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Utilizing Reduced Risk Pesticides and IPM Strategies to Mitigate Golfer Exposure and Hazard

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RESEARCH SUMMARY

This ongoing study seeks best management practices for reduced golfer exposure to "**reduced risk"** turfgrass pesticides. We have previously evaluated exposure in over 150 rounds of golf following the application of standard turfgrass insecticides (chlorpyrifos, cyfluthrin, carbaryl, imidacloprid), herbicide (2,4-D) and a fungicide (chlorothalonil). Exposure estimates made using biomonitoring and dosimetry data are significantly less (up to 15-fold) than estimates made using volatile and dislodgeable foliar residues. This type of information is absolutely critical to reduce individual contributions of pesticides to the USEPA/FQPA "Risk Cup" evaluation of agrochemicals, including turfgrass pesticides. While many standard pesticides have been removed from use, new "reduced risk" pesticides are being added to the IPM practitioner's toolbox. To date, there is no similar data on "reduced risk" pesticides, which elicit low mammalian and environmental toxicity, low potential for groundwater contamination, low pest resistance potential, and are compatible with IPM, due to their novel physical and chemical properties. This growing season (Summer 2007) we evaluated pesticide exposure following two applications of carfentrazone-ethyl. Future work will involve determining exposure for azoxystrobin (Summer 2008) and halofenozide (2009).

Accurate assessment of golfer exposure to pesticides requires knowledge of the availability of pesticide residues following application, transfer and absorption kinetics of these residues, and major routes of entry into the body. Determination of the actual transfer of available environmental residues (dislodgeable foliar residues, DFRs) to golfers during a round of golf and the subsequent penetration of the transferred residues was achieved by measuring the exposure of volunteers using dosimetry (pesticide residues on full body cotton suits and personal air samplers) and biomonitoring (measuring urinary metabolites), respectively.

Dosimetry and biomonitoring, together with concurrently collected dislodgeable and volatile residue data, provides a unique and complete database on golfer exposure and has allowed us to develop two *golfer exposure models*. Using the total pesticide dose derived from dosimetry or biomonitoring data, these models accurately predict golfer exposure based solely on DFRs. With this information, a simple wipe sample from the turfgrass surface is sufficient to realistically predict exposure in most situations.

The central predictor of exposure in our model is the transfer factor (TF), which is the ratio between the amounts collected on the dosimeter suits versus environmental residues (DFR). By combining information determined for carfentrazone-ethyl with our previous research on chlorpyrifos, cyfluthrin, carbaryl, imidacloprid (with post-application irrigation), 2,4-D, mecoprop-p, chlorothalonil and cyfluthrin (without post-application irrigation), we will validate our golfer exposure model and amend it for use with pesticides that vary widely in their physical and chemical properties. Regulators and health professionals now consider biomonitoring data the "gold standard" for measuring pesticide exposure, and we have validated our TF model using this approach for carfentrazone-ethyl. New data generated will be completely novel and will establish the potential benefits to golf of using "reduced risk" pesticide approaches.

With our empirically derived TF model, pesticide dose can be predicted using environmental residues (airborne and DFR).This pesticide dose can then be used to calculate a Hazard Quotient (HQ) using the US EPA's established reference dose (RfD). HQs less than or equal to one indicate that exposure resulted in a pesticide dose at which adverse effects are unlikely, even if that dose is received every day over an individual's lifetime. A HQ greater than

1.0 does not necessarily infer the exposure will cause adverse effects, but rather that the absence of adverse effects is less certain.

Last season (2007) we evaluated exposure in 16 rounds of golf following the application carfentrazone-ethyl without post-application irrigation. Analysis of these dosimetry samples is complete and data analysis is in progress.

Experimentally-derived TFs from our previous research range from a low of 570 (2,4-D) to a high of 6300 cm^2/hr (chlorpyrifos). Using our established experimental design based on concurrently collected dosimetry, biomonitoring and environmental samples we have calculated a preliminary transfer factor of 1650 for carfentrazone-ethyl and a preliminary dermal absorbed dose of 0.004 µg/kg, resulting in a dermal HQ of **0.0000008**. It is important to note that this is the dermal HQ only, and that the air samplers need to be analyzed to determine the inhalation HQ. These results validate our original assumption that the use of reduced risk pesticides will result in lower HQs.

