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Dermal Pesticide Exposure During Seed Corn Production

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The US Environmental Protection Agency's (EPA) pesticide risk assessment includes an evaluation of the occupational risks from pesticide exposures to agricultural workers reentering fields. These risk assessments rely on default values in the absence of actual field data. Conservative assumptions may involve parameters such as use rates, residue dissipation, pesticide transfer, use of protective clothing, and contact time. Better worker exposure estimates are needed as defined by the Worker Protection Standard for those who have incidental pesticide exposure in the course of their normal work activities.

The USEPA, in conducting agriculturally related occupational risk assessments, categorizes work practices occurring in food production into crop/activities groups. Clustering the different crop/activities allows for approximately 50 worker re-entry monitoring studies to represent the various types of probable exposures incurring over 1200 crop/activity combinations in various cropping systems and allows for a more streamline approach to assessing risk (USEPA 2000).

Seed corn belongs to the crop/activity group known as "tall/row" crop which includes sorghum, sweet corn, and other commodities. However, not all worker activities in this crop have been characterized by EPA especially those practices such as rogueing and detasseling which are unique to seed corn production. Currently high contact re-entry risks to crops in this cluster are based on corn harvesting re-entry data; exposure during other high contact activities, such as rogueing and detasseling specific for seed corn, have not been investigated.

Furthermore, there is concern that certain sub-populations such as adolescents who are typically hired for rogueing and detasselling during the summer months may be more sensitive than the typical adult worker. This study was conducted to characterize activities specific to seed corn production and to assess the dermal exposures/risks to two commonly used pesticides, propiconazole and lambda-cyhalothrin upon reentry. Occupational risks were assessed by: 1) determining dislodgeable foliar leaf residues, 2) measuring dermal exposure to workers conducting re-entry activities, and 3) calculating a generic transfer coefficient (TC) for the high contact activities in seed corn to be used in risk assessments. Rogueing was used as the activity of choice because it requires all manual labor near the time of pesticide application. Detasselling can be conducted mechanically with followup hand removal by either walking the rows or with workers operating in buckets above the stalks.

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MATERIALS AND METHODS

The target site was a 152-acre field located in eastern Michigan's Lower Peninsula, an area traditionally used for seed corn production. Two active ingredients were used as test substances, propiconazole and lambda-cyhalothrin (Tilt fungicide, 41.8% and Warrior T Insecticide, 11.4%, Syngenta Crop Protection, Inc., respectively). The application rate, as formulated product, was 3.0 ounces of lambda-cyhalothrin and 4 ounces of propiconazole in 15 gallons of water per acre as one tank mix and applied to the same field. Application equipment consisted of a Wilmar Highboy with a 90 foot spray boom with 55 AG6 nozzles. Applications were made by a professional applicator from a local crop protection service. Application rates were monitored for accuracy by boom pressure gauge and an onboard computer that indicated acres sprayed per load. Application height was approximately 4 feet. Weather conditions were sunny, 80^0F with a wind speed of 10 mph WNW. Samples of the tank mixtures were taken for future analysis.

Fifteen participants were selected for this study. All study subjects were volunteers who routinely worked rogueing, detasseling, and weeding in seed corn fields. Informed consent procedures and forms were approved by Michigan State University's Committee on Research Involving Human Subjects. Each participant signed informed consent. If the participant was less than 18 years old, parental consent was also obtained. The participants were 16 to 19 years old, 5 were female and 10 were male. All participants had 3 to 7 years of on-farm experience.

Individuals were assigned to destroy or "rogue/hoe out" the plants with undesirable genetic qualities in the sprayed field for at least 4 hours a day. The individuals work standing upright in crews with hoes traveling down an entire row of seed corn. Plants were 3 to 6 feet in height. Each individual can rogue about 2 to 3 acres per hour. Each participant was instructed to bathe or shower prior to entering the field. Face wipes and hand washes were conducted prior to donning inner and outer dosimeters. A changing area was provided for the study subjects.

The study participants wore inner and outer whole body dosimeters. The inner dosimeter is used as a surrogate for the workers skin and consists of a pair of 100% cotton, white, long underwear with long sleeves and round neckline and no elastic. The outer dosimeter represents the workers normal outer work clothing and is worn directly over the inner dosimeter consisting of a white 100% cotton long-sleeved work shirt and a pair of white, 100% cotton pants.

