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

The concentration of ethoprop, chlorpyrifos, and isofenphos in air following application to a golf course fairway was determined. Appreciable airborne pesticide residue was observed over a three-day measurement period. The highest concentration was found for ethoprop (33 $\mu g\ m^{-3}$). Chlorpyrifos had a maximum concentration of 4.0 $\mu g\ m^{-3}$, and the maximum for isofenphos was 1.7 $\mu g\ m^{-3}$, with all three maximum concentrations occurring on the day of application. There was a general trend for decreasing concentrations of all three pesticides over time, but mid-day increases in concentration generally were evident. A risk analysis for chlorpyrifos indicated that golfer exposure to airborne residues of this pesticide posed no health risk. A similar assessment using data from past-year experiments indicated little health risk for inhalation of fenamiphos or fonofos applied to golf turf. Nevertheless, the amount of each of the four pesticides that was lost by volatilization this year, or in a 1999 trial, greatly exceeded that lost by leaching or clipping removal in previous USGA-sponsored studies we have conducted.

The effect of a stabilized organic polymer (SOP) incorporated in a USGA green on leaching losses of Fenamiphos and fenamiphos metabolite was investigated approximately two years after incorporation. Leaching of fenamiphos and its metabolites during the 91-day period after fenamiphos application was reduced 88 and 83%, respectively, by the SOP.

Mr. David Rich, Chemist, emptying XAD-4 resin used to adsorb air-borne pesticide from an air sampler during a pesticide volatilization experiment.

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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

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ABSTRACT

The concentration of ethoprop, chlorpyrifos, and isofenphos in air following application to a golf course fairway was determined. Appreciable airborne pesticide residue was observed over a three-day measurement period. The highest concentration was found for ethoprop (33 $\mu g\ m^{-3}$). Chlorpyrifos had a maximum concentration of 4.0 $\mu g\ m^{-3}$, and the maximum for isofenphos was 1.7 $\mu g\ m^{-3}$, with all three maximum concentrations occurring on the day of application. There was a general trend for decreasing concentrations of all three pesticides over time, but mid-day increases in concentration generally were evident. A risk analysis for chlorpyrifos indicated that golfer exposure to airborne residues of this pesticide posed no health risk. A similar assessment using data from past-year experiments indicated little health risk for inhalation of fenamiphos or fonofos applied to golf turf. Nevertheless, the amount of each of the four pesticides that was lost by volatilization this year, or in a 1999 trial, greatly exceeded that lost by leaching or clipping removal in previous USGA-sponsored studies we have conducted.

The effect of a stabilized organic polymer (SOP) incorporated in a USGA green on leaching losses of fenamiphos and fenamiphos metabolite was investigated approximately two years after incorporation. Leaching of fenamiphos and its metabolites during the 91-day period after fenamiphos application was reduced 88 and 83%, respectively, by the SOP. 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. It is unfortunate that for the purpose of making risk assessments we have not had the biological data, such as a physiological model of pesticide absorption from inhalation exposure, that the Clark project would have provided. Lacking such data, we have had to rely on default exposure parameters found in EPA guidance documents on risk assessment, which are essentially policy decisions about how to estimate doses and risks in the absence of scientific data. Furthermore, even these figures are not available for all of the pesticides used in our studies.

In 2000, a pesticide volatilization study was conducted at Banyon Golf Course in West Palm Beach, Florida as a replicate of the study conducted in the previous year. However, because of the unavailability of one pesticide (fonofos) used last year, chlorpyrifos was included in this year's study. Using data from the study conducted this year and from past-year studies, the risk associated with golfer exposure to volatilized chlorpyrifos, fenamiphos, and fonofos was made using EPA chronic reference dose (RfD) data. Although not a specifically stated objective for the current project, an evaluation of the ability of a Stabilized Organic Polymer (SOP) to reduced fenamiphos and fenamiphos metabolite leaching in a USGA green was conducted, as referred to in the 'Current Project Status and Future Plans' section of the 1999 report. The SOP was developed as part of a previous USGA project, and the University of Florida is pursuing a patent on this product. The evaluation conducted this year represented a test of the SOP 25 months after it was incorporated into the soil.

