ANNUAL REPORT - NOVEMBER - 1999

AN ASSESSMENT OF THE RISKS ASSOCIATED WITH PESTICIDES VOLATILIZED AND DISLODGED FROM GOLF TURF

Submitted to: Dr. Michael P. Kenna
United States Golf Association
Green Section Research
P. O. Box 2227
Stillwater, OK 74076

Submitted by: Dr. George H. Snyder
University of Florida, IFAS
Everglades Research and Education Center
P. O. Box 8003
Belle Glade, FL 33430

and

Dr. John L. Cisar
University of Florida, IFAS
Ft. Lauderdale Research and Education Center
3205 S. W. College Avenue
Ft. Lauderdale, FL 33314

in cooperation with

Dr. Christopher Borgert
Applied Pharmacology and Toxicology, Inc.
Alachua, FL 32601

AN ASSESSMENT OF THE RISKS ASSOCIATED WITH PESTICIDES VOLATILIZED AND DISLODGED FROM GOLF TURF

George H. Snyder and John L. Cisar
University of Florida, IFAS

EXECUTIVE SUMMARY

Following laboratory studies to verify methodology, the concentration of ethoprop, fonofos, and isofenphos in air following application to a golf course fairway was determined. Although the weather was cloudy and rainy during the study, appreciable airborne pesticide residue was observed over a three-day measurement period. The highest concentration was found for ethoprop (20 $\mu g\ m^{-3}$ on day 2). Fonofos had a maximum concentration of 5.9 $\mu g\ m^{-3}$ on day 2, and isofenphos was 1.0 $\mu g\ m^{-3}$ on day 3. Although there was a general trend for increasing concentrations of ethoprop on the morning of the second day after application and a decline thereafter, trends were less evident for the other two pesticides. The study will be repeated in 2000, and an assessment of risks to golfers from inhalation of these pesticides will be conducted using available USEPA chronic reference dose data. An assessment using isazophos volatilized residues data from two previous studies indicated values exceeding the USEPA chronic reference dose for 18 - 19 hours after application. Of course, this assessment assumes inhalation of the residues by a golfer playing every day for 70 years. For a more realistic assessment, the risk can be reduced in proportion to the actual amount of exposure.

A series of pesticide dislodgeability studies were conducted to evaluate the risks associated with golfer exposure to dislodged pesticides as a result of application to greens. The work, which was performed by Mr. Raymond H. Snyder as part of a master of science degree program at the University of Florida, involved 2,4-D, Dicamba, isazofos, chlorpyrifos, and fenamiphos. The full report of this work is contained in his M.S. thesis.

Generally, the amount of pesticide dislodged decreased with time after application, and was greatly reduced following irrigation. By combining the data, risk assessment calculations could be made for various scenarios. The lowest risks were found for dicamba and chlorpyrifos. Even for fenamiphos, the pesticide from the group that posed the greatest risk from dislodgeable residues, little risk was calculated for a golfer who plays the day after pesticide application and irrigation everyday for 70 years.

TABLE OF CONTENTS

AN ASSESSMENT OF THE RISKS ASSOCIATED WITH PESTICIDES VOLATILIZED AND DISLODGED FROM GOLF TURF

George H. Snyder and John L. Cisar
University of Florida, IFAS

ABSTRACT

Following laboratory studies to verify methodology, the concentration of ethoprop, fonofos, and isofenphos in air following application to a golf course fairway was determined. Although the weather was cloudy and rainy during the study, appreciable airborne pesticide residue was observed over a three-day measurement period. The highest concentration was found for ethoprop (20 $\mu g\ m^{-3}$ on day 2). Fonofos had a maximum concentration of 5.9 $\mu g\ m^{-3}$ on day 2, and isofenphos was 1.0 $\mu g\ m^{-3}$ on day 3. Although there was a general trend for increasing concentrations of ethoprop on the morning of the second day after application and a decline thereafter, trends were less evident for the other two pesticides. The study will be repeated in 2000, and an assessment of risks to golfers from inhalation of these pesticides will be conducted using available USEPA chronic reference dose data. An assessment using isazophos volatilized residues data from two previous studies indicated values exceeding the USEPA chronic reference dose for 18 - 19 hours after application. Of course, this assessment assumes inhalation of the residues by a golfer playing every day for 70 years. For a more realistic assessment, the risk can be reduced in proportion to the actual amount of exposure.

