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

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SUMMARY

Researchers at the University of Massachusetts quantified dermal, airborne and **D**islodgeable **F**oliar **R**esidues (DFR) of three reduced risk pesticides, azoxystrobin, carfentrazone-ethyl, and halofenozide. Dosimetry techniques were used to assess the exposure of volunteer golfers to these pesticides under worst-case scenarios during the play of 32 rounds of simulated golf. All exposures resulted in acquired doses significantly less than the reference doses (RfD) established for each pesticide by the USEPA Office of Pesticide Programs (USEPA/OPP). The RfD is then used to calculate a hazard quotient (HQ) by dividing the acquired dose by the RfD. HQs ≤ 1.0 are indicative of a safe exposure. HQs >1.0 do not necessarily mean that the exposure is unsafe, only that the absence of adverse effects is less certain. Other findings include:

- Dermal absorption is the principle route of exposure to golfers following application of these reduced risk compounds. Hands, lower legs and upper socks were the main routes of exposure.
- Halofenozide exposure resulted in the highest combined hazard quotient (CHQ, sum of dermal and inhalation hazard quotients, 0.030) of the reduced risk pesticides tested following application at its highest labeled rate with 0.25”of post-application irrigation. It should be noted that halofenozide has recently lost its reduced risk pesticide designation. The CHQ calculation for halofenozide is only about ½ of that determined by dosimetry for chlorpyrifos (0.059) (1). In this case, the application of halofenozide is considered safe but does not greatly reduce golfer hazard.
- The CHQ established for the fungicide azoxystrobin (0.0039) was about an order of magnitude less than that determined for the fungicide chlorothalonil (0.043). The CHQ determined for the herbicide carfentrazone-ethyl (0.00014) was ~ 700-fold less than that determined for the herbicide MCPP (0.1).
- In the cases examined, the use of reduced risk pesticides can lessen golfer exposure and hazard. The application of azoxystrobin brought about an ~ 10-fold reduction in CHQ compared to chlorothalonil. The use of carfentrazone-ethyl produced an ~ 700 fold reduction in CHQ versus the use of MCPP, and the application of halofenozide led to a ~ 2-fold reduction in HQ compared to the use of chlorpyrifos.
- A 1 hour reentry interval generally reduces exposure.

INTRODUCTION

Golf and Pesticide Exposures

Pesticide exposure following application to turfgrass is of concern to turf managers, golfers, and regulators. Although most consumers are not well informed about pesticide use on golf courses, well-publicized examples of environmental contamination from agrochemicals have caused many individuals to develop negative attitudes toward golf course management practices. These concerns arise from the variety, amount and frequency of pesticide use on turf, the amount of time adults and especially children and infants spend on turfgrass, and the potential for unsafe levels of exposure that may occur in these situations. There has been a great deal of focus in the past on the exposures of

mixers, loaders and applicators to pesticides. The potential for exposure, however, exists for all who reenter pesticide treated turf areas.

Previous Studies

Our previous results indicate that the overall "golfer" exposure received following full-course and full-rate applications of chlorpyrifos, carbaryl, and cyfluthrin, under worst case scenarios, are substantially below USEPA RfD values, indicating safe exposures (CHQ ≤ 1.0, Clark, 2005, USGA Program Report). The initial phase of this project focused on studying the well-characterized conventional insecticides chlorpyrifos and carbaryl, as well as a more modern insecticide, cyfluthrin. Insecticides were chosen in the belief that these neurotoxins would present the most hazard to golfers. All insecticides received 0.25" of post-application irrigation. Putnam and Clark determined CHQs for golfer exposure to chlorpyrifos (0.059), carbaryl (0.014) and cyfluthrin (0.004) (Clark, 2005, USGA Program Report). All CHQs were well below 1.0, indicating safe exposures. It was also determined that the lower body was the major route of exposure.

The next phase of the project looked at conventional herbicides (2,4-D, MCPP), a commonly used fungicide (chlorothalonil), and a more modern insecticide (imidacloprid). As with the other insecticides, imidacloprid received 0.25" of post-application irrigation. Herbicides and fungicides did not receive post-application irrigation. This study determined that the CHQs for 2,4-D (0.011) MCPP (0.55) imidacloprid (0.0097), and chlorothalonil (0.043) were also well below USEPA HQ values. Golfer exposure to MCPP, an herbicide, resulted in the highest CHQ generated in this project. Without post-application irrigation (2,4-D, MCPP, chlorothalonil), the primary route of exposure was through the hands. With post-application irrigation, imidacloprid exposure was determined to be through the lower body, much like the exposure scenarios of the previously studied insecticides.

Justification of Worst Case Scenarios

In all these studies, we consider these exposure estimates to be 'worst-case scenarios' for the following reasons:

- All pesticides were applied at maximum-labeled rates;
- Pesticide applications were made to the entire "course", including tees, greens, collars and fairways;
- Volunteer golfers spent the entire four-hour round of golf on the treated turf;
- USEPA chronic RfDs, which assume no harmful effects following daily exposure over a 70 year lifespan, were used to generate the HQs;

In this study, we measured environmental residues (DFR) available for transfer from treated turf, and residues on dosimeters (whole-body cotton suits and personal air samplers) to measure the amount of pesticide on the body surface available for dermal penetration and that in the personal breathing space available for inhalation, respectively. This information provides a novel and complete database for the assessment of pesticide exposure from treated turf.

Our previous work focused on strategies for mitigating golfer exposure to turfgrass pesticides such as half-course applications, application only to tees and greens and use of post-application irrigation when appropriate. These strategies were found to reduce golfer exposure and hazard. Reduced risk pesticides, which typically have reduced mammalian toxicity, may be yet another strategy to reduce golfer exposure and hazard. For this reason, we chose to examine the effect of the use of reduced risk pesticides on golfer exposure and hazard.