VOLATILIZATION OF ETHOPROP, CHLORPYRIFOS, AND ISOFENPHOS APPLIED TO TURFGRASS

METHODS AND MATERIALS

An assessment of volatilization of ethoprop, chlorpyrifos, and isofenphos applied to a golf course fairway was made June 5 - 7, 2000, 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 1.13 g A.I. m^{-2} (2.3 lb product/1000 sq. ft.). The application rate for Ethoprop in 1999 was 1.25 g A.I. m^{-2} (2.6 lb product/1000 sq. ft.), but was incorrectly stated as 2.25 g A.I. m^{-2} (4.6 lb product/1000 sq ft.) in the 1999 Annual Report. Chlorpyrifos was applied as Dursban 1G 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 and 4.6 mm irrigation, 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 in an inner and outer chamber (each 8.8 cm dia. x 2.0 cm deep). Data from both 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. Data were calculated both as pesticide concentration in the air over the application site (µg pesticide m^{-3} air), and as pesticide volatilized from the turfgrass surface (µg pesticide m^{-2} $hour^{-1}$). The data collected in the 1999 study also were calculated in the latter fashion, since this had not been done in 1999.

In contrast to the 1999 experiment when the weather during the entire study period was cloudy and rainy, there was no rain (or irrigation) during the 2000 study except for 1.3 mm rainfall during the second night.

RESULTS AND DISCUSSION

For all three pesticides, there was a general decline in airborne pesticide for corresponding time periods over the three days of the study, with small but clear increases during the late morning and early afternoon (Table 1). Ethoprop was applied at 2.6 and 5.1 times the concentration (A.I.) of chlorpyrifos and isofenphos, respectively. However, the airborne concentration of ethoprop was greater, relative to the other pesticides, than could be accounted for by the differences in application rate. Considerable ethoprop was observed on the third day.

Table 1. Concentration of ethoprop, chlorpyrifos, and isofenphos in air following application to a golf course fairway in June, 2000.

Date	Time period	Ethoprop	Chlorpyrifos	Isofenphos
		($\mu g\ m^{-3}$)		
June 5	11.00 - 1.00 PM	20.4	3.8	1.7
	1:00 - 3:00 PM	32.7	4.0	1.7
	3:00 - 5:00 PM	17.1	3.8	0.7
	5:00 - 7:00 PM	11.2	3.0	1.0
June 6	8:00 - 10:00 AM	13.9	3.1	1.0
	10:00 - 12:00 Noon	15.6	2.1	1.0
	12:00 - 2:00 PM	17.1	2.8	0.3
	2:00 - 4:00 PM	17.7	2.8	0.5
	4:00 - 6:00 PM	9.5	2.2	0.0
June 7	8:00 - 10:00 AM	5.4	1.3	0.1
	10:00 - 12:00 Noon	9.7	1.4	0.1
	12:00 - 2:00 PM	8.5	1.9	0.3
	2:00 - 4:00 PM	7.1	0.5	0.0
	4:00 - 6:00 PM	1.9	0.2	0.1

In a previous USGA report (1997), chlorpyrifos volatilization data for two weather conditions were presented. The application rate was 0.229 g A.I. m^{-2}, which is somewhat lower than used this year. Study 1 was conducted on a cloudy, rainy day, and study 2 was conducted on a clear, dry day. In the 1999 report, these data were calculated in terms of pesticide concentration in air (Table 2). The concentrations measured this year (2000, Table 1) were in the same general range as those measured in 1997.

Table 2. Concentration of chlorpyrifos and fenamiphos in air following application to bermudagrass turf.

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

RISK ASSESSMENT CALCULATIONS

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 chlorpyrifos, the USEPA chronic reference dose (RfD, $\mu g\ kg^{-1}\ d^{-1}$) is 3.0 $\mu g\ kg^{-1}\ d^{-1}$. Using equation 1, and assuming that all inhaled pesticide is absorbed by the body, it can be calculated that the concentration (C) of chlorpyrifos in air that provides a daily inhaled dose (D) equal to the RfD is 21 $\mu g\ m^{-3}$. This value was not exceeded in any of the three studies we have conducted (Tables 1 and 2), indicating that golfer exposure to volatile losses of chlorpyrifos pose little health hazard. However, it should be noted that the RfD for chlorpyrifos is rather high compared to certain other organophosphate pesticides, so the lack of a health hazard for chlorpyrifos should not be taken as a generalized lack of health hazard for other pesticides

For example, fenamiphos has a RfD of only 0.25 $\mu g\ kg^{-1}\ d^{-1}$. Based on equation 1, above, C is only 1.75. However, this value was exceeded for only a short time in one of two studies conducted on fenamiphos volatilization, as presented in the 1999 USGA report (Table 2). Of course, the calculations assume exposure to the corresponding concentration of pesticide every day for a lifetime, which will not occur based on the data from our study (Table 2), and the requirement that fenamiphos be used no more than twice per year.