A series of pesticide dislodgeability studies were conducted to evaluate the risks associated with golfer exposure to dislodged pesticides as a result of application to greens. The work, which was performed by Mr. Raymond H. Snyder as part of a master of science degree program at the University of Florida, involved 2,4-D, Dicamba, isazofos, chlorpyrifos, and fenamiphos. The full report of this work is contained in his M.S. thesis.

Generally, the amount of pesticide dislodged decreased with time after application, and was greatly reduced following irrigation. By combining the data, risk assessment calculations could be made for various scenarios. The lowest risks were found for dicamba and chlorpyrifos. Even for fenamiphos, the pesticide from the group that posed the greatest risk from dislodgeable residues, little risk was calculated for a golfer who plays the day after pesticide application and irrigation everyday for 70 years.

In the coming year, in addition to conducting a second pesticide volatilization study we anticipate making another evaluation of the ability of a Stabilized Organic Polymer (SOP) to reduced fenamiphos and fenamiphos leaching in a USGA green. The SOP was developed as part of a previous USGA project, and the University of Florida is pursuing a patent on this product.

INTRODUCTION

The project was designed to be in collaboration with a project headed by Dr. John Clark, University of Massachusetts. However, that project was not funded by the USGA, so our project has and will continue to undergo appropriate modification.

In 1999, a pesticide volatilization study was conducted at Banyon Golf Course in West Palm Beach, Florida. In addition, as promised in the 1998 report, a series of risk assessment scenarios based on field measurements of dislodgeable pesticides was performed as part of the M.S. degree thesis work of Mr. Raymond Snyder, graduate student in the Soil and Water Science Department of the University of Florida, which was partially supported by the United States Golf Association. The full thesis is included with this report.

VOLATILIZATION OF ETHOPROP, FONOFOS, AND ISOFENPHOS APPLIED TO TURFGRASS

A. Laboratory Study.

Prior to conducting a field study, an evaluation of pesticide absorption by a Staplex Model TFIA air sampler was conducted in the laboratory. The pesticides ethoprop, fonofos, and isofenphos were applied to cheese cloth placed on the intake side of the sampler. Because it was found that Amberlite XAD-4 resin passed through the retention screens suppled with the sampler, the screens were replaced with 100 mesh stainless steel screen. Two chambers for holding adsorbent were placed in the sampler; an outer chamber (O) holding adsorbent that first contacted the pesticide/air mix, and an inner chamber (I) that was used to adsorb pesticide that escaped the outer chamber. Following exposure to pesticide, the resin was extracted with methylene chloride, concentrated, and pesticides were analyzed with a Hewlet-Packard 5890 gas chromatograph. The rates of application to the cheese cloth were 8000 μg for ethoprop, 1600 μg for fonofos, and 830 μg for isofenphos. Adsorption was determined under a variety of conditions involving resin type, run time, and air speed (Table 1). Clearly, maximum adsorption in the outer chamber, minimum adsorption on the inner chamber (indicating less bleed-through), and maximum total adsorption was achieved with XAD-4 resin, a 2 hour adsorption period, and fan speed of 10 cfm (283.7 liters min^{-1}). Therefore, it was decided that these conditions would be used in the field study.

Table 1. Effect of resin type, run time, and sampler air speed on adsorption of ethoprop, fonofos, and isofenphos with a Staplex model TFIA air sampler, separated by inner chamber (I), outer chamber (O), and the summation of the two chambers (T).

Experimental condition			Recovery (% of volatilized pesticide)								
			Ethoprop			Fonofos			Isofenphos		
Resin	Time (hours)	Speed	I	O	T	I	O	T	I	O	T
XAD-4	18	full	0.5	38.9	39.4	0.6	30.4	31.0	0.0	3.7	3.7
XAD-4	4	full	2.5	67.3	69.8	2.4	61.7	64.1	0.1	14.7	14.8
XAD-4	2	10 cfm	0.6	89.3	89.9	0.9	84.7	85.6	1.3	67.8	69.1
SOP	18	full	3.3	5.3	8.6	0.9	1.3	2.2	6.6	5.0	11.6
SOP	4	full	2.2	2.5	4.7	0.6	0.7	1.3	1.9	3.6	5.5
SOP	4	10 cfm	12.8	12.9	25.7	4.5	4.3	8.8	4.6	14.7	19.3

