Turfgrass and Environmental Research Online

...Using Science to Benefit Golf

University of Massachussets scientists quantified foliar dislodgeable residues and utilized dosimetry and biomonitoring techniques to assess exposure of volunteers to commonly used pesticides as volunteers were simulating rounds of golf. The data obtained show that there is a wide safety margin for golfers regarding the hazard of pesticide exposure and certain management strategies including re-entry intervals and post-application irrigation can lower the hazard even further.

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PURPOSE

The purpose of *USGA Turfgrass and Environmental Research Online* is to effectively communicate the results of research projects funded under USGA's Turfgrass and Environmental Research Program to all who can benefit from such knowledge. Since 1983, the USGA has funded more than 290 projects at a cost of $25 million. The private, non-profit research program provides funding opportunities to university faculty interested in working on environmental and turf management problems affecting golf courses. The outstanding playing conditions of today's golf courses are a direct result of ***using science to benefit golf***.

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Managing Pesticide Exposure from Turfgrass

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SUMMARY

University of Massachussets scientists quantified foliar dislodgeable residues and utilized dosimetry and biomonitoring techniques to assess exposure of volunteers to commonly used pesticides as volunteers were simulating rounds of golf. Three widely used insecticides, chlorpyrifos, cyfluthrin, and carbaryl were evaluated in over 150 rounds of golf. In all cases, exposure to these insecticides under worst case scenarios were significantly less than established acceptable daily dose (ADI) and USEPA Office of Pesticide Program reference dose (Rfd) criteria. Other findings include:

- Dermal absorption is the most significant route of exposure to golfers following application of currently-used turfgrass pesticides. Lower legs, arms and hands are most vulnerable.
- Exposure estimates using biomonitoring data are 2 to15-fold less than previous estimates using environmental (airborne and dislodgeable foliar) residue data.
- Exposure to chlorpyrifos (new rate), carbaryl, and cyfluthrin under worst case scenarios are all significantly less than established acceptable daily dose (ADI) and USEPA/OPP reference dose based Hazard Quotient (HQ) criteria.
- The highest USEPA Hazard Quotient value determined (0.079) using dosimetry and/or biomonitoring techniques following application of chlorpyrifos at the current USEPA approved maximum label rate occurred during the full-course applications, indicating that additional management practices will lead to even greater safety margins.
- Several management practices, including the optimal use of post-application irrigation, enforcement of reentry intervals, use of less-toxic pesticides, and partial course applications significantly reduced exposure.

There is great concern over human exposure following the application of pesticides for the proper management of turf environments. This concern is expected and germane given the level and frequency of pesticide use, the extent of activities and time spent on turfgrass, and the exposure potential for infants, children, and adults alike. Much effort has been expended in the determination of applicator exposure issues and the means to mitigate problematic exposure situations before and during application of pesticides. However, there are potential exposure concerns for all who reenter turfgrass areas following pesticide applications (14).

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Pesticide Exposure

The primary route of pesticide exposure involves dermal uptake from dislodgeable foliar residues (DFRs, pesticide residues available by contact or abrasion for skin absorption) present on treated turfgrass foliage. It is expected that a larger proportion of the applied pesticide will remain on the turfgrass leaves because of the dense canopy inherent in turfgrasses compared to agricultural cropping situations where a substantial

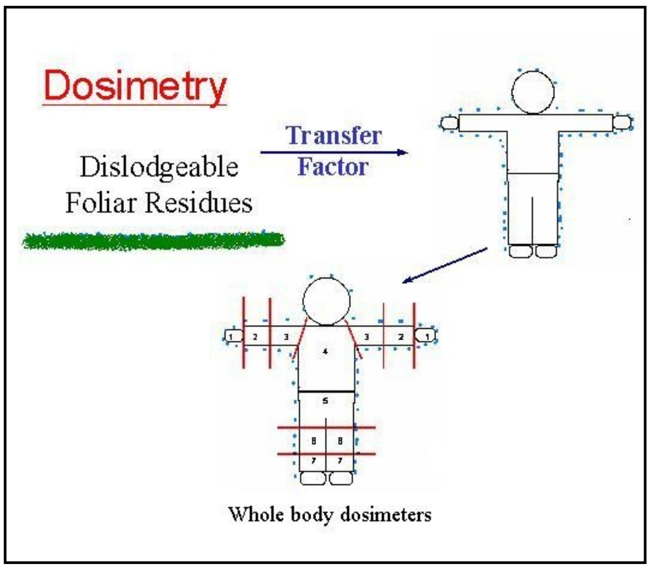

Figure 1. The pesticide transfer factor is the difference between available residues on the turfgrass surface (dislodgeable foliar residues, DFR) and those that are transferred to a golfer during a normal round of golf (determined by dosimetry).

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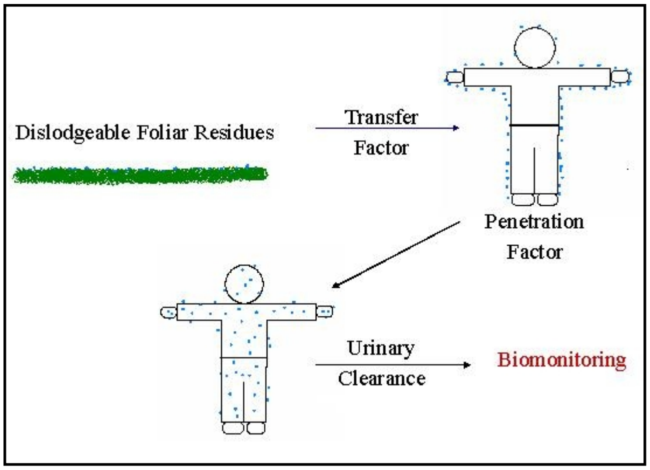

Figure 2. Only a certain portion of pesticide residues transferred from the treated turf to the golfer actually penetrates through the cloths and skin. This penetration factor can vary between pesticides. The actual absorbed dose is determined by the urinary excretion of pesticide metabolites (biomonitoring).

proportion of the pesticide reaches the soil surface directly. Thus, dermal exposure to dislodgeable foliar residues on turfgrass is expected to be significant. Nevertheless, most turfgrass cultivars used for lawns, golf courses, and other turfed areas have substantial waxy layers associated with the external surfaces of their blades and all grasses produce organically rich thatch/mat layers. These aspects of the turfgrass plant are expected to compete with transfer of pesticides to exposed hands, legs, etc. and reduce dermal exposure levels.

The next most significant exposure route involves inhalation of airborne pesticide residues (volatile pesticides and residues associated with particulates such as aerosols and dust particles) by the lung during breathing. Although usually not considered as significant as dermal exposure, the respiratory route is toxicologically relevant due to its high rate of absorption and direct interaction with the circulatory system, allowing rapid and wide distribution in the body of airborne pesticides.

The oral route of exposure via the gastrointestinal tract is considered the least extensive and occurs primarily via hand-to-mouth contact, a situation more relevant for children than adults. Preliminary evidence has indicated that golf balls, tees, etc. do not acquire large amounts of pesticides and are not efficient means to transfer significant levels of pesticides to golfers (2).

