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Exposure of a Mixer-Loader to Insecticides Applied to Corn via a Center-Pivot Irrigation System

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Human exposure to insecticides can occur during storage, transport, mixing-loading and application (Coutts 1980). In general, applicators primarily contact chemicals during the mixing-loading phase of application (Lavy and Mattice 1985). The major routes of insecticide exposure to agricultural workers include dermal and respiratory (Durham and Wolfe 1962). The use of insecticides via center-pivot irrigation systems (chemigation) may reduce exposure because the mixer-loader does not have to be at the pivot site all the time except to check it periodically (Threadgill 1981). Pesticide exposure studies have been conducted for various agricultural pesticide exposure situations (Batchelor and Walker 1954; Coutts 1980; Knaak et al. 1980; Wicker and Guthrie 1980; Wolfe et al. 1967). However, to date, no data are published concerning mixer-loader insecticide exposure during chemigation. This research was undertaken to determine the dermal and respiratory exposure of a mixer-loader to three insecticides applied through chemigation to corn, Zea mays (L) and to assess the potential risk to the mixer-loader.

MATERIALS AND METHODS

In 1987, chlorpyrifos (Lorsban® 4E), carbaryl (Sevin® 80S) and permethrin (Pounce® 3.2EC) were applied to corn at rates of 1.12, 1.68 and 0.22 kg active ingredient (AI) per ha, respectively. In 1988, chlorpyrifos (Lorsban® 4E) with and without crop oil (Sunoco 11N, Cornbelt Chemicals, McCook, Nebraska) was applied at a rate of 1.12 kg AI per ha. Crop oil was added at a rate of 0.45 L/ha. All insecticide applications were made to wedge-shaped quadrants (approximately 2.05 ha) of field corn at the R3 (milk) stage (Ritchie et al. 1986) near Concord (Dixon County), Nebraska. Each insecticide was applied in 0.64 cm of irrigation water with a high angle, high pressure (4.23 kg/cm, 414 KPa), 384.3 m center-pivot irrigation system (Lindsey® Model 410, Lindsey, Nebraska). Insecticides were injected midstream into the irrigation line through a one-way check valve by a positive displacement diaphragm pump (PULSA-feeder Microflo 680, Interpace Corp., Rochester, New York). Weather data collected in 1987 and 1988 during

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insecticide applications included: mean temperatures, 22.9 ± 1.6 and 24.6 ± 2.4 °C; mean humidities, 83.9 ± 5.8 and 80.0 ± 15.6 %RH; and mean wind speeds, 3.2 ± 2.2 and 2.1 ± 0.3 m/second, respectively. The experimental design was randomized complete block with each treatment replicated three times.

Mixer-loader used in this study was the subject for evaluating human exposure. He is a technician with formal education in agricultural sciences and more than five years of experience in pesticide applications. He is state certified to use "Restricted Use Pesticides" and to perform the "Chemigation". His duties were to handle insecticide containers, pour, mix, calibrate and apply insecticides through a center pivot irrigation system. The subject was monitored for dermal and respiratory exposure for 0.63 hour.

The mixer-loader's dermal exposure to insecticides was monitored using adsorbent gauze pad technique modified from Durham and Wolfe (1962). The construction of each gauze pad included three layers: bottom layer of glassine paper (10.2 x 10.2 cm), middle layer of tagboard (10.2 x 10.2) and top layer of 12-ply surgical gauze (10.2 x 10.2 cm) (Johnson and Johnson Co., New Brunswick, N.J.). The three layers were bound with adhesive masking tape, leaving an exposed gauze surface of 6.4 x 6.4 cm. Preliminary analysis indicated that the exposure pads contained no materials that would interfere with chlorpyrifos, permethrin and carbaryl detection. Mixer-loader wore a different protective one piece, hooded Tyvek® coverall (Kappler Inc., Guntersville, Al) during each treatment. Eighteen gauze pads were used to monitor the dermal exposure. Ten gauze pads were attached to the exterior of the coverall (as exterior pads with gauze side exposed) as follows, one each on: both shoulders, both forearms, both thighs, both ankles, chest (front trunk) and upper back (back trunk). The gauze side of the remaining eight pads was covered with a 10.2 X 10.2 cm cotton/polyester (50:50 blend, light weight with even weave) cloth swatch overlay, representing the mixer-loader's clothing fabric. These eight pads were attached to the coverall (as inner pads representing exposure to bare skin), one each on: both shoulders, both thighs, both ankles, chest (front trunk) and upper back (back trunk). Penetration of the insecticide through the swatch onto gauze pad was meant to be analogous to penetration of an insecticide through a clothing layer to the bare skin. Percent penetration was calculated by dividing the insecticide quantity penetrated to the gauze through the swatch by total quantity on swatch plus gauze and multiplied by 100. Total hand exposure was determined using 100% cotton beauty gloves (Donley Medical Supply Company, Lincoln, NE) over protective polyvinyl chloride gloves. Following mixing, loading and application, gauze pads, swatches and cotton gloves were removed and placed individually in ziploc bags (DowConsumer Products Inc, Indianapolis, IN), stored on ice in coolers, transported to the laboratory and stored at -20 °C until extraction. The Tyvek coveralls were discarded after each treatment. Field fortified samples were prepared and later analyzed to determine insecticide stability during handling and storage of samples. This procedure consisted of spiking gauze pads ($n=3$) with 10 μg (AI) of each insecticide in 1 mL of hexane applied with a pipetman (Reinen