SOP refers to a resin made in-house, cmf = cubic feet per minute (multiply by 28.37 for liters/min)

B. Field Study

An assessment of volatilization of ethoprop, fonofos, and isofenphos applied to a golf course fairway was made in June, 1999, at Banyon Golf Course in Palm Beach County, with the cooperation of Mr. Clint Smallridge CGCS. Ethoprop was applied as Mocap 10G at the rate of 2.25 g A.I. m^{-2} (4.6 lb product/1000 sq ft.). Fonofos was applied as Crusade 5G at 0.44 g A.I. m^{-2} (1.8 lb product/1000 sq. ft.). Isofenphos was applied as Oftenol 1.5G at 0.22 g A.I. m^{-2} (3 lb product/1000 sq. ft.). The study was conducted using the Theoretical Profile Shape technique described by Jenkins et al. (1993). The products were applied with a Gandy drop-type spreader over a circular area with a 20 m radius. Following application, air was sampled with a Staplex Model TFIA air sampler placed in the center of the circle at a height of 73 cm, operated at a speed of 284 L min^{-1} (10 cfm) over 2 hour intervals. Pesticide was sorbed on XAD-4 resin. Data from the inner and outer chambers were combined. The resin was extracted with methylene chloride, concentrated, and pesticides were analyzed with a Hewlet-Packard 5890 gas chromatograph. An anemometer was used to measure wind speed during the study. However, because the purpose of the study was to obtain data that can be used to make a risk assessment, and not to determine the total quantity of pesticide volatilized, the anemometer data are not presented at this time. Data are presented as µg pesticide m^{-3} of air over the application site, calculated at the quantity of pesticide adsorbed over approximately two-hour periods, divided by the quantity of air drawn in by the air sampler (284 L min^{-1}).

The weather during the entire study period was cloudy and rainy, although intense, heavy rainfall was not observed until the last night before the conclusion of the study. The rainfall and applied irrigation after the pesticides were applied totaled approximately 13 mm on the first day. That night there was another 4 mm of rainfall. On the next day (June 2), there was 12.5 mm rainfall by 7:30 PM. During the night, an additional 130 mm of rainfall was observed, and the weather was overcast for the final day of the study.

Table 2. Concentration of ethoprop, fonofos, and isofenphos in air following application to a golf course fairway in June, 1999.

Date	Time period	Ethoprop	Fonofos	Isofenphos
			(μg m^{-3})	
June 1	1:20 - 3:20 PM	13.2	2.54	0.30
	3:21 - 5.21 PM	11.7	1.59	0.38
	5:22 - 7:15 PM	10.1	1.69	0.15
June 2	7:25 - 9:25 AM	14.5	2.63	0.16
	9:25 - 11:25 AM	29.2	5.86	0.87
	11:25 - 1:25 PM	10.9	2.20	0.14
	1:25 - 3:20 PM	13.6	3.41	0.31
	3:20 - 5:21 PM	5.7	1.70	0.26
	5.21 - 7:28 PM	2.4	0.88	0.29
June 3	7:25 - 9:25 AM	2.2	0.79	0.37
	9:25 - 11:25 AM	4.3	1.52	0.31
	11:25 - 1:30 PM	3.8	1.56	0.58
	1:30 - 3:30 PM	7.4	2.24	1.02

For ethoprop and fonofos, there was a general decline in airborne pesticide for corresponding time periods over the three days of the study, but surprisingly high concentrations of pesticides, relative to the initial amounts, were observed even on the third day following heavy overnight rainfall. On the third day, it was still possible to detect pesticide (probably ethoprop) by smelling the soil surface. Air concentration values for isofenphos were lower than for the other pesticides, but they were actually higher on the third day than for the corresponding time periods on the first two days. This study will be repeated in 2000, and a risk assessment analysis will be made using available USEPA chronic reference dose data (Rfd, μg kg^{-1} d^{-1}) or other available information.