In this article, we review research that evaluated best management practices for the reduction of golfer/bystander exposure to turfgrass pesticides. Because golfers elicit unique behaviors playing golf not usually mimicked by pesticide applicators or agricultural workers, a comprehensive evaluation of the exact exposures that a golfer receives while playing golf and the health implications, if any, of that exposure are necessary. Proper safeguards can then be developed to eliminate or reduce future exposures.

Exposure and Hazard from Airborne and Dislodgeable Foliar Pesticide Residues

The hazard associated with the inhalation of volatile pesticides or those associated with the particulate have been indirectly determined by various methods following their application to turfgrass. The most common means involve the use of high-volume air samplers, breathing zone estimates using personal air samplers, and a variety of small plot techniques. Dislodgeable foliar residues, likewise, have been determined by a variety of means, including solvent- or surfactant-based extractions, surface wipes using water-dampened cheesecloth, cloth-covered sleds, shoes and weighted roller devices, and used to estimate dermal exposures and associated hazard (4).

We have used high-volume air samplers located in the middle of 20-meter circular plots to determine airborne pesticide concentrations and water-dampened cheesecloth wipes to estimate dislodgeable foliar residues. Inhalation and dermal doses were determined from these respective residues and hazard evaluated using the USEPA hazard quotient determination (9, 10). The estimated inhaled dose ($D_{i)}$ is divided by the chronic reference dose of a particular pesticide (15), resulting in the Inhalation Hazard Quotient (D_i/Rfd = IHQ).

Similarly, the estimated dermal dose (D_d) is divided by the Rfd yielding the Dermal Hazard Quotient (DHQ). A hazard quotient value less than or equal to 1.0 indicates that the residues present are at concentrations below those that are expected to cause adverse effects to humans. A hazard quotient value greater than 1.0 does not necessarilly infer that adverse effect will occur, but rather that the absence of adverse effects is less certain. In these circumstances, more direct approaches to estimate hazard are necessary.

Using this experimental plan, a large field study was conducted that evaluated 14 commonly used turfgrass pesticides (3). Only three pesticides (ethoprop, diazinon, isazofos) resulted in IHQ values greater than 1.0 over the entire time course of the study. Only seven pesticides (ethoprop, isazofos, diazinon, isofenphos, trichlorofon, chlorpyrifos, bendiocarb) resulted in DHQ values greater than 1.0 and only ethoprop, isazofos, diazinon, and isofenphos had values greater than 5.0. The potentially hazardous pesticides (ethoprop, diazinon, isazofos, and isofenphos) were all organophosphorous insecticides that share common chemistry, have high vapor pressures (high volatility), and high inherent toxicity (low Rfds). Thus, this approach identified related pesticides that may result in exposure situations that cannot be deemed completely safe using the USEPA hazard quotient criteria.

This assessment must be viewed in terms of the assumptions that were used in making these estimates. In all instances, maximum pesticide concentrations were used for the entire four-hour exposure period, maximum rates for pesticide applications were used, and dermal transfer coefficients and penetration factors were taken from non-turfgrass situations that likely overestimate exposure that would occur during the play of golf, indicating that HQ values were estimated under worst-case scenarios (4). To more accurately predict the health implications of pesticide exposure of golfers and during other turfgrass activities, a relevant dosimetry and biomonitoring evaluation was necessary.

Figure 3. Collecting dislodgeable foliar residues (DFR) with the California roller (CA roller). The 32-lb roller is slowly rolled over a 6 ft^2 cloth 10 times. Pesticide residues transferred to the cloth are considered dislodgeable.

Operational and Cultural Practices

The watering-in of pesticides immediately following application (post-application irrigation) to turfgrass has long been a suggested and sometimes a necessary practice to insure efficacious pest control and to minimize dermal and inhalation exposures upon reentry. Our previous research (3, 9, 10), quantitatively assessed the effects of post-application irrigation on the reduction of airborne and dislodgeable foliar residues and the HQ values estimated from them. Both 0.65 cm (1/4 inch) and 1.3 cm (1/2 inch) of irrigation substantially reduced airborne and dislodgeable foliar pesticide residues when applied immediately following application (at least 80-90% reduction depending on pesticide applied) and resulted in substantial reductions in the HQ estimations. Post-application irrigation at 0.32 cm (1/8 inch) was not an effective means to reduce pesticide residues. These findings indicate that the judicial use of post-application irrigation in combination with managed spray volume and sprayer configurations may be an effective means to reduce the hazard associated exposure to turfgrass pesticides.

To mitigate the exposure potential of potentially problematic turfgrass pesticides (e.g., organophosphorous insecticides), the practical use of spray tank adjuvants and the importance of thatch accumulation on the dissipation of airborne and dislodgeable foliar pesticide residues follow-

Figure 4. Whole body dosimetry suit, including socks, double gloves, and a cotton veil attached to hat.

ing their application to turfgrass has been assessed (3). Two adjuvants, Aqua Gro-L, a nonionic wetting agent/penetrant, or Exhalt 800, an encapsulating spreader/sticker, were applied individually with either ethoprop or isofenphos to a mature turfgrass plot (nine-years-old) and to a newly established plot (one-year-old) and HQ values determined as described previously. To evaluate the effects of thatch accumulation, applications of ethoprop were made without adjuvants to mature and newly established plots. In a second experiment, ethoprop was applied to the mature plot that had been dethatched by vericutting in two directions, and the results compared to those obtained from the same plot prior to dethatching.

In no instance did the addition of spray tank adjuvants result in substantial reductions of airborne or dislodgeable foliar residues or in their estimated HQ values. Similarly, no substantial or consistent reductions in IHQ or DHQ values were determined following the application of ethoprop or isofenphos to mature or recently established turfgrass plots or to plots that were thatched or recently dethatched. These preliminary results indicate that neither the use of spray tank adjuvants nor thatch management may result in the reduction of environmental pesticide residues following their application to turfgrass and in the reduction of their relevant HQ values.

Current Research Approaches Emphasizing Dosimetry and Biomonitoring

Accurate assessment of pesticide exposures to golfers requires the knowledge of the availability of pesticide residues following application, transfer and absorption processes of these residues, and major routes of entry into the body. We are currently evaluating the optimal use of post-application irrigation, re-entry intervals, application of less toxic and volatile pesticides, and application strategies that result in less than full coverage (e.g., tees and greens only) to minimize exposure.

To date, we have evaluated golfer exposure in over 150 rounds of golf following the application of three turfgrass insecticides, chlorpyrifos (Dursban), cyfluthrin (Tempo), and carbaryl (Sevin) in a three-year study jointly funded by the USGA, the U.S. Department of Agriculture, and the New England Regional Turfgrass Foundation. This current study emphasizes dosimetry (measuring pesticide residue on full body cotton suits, gloves, veils, and personal air samplers) and biomonitoring (measuring pesticide metabolites in collected urine).

