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USGA ANNUAL REPORT

Best Management of Post-Application Irrigation on Turfgrass to Minimize Exposure to Volatile and Dislodgeable Foliar Pesticide Residues and Their Breakdown Products

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Dr. J. Marshall Clark (Principal Investigator)
Ray Putnam (Ph.D. Candidate)
Scott A. Carrier (M.S. Candidate)
Robin Edwards (Technician, MPAL)

EXECUTIVE SUMMARY

This ongoing study seeks the best management practices that reduce the potential for golfer exposure to volatile and dislodgeable foliar residues of turfgrass pesticides. Major routes of pesticide exposure for humans are primarily through inhalation and dermal penetration. Our past research has determined that pesticides with high vapor pressures and inherent high toxicities result in Inhalation Hazard Quotients (IHQs) and Dermal Hazard Quotients (DHQs) greater than 1.0 and has established that there are volatile and dislodgeable residues, particularly from organophosphorous insecticides, available for golfer/bystander exposure, and not all of these exposures can be deemed "safe" using the USEPA Hazard Quotient (HQ) criteria. We have begun to evaluate the optimal use of post-application irrigation of turfgrass to minimize human exposure to problematic pesticides and environmental impact of their breakdown products. This part of the project emphasizes concurrent dosimetry and biomonitoring studies of chlorpyrifos to determine transfer and penetration factors and whole body dose for golfers. These direct and realistic exposure measurements will allow us to predict the actual, if any, health implications to golfers and other recreational turfgrass users.

To date, 140 volatile and foliar dislodgeable samples have been collected during the two three-day monitoring experiments. These samples have been solvent extracted and are currently being analyzed as described previously (to be concluded by 2/2001). Before, during and following these experiments, 25 soil cores have been collected, sectioned and stored for analysis of breakdown products of chlorpyrifos, trichlorfon and triadimefon (to be concluded late Spring 2001).

Methods for the analysis chlorpyrifos in whole body dosimeters, hand rinses, urinary TCP, which were taken from Dow AgroSciences, and the OSHA method of analysis for chlorpyrifos from personal air samplers, were validated in-house through chlorpyrifos recovery and storage, method linearity and detection limit evaluations.

From dosimetry experiments following chlorpyrifos application, the lower leg consistently was the most available collector, followed by pants and torso. Overall, a total of 320 $\pm$ 33 and 303 $\pm$ 18 μg of chlorpyrifos were collected during the dosimetry study at 0.65 and 1.3 cm post-application irrigation, respectively.

Chlorpyrifos levels collected onto individual personal air samplers by the dosimetry group ranged from 8.8 to 14.8 μg for the 4 hour exposure.

The actual whole body dose of absorbed chlorpyrifos from the biomonitoring group as judged by the urinary clearance of the metabolite, 3,5,6-trichloro-2-pyridinol (TCP) resulted in a mean exposure of 1.15 $\pm$ 0.37 μg/Kg/d, which is not significantly different from the current ADI value assigned to chlorpyrifos. Using this actual dose, the USEPA hazard quotient for this exposure is estimated as 0.38. As expected, this actual value is well below the concern level of 1.0 and is ~ 6-fold less than the DHQ value estimated previously by us using dislodgeable foliar residues levels.

I. OBJECTIVES OF THE PROPOSAL:

Objective 1: Effect of post-application irrigation on the level and hazard of volatile and foliar dislodgeable pesticide residues and on the formation of environmental degradation products following application of chlopyrifos, trichlorfon and triadimefon at full (1.0X)-labeled rates (Year 1).

Objective 2: Effect of post-application irrigation on the level and hazard of volatile and foliar dislodgeable pesticide residues and on the formation of environmental degradation products following application of chlopyrifos, trichlorfon and triadimefon at 0.5X-labeled rates (Year 2).

Objective 3: Effect of post-application irrigation on the level and hazard of volatile and foliar dislodgeable pesticide residues and on the formation of environmental degradation products following application of chlopyrifos, trichlorfon and triadimefon at 0.25X-labeled rates (Year 3).

Objective 4: Concurrent determination of active and passive dosimetry and urinary biological monitoring of researchers simulating a 18-hole round of golf following application of chlorpyrifos to turfgrass maintained as a golf course fairway (Years 1, 2, & 3). **NOTE:** This aspect of the proposal is funded and carried out under a separate agreement with the United States Department of Agriculture through my collaboration with the USDA Regional Research Project, NE-187 "Best Management Practices for Turf Systems in the East" and through a three year grant funded by the NE Regional Turf Foundation, "Reduced Golfer Exposure to Pesticides".