To date, HQs determined for carfentrazone-ethyl as well as the previously studied pesticides chlorpyrifos, carbaryl, and cyfluthrin with post-application irrigation, and 2,4-D, MCPP, cyfluthrin, and chlorothalonil without post-application irrigation have all been below 1.0, indicating safe exposure levels.

It should be noted that the US EPA recently released a new reference dose (RfD) of 1.7 mg/kg/day (1) for acute dietary exposure to MCPP-p (August 29 2007). Therefore, we have recalculated the RfD for MCPP-p. In the absence of post-application irrigation, this new RfD resulted in a HQ of 0.0011. The new RfD for MCPP-p is considerably higher than the previously available chronic dietary reference dose of 0.001 mg/kg/day, which resulted in a HQ >1.0 (1.8).

By choosing "reduced risk" pesticides with novel physical and chemical properties, our models will be expanded to provide golf course managers and regulators a range of exposure factors to accurately predict exposure (dose) following a variety of application scenarios. It is imperative to test "reduced risk" pesticides in IPM programs to document their impacts. First, our data will establish the benefits (e.g., protection of the health of workers, golfers, and wildlife, decrease potential for resistance, etc) of reduced risk materials. Second, EPA offers an expedited registration review for them. Third, there is a critical need for this type of regulatory information, and our accurate estimates of exposure will allow appropriate risk assessments to be made for the vast majority of commercial pesticides for which there is no suitable urinary metabolite (i.e., not amenable to biomonitoring studies). Lastly, we have determined that estimates of golfer exposure are significantly less by determining dose directly (biomonitoring) and indirectly (dosimetry) than previous estimates made using volatile and dislodgeable foliar residues. Hazard assessment of "reduced risk" pesticides will even be lower as evidenced by carfentrazone-ethyl.

I: OBJECTIVES:

Objective 1: Determination of the level and hazard of volatile and foliar dislodgeable residues of the reduced risk pesticides, halofenozide, carfentrazone-ethyl and azoxystrobin, following full course-full rate applications.

Objective 2: Effect of partial course application strategies (e.g., tees and greens) and post-application irrigation on volatile and foliar dislodgeable pesticide residues following full-rate applications of halofenozide, carfentrazone-ethyl and azoxystrobin.

Objective 3: Concurrent determination of dosimetry and urinary biological monitoring of researchers simulating an 18-hole round of golf following application of halofenozide, carfentrazone-ethyl and azoxystrobin to turfgrass. **NOTE: This aspect of the proposal will be funded and carried out under separate agreements with the New England Regional Turfgrass Foundation.**

Objective 4: Model the relationship between volatile and dislodgeable foliar residues vs. actual golfer exposure using urinary biological monitoring techniques (*Biomonitoring Exposure Model*) or, for pesticides that are not amenable to biomonitoring, using dosimetry techniques (*Dosimetry Exposure Model*) for a wide range of pesticides and application scenarios.

II: WORK COMPLETED:

We are continuing to determine dislodgeable foliar residues (DFRs) with the EPA recommended *California Roller* method. The use of this validated method consistently results in approximately 50% less pesticide residues available for transfer to golfers than the previous cheesecloth wipe method, reducing total exposure estimates.

Two separate applications of carfentrazone-ethyl without post-application irrigation have been completed (2007). Two groups of research subjects played a simulated round of golf (4 hrs) following each application. A dosimetry group (n=4) wore cotton overalls, gloves, a veil, and personal air samplers containing XAD-2 resin. A biomonitoring group (n=4) collected urine over a one day (24 hrs) period post-exposure. Samples representing a total of 16 rounds of golf were collected. We have collected 154 samples, of which 138 (90%) have been analyzed (Table 1).