Dosimetry together with concurrently collected dislodgeable foliar and airborne residue data provides the basis for modeling exactly how much pesticide is transferred from the turfgrass to an individual during a round of golf (Figure 1). Biomonitoring offers a direct measurement of the total pesticide dose (actual amount of pesticide from all routes of exposure that are absorbed into the body) (Figure 2). Additionally, no assumptions of clothing protection, routes or rates of transfer, or skin absorption rates are needed. Thus, the direct and simultaneous determination of dosimetry and biomonitoring data, along with concurrently collect environmental residues (dislodgeable and airborne), provides a novel and complete information base on how much pesticide is actually transferred to and absorbed by a golfer playing golf. Information generated by this experimental approach will have significant impact on the re-registration processes for pesticides under the 1996 Food Quality Protection Act criteria.

Methodology

All experiments were conducted at the University of Massachusetts Turfgrass Research Center in South Deerfield, MA. Two circular (10-meter radius) turfgrass plots with established 'Penncross' creeping bentgrass were used for the collection of environmental residues (airborne and dislodgeable foliar pesticide residues) as previously described (3, 10). Additionally, a 120 X 100 meter rectangular bentgrass turfgrass plot was used for the concurrent collection of dosimetry and biomonitoring data. All plots were maintained as golf course fairways--mowed at a height of 1.3 cm (1/2 inch) three times per week and irrigated as needed to prevent drought stress.

Pesticide Applications

A Rogers Sprayer (35-40 psi), equipped with a wind foil, skirt, and twelve spray nozzles fitted with VisiFlo Flat Spray Tips, was used for all applications. Post-application irrigation (1.3 cm, 1/2 inch) was applied immediately following spraying to water-in the pesticides.

Dursban Pro® (23.5% chlorpyrifos) was applied at two rates. A label change was promulgated prior to the 2002 growing season. The maximum labeled USEPA approved rate prior to 2002 was 4 lbs a.i./acre, which was reduced to 1 lb a.i./acre for the 2002 season. One gallon (4 lbs a.i./acre) or 0.25 gallon (1 lb a.i./acre) of formulated product was mixed into 50 gallons of water and applied at approximately 100 gallons/acre.

Tempo 20 WP Golf Course Insecticide (20% cyfluthrin) was applied at its maximum USEPA accepted labeled rate of 0.13 lbs a.i./acre. 165 g (5.82 ounces) of formulated product was mixed into 50 gallons of water and applied at approximately 100 gallons/acre.

Sevin SL (43.0% carbaryl) was applied at the maximum USEPA accepted labeled rate of 7 lbs a.i./acre. One gallon of formulated product was mixed into 50 gallons of water and applied at approximately 100 gallons/acre.

Airborne and Dislodgeable Foliar Residues

These experiments were carried out on 20-meter circular bentgrass plots. Airborne residues of chlorpyrifos (μg/ m^3) were determined with a single TF1A high-volume air sampler placed in the center of each circular plot using the methodology of Kilgore et al., (6) as modified by Murphy et al. (11).

Dislodgeable foliar residues (DFRs) were determined using a water-dampened cheesecloth wipe (3) or with the Outdoor Residential Exposure Task Force-recommended California roller (CA roller, Figure 3) (5). Cloth wipe samples were collected in triplicate at each plot at 0.25, 1, 2, and 5 hours after application. California roller samples were collected in triplicate at each plot at 1, 2, and 5 hours after pesticide application.

Figure 5. Personal air sampling consists of an air sampling pump attached to the pants and pesticide collection tube attached to the collar.

Application Type/Rate	Experimental Design	Exposure (h)	Field Trials
Chlorpyrifos			
Dursban 4 lbs a.i./acre	full-course, 1 hr re-entry	4	6
Dursban 4 lbs a.i./acre	tees & greens, 1 hr re-entry	4	2
Dursban 1 lbs a.i./acre	full-course, 1 hr re-entry	4	6
Dursban 1 lbs a.i./acre	half-course, 1 hr re-entry	2	2
Dursban 1 lbs a.i./acre	full-course, 12 hr re-entry	4	1
Cyfluthrin			
Tempo WP 0.14 lbs a.i./acre	full-course, 1 hr re-entry	4	2
Carbaryl			
Sevin 7 lbs a.i./acre	full-course, 1 hr re-entry	4	2

Table 1. Application and exposure summary

Dosimetry and Biomonitoring

At the same time that airborne and dislodgeable foliar pesticide residues were being collected, exposure to researchers simulating the play of golf were determined by dosimetry and biomonitoring (urinary metabolites) studies. Individual golfer exposure in over 150 rounds of golf has been evaluated in a total of 21 field application (Table 1). One set of golfers (dosimetry group) wore white, 100 % cotton long-sleeved shirts, long pants, gloves, and veils attached to their hats (Figure 4) that served as a passive collection media for pesticide residues from treated turfgrass (1, 7).

Inhalation exposure of the dosimetry group was measured using personal air sampling pumps equipped with special air sampling tubes attached to the volunteers' collars (Figure 5) (12). Particles and pesticide vapors are absorbed within the sampling tubes. To estimate the total amount of pesticide inhaled, the air concentration was multiplied by an inhalation rate for light workloads (21 L/min) and the time over which the exposure occurred (two or four hours).

The biomonitoring group wore short sleeve shirts, shorts, ankle socks and golf shoes. 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 (13). Urine samples were collected and analyzed for TCP the day before exposure, and then for 26 hrs following the chlorpyrifos exposure (the estimated time to excrete ½ of the total TCP urinary metabolite of chlorpyrifos).

To estimate the total absorbed dose following cyfluthrin exposure, urinary biomonitoring was conducted on the major urinary metabolites of cyfluthrin: methyl 4-fluoro-3-phenoxybenzoate (FPBA), 4-fluoro-3-(4-hydroxyphenoxy)-benzoic acid (FPBA-OH), and methyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclo-propanecarboxylate (DBCA) (8, 16). Urine samples were collected and analyzed the day before exposure, and then for six hours (the elimination half-life for these metabolites) and 26 hours following exposure.

Volunteers for the dosimetry and biomonitoring groups were from the UMASS Environmental Toxicology and Risk Assessment Program (School of Public Health) and the Department of Veterinary and Animal Science. A protocol that described the work to be done and protected the rights of the volunteers has been approved by the Human Subjects Review

Committee, UMASS. The approved protocol, including an informed consent form, was reviewed with potential participants at an orientation meeting prior to their participation.

Golfer Activities and Exposure Scenarios

Chlorpyrifos, cyfluthrin and carbaryl were applied to a rectangular bentgrass plot. At the same time airborne and foliar dislodgeable residues were being collected from the circular plots, exposure to volunteers simulating the play of golf was determined by dosimetry and biomonitoring studies. Each experiment utilized eight volunteers (one foursome for dosimetry, a second foursome for biomonitoring) simulating the play of a 9- or 18-hole round of golf over a period of two or four hours, respectively. In the "standardized" 18-hole round of golf, each player walked 6,500 yards, hit a ball 85 times and took 85 practice swings. Clubs were rotated in an appropriate way, balls teed-up, divots replaced, two putts taken each hole, and clubs wiped clean between shots using a golf bag towel. Each "round" of golf started one hour following the completion of post-application irrigation.