For a pesticide to be considered reduced risk, it must meet one or more of the following criteria:

- Human Health Effects
    - very low mammalian toxicity

    - toxicity generally lower than alternatives (10-100x)
    - displaces chemicals that pose potential human health concerns (e.g. organophosphates, or probable carcinogens)
    - reduces exposure to mixers, loaders, applicators, and reentry workers
- Non-Target Organism Effects (birds)
    - very low toxicity to birds and beneficial insects
    - very low toxicity to honeybees
    - significantly less toxic to birds than alternatives
    - not harmful to beneficial insects, highly selective pest impacts
- Non-Target Organism effects (fish)
    - very low toxicity to fish
    - less toxicity/risk to fish than alternatives
    - potential toxicity/risk to fish mitigatable
    - similar toxicity to fish as alternatives but significantly less exposure
- Groundwater Issues
    - low potential for groundwater contamination
    - low drift, runoff potential
    - runoff mitigatable
- lower use rates than alternatives
- low pest resistance potential (e.g. new mode of action)
- highly compatible with IPM
- efficacy (effective at very low use rates)

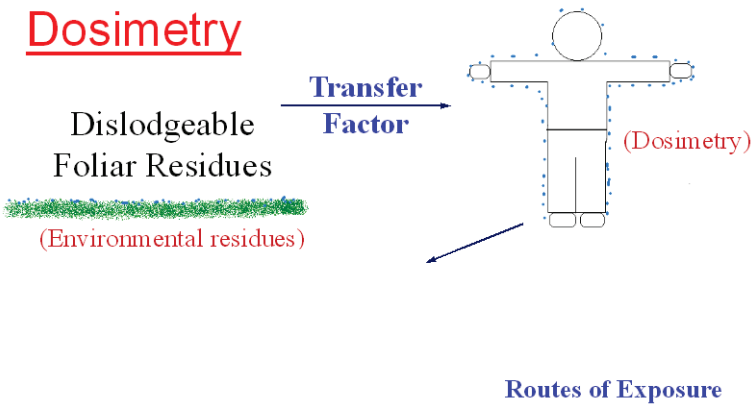
Routes of Pesticide Exposure

Pesticide exposure to golfers is principally through the dermal contact with DFRs on treated turfgrass foliage. The dense canopy of the turfgrass system is likely to intercept a greater percentage of applied pesticide than typical agricultural systems where much of the applied pesticide reaches the soil surface. Therefore, dermal exposure may be significant. Turfgrass plants also have a waxy layer on their surface and also produce an organically rich thatch layer. These factors are expected to compete with the transfer of pesticides to golfers.

Inhalation is a second possible route of golfer exposure. These reduced risk pesticides are relatively non-volatile, making airborne exposure to these compounds less of a concern. This exposure route is still toxicologically relevant, however, because inhalation exposure results in a high level of absorption. The lungs highly vasculated circulatory system allows for extremely rapid transfer of volatiles and small particulates in inhaled air to the bloodstream and widespread distribution throughout the body.

Oral exposure is the third possible route but is generally considered the least important in a golfer exposure scenario. This type of exposure would primarily be through hand-to-mouth contact. Evidence has shown that golf balls, tees, etc. do not transfer significant amounts of pesticides to golfers (2).

Figure 1. The transfer factor is the difference between the dislodgeable foliar residues on the turfgrass and the amounts determined on the dosimetry suits worn by a volunteer golfer simulating a round of golf. By segmenting the suits the routes of exposure can be determined (from Putnam and Clark, 2004. See reference 1).



Whole Body Dosimeter (WBD)

MATERIALS AND METHODS

Field Study Site

All experiments were performed at the University of Massachusetts Joseph Troll Turfgrass Research Center in South Deerfield MA. A 130 X 30 yard plot consisting of 'Penncross' creeping bentgrass was used for the concurrent collection of DFR and dosimetry samples. This plot was maintained as a golf course fairway, mowed three times a week at 0.5", and irrigated as needed to prevent drought stress. Additionally, the plot was fertilized with 3 lbs N/year in three 1 lb applications, and treated with fungicides not used in the current study to control fungal diseases; dollar spot (*S. homeocarpa*), brown patch (*R. solani*) and pythium blight (*Pythium spp.*) as needed.

Pesticide Applications

A Toro Multipro 1200 boom sprayer fitted with eleven VisiFlo® flat spray tips (TeeJet® Technologies) was used for all applications (Fig. 2). All treatments with Mach II 2SC® (halofenozide, Syngenta) were followed by 0.64 cm (0.25") of irrigation immediately after application.

Figure 2. All pesticides were applied with a Toro® Multipro 1200.

Heritage® (50% azoxystyrobin, Dow Agrosciences) was applied at a rate of 0.2 oz a.i./1000ft^2. Heritage® was not applied at the maximum label rate of 0.35 oz. a.i./1000ft^2 used for snow mold control because these applications take place shortly before snow cover when the golf season is already over. This would, therefore, present an unrealistic exposure scenario. Briefly, 16 oz. of formulated product was mixed with 80 gallons of water and applied at a rate of 2 gallons/1000ft^2.

Quicksilver T & O Herbicide® (21.3.0% carfentrazone-ethyl, FMC Corp.) was applied at the USEPA maximum label rate of 0.036 oz. a.i./1000ft^2. For the Quicksilver application, 6.16 oz. of formulated product was mixed with 80 gallons of water and applied at a rate of 2 gallons/1000ft^2.

Mach II 2SC® (22.3% halofenozide, Syngenta) was applied at the USEPA maximum label rate of 0.65 oz. a.i./1000ft^2. For the Mach II application, 7.25 qt. (116 fluid oz.) of formulated product was mixed into 80 gallons of water and applied at a rate of 2 gallons/1000ft^2.

Golfer Activities and Exposure Scenarios

Azoxystrobin, carfentrazone-ethyl, and halofenozide were applied to a rectangular bentgrass plot maintained as a fairway. Exposure to volunteers simulating the play of a round of golf was determined by a dosimetry study. Concurrent with this study, DFR samples were collected from the same plot. Each experiment utilized four volunteers wearing dosimetry suits simulating the play of an 18 hole round of golf over a period of four hours. The round of golf was standardized in an attempt to ensure consistent behaviors amongst the different volunteers. The template was based on all volunteers playing bogey golf (par plus one stroke per hole). Each player hit the ball 90 times, additionally taking 90 practice swings, while walking the 6500 yard layout of a local course. Clubs were rotated in an appropriate manner, balls were teed up on tee shots, divots were replaced, and clubs were wiped clean between shots using a golf towel. Each simulated round of golf commenced either one-hour after application (azoxystrobin, carfentrazone-ethyl) or one hour after the end of post-application irrigation (halofenozide).

Dislodgeable Foliar Residues (DFR)

These experiments were carried out on the same plot concurrent with the exposure study. DFR were determined using the Outdoor Residential Task Force recommended California roller (CA roller, Fig. 5) (3) Three 7' x 12' sections of the study site were cordoned off to prevent foot traffic by the study participants. One 2' x 3' DFR sample was collected from each section at 0.25, 1,2, and 5 hours after pesticide application. Sections that were sampled had their perimeters marked using turf paint to prevent re-sampling of an area.