Table 1. Samples collected and analyzed over the course of the project.

Pesticide	2007		2008		2009	
	collected	analyzed	collected	analyzed	collected	analyzed
Carfentrazone-ethyl						
DFR	26	26				
Dosimeters	112	112				
Airborne	8	0				
Urine	8	0				
Azoxystrobin						
DFR			----------	----------		
Dosimeters			---------	----------		
Airborne			---------	---------		
Urine			---------	---------		
Halofenozide						
DFR					---------	---------
Dosimeters					---------	---------
Airborne					---------	---------
Urine					---------	---------

90% of the samples collected in 2007 have been analyzed.

Environmental Residues: This season (2007), 26 California roller samples were collected following application of carfentrazone-ethyl. 26 samples have been analyzed and data analysis is in progress.

Whole Body Dosimeters (passive dosimetry): One set of golfers (dosimetry group) wore overalls that consisted of a single layer of white, 100% cotton and cotton gloves. This cotton clothing served as a passive collection medium for DFR from treated turfgrass. Overalls were removed at the end of the golf round and sectioned as follows for analysis: lower arms, upper arms, torso, lower legs, and upper legs/waist (2-5). Additional dosimetry samples include a veil and upper socks. Another set of golfers (biomonitoring group) wore partial dosimeters consisting of upper arms, torso, and upper legs/waist.

This season (2007), 8 full and 8 partial dosimetry suits were collected following carfentrazone-ethyl application for a total of 112 samples. 112 of these samples have been analyzed and data analysis is in progress.

Personal Air Samplers (active dosimetry): Inhalation exposure was measured using personal air sampling pumps containing XAD-2 resin (NIOSH 5602) calibrated to a flow of 1.0 liter of air per minute with special air sampling tubes attached to volunteers' collars of the dosimetry group (6-8). Particles are retained on a glass microfiber and pesticide vapors are absorbed on a two-section sorbent contained 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 workloads (21 liters/min) and the time over which the exposure occurred (4 hrs).

This season (2007), 8 personal air samplers were collected and will be analyzed for carfentrazone-ethyl in the following manner. Subsequent to sampling, the front sorbent section and the glass microfiber will be combined into an 8 ml vial and the rear sorbent bed into another. Pesticide residues are desorbed for 1 hr with 2.0 ml hexane. Samples will be analyzed by GC/MS.

Urine Samples: To estimate the total absorbed dose following carfentrazone-ethyl exposure, urinary biomonitoring was conducted for the metabolite carfentrazone-chloropropionic acid (alpha,2-dichloro-5-[4-difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid). Urine samples were collected 24 hrs before exposure, and then collected for one 24 hr period following exposure (the estimated time to excrete ½ of the total dose of carfentrazone-ethyl) (9).

This season (2007), 8 urine samples were collected and method development for the above compound is in progress.

III: RESEARCH FINDINGS

Golfer Exposure Models

Multipathway exposures will be evaluated by comparing pesticide residues on dosimetry media and/or 24 hr post-exposure urine (biomonitoring group) to volatile and dislodgeable foliar residues (DFR). The direct and simultaneous determination of dosimetry and biomonitoring data provides a novel and complete database on how much pesticide is transferred from the treated turf to the golfer during the play of a round of golf, and subsequently how much pesticide is actually absorbed. This exposure data, together with dislodgeable and volatile residue data, has

allowed us to develop a new golfer exposure model. Using the total pesticide dose derived from dosimetry and/or biomonitoring data, these models can be used to accurately predict golfer exposure based solely on dislodgeable foliar residues (DFR). The transfer factor (TF, Equation 1) is derived from a comparison of the residues determined from the whole body dosimeters with the DFRs. With this information, a simple California Roller wipe sample from the turfgrass surface is sufficient to realistically predict exposure in most situations (Equation. 2).