In a previous USGA report (1977), data were presented for isazophos, chlorpyrifos, and fenamiphos volatilization relative to the amount applied for two weather conditions. Study 1 was conducted on a cloudy, rainy day, and study 2 was conducted on a clear, dry day. However, data were not presented in terms of pesticide concentration in air. Data of this type can be used for risk assessments, and therefore are presented herein (Table 3).

Table 3. Concentration of three pesticides in air ($\mu g\ m^{-3}$) following application to bermudagrass turf.

Sample time following application		Isazophos		Chlorpyrifos		Fenamiphos	
Study 1	Study 2	Study 1	Study 2	Study 1	Study 2	Study 1	Study 2
--- (hours) ---		($\mu g\ m^{-3}$)					
0 - 2	0 - 1	1.61	5.76	4.24	6.39	0.39	3.15
2 - 4	1 - 2	0.29	5.54	1.02	6.48	0.00	0.04
4 - 6	2 - 3	0.58	2.99	1.22	5.27	0.09	0.02
6 - 18	3 - 4	0.18	2.65	0.32	3.52	0.00	0.02
18 - 24	4 - 5	0.07	1.84	0.19	3.18	0.00	0.02
24 - 27	5 - 19	0.01	0.57	0.08	0.51	0.01	0.01

The average daily inhaled dose of pesticide for a 70 kg adult playing a 4-hour round of golf can be estimated as (Murphy et al., 1996):

$$D = (C * R * 4\ h)/70\ kg \qquad \text{(equation 1)}$$

where D = daily inhaled dose of pesticide ($\mu g\ kg^{-1}$), C = measured air concentration of pesticide ($\mu g\ m^{-3}$), and R = adult breathing rate during moderate activity ($2.5\ m^3\ h^{-1}$).

For isazophos, the USEPA chronic reference dose (Rfd, $\mu g\ kg^{-1}\ d^{-1}$) is 0.02 $\mu g\ kg^{-1}\ d^{-1}$ (Murphy et al, 1996). Using equation 1, it can be calculated that the concentration of isazophos in air that provides a daily inhaled dose (D) equal to the Rfd is 0.14 $\mu g\ m^{-3}$. This value was exceeded for the first 18 hours in Study 1, and was exceeded thoughout Study 2. Murphy et al. (1996) also reported values exceeding the Rfd for three days following isazophos application. Of course, a golfer will not play on a course following isazophos application every day of his life, so the risk will be proportionally reduced. Nevertheless, pesticide volatilization appears to represent a significant pathway for golfer exposure, which may be greater than that of dislodgeable residues. A risk assessment analysis will be conducted for the other pesticides used in our studies as Rfd data become available.

RISK ASSESSMENT SCENARIOS BASED UPON FIELD STUDIES OF PESTICIDE DISLODGEABILITY

A variety of methods were used to measure the dislodgeability of various pesticides applied to bermudagrass turf. A summary of the methodology was presented in the 1998 USGA report, and the full methodology is provided in the M.S. degree thesis included with this report. The information provided herein is a listing of Hazard Quotients for various scenarios that might be encountered by golfers, based on play on and around greens, although for the sake of safety it is unlikely that many golfers would encounter the extreme nature of most of these scenarios.

EXPOSURE AND RISK ASSESSMENT

1. Exposure Setting

A short, dense turfgrass surface serves as media upon which golfers compete. A variety of turfgrasses are used depending on the location of the golf course and the intended use of the turfgrass (tee, fairway, rough, and putting green). In Florida, a hybrid bermudagrass is most often the turfgrass of choice.

2. Identification of Exposure Pathways

Several pathways by which golfers may encounter pesticide residues exists. Direct and indirect contact may occur with the turfgrass surface. Direct dermal contact includes placement of the hand or fingers onto the turfgrass surface. This behavior is often exhibited by golfers during preparation for putting. Indirect dermal contact generally occurs when handling golf equipment such as golf balls, golf grips, and club faces that have direct contact with the turfgrass surface. Individually, these indirect pathways may not transfer a great deal of residues, however, the sum of the pathways can be appreciable especially if dermal contact leads to oral ingestion via hand-to-mouth contact.