The workers entered the fields 2 days after application and rogued for 4 hours. After rogueing, the participants were assisted with removal of the dosimeters. Collection and processing procedures followed standard protocols (ARTF 2000a, ARTF 2000b). Field fortification spikes of the inner dosimeters, outer dosimeter shirt, and outer dosimeter pants were taken to determine the stability of the compounds. Field fortification levels were conducted in triplicate at three different rates: 20, 50, and 100 μg/sample for each active ingredient on the day the workers re-entered the fields (ARTF 2000c). Field fortifications were exposed to the same weather conditions as the workers for the 4-hour duration. The overall percent recoveries for the pants, shirt and inner dosimeter are given in Table 1.

Table 1. Field fortification recoveries.

Matrix	Average Percent Recoveries (Standard Deviation)	
	Lambda-cyhalothrin (Low, Medium, and High)	Propiconazole (Low, Medium, and High)
Hand Washes	107% (SD=11%)	108% (SD=28%)
Face Wipes	81% (SD=16%)	96% (SD=2%)
Outer Shirt	69% (SD=9%)	62% (SD=22%)
Outer Pants	61% (SD=5%)	64% (SD=25%)
Inner Dosimeter	71% (SD=18%)	81% (SD=12%)
Dislodgeable Foliar Residue	58% (SD=27%)	64% (SD=35%)

Dislodgeable foliar residues (DFRs) were collected and processed according to previously described procedures (ARTF 2000d, USEPA 1996). Forty leaf punches of 1 inch diameter (approximately 400 cm^2 of leaf material) were randomly collected throughout the seed corn field on days 0 through day 7 in triplicate. Punches were washed twice with a 0.01% Aerosol® OT (Fisher Scientific, Lot No. 001533) solution. The washes were collected and frozen for later analysis. The wash solutions were analyzed according to the Michigan Department of Agriculture (MDA) standard operating procedure (2004a). Field fortification spikes of the leaf washes were taken to determine the stability of the compounds and recovery at three different rates: 40, 100, and 200 µg/sample (ARTF 2000c). Percent recoveries for the DFR samples are given in Table 1. DFR field fortifications were analyzed after field samples. The lower recoveries may reflect degradation of the sample during refrigeration in an aqueous matrix.

Hand washes were collected and processed according to standard procedures (ARTF 2000e). The wash solutions were analyzed according to MDA procedure (2004a). Field fortification spikes of the hand wash solutions were taken to determine the stability of the compounds and recoveries at three different rates: 40, 100, and 200 µg/sample (ARTF 2000c). Percent recoveries for the hand washes are given in Table 1.

Face and neck wipes were collected and processed according to standard procedures (ARTF 2000f). The wash solution was analyzed according to MDA protocol (2004a). Field fortification spikes of the face and neck wipes were taken to determine the stability of the compounds and recoveries at three different rates: 40, 100, and 200 µg/sample (ARTF 2000c). Percent recoveries for the face and neck wipes are given in Table 1.

Lambda-cyhalothrin and propiconazole concentrations from the face and neck wipes, hand washes and the DFR samples were determined using a Varian Gas Chromatograph with tandem mass spectroscopy. Samples were injected onto a J&W DB-5MS capillary column, 30m x 0.23mm designed to separate neutral compounds. Instrument parameters include: 3 µL sample volume, 3.0 µL injection rate, injection temperate of 265°C and a helium flow rate of 1 mL/minute. The oven temperature was ramped at 60°C for 1 minute then 20°C per minute until 230°C and maintained for 10 minutes then increased 25°C per minute to 280°C and held for 8.5 minutes. The mass spectrometer had a mass

range of 75 m/z to 450 m/z and a scan rate of 1 second. The internal standard for lambda-cyhalothrin was cyfluthrin. The internal standard for propiconazole was triadimefon. Lambda-cyhalothrin on cloth samples from the inner and outer dosimeters were also analyzed by GC/MS.

Propiconazole concentrations on the inner and outer dosimeters were determined using a Hewlett Package Gas Chromatograph with electron capture detector (ECD). Samples were injected onto a J&W DB-17 capillary column, 30m x 0.53mm designed to separate neutral compounds. Instrument parameters include: 2μL sample volume, 3.0 μL injection rate, 320^{0}C ECD temperature, injection temperature of 200^{0}C and a helium flow rate of 1 mL/minute. The oven temperature was ramped between 100^{0}C to 260^{0}C for 30 minutes. The results were confirmed on GC/MS and the results averaged.