Dosimetry

Exposure of volunteer 'golfers' simulating the play of an 18-hole round of golf was determined by dosimetry. Exposure to individual volunteers has been evaluated following 32 rounds of golf derived from 8 pesticide applications to the study site (Table 1). The dosimetry group of volunteers wore white, 100% cotton, long johns (Indera Mills Co., Yadkinville, NC), white cotton gloves, and veils attached to the back of their hats (Fig. 3), which served as passive collection media for pesticide residues from treated turfgrass (4,5).

Figure 3. Group. Volunteer golfers wore whole body dosimetry suits and socks, double gloves, and a cotton veil on the hat.

Table 1. Summary of reduced risk pesticides tested, applications, rates and conditions, and duration and frequency of exposures.

	Post-application Irrigation	Exposure (h)	Field Trials
Azoxystrobin Heritage 0.2 oz. a.i./1000 ft^2	None	4	3
Carfentrazone-ethyl Quicksilver T&O 0.036 oz. a.i./1000ft^2	None	4	2
Halofenozide Mach II 2SC 0.65 oz. a.i./1000ft^2	0.25"	4	3

Inhalation exposure to the dosimetry group was measured utilizing personal air samplers (Aircheck52, SKC Inc., Eighty Four PA) equipped with OVS air sampling tubes (SKC Inc.) attached to the front collar of each volunteer near the breathing zone (Fig. 4)(4,6). These sampling tubes trap three types of pesticide residues: those sorbed onto particulates (e.g., dust) and those found in aerosols are trapped by a quartz filter, and pesticide vapors, which are trapped on XAD-2 resin in the tubes. Air samples were collected at 2.0 L/min. To estimate total airborne dose of the pesticide, the residues found in the sampling tubes were multiplied by 10.5 to arrive at the dose correlated with a moderate breathing rate of 21 L/min.

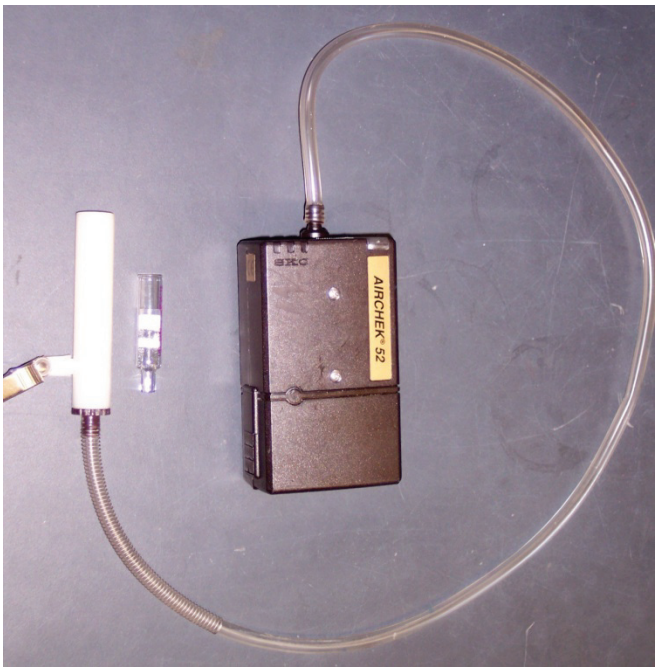


Figure 4. Volunteer golfers wore personal air samplers consisting of a pump attached to a pesticide collection tube that was clipped onto the collar of the dosimetry suit.

Volunteers were from the Department of Veterinary and Animal Science at the University of Massachusetts/Amherst. A protocol that describes the study and the protected rights of the volunteers was approved by the Human Subjects Review Committee at UMASS (OGCA# 107-0889). The approved protocol, including an informed consent form, was reviewed with potential participants at an orientation meeting prior to their participation.

Pesticide Analysis

All pesticide analysis was carried out at the Massachusetts Pesticide Analysis Laboratory (MPAL), a USEPA/MA Department of Agricultural Resources (DAR)-supported pesticide analytical laboratory using standard protocols and QA/QC procedures.

RESULTS

Dislodgeable Foliar Residues (DFR)

Airborne and DFR were determined for a period of 4.75 hours following pesticide application, or 4.75 hours after the end of post-application irrigation in the case of halofenozide. Foliar dislodgeable residues were quantified using the CA roller device, and airborne residues were

determined by personal air samplers. These environmental samples were collected concurrent with the dosimetry exposure study on the same plot.

Azoxystrobin DFR

In agreement with previous research on chlorpyrifos and carbaryl (4), azoxystrobin residues declined rapidly in the first hour following application, then exhibited a slower decline over the next four hours (Fig. 6). Azoxystrobin DFR declined from 0.60 µg/cm^2 (± 0.04 S.E) at 0.25 hours to 0.34 µg/cm^2 (± 0.03) at one hour (43% reduction) and then to 0.02 µg/cm^2 (± 0.005) in the next four hours for a total reduction of 97% in available residues over the 4.75 hours of the experiment. This dissipation pattern indicates that it is appropriate for DFRs to be averaged over a four hour period, our standardized playing time for an 18 hole round of golf, for use in exposure estimates (1). Using this approach, a mean DFR of 0.146 (±0.015) µg azoxystrobin/cm^2 was calculated for the time course of the experiment (hours 1-5) following application at a rate of 0.2 oz. a.i./1000ft^2.

Carfentrazone-ethyl DFR

Dissipation of DFR of carfentrazone-ethyl followed a similar pattern (Fig. 7). DFR of carfentrazone-ethyl declined from 0.00082 µg/cm^2 (± 0.000011) to 0.00052 µg/cm^2 (± 0.000016) at one hour (a 37% reduction) and then to 0.00026 µg/cm^2 (±0.000030) in the next four hours, resulting in an overall reduction of 68% in available residues. A mean DFR was calculated as 0.0005 (±0.000014) µg carfentrazone-ethyl/cm^2 for the time course of the experiment (hours 1-5) following application at a rate of 0.035 oz. a.i./1000ft^2.

Halofenozide DFR

The dissipation pattern of halofenozide was not consistent with previous results (Fig. 8). Halofenozide residues did not significantly decline in the first hour following application. Dislodgeable foliar halofenozide residues only declined from 0.295µg halofenozide/cm^2 (± 0.072) at 0.25 hours to 0.276 µg/cm^2 (± 0.078) at one hour and this reduction was not significantly different. Residues then declined to 0.023 µg/cm^2 (± 0.01) over the next four hours for an overall reduction of 92% of available residues. A mean DFR was determined to be 0.115 µg/cm^2 (±0.022) for the time course of the experiment (hours 1-5) following application at

Figure 5. Dislodgeable foliar residues (DFR) were collected with a California roller (CA roller). A 6 ft2 piece of cloth was placed over a frame and the 32-lb CA roller was slowly rolled across the cloth 10 times. Pesticide residues were considered dislodgeable if they were transferred to the cloth.