3. Quantification of Exposure

Dislodgeable residues of two herbicides, two insecticides, and one nematicide were determined by various methods which attempt to simulate the previously noted exposure pathways. Damp cheesecloth wipe residues was used to provide the quantity of residues dislodged by human hand - turfgrass contact. Residues dislodged by the golf ball putt method served to provide the quantity of residues available for both dermal and oral exposure. The golf grip roll, and chip and wipe methods provided the quantity of residues available for dermal contact.

For purposes of this study, a theoretical golfer was generated. This theoretical golfer was intended to serve as an extreme case of dermal and oral exposure. It is likely that most golfers will not exhibit the same behavior or receive as high a level of exposure as the theoretical golfer developed in this study.

Behavior Assumptions of the theoretical golfer

1.) One time placement of a single hand on the putting green surface.
2.) Handling of a golf grip following placement of the golf club on the putting green surface.
3.) Handling of a golf ball following two putts on the putting green surface.
4.) Handling of a golf club face and back following chipping (one chip per hole) onto the putting green surface.
5.) One placement of a the golf ball into the mouth following its use on the putting green surface.
6.) The golfer uses a bare hand to handle the golf grip and golf ball, remove debris from the club head, and touch the turfgrass surface of the putting green.

4. <u>Risk Assessment</u>

None of the pesticides used in this study have shown any carcinogenic effects. Therefore, assessing risk using the hazard index approach to assess potential non-cancer effects is appropriate and necessary. This approach compares the average daily intake (dermal and oral) of each pesticide to a published acceptable level of daily intake for chronic or subchronic exposure (RfD) (Borgert et. al., 1994). If the resulting hazard index is less than or equal to one, the chemicals are considered unlikely to represent a risk to human health. If the hazard index is greater than one, a potential risk to human health may exist (Davis and Klein, 1996).

Several exposure models have been used in determining risk (Ross, 1990, Zweig et al, 1985, and USEPA, 1989). The Ross (1990) and Zweig et. al. (1985) models determined the transfer coefficients for their individual exposure environments. For example, in Ross's et. al. (1990) model subjects performed Jazzercise routines for 20 min. on carpet in pesticide-treated room. It is questionable as to whether a golfer's activity on a golf course is similar or can be related to a person performing a Jazzercise routine. In Zweig's et. al. (1985) model, the dermal transfer coefficient was based on harvesters' dermal exposure upon reentering pesticide-treated crops. Again, exposure using this model would likely be exaggerated since golfers probably do not have the same or as frequent contact with vegetation as harvesters. Consequently, the use of such models could result in an overestimation of exposure and potentially cause unwarranted concern.

Several models, all of which are based on the USEPA (1989) model, were used in this study to determine if a significant toxilogical risk is present. In these models, a transfer coefficient of 1.0 is assumed. For example, 100% of the pesticide dislodged by the golf ball is assumed to transfer from the golf ball to a persons hand. This is a conservative estimate. In reality 100% transfer is not likely. The exposure points used in the models were based on the theoretical golfer previously described in this chapter. The following equations which represent the dermal and oral doses are the basis upon which all of the equations used in the models are built.

Dermal Dose:

$$\frac{(QP_H + QP_B + QP_G + QP_{CF}) \times DP}{BW}$$

Oral Dose:

$$\frac{QP_B \times DP}{BW}$$

QP_H = Quantity of pesticide dislodged by a hand.
QP_B = Quantity of pesticide dislodged by a golf ball.
QP_G = Quantity of pesticide dislodged by a golf grip.
QP_{CF} = Quantity of pesticide dislodged by a golf club head
DP = Dermal permeability coefficient.
BW = Female body weight.

Total Dose: Dermal Dose + Oral Dose = Total Dose

Hazard Quotient: Total Dose / RfD Dose = Hazard Quotient

It is important to note that in the 2,4 - D and dicamba models, the QP_G is not include since a method for the extraction of 2,4 - D and dicamba from golf grips could not be developed during the course of this study. Hazard Quotients of 1.0 or less indicate little probability of harm to the golfer.

The data in Table 4 indicate that even under extreme circumstances, golfers will experience little risk from dislodgeable residues of chlorpyrifos or dicamba, and probably from 2, 4-D as well. While the data for isazophos and fenamiphos appear more threatening, it should be remembered that golfers are unlikely to encounter these pesticides on every round of golf they play over a period of many years. For example, fenamiphos is labeled for use only twice per year on golf courses. Therefore, the risk calculations can be reduced proportionally.