A) Dermal Hazard Quotient

EQUATION 1:

TF(cm^2/hr) = µg on dosimeter/DFR(µg/cm^2)/4 hrs

EQUATION 2:

Dermal Pesticide Dose (µg/Kg body weight/d) =
DFR (µg/cm^2) x TF (cm^2/hr) x dermal penetration x 4hr /body weight (70kg)
Where TF = transfer factor and DFR = dislodgeable foliar residues

The DFR, transfer factor and dermal penetration factor are used subsequently to calculate a dermal hazard quotient using the EPA RfD.

EQUATION 3:

DHQ = Dermal Dose (µg/Kg body weight/d) /EPA RfD (µg/Kg body weight/d)

Transfer Factors

A transfer factor has now been calculated for carfentrazone-ethyl (Table 2).

Table 2. Summary of golfer transfer factors.

Pesticide	Transfer Factor (cm^2/hr)
Carfentrazone-ethyl	1650

A dermal hazard quotient has been calculated for carfentrazone-ethyl (Table 3).

Table 3: Dermal hazard quotients (DHQ) calculated for carfentrazone-ethyl from DFR and dosimetry.

Pesticide	DFR (µg/cm^2)	TF(cm^2/hr)	Dermal Penetration	Dermal Dose (µg/kg)	RfD (µg/kg/day)	HQ
Carfentrazone-ethyl	0.00044	1650	10%	0.004	5000	0.000008

Hazard quotients less than or equal to one indicate that exposure resulted in a pesticide dose at which adverse effects are unlikely. A HQ greater than 1.0 does not necessarily infer the exposure will cause adverse effects, but rather that the absence of adverse effects is less certain.
DFR = Dislodgeable Foliar Residues, TF = Transfer Factor from the turf to the dosimeter. RfD = EPA Reference Dose. HQ = Hazard Quotient. carfentrazone-ethyl, mean of two applications.

The DHQ for carfentrazone-ethyl is 0.000008, indicating that adverse effects are unlikely, as determined by the US EPA HQ criteria. This hazard quotient will be combined with that generated from the airborne residue data in the following manner:

B) Inhalation Hazard Quotient

The inhalation dose is calculated by determining pesticide residues collected by a personal air sampler following four hours of simulated golf. Airborne concentrations are calculated by totaling the amount of pesticide collected in the tube divided by the amount of air sampled (2 L/min). To estimate the total inhalation exposure over the four hour exposure (240 min), airborne concentrations (µg/L) are multiplied by an inhalation rate for light workloads (21 L/min).

EQUATION 4:

Airborne dose (µg/240 min) = collected residues (µg/240 min) x $\frac{\text{21L/min/240 min}}{\text{2L/min/240 min}}$

EQUATION 5:

Inhalation Dose (µg/kg) = airborne dose (µg) x 100 % penetration /70 Kg

EQUATION 6:

IHQ = inhalation dose (µg/Kg body weight)/reference dose (µg/Kg body weight/d)

C) Combined Hazard Quotients

Finally, total dose is calculated by combining the dermal dose (µg/Kg) with the inhalation dose (µg/Kg) for use in the calculation of an overall hazard quotient.

EQUATION 7:

Total Dose = DFR (µg/cm^2) x TF (cm^2/hr) x dermal penetration x 4hr + inhaled dose/body weight (70kg)

OR

EQUATION 8:

Total Dose = dermal dose (µg/Kg) + inhalation dose (µg/Kg)

EQUATION 9:

Combined HQ = DHQ + IHQ

OR

EQUATION 10:
Combined HQ = total dose/RfD

This transformation provides a method for directly and realistically evaluating exposure levels of golfers in order to *establish safe reentry intervals without involvement of human subjects.* Our experimentally derived exposure ratios (transfer factor and penetration factors) are consistently 2 to15-fold less than previous estimates using volatile and dislodgeable foliar residue data.

IV. FUTURE RESEARCH PLANS:

1) Expected completion dates for remaining analyses:
carfentrazone-ethyl air samplers: 1/30/08
carfentrazone-ethyl urine: 3/15/08

2). Complete application and analysis of azoxystrobin - 2008.

3). Complete application and analysis of halofenozide - 2009.

V. PUBLICATIONS

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