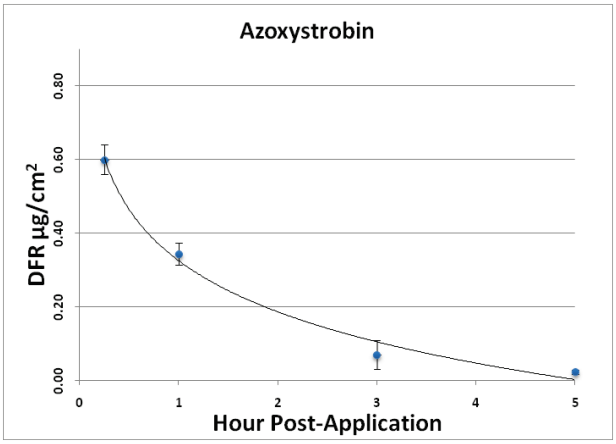


Figure 6. Availability of azoxystrobin dislodgeable foliar residues (DFR) over the first five hours following application.

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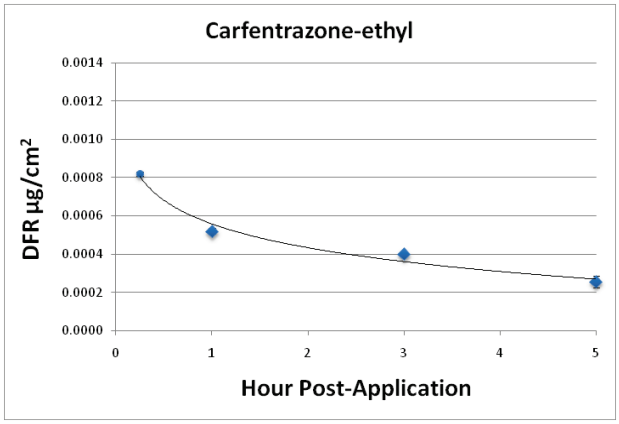

Figure 7. Availability of carfentrazone-ethyl dislodgeable foliar residues (DFR) over the first five hours following application..

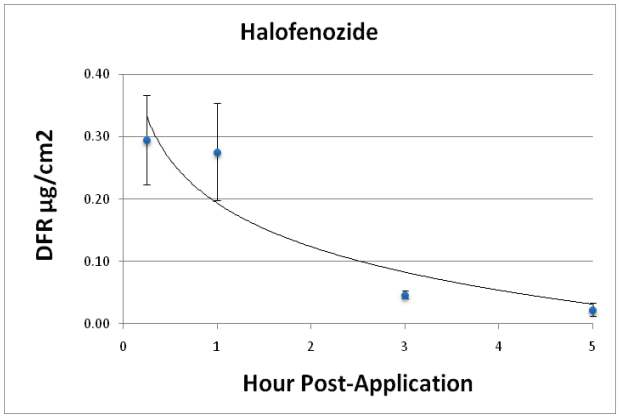

Figure 8. Availability of halofenozide dislodgeable foliar residues (DFR) over the first five hours following application.

a rate of 0.65 oz. a.i./1000ft^2. It should be noted that halofenozide is a systemic insecticide taken up by the roots and has a relatively high water solubility of 12.3 ppm (7).

The dissipation pattern for 2,4-D, MCPP, chlorothalonil, and imidacloprid were consistent with the results for azoxystrobin, carfentrazone-ethyl, and the insecticides studied earlier (chlorpyrifos, carbaryl, and cyfluthrin). The dissipation pattern of halofenozide is unique to all the pesticides we have studied to date.

Determination of Exposure by Dosimetry

The total residues of azoxystrobin, carfentrazone-ethyl, and halofenozide collected on whole body dosimeters and personal air samplers during the simulated play of an 18-hole round of golf are given in Table 2. An average of ~ 800 µg of azoxystrobin was collected on the whole body dosimeters following three applications of Heritage® at a rate of 0.2 oz. a.i./1000ft^2 (Table 2). After adjusting for a moderate breathing rate (21L/min.), personal air samplers worn by the dosimetry group collected an average of 0.156 µg of azoxystrobin. As shown previously (4), the principle route of exposure to golfers was dermal following chlorpyrifos application. In the case of azoxystrobin, similar results were found. Dermal residues account for >99.9% of all transferred residues.

Table 2. Dermal hazard quotients (DHQ), inhalation hazard quotients (IHQ) and overall hazard quotients (Overall HQ) calculated from dosimetry data for the three pesticides studied. No detectable carfentrazone-ethyl residues were found. The value given is determined as ½ of the limit of detection for the sample.

Application Rate	Mean Suit Residues (µg)	Mean airborne Residues (µg)	DHQ	IHQ	Combined HQ
Azoxystrobin 0.2 oz a.i./1000ft^2	805	0.156	0.0039	0.000012	0.003912
Carfentrazone 0.036 oz. a.i./1000ft^2	2.86	0.0055	0.00014	0.0000026	0.0014
Halofenozide 0.65 oz. a.i./1000ft^2	944	0.095	0.030	0.0014	0.03014

The distribution of azoxystrobin on the various dosimeter segments is shown in Figure 9. The hands were the primary route of exposure to axoxystrobin, accounting for ~ 55% of the total residues on the dosimeters, while the upper sock accounted for an additional ~ 27%. Together, the hands and lower sock account for ~ 82% of the total pesticide residues transferred to the dosimeter. The remaining dosimeter segments (veil, upper and lower arm, torso, pant and lower leg) accounted for ~ 18% of the total residues combined.

Total residues of carfentrazone-ethyl found on the dosimeters following two applications of Quicksilver T&O® at a rate of 0.036 oz. a.i./1000ft^2 were determined to be ~ 2.9 µg (Table 2). No carfentrazone-ethyl was detected in the personal air samplers, so these samples were assumed to contain residues equal to ½ the limit of detection for these samples. After adjusting for a moderate breathing rate, the estimated airborne exposure to carfentrazone-ethyl was 0.006 µg. Dermal residues accounted for 99% of all transferred residues.