Exposure scenarios simulating the applications to only nine holes were also conducted using chlorpyrifos where simulated play occurred for only two hours. To measure the effect of an increased re-entry interval, one application was also performed in the evening (8 p.m.) with relevant exposure samples, including golfer dosimetry and biomonitoring, collected the next morning. Chlorpyrifos was applied also in a manner that simulated a treatment to just the tees and greens. During each hole, golfers spent three minutes on the treated tee boxes, continued light activity for seven minutes on the untreated surface, and three minutes putting on the treated greens.

All pesticide analyses occurred at the MA Pesticide Analysis Laboratory (MPAL), a USEPA/MA Department of Agricultural Resources (MADAR)- supported FIFRA pesticide analytical laboratory using standard protocols and QA-QC procedures.

Results

Foliar dislodgeable and airborne concentrations of pesticides were determined for approximately five hours following pesticide applications and irrigation to small circular turfgrass plots by the cloth wipe and CA roller techniques

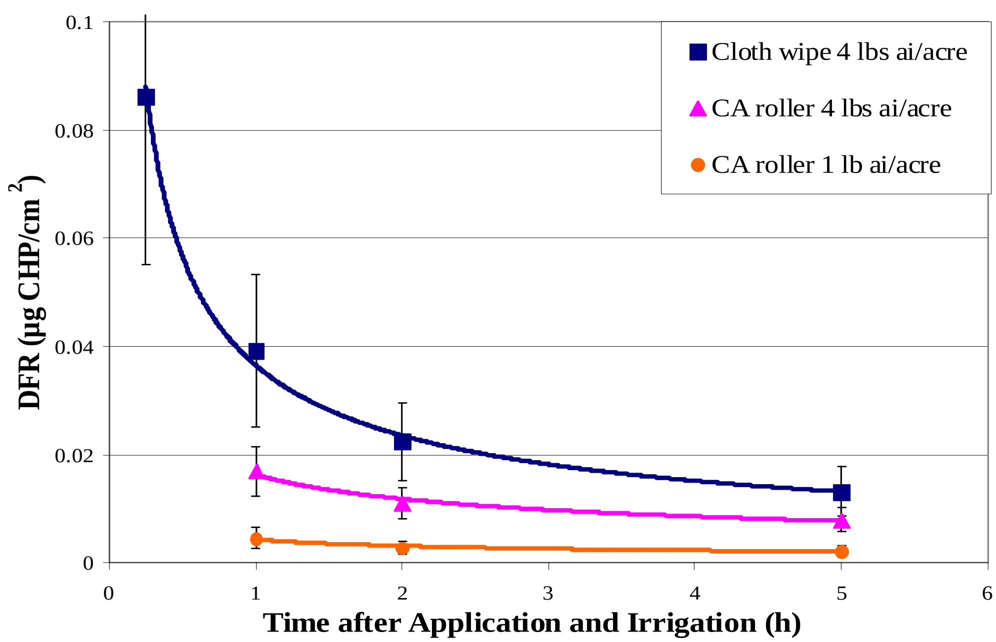

Figure 6. Availability of dislodgeable foliar residues (DFR) of chlorpyrifos during the first five hours following post-application irrigation

and by high-volume air sampling, respectively.

Dislodgeable Foliar Residues (DFRs)

As evidenced by chlorpyrifos DFRs determined by cloth wipe samples, a dramatic decline occurs during the first hour following post-application irrigation, followed by a slower but steady decline over the next four hours (Figure 6). Chlorpyrifos declined from 0.09 μg/cm^2 at 0.25 hours to 0.04 μg/cm^2 at one hour (55 % reduction), and then to 0.01 μg/cm^2 over the next four hours (an additional 49% reduction). Due to this dissipation pattern, it is appropriate that DFRs be averaged over a 4-hour period (average time for 18-hole round of golf) when exposure would take place (1-5 hour post-application and irrigation) for use in exposure estimates.

Using this procedure, a mean DFR value (± S.E.) of 0.0249 ± 0.013 μg chlorpyrifos/cm^2 was determined when applied at its high rate (4 lbs a.i./acre). Our previous research established that DFRs at this same high rate are reduced by approximately 80 % by post-application irrigation. Our current dissipation study reveals that DFRs are reduced by an additional 50% simply by enforcing a one-hour re-entry interval (Figure 6). These new findings are encouraging and indicate that future studies of operational practices to attenuate exposure (e.g. re-entry intervals, irrigation, application strategies, alternative chemicals, and IPM strategies) are highly likely to be effective.

Chlorpyrifos DFRs determined from CA roller samples show a similar dissipation pattern compared to that obtained with cloth wipe samples except that the levels of DFRs are reduced approximately 50 % at all time intervals examined (Figure 6). Additionally, the DFRs averaged over the four-hour golfing period were 73 % less following the 1 lb a.i./acre compared to the 4 lb a.i./acre chlorpyrifos applications. Because the CA roller technique was developed to give a more realistic estimate of the amount of DFRs that are available for transfer to recreational users of treated turf (5), its adoption as the standard method will result in lower exposure estimates. Likewise, lower use rates for pesticides have a high potential

Application Rate	Sampling Method	Exposure Period	Mean DFR (μg/cm^2)	DHQ
Chlorpyrifos				
4 lbs ai/acre	cloth wipe	0.25-4.25 hrs	0.041	0.097
	cloth wipe	1-5 hours	0.025	0.061
	CA roller	1-5 hours	0.012	0.029
1 lb ai/acre	CA roller	1-5 hours	0.003	0.007
Cyfluthrin				
0.14 lbs ai/acre	CA roller	1-5 hours	0.001	<0.001
Carbaryl				
7 lbs ai/acre	cloth wipe	1-5 hours	0.112	0.057
	CA roller	1-5 hours	0.0185	0.009

Table 2. Dermal hazard quotients (DHQ) estimated using dislodgeable foliar residues (DFR)

in reducing exposure estimates.

Dislodgeable foliar residues of both cyfluthrin and carbaryl dissipated in a similar manner to chlorpyrifos (data not shown). Mean DFR values for cyfluthrin and carbaryl were determined as for chlorpyrifos over the four-hour round of golf and are given for comparative purposes in Table 2. The DFR values can be used to estimate the dermal exposures for golfers by using the USEPA Hazard Quotient (1). An average daily dermal dose (D_d) was calculated using Equation 1.

Equation 1

$$D_d \quad = \quad S \times P / 70 \text{ Kg}$$

where S is determined by multiplying the mean DFR value determined from cloth wipe or CA roller techniques by a dermal transfer coefficient of 5×10^3 cm h^{-1}, P = dermal permeability (0.1, USEPA default value, 6). The estimated dermal dose is divided by the chronic EPA OPP reference dose (Rfd) to give a Dermal Hazard Quotient (D_d/Rfd =DHQ). Chlorpyrifos, the most toxic of the three insecticides studied, has a reference dose of 3µg/Kg/day, cyfluthrin is 25µg/Kg/day, and carbaryl is 14µg/Kg/day.