II. RESULTS:

A. Research Summary.

Our ongoing research has established that there are volatile and dislodgeable residues, particularly from organophosphorous insecticides, available for golfer/bystander exposure, and not all of these exposures can be deemed "safe" using the USEPA Hazard Quotient (HQ) criteria. We plan to evaluate the optimal use of post-application irrigation, reentry intervals and application strategies to minimize human exposure to problematic turfgrass pesticides and environmental impact of their breakdown products. Ultimately, new and novel-acting turfgrass pesticides currently being used will be evaluated in a similar fashion. This part of the project will emphasize concurrent dosimetry and biomonitoring studies of chlorpyrifos to determine transfer and penetration factors and whole body dose for golfers. These direct and realistic exposure measurements will allow us to predict the actual, if any, health implications to golfers and other recreational turfgrass users.

Work Completed (10-31-00).

Two field-monitoring experiments to determine the effect of post-application irrigation (0.63- 1.3 cm) on the level and hazard of volatile and foliar dislodgeable pesticides residues and on the formation of environmental degradation products following application of chlorpyrifos, trichlorfon and triadimefon, were completed this summer (2000). Soil cores also were collected from each plot to monitor the fate of chlorpyrifos, triadimefon, and their breakdown products.

These experiments were carried out on 10 M radius bentgrass plots as described previously (Murphy et al. 1996). Volatile and dislodgeable foliar residues from the treated plots were collected using high volume air samplers (Staplex) packed with XAD-4 resin (Rohm and Haas) and with a dampened cheesecloth, respectively. Both the resin and cheesecloth samples were solvent extracted and concentrated using a previous method (1), and freezer stored until analyzed. Soil samples are being analyzed for triadimefon and triadimenol (2), and chlorpyrifos and its major degradative product, 3,5,6-trichloro-2-pyridinol (TCP) (3).

At the same time that volatile and foliar dislodgeable residues are being collected, chlorpyrifos exposure to researchers simulating the play of golf were determined by dosimetry (cotton pants and shirts, hand rinses, and personal air samplers) (4) and biomonitoring (urine and blood analysis) (5) studies. Chlorpyrifos was applied to a 100 x 20 m rectangular bentgrass plot. Each experiment consisted of an eight volunteer researchers simulating the play of an 18-hole round of golf over a period of 4 hours. As in the monitoring study, chlorpyrifos will be applied using a range of post-application irrigation volumes.

Whole Body Dosimeters: One set of golfers (dosimetry group) wore a single layer of white, 100 % cotton long-sleeved shirt and long pants provided by Dow AgroSciences. This cotton clothing served as a passive collection medium for dislodgeable pesticide residues from treated turfgrass. It is removed at the end of the golf round and sectioned as follows for analysis: lower arms, upper arms, torso, lower legs, upper legs/waist (6).

Hand Rinses: Hand rinses were obtained from the volunteers at the end of each "round of golf". Hand rinses consisted of placing 200 ml of a dilute surfactant solution into 2 quart heavy duty zip lock freezer bags. Each hand was placed into a separate bag and shaken for 2 minutes. The hand washes were analyzed for residues of chlorpyrifos (7).

Face and Neck Wipes: Face and neck exposure were determined by wiping the respective exposed areas with two cheesecloth pads, sequentially, that have been wetted with fresh hand rinse solution (8).

Personal Air Samplers: Inhalation exposure was measured using personal air sampling pumps calibrated to a flow of 1.0 liter of air per minute with special air sampling tubes attached to the volunteers' collar. Particles are retained on a glass microfiber and pesticide vapors are absorbed on a two-section sorbent all within the sampling tubes. Total air concentration is estimated by summing the amount of pesticide collected in the tube divided by the amount of air sampled. To estimate the total amount of pesticide inhaled during the exposure period, the air concentration will be multiplied by an inhalation rate for light work loads (29 liters/minute) and the time over which the exposure occurred (9).

Urine Samples: To estimate the total absorbed dose following chlorpyrifos exposure, urinary biomonitoring was conducted for 3,5,6-trichloro-2-pyridinol (TCP), the major urinary metabolite of chlorpyrifos. When the pharmacokinetics of a compound is known, biological monitoring of major urinary metabolites presents the most complete picture for assessing whole body dose. Urine samples were collected and analyzed for TCP the day before exposure, and then for 23 hrs following the chlorpyrifos exposure (total collection interval was 27 hrs).

Blood Samples: Blood samples were collected from each volunteer 24 hours prior to exposure, and then again 72 hours post-exposure. Blood samples were analyzed for red blood cell cholinesterase activity.

Chlorpyrifos, triadimefon, triadimenol, and TCP residues are being analyzed using a Hewlett Packard 6890 gas chromatograph (GC) equipped with a Nitrogen Phosphorous Detector and/or a Hewlett Packard 5890 GC equipped with a mass selective detector. Trichlorfon and DDVP are being analyzed by Hewlett Packard 5890 GC equipped with a Flame Photometric Detector.