Pesticides were extracted from inner and outer dosimeters using the method of Williams and Matheson (1999) with minor modifications as outlined in the MDA procedure (2004b). These modifications include using a 2-liter separatory funnel in the initial extraction without the use of a 1% NaCl solution. A cis-permethrin process standard was included in the extraction process. A 300-ml flask was used to mix 100 mls of the initial extract of the cloth material with an additional 150 mls of water. This mixture was vacuum filtered and washed with a solution of 1:1.5 methanol:water. The resulting mixture was applied to a 820 mg tC18 SepPak cartridge sequentially conditioned with 25 ml acetonitrile and then with 25 mL water. The compounds were then eluted off the column with 25 mL of acetone. Each extract was concentrated below 1 mL under a nitrogen stream and then brought up to 1 mL in acetone and analyzed.

Field samples were fortified with propiconazole and lambda-cyhalothrin at low, medium, and high concentrations. These samples were stored and analyzed concurrently with in-field exposure samples. The field fortifications are used to establish a recovery correction factor for each matrix of interest. Each sample was corrected with the recovery from the field fortification at or near the level of the field samples.

RESULTS AND DISCUSSION

Table 2 gives the distribution of pesticide residues on the outer and inner dosimeters of the rogueing crew. The values are adjusted by the field fortification data from the outer and inner dosimeter for each respective compound. The highest residues on both the inner and outer dosimeters were found on the upper leg and lower leg, followed by the lower arm.

The pesticide penetration from the inner and outer dosimeter was calculated for each compound by summing the concentrations of each section of the outer dosimeters and dividing by the residues found on the inner dosimeters. This assumes that the surface areas of the inner and outer dosimeters are approximately equal. For lambda-cyhalothrin, the penetration through a layer of clothing ranged from 2.9% to 9.4%; the average of all the dosimeters was 5.3% (SD=1.9, N=14). For propiconazole, the penetration ranged from 2.1% to 27.5%, the average range of all the dosimeters was 7.7% (SD=6.1, N=14). Honeycutt et al. (2001) examined the pesticide penetration through one layer of clothing for

Table 2. Average residue found on inner and outer dosimeters, hand washes and face wipes.

Propiconazole μg/sample/4 hours		
Section	Outer Dosimeter (n=15)	Inner Dosimeter (n=14)
Front Torso	12.0 (SD = 4.3)	1.6 (SD = 0.9)
Rear Torso	8.7 (SD = 9.5)	1.3 (SD = 1.0)
Upper Arm	6.0 (SD = 3.0)	1*
Lower Arm	19.1 (SD = 4.5)	3.4 (SD = 1.8)
Upper Leg	115.3 (SD = 39.4)	8.3 (SD = 4.1)
Lower Leg	111.5 (SD = 43.1)	6.1 (SD = 4.3)
Total	272.6	21.7
Face and Neck Wipes	0.25*	
Hand washes	4.4 (SD=2.2)	
Lambda-cyhalothrin μg/sample/4 hours		
Section	Outer Dosimeter (n=15)	Inner Dosimeter (n=14)
Front Torso	16.1 (SD = 11.9)	1.1 (SD = 0.5)
Rear Torso	9.0 (SD = 4.0)	0.8 (SD = 0.4)
Upper Arm	7.2 (SD = 4.3)	0.6 (SD = 0.3)
Lower Arm	34.6 (SD = 15.5)	3.0 (SD = 1.8)
Upper Leg	147.9 (SD = 56.8)	4.8 (SD = 1.4)
Lower Leg	87.4 (SD = 29.2)	3.0 (SD = 1.0)
Total	302.2	13.3
Face and Neck Wipes	0.25*	
Hand washes	2.3 (SD=1.8)	

*1/2 LOD: LOD(limit of detection)s for the different matrices are: Inner and outer dosimeters, lambda-cyhalothrin = 1 ug/sample, propiconazole = 2 ug/sample, face wipes = 0.5 ug/sample for propiconazole and lambda-cyhalothrin, DFRs, and hand washes = 1.0 ug/sample for propiconazole and lambda-cyhalothrin.

various types of activities including mixer/loaders, applicators, and various reentry activities. These penetration factors ranged from 4.8 to 12.4%. Our results are in close agreement with these previously published results.