Table 4 (Continued). Hazard Quotients calculated for various pesticides and behavioral scenarios

Pesticide	Behavior	Hazard Quotient
Dicamba	Golfer plays on 18 greens 30 minutes after pesticide application every day for a lifetime (70 years)	0.04
	Golfer plays on one green 30 minutes after pesticide application and on the remaining 17 greens 4 - 5 hours after application every day for a lifetime	0.02
	Golfer plays on 18 greens 4 - 5 hours after application every day for a lifetime	0.02
	Golfer plays on 18 greens 24 hours after application every day for a lifetime	0.01
	Golfer plays on 18 greens 30 minutes after pesticide application two times a week for 35 years.	0.005
	Golfer plays on one green 30 minutes after pesticide application and on the remaining 17 greens 4 - 5 hours after application two times a week for 35 years	0.004
	Golfer plays on 18 greens 4 - 5 hours after application two times a week for 35 years	0.003
	Golfer plays on 18 greens 24 hours after application two times a week for 35 years	0.001

Table 4 (Continued). Hazard Quotients calculated for various pesticides and behavioral scenarios

Pesticide	Behavior	Hazard Quotient
Fenamiphos	Golfer plays on 18 greens within 1 hour after pesticide application every day for a lifetime (70 years)	152.00
	Golfer plays on one green immediately after pesticide application and on the remaining 17 greens after application and irrigation every day for a lifetime	17.05
	Golfer plays on 18 greens after pesticide application and irrigation every day for a lifetime	9.08
	Golfer plays on 18 greens the day after application and irrigation every day for a lifetime	0.84
	Golfer plays on 18 greens within 1 hour after pesticide application two times a week for 35 years.	21.65
	Golfer plays on one green immediately after pesticide application and on the remaining 17 greens after application and irrigation two times a week for 35 years	2.43
	Golfer plays on 18 greens after application and irrigation two times a week for 35 years	1.29
	Golfer plays on 18 greens the day after application and irrigation two times a week for 35 years	0.12

* Hazard Quotients of 1.0 or less indicate little risk to the golfer

CURRENT PROJECT STATUS AND FUTURE PLANS

A second pesticide volatilization study is planned. Risk assessment calculations will be completed for all remaining volatilization data. Although not specifically a part of the current project, another evaluation of the ability of a Stabilized Organic Polymer (SOP) to reduced fenamiphos and fenamiphos leaching in a USGA green will be conducted. The SOP was developed as part of a previous USGA project, and the University of Florida is pursuing a patent on this product.

LITERATURE CITED

Borgert, C. J., S. M. Roberts, R. D. Harbison, J. L. Cisar, and G. H. Snyder. 1994. Assessing Chemical Hazards on Golf Courses. USGA Green Section Record. March\April

Davis, B.K.; and A. K. Klien, 1996. Medium-Specific and Multimedium Risk Assessment. In *Toxicology and Risk Assessment*. Fan A. M. and Chang L.W., Eds.; Marcel Dekker, Inc. New York, Chapter 16, p 271.

Jenkins, J. J., A. S. Curtis, and R. J. Cooper. 1993. Two small-plot techniques for measuring airborne and dislodgeable residues of pendimethalin following applications to turfgrass. Chapt. 20 In K. D. Racke and A. R. Leslie (eds.) Pesticides in Urban Environments - Fate and Significance. Amer. Chem. Soc. Series 522. Amer. Chem. Soc. Washington, D.C. p. 228-242.

Murphy, K. C., R. J. Cooper, and J. M. Clark. 1996. Volatile and dislodgeable residues following trichlorfon and isazofos application to turfgrass and implications for human exposure. Crop Sci. 36:1446 - 1454.

Ross, J., 1990. Measuring potential dermal transfer of surface pesticide residues generated from an indoor fogger. Chemosphere 20:349-361.

USEPA. 1989. Risk Assessment Guidance for Superfund. Vol. 1. Human Health Evaluation Manual, Part A. EPA/540/1-89/002.

Zweig, G., J. T. Leffingwell, and W. Popenforf. 1985. The relationship between dermal pesticide exposure by fruit harvesters and dislodgeable foliar residues. Environ. Sci. Health. B 20 (1):27-59.