Carfentrazone-ethyl distribution on the dosimeters is shown in Figure 10. Again, the hands (~ 28% of transferable residues) were the primary route of exposure, but the pants held the next highest percentage of residues at ~ 22%. These two segments account for ~ 50% of all dermal residues of carfentrazone-ethyl. Overall, carfentrazone-ethyl was more widely distributed on the dosimeter than the other two compounds in this study. It is important to note that roughly ½ the dosimeter segments analyzed for carfentrazone-ethyl were negative, including all the veils. Because of this, many suit segments were assigned a residue concentration equal to ½ the limit of detection (0.1µg/segment). Comparatively, all

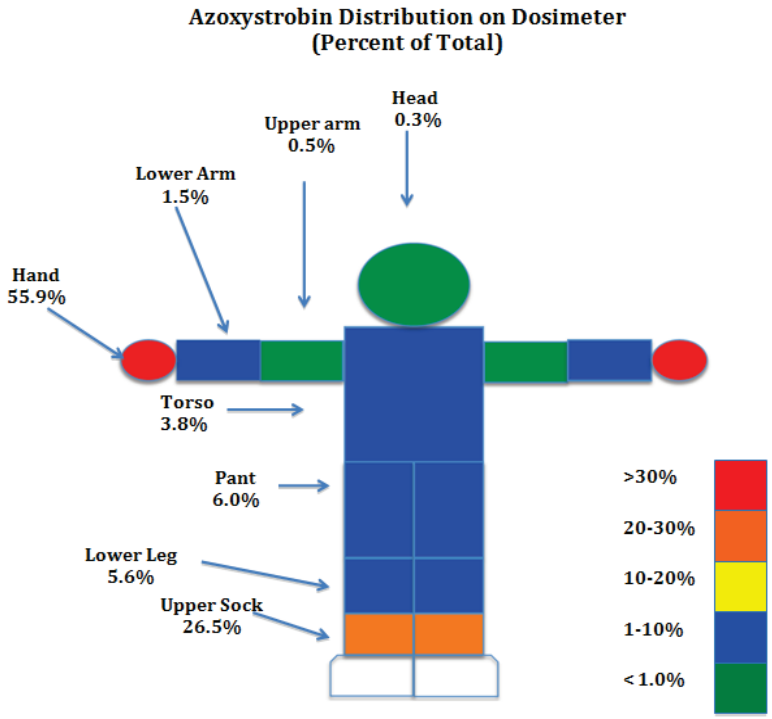

Figure 9. The distribution of azoxystrobin on whole body dosimeters.

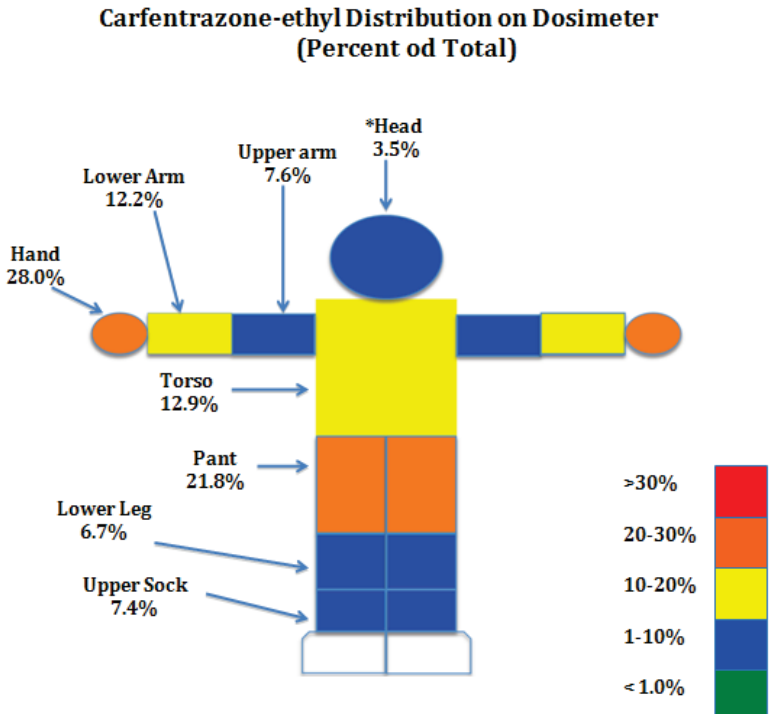

Figure 10. The distribution of carfentrazone-ethyl on whole body dosimeters. Hands and pants received almost ½ the dose. * Veils (head) had no detectable residues. Pants were the only segment with all samples being positive for carfentrazone-ethyl. 25% to 75% of the individual samples for all other segments had no detectable residues.

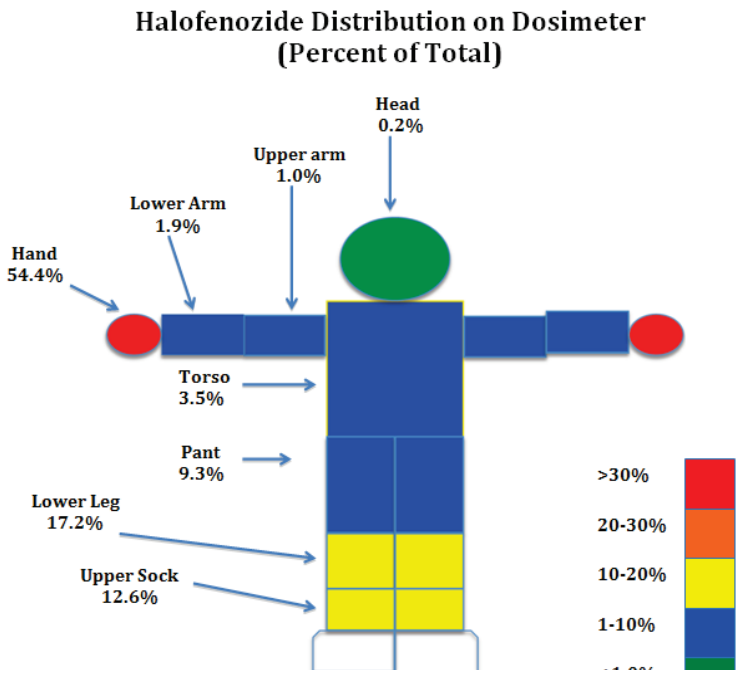

Figure 11. The distribution of halofenozide on whole body dosimeters. Hands, upper sock, and lower leg received the majority of the dose.

dosimeter suit segments from the azoxystrobin and halofenozide analyses were positive for those pesticides (above the limit of detection).

An average of approximately 940 µg of halofenozide was found on the whole body dosimeters following three applications of MachII SC® at a rate of 0.65 oz. a.i./1000ft^2 (Table 2). Halofenozide was the only one of the three pesticides that received post-application irrigation. Personal air samplers worn by the dosimetry group collected an average of 0.095 µg of halofenozide, assuming a moderate breathing rate, over the four hour simulated round of golf. Again, the principle route of exposure was dermal. With halofenozide, > 99.99% of the transferred residues were dermal.