All DHQs calculated in this manner are substantially less than 1.0, indicating wide margins of safety (Table 2). The DHQs determined using mean DFRs are substantially less than those previously reported under the same exposure scenarios (4). Previous techniques assumed DFRs available at the start of a round of golf were constant, when in fact, these residues rapidly decline over the first four hours following application (Figure 6). Additionally, DHQs calculated using

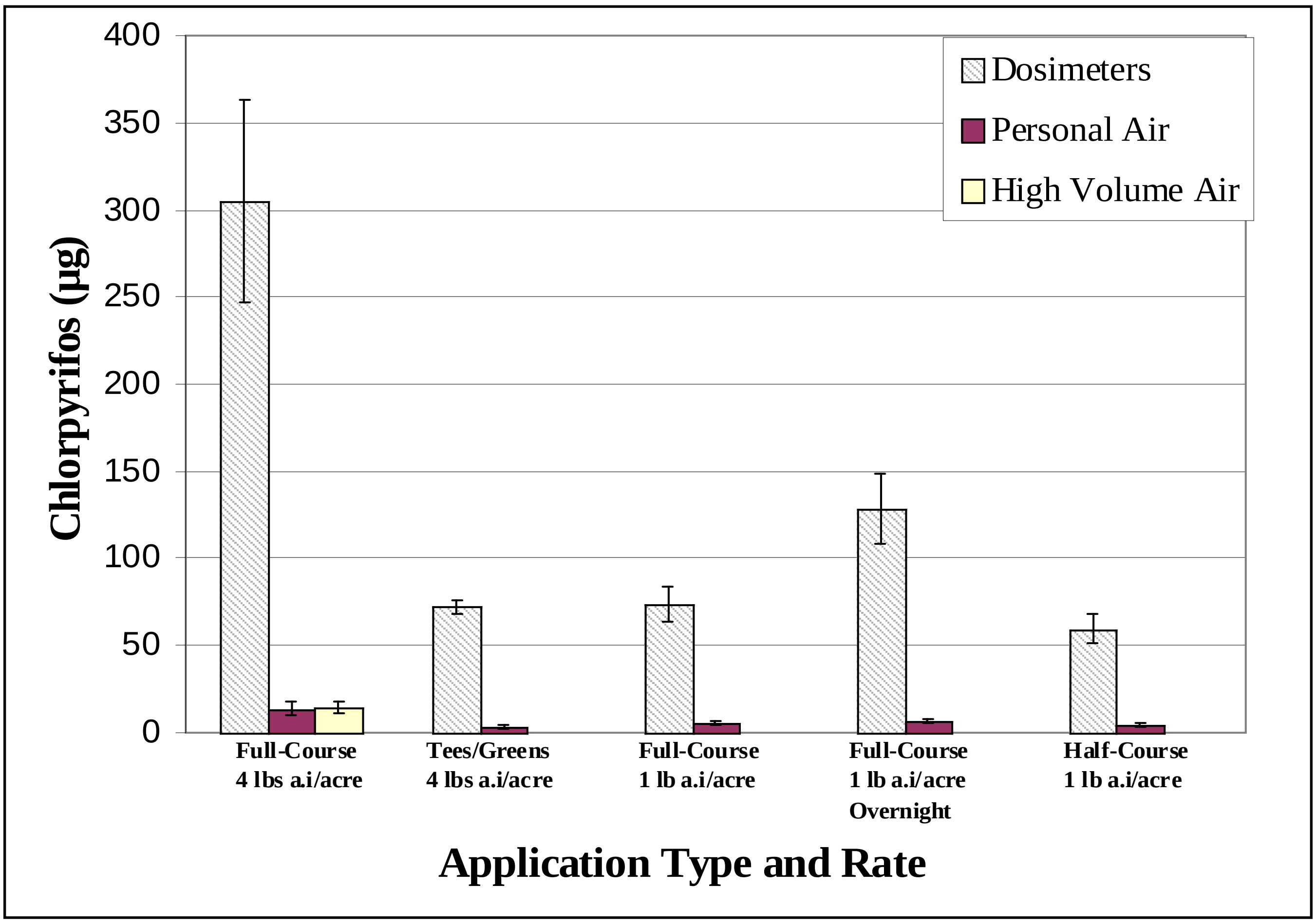

Figure 7. Total chlorpyrifos residues (exposure) collected on whole body dosimeters and onto individual personal and high volume air samplers

the CA Roller technique are significantly less than DHQs calculated using the cloth wipe technique, further reducing exposure estimates.

Several experiments were conducted that applied chlorpyrifos at the old label rate of 4 lbs a.i./acre (Table 2). Even at this high rate, the DHQs are still significantly less than 1.0. Dermal Hazard Quotients were further reduced when the chlorpyrifos rate was reduced to 1 lb a.i./acre.

Similar to estimating a dermal dose from DFRs, an average inhaled dose (D_i) of chlorpyrifos was also estimated. Using the measured air concentration of chlorpyrifos determined by high-volume air sampling, an average D_i for a 70 Kg adult playing an 18-hole round of golf was estimated by Equation. 2.

Equation 2

$$D_i = C \times R \times 4 \text{ hr}/70\text{Kg}$$

where C = average concentration of pesticides in air determined by high-volume air sampling, R = adult breathing rate during light activity (2.5 m^3 h^{-1} or 21 L /min), and D_i = inhaled dose of pesticides. An average of 13 µg (± 4) of chlorpyrifos was determined to be absorbed at this moderate breathing rate following application at its high rate (4 lbs a.i./acre) (Figure 7). Factoring in a 70 Kg body weight, the estimated dose of inhaled pesticide (0.186 µg/Kg) is divided by the reference dose (Rfd) to give and Inhalation Hazard Quotient (IHQ) of 0.062.

Determination of Exposure by Dosimetry

Figure 7 presents the total chlorpyrifos residues collected on whole body dosimeters and onto individual personal air samplers by the dosimetry group while simulating the play of an 18-hole round of golf. Whole body dosimeters collected ~300 µg chlorpyrifos when applied at 4 lbs a.i./acre. Personal air samples, assuming a light activity breathing rate, collected ~13 µg chlorpyrifos, a value similar to that obtained using the high volume air sampling technique on small