Using similar calculations for fonofos, which has a RfD of 2 $\mu g\ kg^{-1}\ d^{-1}$, the daily inhaled dose is 14 $\mu g\ m^{-3}$. This value was not exceeded during the three days following fonofos application to a golf course fairway in 1999 (Table 3, adapted from the 1999 USGA report).

Table 3. Concentration of fonofos in air following application to a golf course fairway in June, 1999.

Date	Time period	Fonofos
		- ($\mu g\ m^{-3}$) -
June 1	1:20 - 3:20 PM	2.54
	3:21 - 5.21 PM	1.59
	5:22 - 7:15 PM	1.69
June 2	7:25 - 9:25 AM	2.63
	9:25 - 11:25 AM	5.86
	11:25 - 1:25 PM	2.20
	1:25 - 3:20 PM	3.41
	3:20 - 5:21 PM	1.70
	5.21 - 7:28 PM	0.88
June 3	7:25 - 9:25 AM	0.79
	9:25 - 11:25 AM	1.52
	11:25 - 1:30 PM	1.56
	1:30 - 3:30 PM	2.24

VOLATILIZATION LOSSES

Data from the 1999 and 2000 studies can be used to calculate the amount of pesticide volatilized during various portions of the three-day observation periods, and the total amount volatilized relative to that applied, excluding the intervening nighttimes when volatilization losses should be relatively small (Jenkins, et al., 1993). The diurnal nature of the volatilization losses is clearly evident (Figs. 1, 2, 3), and was magnified relative to the increased concentration in the air (Table 1) by the increased wind that occurred during daytime periods. Volatilization of ethoprop (Fig. 1), which was applied at the highest rate, greatly exceeded that of the other pesticides, and volatilization of isofenphos (Fig. 2), which was applied at the lowest rate, was the lowest. However, even when calculated relative to the amount applied, ethoprop had the greatest volatilization and isofenphos the least (Table 4). Furthermore, even without the nighttime losses, the calculated amounts are substantial (Table 4), particularly when compared to other loss pathways. In previous work, we have observed losses of these pesticides of less than 1% in percolate and clippings (Cisar and Snyder, 1996).

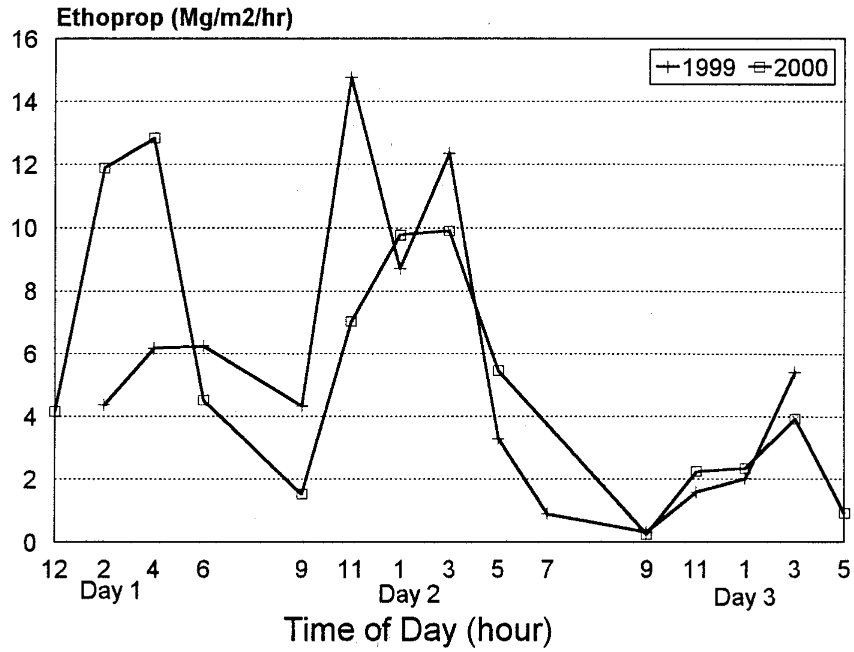

Fig. 1. Volatilization losses of ethoprop applied to a bermudagrass fairway in 1999 and 2000.