As with azoxystrobin, the hands were the principle route of exposure to halofenozide, accounting for ~ 54% of the total dermal exposure (Fig. 11). The lower leg (~ 17%) and the upper sock (~ 13%) account for an additional ~ 30% of the dosimeter residues. The rest of the dosimeter (veil, upper arm, lower arm, torso, and pant) contained ~ 16% of the total dermal residues combined.

Calculation of Dermal, Airborne and Combined Hazard Quotients

Dosimetry data alone can be used to directly calculate a dermal hazard quotient (DHQ). Using azoxystrobin as an example, we have determined the total residues of azoxystrobin on the dosimeter to be 805 µg following application of Heritage® at 0.2 oz. a.i./1000ft^2 . Using USEPA or EU Pesticide Properties Database established values for dermal penetration (6.1% for azoxystrobin), USEPA values for the weight of an average person (70kg), and the chronic RfD (0.18 mg/kg/d for azoxystrobin), the DHQ for azoxystrobin is determined using equation 1.

Equation 1

$$DHQ = \frac{805\ \mu g\ azoxystrobin \times 6.1\%\ penetration\ factor/70\ kg}{180\ \mu g/kg/day\ (USEPA\ Azoxystrobin\ RfD)}$$

DHQ = **0.0039**

Using the same approach, we calculated a DHQ for carfentrazone-ethyl of **0.00014** (Table 2).

Halofenozide has no established EPA dermal penetration factor, so a default value of 20% was used. Since halofenozide is not registered for any food crop uses, there is no USEPA established RfD either. Using standard EPA methodology, a chronic RfD of 38 µg/kg/day has been calculated (8). Using this estimated penetration factor and RfD for halofenozide, a dermal hazard quotient of **0.030** is calculated.

The residues collected on the personal air samplers can also be used to calculate an inhalation hazard quotients (IHQ). Again using azoxystrobin as an example, the average residues found on the air samplers following application of Heritage® at 0.2 oz. a.i./1000ft^2 was 0.156 µg. The IHQ can be calculated in a manner similar to the DHQ.

Equation 2

$$IHQ = \frac{0.156\ \mu g/70\ kg}{180\ \mu g/kg/day\ (USEPA\ Azoxystrobin\ RfD)}$$

IHQ = **0.000012**

Using the same approach, we calculated IHQs for carfentrazone-ethyl and halofenozide (Table 2). No carfentrazone-ethyl residues were ever detected in the personal air samplers. We therefore assigned these residues a value ½ that of the limit if detection to arrive at an IHQ of **0.0000026** for carfentrazone-ethyl. The calculation for the IHQ of halofenozide resulted in an IHQ of **0.000037**.

These hazard quotients can then simply be summed to determine a CHQ as follows:

Azoxystrobin Combined HQ

0.0039 DHQ + 0.000012 IHQ = **0.003912**

Carfentrazone-ethyl Combined HQ

0.00014 DHQ + 0.0000026 IHQ = **0.0001426**

Halofenozide Combined HQ

0.030 DHQ + 0.000037 IHQ = **0.030037**

These data clearly show that airborne residues of the three reduced risk pesticides examined contribute very little to the CHQ of each of the three pesticides. It should also be noted that all three CHQs are significantly less than 1.0, indicating a wide safety margin. The CHQs of azoxystrobin, carfentrazone-ethyl and halofenozide were 250-, 7000-, and 14-fold below the current USEPA level of concern respectively. The use of the chronic RfD also adds to this safety margin. A chronic RfD is one that can be received daily over a 70-year lifespan with no adverse effects.

Using the same experimental design, we have previously calculated CHQs for 2,4-D (**0.011**), MCPP (**0.55**), chlorothalonil (**0.043**), and imidacloprid (**0.01**) using dosimetry.

Transfer Factors

Using the dermal dose derived from dosimetry and the DFR determined from the environmental residues we can calculate a transfer factor (TF) using the method of Zweig et al. (1985):

Equation 3

$$TF(cm^2/h) = \text{dermal exposure } (\mu g)/DFR\ (\mu g/cm^2)/4h$$

Using azoxystrobin as an example, we can calculate a TF as follows:

Azoxystrobin TF = 805 µg/0.146 µg/cm^2/4h

Azoxystrobin TF ~ **1380**

Employing the same methodology, transfer factors have been calculated for carfentrazone-ethyl (**1440)** and halofenozide **(2050)**. Transfer factors have also been calculated for 2,4-D (**570**), MCPP (**1300**), chlorothalonil (**1150**), and imidacloprid (**3300**).

Knowing the DFR and the TF allows an absorbed dose to be established solely from these two values as well as the dermal penetration of the pesticide. The estimated absorbed dose is determined as follows where AD = absorbed dose and DP = dermal penetration.

Equation 4

AD = DFR (µg/cm^2) x TF (cm^2/h) x DP x 4h/70kg

Utilizing this equation allows an absorbed dose to be estimated without the need for time-consuming and expensive golfer exposure studies using human volunteers.

DISCUSSION

Dermal exposure estimates based on full-course applications at the maximum label rates with a one-hour re-entry interval for azoxystrobin, carfentrazone-ethyl, and halofenozide resulted in USEPA HQ values substantially below 1.0, indicating safe exposures. Previously, Putnam and Clark (2008) showed good agreement between HQs generated by dosimetry and biomonitoring data. This finding indicates that in the absence of voided urinary metabolites, dosimetry can be an adequate surrogate for biomonitoring if transfer and penetration factors are known. The measurement of dosimetry residues combined with airborne residues and DFR provide a complete and accurate account of pesticide availability for golfer exposure. Pesticide regulators have a critical need for this type of data.

The current study evaluated whether reduced risk pesticides could lessen golfer hazard. Reduced risk pesticides typically have lower mammalian toxicities and lower application rates in addition to their other environmental benefits compared to conventional pesticides. These factors indicate that reduced risk pesticides should lessen golfer hazard. This proved to be the case for azoxystrobin and carfentrazone-ethyl when compared to chlorothalonil and MCPP, respectively. Halofenozide on the other hand, did not result in lower HQs when compared to chlorpyrifos, and was actually significantly higher than that found for cyfluthrin. Nevertheless, all pesticide exposures resulted in HQs less than 1.0.

