treated corn less than 1 m tall (7-26 through 8-11) was near or less than the lower limits of detection. At later intervals when corn was at least as tall as workers, up to 1.8 μg of chlorpyrifos per 100 cm^2 of filter of respirators at 4 hours post-treatment. No chlorpyrifos was detected in outer filters at other times or in inner filters of foam after 0.5 hour exposures at any sampling time (Table 3).

Results of tests to determine the recovery of dislodgeable residues and total chlorpyrifos from foliage are presented in Table 5. A significant amount of chlorpyrifos remained on leaf discs after washing of discs in sur-ten solution Table 5). At five minutes post-treatment, about 30% of the dose of chlorpyrifos applied in aqueous or methanol medium was not removed from the leaf surface. Less chlorpyrifos was dislodged with increasing time after treatment.

Comparison of levels of chlorpyrifos on workers exposed by dermal (Table 2) and respiratory (Table 3) routes demonstrates well that most contamination of workers occurs by the dermal route. These findings are in good agreement with previous studies on exposure of agricultural workers to pesticides (Durham and Wolfe, 1962; Popendorf, 1980).

A strong correlation is indicated between dermal exposure of workers and dislodgable residues of chlorpyrifos on corn foliage (Figure 1). At 4 hours and 48 hours post-treatment, two and three times more chlorpyrifos, respectively, was measured per unit area of dermal surface than foliar surface. Our findings generally support work of others (Popendorf, 1980; Nigg et al., 1984) in suggesting that dermal exposure of agricultural workers to pesticides can be quantitatively predicted on the basis of foliar dislodgable residues.

Acknowledgment. This paper was completed after the untimely death of U. Eugene Brady, and is dedicated to his memory.

REFERENCES

Brady UE, Berisford CW, Hall TL, Hamilton JS (1980) Efficacy and persistence of chlorpyrifos, chlorpyrifos-methyl and lindane for preventative and remedial control of the southern pine beetle. J Econ Entomol 73:639-41

Chalfont RB, Young JR (1982) Chemigation, or application of insecticide through overhead sprinkler irrigation systems, to manage insect pests infesting vegetable and agronomic crops. J Econ Entomol 75:237-241

Davis JE (1980) Minimizing occupational exposure to pesticides: Personnel monitoring. Residue Rev 75:33-50

Durham WF, Wolfe HR (1962) Measurement of the exposure of workers to pesticides. Bull World Health Org 26:75-91

Gesser HD, Chow A, Davis FC, Uthe JF, Reinke J (1971) The extraction and recovery of polychlorinated biphenyls (PCB) using porous polyurethane foam. Anal Lett 4:883-886

Iwata Y, Knaak JB, Spear RC, Foster RJ (1977) Worker re-entry into pesticide-treated crops. 1. Procedure for the determination of dislodgable pesticide residues on foliage. Bull Environ Contam and Toxicol 18:649-655

Matsumura F, Madhukar BV (1980) Exposure to insecticides. Pharmacol Ther 9:27-49

Musty PR, Nickless J (1974) The extraction and recovery of chlorinated insecticides and polychlorinated biphenyls from water using porous polyurethane foams. J Chromatogr 100:83

Nigg HN, Stamper JH, Queen RM (1984) The development and use of a universal model to predict tree crop harvester pesticide exposure. Am Ind Hyg Assoc J 45:182-186

Popendorf W (1980) Exploring citrus harvesters' exposure to pesticide contaminated foliar dust. Am Ind Hyg J 41:552-559

Wolfe HR (1976) Field exposure to airborne pesticides. In: Lee RE (ed) Air pollution from Pesticides and Agricultural Processes. CRC Press, Cleveland, Ohio pp 137

Young JR (1981) Chemigation: Insecticides applied in irrigation water for control of the corn earworm and fall armyworm in sweet and field corn. In: Young, JR (ed) Proc. National Symp. on Chemigation, Tifton, GA, Aug. 20-21. Univ. GA Cooperative Extension Service Rural Development Center, Tifton, GA. pp 156-64

Received August 1, 1989; accepted August 1, 1990.