Research Findings:

Monitoring of Volatile and Foliar Dislodgeable Residues.

To date, 140 volatile and foliar dislodgeable samples have been collected during the two three-day monitoring experiments. These samples have been solvent extracted and are currently being analyzed as described previously (to be concluded by 2/2001). Before, during and following these experiments, 25 soil cores have been collected, sectioned and stored for analysis of breakdown products of chlorpyrifos, trichlorfon and triadimefon (to be concluded late Spring 2001).

Dosimetry and Biomonitoring of Chlorpyrifos.

Validation of methods and instrumental analysis. Methods for the analysis chlorpyrifos in whole body dosimeters and hand rinses, and TCP in golfer volunteer urine were taken from Dow AgroSciences (5 & 11, respectively). The method of analysis for chlorpyrifos on the personal air sampler media was modified from OSHA (10). Several method modifications were needed to adapt these methods to our laboratory. All final methods were validated in-house through chlorpyrifos recovery and storage, method linearity and detection limit evaluations. The limit-of-detection and recovery of chlorpyrifos or TCP are summarized in Table 1.

Preliminary findings from YEAR 1. A dosimetry group (three individuals) and a biomonitoring group (four individuals) simulated the play of a 18-hole round of golf in 4 hours using the yardage from a local golf course (~6800 yards). All biomonitored individuals wore shorts and short sleeve shirts. Play began 15 minutes following the post-irrigation event that was applied immediately following the pesticide treatment. All 'players' took a practice swing, exchanged clubs appropriately, used tees, replaced divots and shot an overall score of 85. The entire simulated playing area, including fairway and greens, received a full-labeled rate application of chlorpyrifos. Thus, these initial two experiments are considered a ***worst-case scenario*** designed to determine the maximal exposure situations and not one that is likely to occur on any operating golf course.

Table 2 presents the amount of chlorpyrifos collected onto various body locations by the dosimeter group during play. The lower leg consistently was the most available collector, followed by pants and torso. Overall, a total of 320 ± 33 and 303 ± 18 μg of chlorpyrifos were collected during the dosimetry study at 0.65 and 1.3 cm post-application irrigation, respectively. These two amounts are not statistically different form each other (*t*-test, $P>0.05$). The lack of any reduction in chlorpyrifos levels at the higher post-application irrigation level (1.3 cm) is unexpected due to previously collected data and may be due to the heavy morning mist encountered during the 1.3 cm collection. Additional experiments are planned. The relatively low level of chlorpyrifos collected by the hand rinses also is unexpected and may indicate a limitation of the surfactant-based method used. This aspect is currently under evaluation.

Table 3 summarizes the initial chlorpyrifos levels collected onto individual personal air samplers by the dosimetry group. The two values obtained at the 0.65 and 1.3 cm levels of post-application irrigation are significantly different from each other. The increased inhalation exposure during the 1.3 cm irrigation event is unexpected due to previously collected data but consistent with the heavy mist that was present during this application.

Table 4 summarizes the biomonitoring data and estimates the actual whole body dose of absorbed chlorpyrifos as judged by the urinary clearance of the metabolite, 3,5,6-trichloro-2-pyridinol (TCP). There was no statistical difference between the means of individual collections, resulting in a mean exposure of 1.15 ± 0.37 μg/Kg/d, which is not significantly different from the current ADI value assigned to chlorpyrifos.

Our preliminary results indicate that overall exposure and actual whole body uptake of chlorpyrifos is low and not significantly different from its current ADI even under experimental conditions designed to give the maximum recreational exposure to chlorpyrifos. Using the mean whole body dose of chlorpyrifos determined by biomonitoring (1.15 μg/Kg/d) and dividing it by the reference dose for chlorpyrifos (0.003) yields a HQ value of 0.38. As expected, this actual value is well below the concern level of 1.0 and is ~ 6-fold less than the DHQ value estimated by us using dislodgeable foliar residues levels (DHQ = 2.3, 5 hrs post-treatment, Table VII, 12). These findings are encouraging and indicate that the future study of operational practices (e.g. reentry intervals, irrigation, application strategies, alternative chemical and IPM strategies) to attenuate exposure are highly likely to be effective. Additionally, chlorpyrifos is a high risk insecticide that has both high volatility and inherent high toxicity (relatively low reference dose). Even with these characteristics, its potential for exposure that would result in human health implications following the play of golf is not likely. Newer pesticides that do not share the potentially harmful chemistry seen with chlorpyrifos are expected to be even at lower risk when evaluated by dosimetry and biomonitoring approaches.