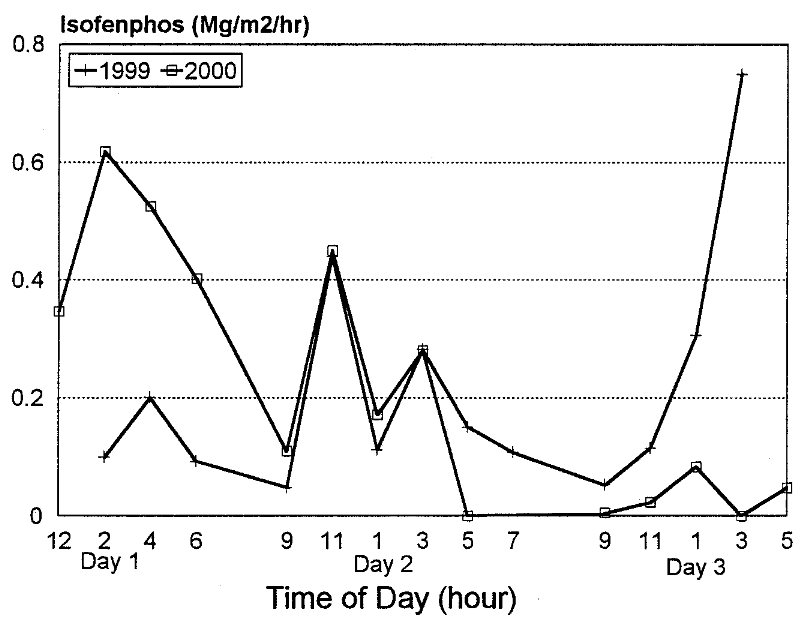

Fig. 2. Volatilization losses of isofenphos applied to a bermudagrass fairway in 1999 and 2000.

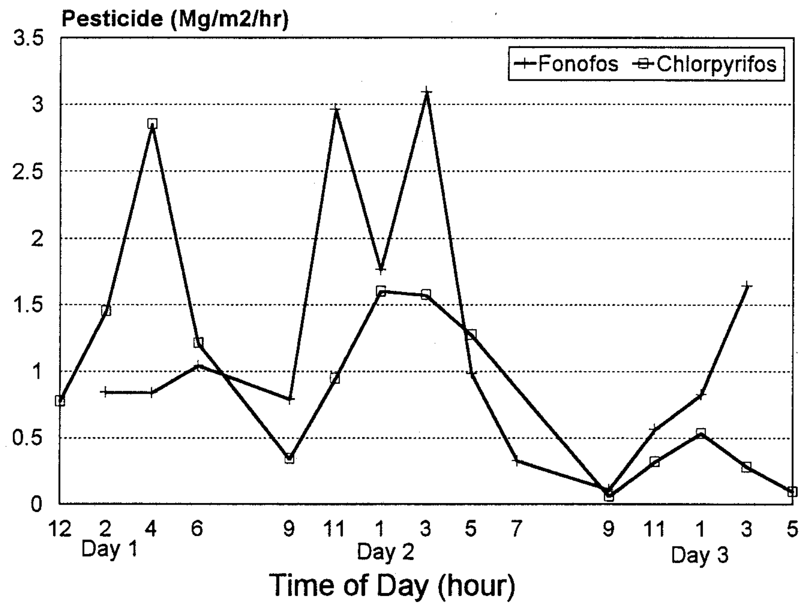

Fig. 3. Volatilization losses of fonofos and chlorpyrifos applied to a bermudagrass fairway in 2000.

Table 4. Pesticide volatilized over a three-day period, excluding nighttime periods, expressed as a percent of the amount applied.