Instrument Co., Waburn, MA) each day of operation. Fortified samples were stored, extracted and analyzed in the same manner as the other pads. Recovery rates of fortified samples for chlorpyrifos, permethrin and carbaryl were 94%, 101% and 100%, respectively.

Respiratory (inhalation) exposure was measured using a portable air sampler (Telematic Model 150A, Bendix Corp., Lewisburg, W.V.) which was calibrated to operate at an intake flow rate of 2 L/min. The air sampler intake tube was attached to one end of a Tygon® tube (15 mm, i.d.) with the other end of the tube attached to a glass sleeve containing a 20 x 35 mm polyurethane foam plug (Dispo-plug®, American Hospital Supply, McGaw Park, IL). The foam plug was used for trapping the insecticide residue in the ambient air of the breathing zone. The air sampler was fastened around the mixer-loader's waist with the glass sleeve attached in the area of the jugular notch ("V" of neck) and inverted to approximate human nostril orientation. Each foam plug was removed from the glass sleeve with acetone-rinsed forceps and individually stored in a prelabeled ziploc bag at -20 ^{0}C until extraction.

Extraction of insecticide from gauze pads involved removing taped borders and using only the central 12 ply-gauze (6.4 X 6.4 cm). Insecticides from pads and foam plugs were extracted by placing each sample in an 250 mL erlenmeyer flask containing 35 mL HPLC grade n-hexane for chlorpyrifos and permethrin, and 35 mL HPLC grade methanol for carbaryl exposed samples. The insecticide from whole gloves was extracted in a similar manner using 70 mL n-hexane or methanol. Flasks were capped with neoprene stoppers wrapped with plastic cling sheets and mechanically agitated for 30 minutes on a wrist action shaker (Burrell® Model 75, Pittsburgh, PA). All extracts were stored at -20 ^{0}C until chemical analysis.

Analysis for chlorpyrifos involved using gas-liquid chromatography (Varian® 6000 Vista Series gas chromatograph, Sunnyvale, CA) equipped with a Ni^{63} Electron Capture Detector (ECD) operated at 350 ^{0}C. The column used was a 2 m x 2 mm (id) glass column packed with 3% OV-101 on gas chrom Q, 80/100 mesh. Injector and column temperatures were set at 250 and 220 ^{0}C, respectively. Carrier gas (nitrogen) flow rate was set at 60 mL/min. The minimal detection for chlorpyrifos was 0.005 ng/μL. Permethrin was analyzed using gas-liquid chromatography (Varian 6000) equipped with Ni^{63} ECD at 350 ^{0}C. Analytical parameters included a 3% OV-210 glass packed column with a nitrogen flow rate of 60 mL/min. The temperatures for injection, column and detector were 250 ^{0}C, 220 ^{0}C and 320 ^{0}C, respectively. Minimal detection for permethrin was 0.1 ng/μL. Carbaryl was analyzed using high performance liquid chromatography (HPLC), (ISCO® Model 2350 Dual-Pump system, Lincoln, NE) coupled with an ultra-violet/visible absorbance detector (ISCO Model V4). The column used was an ISCO C18 operated in a reverse phase mode. A methanol-water mixture (70:30 by volume) was used to elute the carbaryl with a minimal detection level of 0.05 ng/μL for carbaryl.