III. FUTURE RESEARCH PLANS:

1). Repeat preliminary experiments at full-rate chlorpyrifos and a 4 hour exposure interval.

2). Reduce exposure intervals to 3, 2, and 1 hour intervals to approximate exposure situations that would normally occur on golf courses that do not treat the entire course during any single day (i.e., 75, 50 and 25% of the total area of the course per day, respectively).

3). Apply pesticide treatment at dusk the day before conducting the dosimetry and biomonitoring studies to determine the role of reentry timing.

4). Conduct dosimetry and biomonitoring experiments with new pesticides (e.g., lambda-cyhalothrin, imidacloprid, etc.).

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Table 1. Method Detection Limits and Analyte Recovery.

Fortification Range	Recovery (CV)[1]	Replicates	Detection Limit
Urine (TCP)			
2 ug/L - 100 ug/L	102.6% (14.0)	10	2 ug/L
Whole Body Dosimeters (Chlorpyrifos)			
10 ug - 50 ug	85.7 % (8.9)	6	1 ug/section clothing
Hand Rinses (Chlorpyrifos)			
5 ug - 200 ug	96.8% (11.0)	6	0.1 ug
Personal Air Sampler Media (Chlorpyrifos)			
0.5 ug - 100 ug	93.5% (4.3)	6	0.02 ug/sampling tube[2]
Face/neck Rinses (Chlorpyrifos)			
10 ug	75.9 % (7.2)	3	1.0 ug

[1] CV= coefficient of variance (relative standard deviation).

[2] Equivalent to 1 ug chlorpyrifos exposure using moderate breathing rate for 4 hours.

Table 2. Individual Hand/Face Rince and Dosimeter Results.

	0.65 cm irrigation			*1.3 cm irrigation*		
	Volunteer			Volunteer		
Location	1	2	3	1	2	3
Hands	0.92 ug	0.89 ug	1.4 ug	1.22 ug	1.21 ug	2.03 ug
Lower Arms	30.81 ug	33.26 ug	31.44 ug	35.71 ug	22.96 ug	31.09 ug
Upper Arms	27.57 ug	20.00 ug	19.72 ug	16.68 ug	22.9 ug	18.42 ug
Torso	50.89 ug	30.00 ug	49.65 ug	48.9 ug	49.8 ug	41.85 ug
Face	NA [1]	NA	NA	nd [2]	nd	nd
Lower Legs	126.02 ug	122.22 ug	71.75 ug	90.42 ug	124.3 ug	81.3 ug
Pants	96.73 ug	138.42 ug	108.69 ug	97.68 ug	103.2 ug	117.2 ug
Total	333 ug	345 ug	283 ug	291 ug	324 ug	294 ug
Average		320 ug +- 33			303 ug +- 18	

[1] Not Analyzed.
[2] Not Detected. The limit of detection is 0.1 ug chlorpyrifos.

Table 3. Personal Air Sampler Monitoring Results

		Total Chlorpyrifos Inhalation Exposure[1]	
Volunteer	Height	0.65 cm Irrigation	1.3 cm Irrigation
1	5' 3"	10.20 ug	17.13 ug
2	5' 10"	7.50 ug	14.64 ug
3	5' 10"	8.60 ug	12.63 ug
Average		8.77 ug +-1.4	14.8 ug +- 2.3

[1] Calculated using moderate breathing rate of 2.5 m^3/hour.

Table 4. Total Amount of Chlorpyrifos Absorbed.

0.65 cm irrigation

Volunteer	Height	Weight	Chlorpyrifos Absorbed from Urine [1]	Chlorpyrifos Dose [2]
1	5' 7"	68.9 Kg	108.3 ug	1.6 ug/Kg
2	5' 10"	81.6 Kg	62.5 ug	0.77 ug/Kg
3	6' 1"	120.2 Kg	130.6 ug	1.1 ug/Kg
4	5' 10"	75.8 Kg	69.4 ug	0.92 ug/Kg

1.3 cm irrigation

Volunteer	Height	Weight	Chlorpyrifos Absorbed from Urine [1]	Chlorpyrifos Dose (ug/Kg)
1	5' 7"	68.9 Kg	97.2 ug	1.4 ug/Kg
2	5' 10"	81.6 Kg	63.1 ug	0.77 ug/Kg
3	6' 1"	120.2 Kg	115.3 ug	0.96 ug/Kg
4	5' 10"	75.8 Kg	132.3 ug	1.7 ug/Kg

[1] Estimated from 24 hour post-exposure TCP excretion.
ug CHP = (ug TCP excreted) / (0.7151) x (0.5) x (198/350)

[2] ADI = 1.0 ug/Kg/d