Pesticide	Study year 1999	2000
Ethoprop	11.3	13.6
Fonofos	7.2	- -
Chlorpyrifos	- -	6.0
Isofenfos	2.5	2.8

AN EVALUATION OF A STABILIZED ORGANIC POLYMER (SOP) FOR REDUCING LEACHING OF FENAMIPHOS AND FENAMIPHOS METABOLITY 25 MONTHS AFTER INCORPORATION INTO A USGA GREEN

INTRODUCTION

In previous investigations of organophosphate pesticide leaching in a United States Golf Association green, we observed little pesticide in percolate water; generally less than 0.1% of applied (Cisar and Snyder, 1996) because of adsorption by the organic thatch layer. The exception to this generalization was the nematicide fenamiphos, and especially its metabolites (sulfoxide and sulfone), for which substantial quantities were found in percolate (Snyder and Cisar, 1993). Fenamiphos (Nemacur) is widely used for nematode control on greens and fairways, and there are few labeled alternatives to this pesticide. Because fenamiphos has been observed in waters in or adjacent to golf courses (Swancar, 1996), and because of a highly publicized fish kill in south Florida that was linked to the use of fenamiphos (Zaneski, 1994), the State of Florida Department of Environmental Protection issued new regulations limiting fenamiphos use on golf courses. They, and the U. S. Environmental Protection Agency, continue to review the situation. Since fenamiphos is important to the golf industry, and there is concern about leaching of fenamiphos and/or its metabolites, practices are needed for minimizing leaching of these compounds. For these reasons, our interest in reducing fenamiphos and fenamiphos metabolite leaching in golf greens led to the development and testing of an adsorbent that could be incorporated into the USGA root zone mix without altering the particle size specifications for golf green construction.

METHODS AND MATERIALS

A. Preparation of a cross-linked phenolic polyether stabilized organic polymer (SOP) coated sand.

In October, 1997, silica sand was coated with a cross-linked phenolic polyether SOP at the rate of 10% by weight. The SOP was made by a University of Florida patent-pending invention of ours (U.S. Serial No. 09/554,897, in the name of the University of Florida Research Foundation, Inc.) in which polyethylene glycol was reacted with phenol using a Williamson ether synthesis (Solomons, 1992), and the resultant product was cross-linked with formaldehyde forming a block polymer. The prepared material had a particle size range well within United States Golf Association (USGA) specifications.

B. Installation of SOP-coated sand in lysimeters.

In July, 1996, a previously described installation of six stainless-steel lysimeters in a USGA green at the University of Florida/IFAS Ft. Lauderdale Research and Education Center (Cisar and Snyder, 1993) was expanded to twelve lysimeters. On November 7, 1997, the twelve lysimeters were excavated to the gravel layer. Five cm of coarse sand, corresponding in size to that used in the original greens construction, were placed over the gravel layer. The SOP-coated sand was mixed at a rate of 20% by volume with freshly-obtained USGA rooting mix sand that corresponded in particle size to that used in the original greens construction (Cisar and Snyder, 1993) to provide a 10 cm deep layer over the coarse sand in six of the twelve lysimeters. Additional freshly-obtained rooting mix sand was used to completely refill the excavated hole, and this sand also was used over the coarse sand layer in the six lysimeters that did not receive the SOP-sand treatment. SOP-sand treated and untreated lysimeters were arranged in blocked pairs. The cv. Tifdwarf bermudagrass (*Cynodon dactylon X C. transvaalensis*) sod cut from over each lysimeter was trimmed to a soil depth of approximately 4 cm and replaced over the lysimeters. The green was maintained using standard practices thereafter, except that no pesticides other than fenamiphos were applied.

C. Evaluations of fenamiphos and fenamiphos metabolite leaching

Over the course of the next 27 months, fenamiphos was applied to the study area three times. Following each application, fenamiphos and fenamiphos metabolite were determined in percolate water collected in the lysimeters. Data for the final collection period (November 22 through Feb. 21, 2000) are presented.

The area containing the lysimeters had been maintained as a golf green since installation of the CCP-coated sand. Periodically, lysimeter water was evacuated and discarded. On the morning of November 18, 1999, the lysimeter water was evacuated and discarded. Fenamiphos (Nemacur 3E) was mixed with 4 liters of water and applied with a sprinkling can over 1 m^2 areas centered over the lysimeters to provide an application rate of 1.125 g A.I. m^{-2}. The plot area was irrigated to provide 0.8 cm water, and maintained as a golf green thereafter. Lysimeter water sampling began on November 22 and continued twice weekly through Feb. 21, 2000. The percolate samples were extracted with methylene chloride which was analyzed for fenamiphos and fenamiphos metabolite with a Hewlet-Packard 5890 gas chromatograph.