No propiconazole or lambda cyhalothrin residues were found on the face wipes of any subject. The values for the face wipes found in Table 2 represent ½ the lower limit of detection. When any value was not detected for any of the matrices, ½ the lower limit of detection was used as the value for data analysis. Similarly, only slight residues were found in the hand washes.

Leaf punch samples for DFRs were collected on days 0 through day 7. Figure 1 depicts the residue decay curves for both pesticides. The R-squared for propiconazole and lambda-cyhalothrin are 0.857 and 0.84, respectively (R Development Core Team 2003).

The actual concentrations remaining on the foliage 2 days after application were 0.017 $\mu g/cm^2$ and 0.015 $\mu g/cm^2$ for lambda-cyhalothrin and propiconazole,

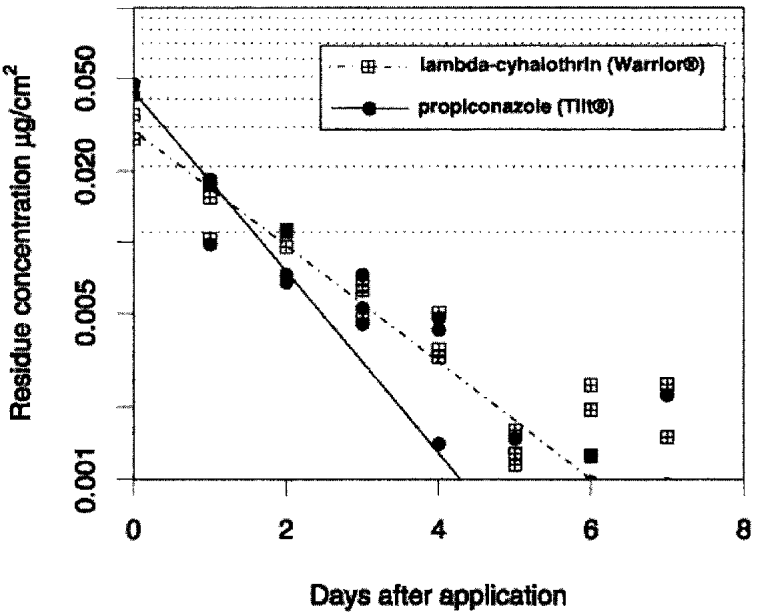

Figure 1. Residue decay curves for propiconazole and lambda-cyhalothrin applied to seed corn in Michigan 2003.

respectively. These values were used to determine the TCs for those workers reentering the fields 2 days after the application using the following equation.

Transfer Coefficient (TC cm2/hr) = Dermal Exposure (µg/hr)/DFR (µg/cm2)

The average TCs for propiconazole and lambda-cyhalothrin are 7800 cm^2/hr and 6800 cm^2/hr, respectively.
The average daily dose (mg/kg/day) can be calculated from the data collected from those workers rogueing seed corn and compared to the appropriate NOEALs for both propiconazole and lambda-cyhalothrin. The equation for the dose calculation is:

Dose (mg/kg/day) = (TC)(DFR)(AT)(AB)/(BW)

Where:
TC (transfer coefficient): propiconazole = 7800 cm^2/hr, lambda-cyhalothrin = 6800 cm^2/hr
DFR (dislodgeable foliar residue at day 2): propiconazole = 0.015 µg/cm^2, lambda-cyhalothrin = 0.017 µg/cm^2

AT (Activity Time): mean = 4.9 hr/day, 95% upper confidence limit of the mean = 5.35 hrs/day, maximum = 11.6 hrs/day
AB (Dermal Absorption): propiconazole = 40%, lambda-cyhalothrin = 1%
(*Personal communication, Mr. William Itterly, Syngenta Crop Protection, Inc.*)

BW (Body Weight): individual body weights ranged from 51.2 to 83.9 kg

The activity times derived from records taken from seed corn farms in 2002 and 2003. Body weights were taken from the actual weight of the seed corn workers.