Insecticide quantities were converted from ng/μL of analyzed sample to ng/cm^2 (based on pad extracts, 41.0 cm^2 gauze pad) and then to mg/hr/body region. The body surface area (cm^2) for the mixer-applicator was calculated from the mixer-loader's height and mass (Dubois and Dubois 1916). Using the procedure of Berkow (1931), the total body surface area was divided into regions. Total dermal exposure was determined by combining the unclothed and clothed body regions' exposure with the hand exposure. The unclothed body regions were: head, face plus "V"-front of neck, back of neck and forearms. The exposure to head was assessed by multiplying the head surface area with mean exposure rate for exterior pads on both shoulders + chest + back. An exposure to remaining unclothed body regions (face plus "V"-front of neck, back of neck and forearms) was estimated by multiplying the area of each region with appropriate exposure rates for exterior pads (chest, back and forearms, respectively). The exposure to clothed body regions (front trunk, back trunk, thighs and lower legs) was determined by multiplying the area of each region with appropriate exposure rates for interior pads (chest, back, thighs and lower legs, respectively). Hand exposure was measured by adding the insecticide amounts detected on right and left gloves. The respiratory exposure in mixer-loader's breathing zone (ng/μL) was calculated from the insecticide extracted from foam plug in the air sampler (ng/μL) and multiplying this amount by the average respiration rate of a man engaged in light work, 1740 L/hr (Durham and Wolfe 1962). Acceptable tolerances for chlorpyrifos and carbaryl in air have been established at 0.2 and 5.0 μg/L, respectively (American Conference of Governmental and Industrial Hygienists [ACGIH] 1989). The ACGIH does not have an acceptable tolerance for permethrin. The percentage of toxic dose per hour (PTDPH) (Durham and Wolfe 1962) was calculated as follows:

$$\text{PTDPH} = \frac{\text{Dermal exp.(mg/hr)} + \text{respir. exp.[(mg/hr)} \times 10]}{\text{Dermal } LD_{50} \text{ (mg/kg)} \times \text{Wt. of Mixer-loader (86.4 kg)}} \times 100\%$$

The dermal LD_{50} for chlorpyrifos, carbaryl and permethrin, are 2,000, 4,000 and 2,000 mg/kg, respectively (Worthing 1987). The margin of safety (MOS) for an insecticide is an index to indicate the degree of risk with lower MOS values corresponding to higher risk. The MOS for mixer-loader was determined using procedure described by Severn (1984) as follows:

$$\text{MOS} = \frac{\text{No Observed Effect Level (NOEL)}}{\text{Quantity Absorbed [derm. exp. (mg/kg/day)} \times 0.1 + \text{respir. exp. (mg/kg/day)]}}$$

The NOEL values for chlorpyrifos, carbaryl and permethrin are 0.03, 200 and 100 mg/kg/day, respectively (Worthing 1987). For MOS calculations, the insecticide absorbed was based on a 10% absorption rate for dermal exposure plus a 100% absorption rate by respiratory exposure. The 10% dermal absorption rate has been commonly used by researchers based on findings of Feldmann and Maibach (1974) who reported that typical absorption for various compounds was between 5% and 20% based on excretion in urine after 120 hrs. Data were subjected to an analysis of variance to establish significant differences in applicator exposure among treatments and body regions (SAS Institute 1985). Mean comparisons were determined by Fisher's protected least significant difference (LSD) test ($P<0.05$) (Snedecor and Cochran 1967).

RESULTS AND DISCUSSION

The estimated mean dermal exposures (μg/body region/hr) of the mixer-loader are listed in Table 1. There were significant differences among body region exposures ($P<0.05$) within each treatment. In general, the exposure patterns indicated that hands were the primary source of dermal contamination during insecticide mixing and application events. For the permethrin and carbaryl in 1987, and chlorpyrifos (with and without crop oil) in 1988, the hands received significantly higher exposure compared to other body regions and the levels of exposure to the hands were 99.8, 66.7, 78.6 and 99.1%, respectively. However, the exposure to chlorpyrifos in 1987 did not significantly differ among hands, front trunk, thighs and lower legs. This was due to chlorpyrifos splatter from a sudden change in wind speed (7.2 m/s) during mixing in one replication.

The chlorpyrifos without oil in 1988 yielded the highest dermal exposures compared to other insecticides both years. This abnormal dermal exposure was caused from accidental spillage on hands during calibration. Chlorpyrifos formulated as Lorsban 4E is a pink-red oily liquid which provided visible pink stains on cotton beauty gloves worn by the mixer-loader in this treatment. The front trunk and face had relatively high levels of exposure which may have been due to accidental touching of the chest area. Permethrin (Pounce 3.2 EC), available in 0.96 L bottles, was easy to pour and that may have attributed to the lack of exposure to body regions other than hands. Carbaryl (Sevin 80S) formulated as soluble powder required mixing and filtering prior to application. Even when exercising extreme precaution, the transfer of soluble powder into a pre-mixing container resulted in increased airborne dust causing hands, forearms, thighs and inhalation as primary sources of exposure.