Summation data for percolate and pesticide leaching were processed by the SAS Institute (1990) ANOVA procedure.

RESULTS

There was no significant ($P < 0.05$) effect of SOP-sand on percolation, which averaged 80.0 cm during the three months following fenamiphos application. At the end of 91 days, the SOP reduced fenamiphos and fenamiphos metabolite leaching by 88 and 83%, respectively, compared to the control treatment (Fig. 4,5). After the initial great adsorption of metabolite by SOP sand, there was a slow desorption of the material, as evidenced by a gradual increase in accumulative metabolite leaching in the SOP-sand lysimeters over time (Fig. 5). Nevertheless, inclusion of SOP-coated sand into the root zone mix greatly reduced fenamiphos and fenamiphos metabolite leaching, especially shortly after pesticide application.

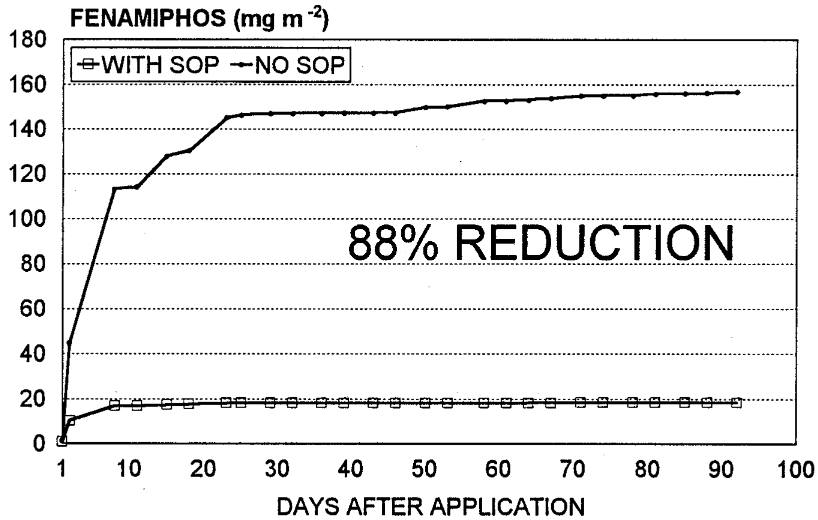

Fig. 4. Accumulative leaching of fenamiphos with and without inclusion of SOP in a USGA green.

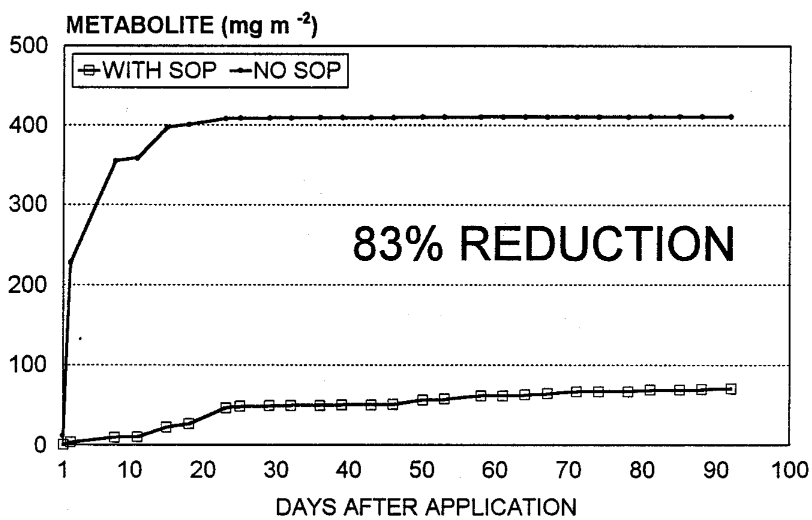

Fig. 5. Accumulative leaching of fenamiphos metabolite with and without inclusion of SOP in a USGA green.

CURRENT PROJECT STATUS AND FUTURE PLANS

Risk assessment calculations will be completed for all remaining volatilization data to the extent that USEPA RfD data are available. We will complete a survey of golfer actions that can lead to pesticide exposure by way of dislodgeable residues.

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