The exposure dose calculations for lambda-cyhalothrin ranged from 8.27E-5, 9.03E-5, and 1.96E-4 mg/kg/day for the mean, 95% upper confidence limit of the mean, and maximal number of hours worked per day, respectively. The exposure dose calculations for propiconazole ranged from 3.34E-3, 3.65E-3, and 7.93E-3 mg/kg/day for the mean, 95% upper confidence limit of the mean, and maximal number of hours worked per day, respectively. For propiconazole only, the dose estimates were calculated for the female (n=5) because the comparison to the acute no-observable-adverse-effect-level (NOAEL) is based on developmental effects for *in utero* exposure. These comparisons are more appropriate to women of reproductive age. For both compounds, the point of departure is the NOAEL. The EPA uses the NOAEL to determine a margin of exposure (MOE) that is based on the following equation.

MOE = NOEAL(mg/kg/day)/Dose(mg/kg/day)

EPA has chosen an MOE of 100 as a guideline for an acceptable level of safety for occupational risk for these two products. This accounts for a 10x difference due to interspecies variability and a 10x difference for the most sensitive in the human population.

The EPA published NOAEL chosen for acute exposure to lambda-cyhalothrin is 0.5 mg/kg/day and based on a chronic oral study in the dog. This value was used for the entire study population. The NOAEL for acute exposure to propiconazole is 30 mg/kg/day and was based on a developmental toxicity study conducted in rats. This exposure scenario is more appropriately applied to females of reproductive age, principally between 13 and 50 years of age. The MOEs based on these NOAELs for the mean, 95% upper confidence limit of the mean (UCL), and maximal time an individual would work are shown in Table 3.

Table 3. Margin of exposure for seed corn workers: roguers.

Compound	Exposure	Mean	95% UCL	Maximum
Lambda-cyhalothrin	Acute	6200	5680	2620
Propiconazole	Acute (female)	7900	7240	3330

The calculations for the MOE on this crop/activity are far greater than EPA benchmark of 100, even for the maximally exposed individual. We compared the MOEs based on a 4.9 hr workday and TCs between 6800 cm^2/hr and 7800 cm^2/hr with EPA's standard default assumptions for high contact activities in corn. These assumptions include an 8-hour workday and a TC of 17,000 cm^2/hr. The results indicated that EPA may overestimate the actual exposure for certain high contact activities by approximately 4-fold.

A more direct measurement of exposure is to calculate a dermal exposure from the field data. The dermal exposure can be calculated by summing the residues on the inner dosimeter, hand washes and face/neck wipe divided by the body

weight. The geometric mean of these exposures multiplied by the absorption factor for these pesticides yields the predicted internal dose from the study. The actual doses incurred during 4 hours of rogueing are 3.52E-6 mg/kg body weight and 2.11E-4 mg/kg body weight for lambda-cyhalothrin and propiconazole, respectively. EPA's predictive methodology using the equation incorporating the TC and DFR with only 4 hours of exposure for comparison purposes yields a dose of 6.61E-5 mg/kg body weight and 2.67E-3 mg/kg body weight for lambda-cyhalothrin and propiconazole, respectively. Based on dose, EPAs predictive measurements are 19 to 12-fold higher for lambda-cyhalothrin and propiconazole, respectively when compared to field data.

Transfer coefficients for seed corn are not statistically significant when comparing the two different active ingredients applied to corn, propiconazole (7800 cm^2/hr) and lambda-cyhalothrin (6800 cm^2/hr). Until this study, the only transfer coefficients to evaluate occupational risk for worker activities involved in seed corn production and other "tall/row" crops was 17,000 cm^2/hr for high contact activities such as detasseling and hand harvesting, and 1,000 cm^2/hr for medium contact activities such as scouting. The industry task force, ARTF (Agricultural Reentry Task Force) generated this data from a hand harvesting and scouting sweet corn study

Previously, seed corn has not been evaluated for the unique activities involved in production. The results from our study are useful in evaluating the occupational risks involved in seed corn production. Through the evaluation, we have determined that actual field data, when incorporated into EPA's deterministic occupational risk assessment paradigm, reduce the estimated risk by nearly 4-fold. This indicates that for some crop/activities in the "tall/row" category, EPA's standard assumptions over-estimate risks and may initiate unnecessary risk mitigation measures. We also characterized rogueing and other activities such as detasseling and inspections as distributions for more refined probabilistic risk assessments.

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