HQ determination depends primarily on the RfD. The USEPA determines the chronic (daily exposure over a lifetime) RfD by first defining the No Observed Adverse Effect Level (NOAEL), which is the highest dose in a chronic toxicological study that induces no adverse effect in the animal. This NOAEL is then divided by an uncertainty factor (UF) taking into account differences between species (10X) and hazard to vulnerable populations such as children (10X). The typical UF is 100X. Only in cases where there is sufficient human data, such as with chlorpyrifos, is the UF = 10. Only three pesticides have UFs of 10 (aldicarb, chlorpyrifos, and malathion), and only acephate (UF = 30) and pirimiphos-methyl (UF = 25) are also below 100. The UF of 10 is due to the fact that differences between species no longer has to be accounted for in the RfD calculation. Such low uncertainty factors are extremely rare. If the USEPA determines that there is insufficient toxicological data such as use of too few species, they will introduce another 10X safety factor, making a UF of 1000. In cases where there is extremely limited toxicological data, they may assign further safety factors such as with MCPP, which has an uncertainty factor of 3000 due to an additional 3X safety factor.

The azoxystrobin RfD is calculated based on a NOAEL of 18.2 mg/kg/d from a chronic rat feeding study as follows using equation 5:

Equation 5

$$RfD = \frac{NOAEL}{UF}$$

$$\text{Azoxystrobin RfD} = \frac{18.2 \text{ mg/kg/d}}{100} = 0.182 \text{ mg/kg/d} = \mathbf{182\ \mu g/kg/d}$$

While the RfD is the driving force behind HQ determination, factors that influence exposure such as application rate, water solubility and K_{oc} can also influence the HQ (Table 3).

Table 3. A summary of the factors influencing the determination of hazard quotients. K_{oc} = water/organic carbon partition coefficient, RfD = USEPA chronic reference dose, CHQ = combined hazard quotient.

Pesticide	Application Rate (oz. a.i./1000ft^2)	Water Solubility (mg/L)	K_{oc}	Transfer Factor	Uncertainty Factor	Dermal Penetration %	RfD (µg/kg/d)	CHQ
Azoxystrobin	0.2	6	482	1378	100	6.1%	180	0.0039
Chlorothalomil	4.16	0.81	5000	1150	100	0.15%	15	0.040
Carfentrazone	0.036	12	866	1436	100	10%	30	0.00014
MCPP	0.13	860	20-43	1300	3000	16.3%	1.0	0.55
Halofenozide	0.65	250	250	2051	1000	20%	38	0.070
Chlorpyrifos	0.38	1.4	9930	6400	10	9.6%	5	0.059
Cyfluthrin	0.053	0.007	64300	1075	100	5%	25	0.004

The HQs of two of the reduced risk pesticides were significantly less than comparable, commonly-used turfgrass pesticides. Azoxystrobin exposure following a simulated round of golf commencing 1 hour after application resulted in a HQ >250-fold below current levels of concern. This compares favorably to the HQ for chlorothalonil of 23-fold below the level of concern following the same exposure scenario. The CHQ generated for carfentrazone-ethyl was >7000-fold below the USEPA's level of concern. This hazard is significantly lower than that found for MCPP, which was 10-fold below this level.

The CHQ resulting from exposure of volunteer golfers to halofenozide 1 hour after post-application irrigation presents a different story. This CHQ was 33-fold below the USEPAs current level of concern. This hazard is about twice that generated for chlorpyrifos in previous work of 17-fold below the current level of concern (Putnam USGA), and is much higher than that determined for cyfluthrin (250-fold below).

The generally higher costs of reduced risk pesticides may give turfgrass managers pause when considering their use. We have demonstrated another benefit in their use by reducing golfer hazard, in addition to their utility in an IPM program. The high margins of safety for azoxystrobin and carfentrazone-ethyl should ensure that these chemicals remain registered for turf, and may help "EPA fast track" approval of similar pesticides for use on turf.

The CHQ generated for the fungicide azoxystrobin (0.0039) was about an order of magnitude less than that determined for chlorothalonil (0.043), a conventional fungicide. This finding roughly parallels 12-fold difference in RfD between azoxystrobin (182 µg/kg/d) and chlorothalonil (15 µg/kg/d).

The RfD does not explain all the difference, however, as the application rate for chlorothalonil was approximately 20 times that of azoxystrobin, and the transfer factors were similar, meaning that roughly the same ratio of available residues were transferred to the dosimeter. The rest of the difference may be explained by the extremely low dermal penetration rate for chlorothalonil (0.15%) compared to azoxystrobin (6.1%).

Exposure to the herbicide carfentrazone-ethyl following simulated golf resulted in a CHQ of 0.00014. The carfentrazone-ethyl CHQ was almost 4000-fold below that determined for MCPP (CHQ=0.55). Some of this higher CHQ can be explained by the RfD for MCPP, which is 30-fold lower than that for carfentrazone-ethyl. All of this difference in RfD can be explained by the UF of 3000 assigned to MCPP. This is 30-fold higher than the UF associated with carfentrazone-ethyl. Additionally, the application rate for carfentrazone-ethyl was ~ 3.6-fold lower than for MCPP.

It is clear from comparing the CHQs of these fungicides and herbicides that the use of reduced risk compounds can reduce golfer hazard. This finding is important for turfgrass managers as it adds another positive factor for the use of reduced risk compounds in addition to their utility in IPM programs due to their novel modes of action, and their enhanced environmental safety.

The above results were in contrast to those found for halofenozide, which recently lost its USEPA reduced risk designation. The CHQ determined for halofenozide (CHQ = 0.070) was close to that determined for chlorpyrifos (CHQ = 0.059) (4), and was ~ 18-fold lower than that determined for cyflythrin (CHQ = 0.004). There are several factors that likely contribute to this result. While the RfD for halofenozide (38 µg/kg/d) is higher than those for chlorpyrifos and cyfluthrin (5 and 25 µg/kg/d, respectively), its application rate was 1.7-fold higher than that for chlorpyrifos and 12-fold higher than that for cyfluthrin. Since halofenozide has no USEPA assigned RfD, it has been calculated by Murphy and Haith (2007). The authors used a conservative UF of 1000 due to the paucity of toxicological data. The halofenozide UF is 100-fold greater than chlorpyrifos (10) and 10-fold higher than cyfluthrin (100). This increased uncertainty also contributes to the relatively high CHQ. Also, there is no established dermal penetration factor for halofenozide, so a default value of 20% was used. This default value most likely overestimates the dermal absorption of halofenozide, and therefore the dose.