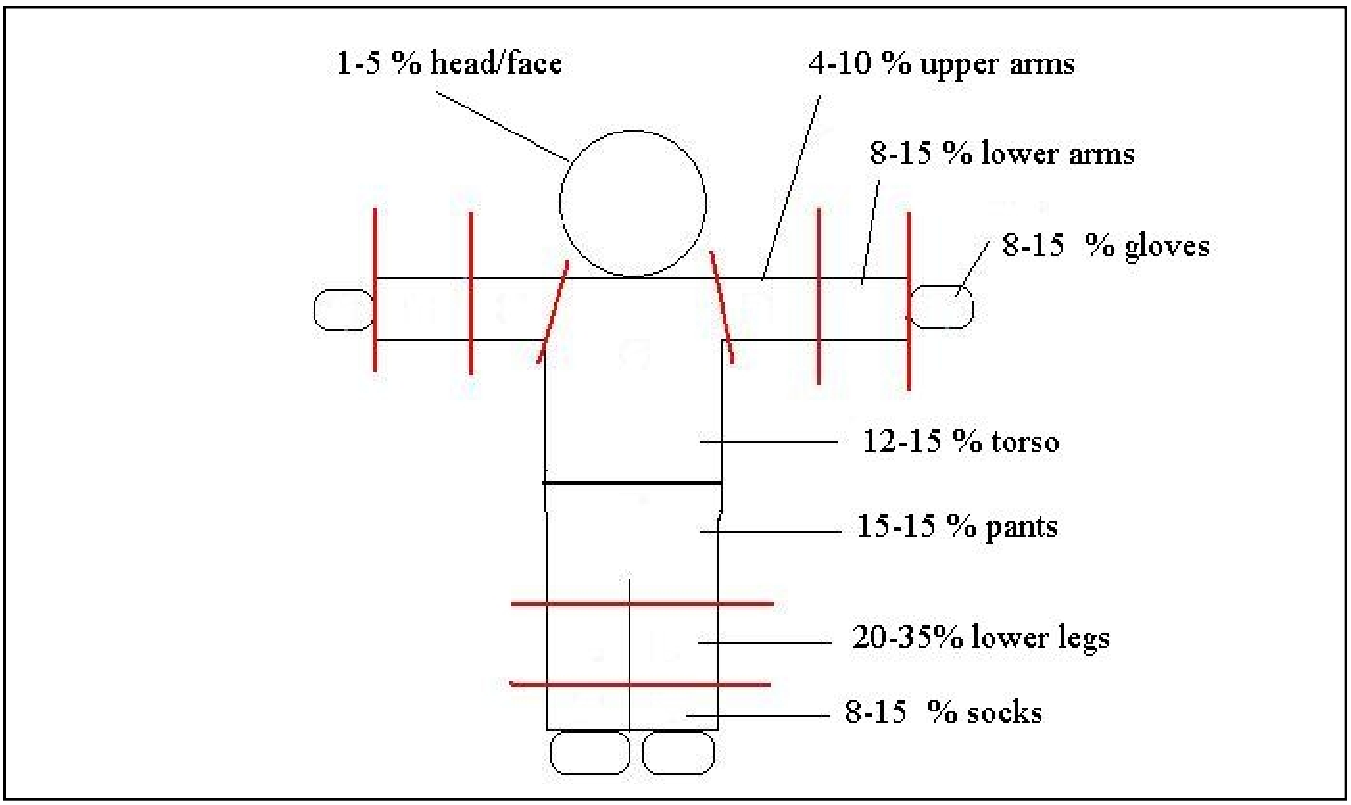

Figure 8. The distribution of chlorpyrifos collected on whole body dosimeters

circular turfgrass plots. One of the most pronounced finding from the dosimetry data was that the major route of exposure to golfers was dermal as it accounted for more than 92% of all transferable residues. This pattern was repeated regardless of the rate or area which chlorpyrifos was applied.

Application of chlorpyrifos at 4 lbs a.i./acre to only tees and greens resulted in a 76-81% reduction in whole body dosimetry and a corresponding 75-84% reduction in airborne residues (Figure 7). Similarly, chlorpyrifos applied at its new label rate of 1 lb a.i./acre resulted in an approximate 60% reduction in residues compared to the high rate of application. Half-course applications (9-holes with a 1-hour re-entry interval) at the new lower rate, likewise, resulted in an additional reduction of appromiately 20 % compared to full-course applications at the lower rate. Taken together, these finding provide compelling evidence that pesticide exposure from treated turfgrass on golf courses can be substantially reduced by reducing rates of application and partial course treatments.

One of the more practical ways to extend the re-entry interval following pesticide application is to apply pesticides after the last golfers finish play in the evening. This process will increase the time to first exposure, should decrease the amount of residues, and minimize exposure. As shown in Figure 7, however, the expected benefit of this practice was not evident. Apparently, evening applications with its cool, stagnant nights and no solar radiation prevented chlorpyrifos from dissipating as expected.

Figure 8 shows the distribution of pesticide collected onto various body regions by the dosimeter groups. It was previously thought that the hands were the primary route for dermal exposure (9, 10). However, we found the major route for exposure is the lower legs. The lower leg consistently was the most highly contaminated collector, followed by pants (upper leg to waist) and torso. When combined with the residues on hands and lower arms (forearms), the areas generally exposed on most golfers, this value accounts for

Application Scenario	REI [a]	DHQ	IHQ	Total [b]
Chlorpyrifos				
4 lbs ai/acre - full course	1 hour	0.145	0.064	0.209
4 lbs ai/acre - tees and greens	1 hour	0.034	0.013	0.047
1 lb ai/acre - full course	1 hour	0.035	0.024	0.059
1 lb ai/acre -full course, night	12 hours	0.061	0.029	0.09
1 lb ai/acre - half course	1 hour	0.028	0.019	0.047
Cyfluthrin				
0.14 lbs ai/acre - full course	1 hour	0.002[c]	0.002[c]	0.004
Carbaryl				
7 lbs ai/acre - full course	1 hour	0.012	0.002[c]	0.014

[a] REI, re-entry interval
[b] Total, combined IHQ and DHQ, representing total exposure measured by whole body dosimetery and air samples
[c] Residues not detected, HQ estimataed from detection limit

Table 3. DHQ and IHQ calculated from whole body dosimeters and personal air samplers