The insecticide penetration through the 50:50 cotton/polyester blend swatches were 0% for permethrin and 33% for carbaryl. The penetration for chlorpyrifos through 50:50 cotton and polyester blends ranged from 16 to 43%. The high chlorpyrifos penetration through the clothing in 1988 indicated the random nature of accidental spillage and how such spillage could potentially increase the dermal exposure. Direct spillage of concentrated insecticide products can penetrate the clothing and cause dermal exposure to regions other than the hands.

Estimated respiratory exposures to all insecticides included in this study were low

Table 1. Estimated dermal exposure to the mixer-loader (n=1, replicates=3) involved in application of insecticides to corn via a center pivot irrigation system near Concord, Nebraska in 1987 and 1988.

Body Region	Area[a] (cm^2)	Permethrin (1987)	Chlorpyrifos (1987)	Carbaryl (1987)	Chlorpyrifos (1988)	Chlorpyrifos + Oil (1988)
		mg/hr[b]				
Hands	990.6	22.78a[c]	4.89 a	14.15 a	35.18 a	26.32 a
Front Trunk	4046.6	0.00[d]b	4.15 ab	0.34 b	5.85 b	0.15 b
Back Trunk	3646.2	0.00 b	1.29 bcd	0.14 b	0.00[d] b	0.00[d] b
Upper Arms	1433.2	0.00 b	1.62 bcd	0.84 b	0.02 b	0.01 b
Head Less Face	485.0	0.00 b	0.26 cd	0.23 b	0.41 b	0.01 b
Face, Front Neck	969.0	0.00 b	0.45 cd	0.67 b	3.25 b	0.03 b
Forearms	1474.4	0.05 b	0.90 cd	2.24 b	0.01 b	0.01 b
Thighs	3899.0	0.00 b	2.37 abcd	1.86 b	0.01 b	0.03 b
Lower Legs	4004.4	0.00 b	3.40 abc	0.72 b	0.04 b	0.01 b
Back Neck	105.4	0.00 b	0.02 d	0.02 b	0.00 b	0.00 b
Dermal Totals	21,053.8	22.83	19.35	21.21	44.77	26.57

[a]Body region surface area for the mixer-loader.
[b]Mean quantity of detected residue (mg/hr) for three replications.
[c]Similar letter designation indicates statistical similarity ($P<0.05$) within each column, determined by Fisher's protected LSD test (SAS Institute 1985).
[d]Below minimal detectable level of 0.005, 0.05 and 0.1 ng/μL for chlorpyrifos, carbaryl and permethrin, respectively.

Table 2. Exposure of the mixer-loader to insecticides applied to corn via a center pivot irrigation system, Concord, Nebraska in 1987 and 1988.

Parameter	Permethrin (1987)	Carbaryl (1987)	Chlorpyrifos (1987)	Chlorpyrifos (1988)	Chlorpyrifos + Oil (1988)
Dermal (mg/kg/d)	6.34	5.89	5.34	12.44	7.38
Respiratory (mg/kg/d)	0.025	0.044	0.011	0.005	0.008
PTDPH[a] (%)	0.014	0.007	0.011	0.026	0.015
MOS[b]	151.740	315.900	0.055	0.024	0.040

[a]Percentage of toxic dose per hr, after Durham and Wolfe (1962).
[b]Margin of safety (insecticide NOEL value divided by 10% of dermal plus 100% respiratory exposure amounts).

when compared to dermal exposures (Table 2). The mean respiratory exposure rate for permethrin was 0.05 μg/L and it amounted to only 0.3% of the total exposure. The ACGIH (1989) has no threshold limit value (TLV) established for permethrin in air. The mean respiratory exposure rates for carbaryl and chlorpyrifos were 0.09 and 0.02 μg/L, respectively, and these rates are well below the established TLVs for carbaryl (5 μg/L) and chlorpyrifos (0.2 μg/L).

Risk analysis included using estimated dermal and respiratory exposure data from this study, and making comparisons to previously generated toxicity data (Gaines 1960 and Worthing 1987). The estimated percentage of toxic dose per hour (PTDPH) ranged from 0.01 to 0.03 (Table 2). The maximum PTDPH values were observed in 1988 during mixing, loading and application of chlorpyrifos (Lorsban 4E). The MOS for permethrin and carbaryl were 152 and 316, respectively (Table 2). However, the MOS for chlorpyrifos was <1 (Table 2) which indicates the need for caution. The low MOS for chlorpyrifos is related to the extremely low value of NOEL (0.03 mg/kg/d).

According to our data, dermal exposure to insecticides was generally confined to hands. The other body regions receiving some exposure were chest (front trunk), forearms, thighs and lower legs.

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