One factor that contributes to the relatively high CHQ is the dissipation of the halofenozide DFRs. Unlike azoxystrobin and carfentrazone-ethyl (and all other pesticides we have studied) where there were significant reductions in available residues (43% and 37%, respectively) in the first hour following application, halofenozide DFRs were essentially unchanged over this time. It has been postulated that pesticide residues on turf may become unavailable through absorption into the waxy layer of the leaf cuticle. Studies have shown that halofenozide penetrates insect cuticles poorly (9). Only 20% of the applied halofenozide penetrated the insect cuticle, compared to 45% for diflubenzuron and 85% for flucycloxuron, two other insect growth regulators. While insect and plant cuticles are different, both have a similar waxy layer at their outermost surfaces. It is possible, therefore, that the highly water soluble halofenozide also penetrates the plant cuticle very slowly. The high water solubility may also influence the availability of halofenozide in other ways. Halofenozide was watered in with 0.25” of irrigation like the other insecticides, so the thatch and verdure were saturated with water. The relatively high water solubility and low K_{oc} (sorption to organic carbon) may mean that more of the halofenozide is in the water phase than bound to the thatch, increasing its availability during sampling. Halofenozide has also shown less vertical movement in bentgrass than in either bare soil or tall fescue (10). This reduced vertical movement may also increase the availability of halofenozide.

The reduction of available residues in the first hour for halofenozide (43%) and carfentrazone-ethyl (37%) is consistent with the ~ 50% reduction noted by Putnam and Clark (1) for a wide variety of pesticides. This new data further strengthens the case for a one-hour re-entry interval for treated turfgrass areas. The halofenozide results over the first hour following application are unique.

Halofenozide was the only compound tested in all the turf pesticides we have evaluated that did not show a significant decline in available residues in the first hour following application. This finding shows that the reduction in residues in the first hour post-application may be widespread, but it is not universal.

The hands were determined to be the principle route of exposure for azoxystrobin (56%), carfentrazone-ethyl (28%) and halofenozide (54%). This route of exposure is in keeping with previous results for MCPP, 2,4-D and chlorothalonil, which like azoxystrobin and carfentrazone-ethyl received no post-application irrigation. The results for halofenozide are contrary to all other results found for insecticides that received post-application irrigation (4). The principle route of exposure for these compounds that received post-application irrigation was the lower body. Putnam and Clark (2004) determined that 43-65% of the chlorpyrifos residues detected on the suit were found on the pants (15%), lower legs (20-35%), and socks (8-15%).

It is possible that the pesticides that did not receive post-application irrigation were sitting on the surface of the leaf and readily available to be picked up by casual hand contact. Following post-application irrigation, it is possible that while the residues could be picked up by the weighted CA roller, they had moved past the verdure and were on/in the thatch and therefore unavailable for casual hand contact. The high level of lower leg exposure for insecticides that received post-application irrigation may be the result of these compounds remaining in the water phase in the saturated thatch and verdure. Even one hour after the end of irrigation, the playing surface was wet. As the volunteer golfers walked across the turf, they may have been kicking up some water containing the pesticide applied thereby contaminating their lower body. It is possible that due to the relatively high water solubility of halofenozide (180-fold greater than chlorpyrifos, 36,000-fold greater than cyfluthrin) there was a much greater concentration of halofenozide in the water on the surface of the thatch, leading to more availability to the hand.

The results from this study indicate that golfer exposure to turfgrass pesticides has a wide safety margin. It has also been shown that in two of the three cases the use of reduced risk pesticides can substantially lower golfer hazard. Excluding halofenozide, it is also clear that a one-hour re-entry interval can also significantly reduce golfer hazard. In the cases examined, the use of reduced risk pesticides can lessen golfer exposure and hazard. Azoxystrobin exposure following a simulated round of golf commencing 1 hour after application resulted in a CHQ (0.0039), >250-fold below current levels of concern. Exposures to carfentrazone-ethyl (CHQ=0.00014, ~ 7000-fold below) and halofenozide (CHQ=0.030, ~ 33-fold below) were also well under the USEPAs current level of concern. The application of azoxystrobin brought about a ~ 10-fold reduction in CHQ compared to chlorothalonil. The use of carfentrazone-ethyl produced an ~ 7000 fold reduction in CHQ versus the use of MCPP, and the application of halofenozide led to a ~ 2-fold reduction in CHQ compared to the use of chlorpyrifos. While the use of halofenozide did not mitigate hazard as effectively as azoxystrobin and carfentrazone-ethyl, it is important to not that the hazard quotients calculated for all three reduced risk compounds are well below the USEPAs level of concern (1.0). Two of the three, azoxystrobin and carfentrazone-ethyl, can substantially reduce an already low risk. It is possible that the exposure profile for halofenozide was a factor in the loss of reduced risk status for this compound.

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REFERENCES

1) Putnam, R.A. and J. M. Clark. 2004. Managing Pesticide exposure from turfgrass. *USGA Turfgrass and Environmental Research Online*. November 1. 3(21): p. [1-17].

2) Cisar, J. L., R. H. Snyder, J. B. Sartain, and C. J. Borget,. 2002. Dislodgeable residues of chlorpyrifos and isazofos and implications for golfer exposure. *USGA Turfgrass and Environmental Research Online* 1(13):1-10. (TGIF Record 82908)

3) Fuller, R., D. Klonne, L. Rosenheck, D. Eberhart, J. Worgan, and J. Ross. 2001. Modified California roller for measuring transferable residues on treated turfgrass. *Bull. Environ Contam. Toxicol.* 67(6):787-794. (TGIF Record 78179)

4) Putnam, R.A., Doherty, J.J. and J.M. Clark. 2008. Golfer exposure to chlorpyrifos and carbaryl following application to turfgrass. *J. Agric. Food Chem*. 56:6616-6622.

5) Bernard, C. E., H. Nuygen, D. Truong, and R. I. Krieger. 2001. Environmental residues and biomonitoring estimates of human insecticide exposure from treated residential turf. *Arch. Environ Contam. Toxicol.* 41(2):237-40. (TGIF Record 98498)

6) Occupational Safety and Health Administration. 1986. Method 62: chlorpyrifos, DDVP, diazinon, malathion and parathion in air. Organic Method Evaluation Branch, Occupational Safety and Health Administration, Analytical Laboratory Salt Lake City, Utah.

7) Pesticide Manual, Fourteenth Edition. 2006. C.D.S. Tomlin, ed. British Crop Protection Council, Hampshire, UK.

8) Murphy, R.R. and D.A. Haith. 2007. Inhalation health risk to golfers from turfgrass pesticides at three northeastern U.S. sites. *Environ. Sci. Technol*. 41(3):1038-1043.

9) Chebira, S., Soltani, N., Muylle, S. and G. Smagghe. 2006. Uptake and distribution of three insect growth regulators – diflubenzuron, flucycloxuron and halofenozide – in pupae and adults of *Tenebrio molitor*. *Phytoparasitica*. 34(2):187-196.

10) Gardner, D.S. and B.E. Branham. 2001. Mobility and dissipation of ethofumesate and halofenozide in turfgrass and bare soil. *J. Agric. Food Chem*. 49:2894-2898.