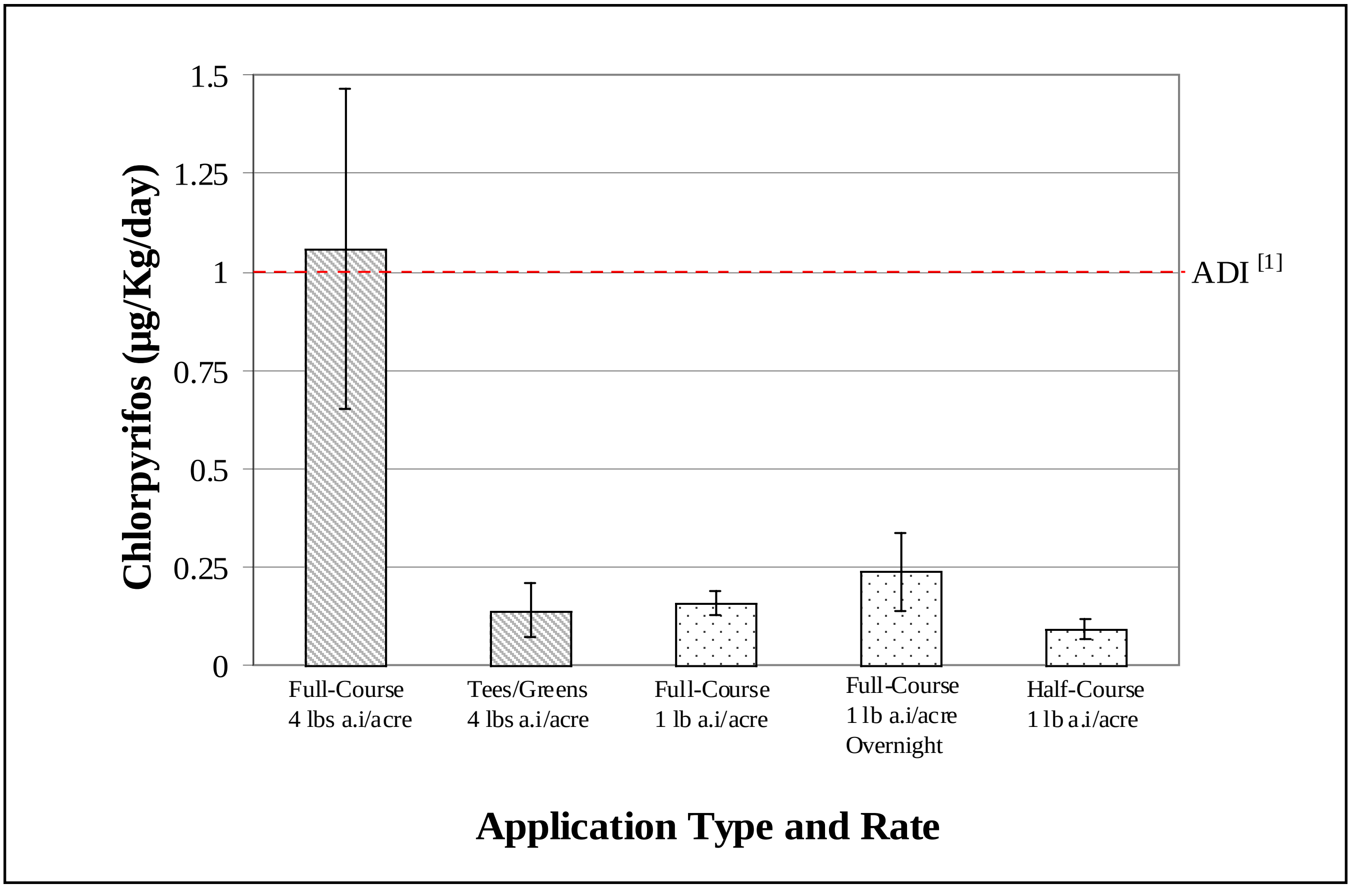

Figure 9. Total dose of chlorpyrifos to individuals following an 18-hole round of golf played in four hours as determined by biomonitoring of its urinary metabolite TCP. ADI is the allowable daily intake of CHP, which is 1.0 µg/Kg/day

approximately 85% of the total pesticide residues transferred to the whole body dosimeters.

Application of cyfluthrin at its full labeled rate and to the entire "golf course" resulted in no detectable residues on either the dosimeters or personal air samplers. The limit of detection (LOD) was 5 µg cyfluthrin per clothing section and 4 µg/4 hours cyfluthrin at a moderate breathing rate on the personal air samplers, respectively.

Although carbaryl was applied at a higher rate than chlorpyrifos, carbaryl residues collected on whole body dosimeters did not increase proportionately. Overall, a total of approximately 120 µg of carbaryl were collected following full course Sevin applications at 7 lbs a.i./acre compared to the high rate of chlorpyrifos (~300 µg). Carbaryl was not detected in the personal air samplers (LOD = 2 µg total exposure), indicating exposure to this insecticide is almost entirely through the dermal route.

Hazard quotients can be calculated directly from the dosimetry data. For example, the average dermal chlorpyrifos exposure collected on the whole body dosimetry suits following full course chlorpyrifos applications at 4 lbs a.i./acre was 305 µg (Figure 7). The dermal hazard quotient can then be calculated as follows:

Equation 3:

$$DHQ = \frac{305\mu g \text{ chlorpyrifos x } 10\% \text{ penetration factor/ } 70 \text{ Kg}}{3\ \mu g/Kg/day \text{ (EPA OPP chlorpyrifos Rfd)}}$$

$$DHQ = 0.145$$

Inhalation Hazard Quotients (IHQs) can also be calculated using the residues collected on the personal air samplers. For example, the average

Application Scenario	Absorbed Dose (µg/Kg)	HQ
4 lbs a.i./acre		
full-course,1 hr re-entry	1.058 ± 0.409	0.352
tees & greens, 1 hr re-entry	0.140 ± 0.069	0.047
1 lb a.i./acre		
full-course, 1 hr re-entry	0.159 ± 0.317	0.053
full-course, 12 hr re-entry	0.238 ± 0.098	0.079
half-course, 1 hr re-entry	0.090 ± 0.027	0.030

Table 4. Total absorbed dose and calculated HQs for chlorpyrifos determined from biomonitoring of its urinary metabolite TCP

total chlorpyrifos inhalation exposure following full course Dursban applications at 4 lbs a.i./acre was 12.65 µg. The inhalation hazard quotient can be calculated as follows:

Equation 4:

$$\text{IHQ} = \frac{12.65\ \mu\text{g chlorpyrifos / 70 Kg}}{3\ \mu\text{g/Kg/day (EPA OPP chlorpyrifos Rfd)}}$$

$$\text{IHQ} = 0.06$$

The estimates of the IHQ using high volume air samplers (0.062, Equation 2) and the personal air samplers (0.06, Equation 4) are in good agreement. This finding is expected because the two methods use similar techniques to estimate the concentration of pesticides in the air. These IHQs are well below 1.0 indicating there is a large safety margin. Hazard quotients can also be estimated in the absence of detectable residues by using the detection limit (LOD) for the pesticide as the maximum amount expected to be present.

Dermal and inhalation chlorpyrifos HQs estimated from whole body dosimeters and personal air samplers, respectively, following various exposure scenarios are summarized in Table 3. The DHQs and IHQs are all substantially below 1.0, indicating a wide margin of safety associated with these exposures. These values are also in good agreement with those calculated from DFR collected by cloth wipes or CA rollers (Table 2) even though the processes involved in acquiring the pesticide residues are distinctly different (dosimetry versus environmental sampling). Additionally, the availability of dosimetry data eliminates a number of assumptions made when using the environmental data, such as the amount of DFRs that are actually transferred to the golfer.

Determination of Exposure by Biomonitoring

Figure 9 summarizes the biomonitoring data and estimates the actual whole body dose of absorbed chlorpyrifos as judged by the urinary clearance of the metabolite, TCP, from volunteer "golfers". At the high rate and full-course application scenario, overall exposure and actual whole body uptake of chlorpyrifos was not significantly different from the current Acceptable Daily Intake (ADI) assigned to chlorpyrifos (1.0 µg/Kg/day, WHO/USEPA). Using the mean whole body dose of chlorpyrifos determined by biomonitoring (1.06 µg/Kg/day) and dividing it by the OPP Rfd for chlorpyrifos (3 µg/Kg/day) yields a HQ value of 0.35. As expected, this actual value determined by biomonitoring is well below the concern level of 1.0 and is in agreement with previous HQ estimates made from environmental sampling and dosimetry procedures previously presented above.

Substantial reductions in whole body doses of chlorpyrifos are also apparent when reduced rates and partial course applications are made, which are consistent with the reductions seen for environmental residues and in dosimetry samples during similar application scenarios. There was an 87 % overall reduction in chlorpyrifos exposure following applications to only tees and greens versus whole course applications, resulting in a HQ of 0.043 (or 13% of the ADI). It should be noted that the data above follows applications using the old label rate of 4 lbs a.i./acre, which is no longer allowed. The new USEPA approved maximum label rate for chlorpyrifos is 4 times less (1 lb a.i/acre). Applications at this new lower rate significantly reduced associated HQs for full course (0.053) and half-course (0.03) applications compared to the older, higher label rate (Table 4).

These findings are encouraging and indicate support the contention that operational practices to attenuate exposure (e.g. reentry intervals, irrigation, application strategies, alternative chemicals, and IPM strategies) are highly likely to be effective. Additionally, chlorpyrifos is a high risk insecticide that has both high volatility and inherent high toxicity (relatively low Rfd). Even with these characteristics, its potential for exposure that would result in hazardous human health implications following the play of golf is not likely. Newer pesticides that do not share the potentially harmful chemistry evident with chlorpyrifos and which are applied at lower rates are expected to pose an even lower risk when evaluated by dosimetry and biomonitoring approaches.

There were no cyfluthrin metabolites detected in any of the pre- or post-exposure urine samples. The analytical limit of detection (LOD) is 0.5 nanograms/L, which is equivalent to approximately 4 µg total cyfluthrin exposure (depending on the volume of urine). Since the analytical method would have detected cyfluthrin exposure up to 4 µg total, it can be assumed that total exposure was less then 4 ug, or < 0.057 µg/Kg. Using this value as the estimated whole body dose of cyfluthrin determined by biomonitoring and dividing it by the reference dose for (25 µg/Kg/day) yields a HQ value of 0.0023. As expected, this value is well below the concern level of 1.0.

Discussion

In the current study, exposure estimates based on a one-hour re-entry interval following full-course and full-rate applications of chlorpyrifos, cyfluthrin, and carbaryl all are substantially below USEPA HQ and Acceptable Daily Intake (ADI) values, indicating safe exposures. Experiments designed to give the maximum exposure using the new chlorpyrifos rate (1 lb a.i./acre) resulted in average HQs of 0.059 (dosimetry) and 0.053 (biomonitoring) and 0.031 (DFRs + airborne concentrations). Biomonitoring is considered the "gold standard" for assessing human exposure as it directly measures the amount of pesticide actually absorbed into the body. Nevertheless, the good agreement among these markedly different techniques indicate that the biomonitoring and dosimetry techniques, combined with the measurement of airborne and DFRs provides a much more complete and accurate picture of pesticide fate and golfer exposure, and the generation of this type of data is absolutely critical for regulatory purposes.

It is noteworthy that chlorpyrifos is a high risk insecticide that has both high volatility and inherent high toxicity (relatively low Rfd). Even with these characteristics, its potential for exposure that would result in hazardous human health implications following the play of golf is not likely. Pesticides that do not share the potentially harmful chemistry evident with chlorpyrifos are expected to pose an even lower risk when evaluated by dosimetry and biomonitoring approaches. It should also be noted that it is unlikely that golfers will encounter worst case exposures on every round of golf play over a period of many years.

These already low exposures were further reduced by applying chlorpyrifos to only nine holes at a time. Hazard Quotients measured by dosimetry and biomonitoring were reduced by approximately 30 % following the simulation of an application to the first 9 holes of the course with a one-hour re-entry interval. Because exposure was not reduced a full 50 % following half-course applications, these results suggest that most exposure occurs in the first two hours following application. Obviously, both DFRs and airborne pesticide concentrations are rapidly declining over the first several hours following application. Thus, partial-course applications apparently only need to be spaced over a day or two to receive significant benefit in exposure reduction.

The highest HQ value determined following applications of chlorpyrifos at the new label rate, 0.079, (biomonitoring) occurred following the night applications. While this value is still significantly below an HQ of 1.0, it is evident that extending the golfer re-entry interval by applying at night was not an effective mitigation strategy. Evening applications with its cool, stagnant nights, no solar radiation, and the formation of morning dew prevented chlorpyrifos from dissipating as expected.

Several experiments were conducted by applying chlorpyrifos at the old label rate of 4 lbs a.i./acre before the label change. Hazard Quotients determined from these high label rate experiments are no longer applicable. Nonetheless, they were critical in developing the relevant exposure models and evaluating exposure reductions studies. Following full-course chlorpyrifos application at the old label rate (4 lbs a.i./acre), the DHQ estimated from dosimetry over a four-hour round of golf following a one-hour re-entry interval was 0.145.

The IHQs from high volume versus personal air samplers were both appromately 0.06 and indicate a large safety margin. Using the mean whole body dose of chlorpyrifos from urinary biomonitoring, a HQ value of 0.35 was obtained, again indicating a safe exposure. As expected, these exposures were successfully attenuated using a partial course application strategy. Overall, there was an 80 % reduction in chlorpyrifos exposure following applications to only tees and greens versus whole course applications as measured by biomonitoring and dosimetry.

Dermal pesticide exposure has been found to be the most significant route of exposure to golfers (> 92 %) for all pesticides studied. The lower legs, hands and lower arms are the most vulnerable routes of exposure. Dermal exposure is thought to occur primarily by the transfer of DFRs to an individual's skin and/or clothing. Exposure estimates determined in this study based on DFRs and airborne pesticide concentrations utilized 4-hour averages of these environmental measurements and overall are less than those previously reported (3).

Previous exposure estimates using environmental measurements assumed that the airborne and DFRs available at the start of a round of golf were constant, when in fact, these residues rapidly decline over the first four hours following application. Indeed, DFRs rapidly declined over the first hour "drying-in" period and the potential for dermal exposure is dramatically reduced following a one-hour post-application and irrigation interval. We have previously reported that DFRs are reduced by approximately 80 % by post-application irrigation. Our new findings show that DFRs are reduced by yet another ~50% simply by enforcing a one-hour re-entry interval. These findings are again encouraging and indicate that operational practices to attenuate exposure (e.g. reentry intervals, irrigation, application strategies, alternative chemicals and IPM strategies) are highly likely to be effective.

We have also replaced the "cheesecloth wipe" method for measuring DFRs with the CA roller method. The use of this new method consistently resulted in about 50% less pesticide residues available for transfer to golfers, reducing total exposure estimates. The adoption of this new technique will help in standardizing such measurements in the future and will reduce the potential hazard estimated previously using methods such as cloth wipes accordingly.

Experiments performed using less toxic and less volatile pesticides (cyfluthrin and carbaryl) resulted in significantly reduced HQs, indicating wide margins of safety for these "lower risk" insecticides. Cyfluthrin residues were not detected (below detection limit) on dosimeter media or in urine. Failure to detect cyfluthrin can be attributed to the reduced application rates and volatility of cyfluthrin, and its low dermal penetration rate. Based on DFRs and air sampler results, HQs for cyfluthrin following worst case scenarios are < 0.001. HQs for carbaryl exposure calculated from dosimetry media have also resulted in large safety factors (DHQ and IHQs < 0.01) following worst case application scenarios.

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