EXECUTIVE SUMMARY

MOBILITY AND PERSISTENCE OF TURFGRASS PESTICIDES IN A USGA GREEN

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The mobility and persistence of the phenoxy-acid herbicides dicamba and 2,4-D were investigated in studies on a USGA green outfitted with lysimeters for collecting percolate water. The herbicides were applied twice at one-week intervals at 58 and 6 mg A.I. m^{-2} for 2,4-D and dicamba, respectively, followed the next day by 9 mm irrigation, and by subsequent irrigations to maintain soil moisture. Samples of thatch, soil, percolate water, and clippings were analyzed for 2,4-D and dicamba. Although the dicamba application rate was only 10% that of 2,4-D, the recovery of these materials (expressed as mass) in percolate water was of the same order of magnitude, being approximately 10% of that applied for dicamba and 1% for 2,4-D. Detectable levels of both herbicides were observed in thatch and soil for several months. Very little ($\leq$ 0.25%) was recovered in clippings.

The use of reduced irrigation for one week following fenamiphos application was studied as a means of reducing fenamiphos/metabolite leaching in a USGA green. Leaching was reduced during the period of limited irrigation, but total leaching was equivalent for low and high irrigation treatments over a longer period that included plentiful irrigation and rainfall. It appeared that the fenamiphos and its metabolites that were not leached when irrigation was restricted eventually leached when excessive irrigation and rainfall occurred.

Volatilization of the organophosphate pesticides isazofos, chlorpyrifos, and fenamiphos was measured in two studies. Volatilization was greatest for chlorpyrifos, and least for fenamiphos. It was less for an application that was followed by rainfall than for one followed by dry weather. Isazofos volatilization amounted to 1 and 9% of that applied for the two rainfall situations, respectively.

The percolate collection system in the USGA green at the Ft. Lauderdale Research and Education Center was expanded to include twelve lysimeters. During excavation it was noted that 7 cm of topdressing had accumulated on the green since the lysimeters were first installed. This layer appeared to hold more water than the underlying media. It contained higher percentages of the finer sand sizes and more organic matter than the original rooting mix. No movement of rootzone mix into the coarse sand layer, or of coarse sand into the underlying gravel was observed during excavation for the newly-added lysimeters.

Fenamiphos and fenamiphos metabolite adsorption by several formulations of a stabilized organic polymer (SOP) was investigated in the laboratory and field. Significant reductions

in pesticide leaching without reductions in percolation have been obtained by the incorporation of SOP in the rootzone media. The University of Florida has applied for a patent on the SOP as a soil amendment for reducing pesticide leaching without affecting the physical parameters of a USGA green, and for other uses. A private company plans to market the product under the trademarked name "Biosand".

USGA green at the University of Florida Ft. Lauderdale Research and Education Center containing lysimeters for collecting percolate waters in studies on the mobility and persistence of pesticides applied to a USGA green. In this photo, a soil amendment is being installed in the lysimeters to test its pesticide-adsorbing characteristics.

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MOBILITY AND PERSISTENCE OF TURFGRASS PESTICIDES IN A USGA GREEN

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ABSTRACT

The mobility and persistence of the phenoxy-acid herbicides dicamba and 2,4-D were investigated in two studies conducted on a USGA green at the Ft. Lauderdale Research and Education Center that is outfitted with lysimeters for collecting percolate water. In each study, the herbicides were applied twice at one-week intervals at 58 and 6 mg A.I. m^{-2} for 2,4-D and dicamba, respectively, followed the next day by 9 mm irrigation, and by subsequent irrigations to maintain soil moisture. Samples of thatch, soil, percolate water, and clippings were analyzed for 2,4-D and dicamba.

Although the dicamba application rate was only 10% that of 2,4-D, the recovery of these materials (expressed as mass) in percolate water was of the same order of magnitude, being approximately 10% of that applied for dicamba and 1% for 2,4-D. Detectable levels of both herbicides were observed in thatch and soil for several months. Very little ($\leq$ 0.25%) was recovered in clippings.

Leaching of the pesticide fenamiphos, and especially of its metabolites, has become a concern because these compounds have been observed in groundwater and surface waters in and around golf courses. The use of reduced irrigation for one week following fenamiphos application was studied as a means of reducing fenamiphos/metabolite leaching in a USGA green in south Florida. Leaching was reduced during the period of limited irrigation, but total leaching was equivalent for low and high irrigation treatments over a longer period that included plentiful irrigation and rainfall. It appeared that the fenamiphos and its metabolites that were not leached when irrigation was restricted eventually leached when excessive irrigation and rainfall occurred.

The percolate collection system in the USGA green at the Ft. Lauderdale Research and Education Center was expanded to include twelve lysimeters. This will permit greater numbers of replications in studies involving two or more treatments, which is very important for pesticide studies. During excavation it was noted that 7 cm of topdressing had accumulated on the green since the lysimeters were first installed. This layer appeared to hold more water than the underlying media. It contained somewhat higher percentages of the finer sand sizes. It also had considerable more organic matter than either the original rooting mix or than the topdressing material. No movement of rootzone mix into the coarse sand layer, or of coarse sand into the

underlying gravel was observed during excavation for the newly-added lysimeters.

Volatilization of the organophosphate pesticides isazofos, chlorpyrifos, and fenamiphos was measured in two studies using the Theoretical Profile Shape technique. Volatilization was greatest for chlorpyrifos, and least for fenamiphos. It was less for an application that was followed by rainfall than for one followed by dry weather. Isazofos volatilization amounted to 1 and 9% of that applied for the two rainfall situations, respectively.

Evaluations of pesticide dislodgeability and subsequent risk assessments were conducted in conjunction with an M.S. graduate student. The initial study was conducted on a 'Tifdwarf' bermudagrass green overseeded with Poa trivialis to provide paired plots that were either overseeded or not overseeded. A second study was conducted with organophosphate pesticides on a bermudagrass green. Dislodgeability methods were: cheesecloth rubbed on the treated turf surfaces, cotton and leather pressed on the turf, a golf ball putted over the turf, and a club grip rolled on the turf. The pesticides also were sprayed on the fringe of the green, and cheese cloth was rubbed on the head of a club that was swung through the turf to simulate a chipping stroke. These treatments were repeated at the end of the day, and again the next morning. The pesticide analyses and risk assessments are incomplete at the time of this writing, although some data are available for the first organophosphate pesticide study. These data demonstrate rapid decreases in dislodgeable pesticides with time after application, and particularly after irrigation.

Fenamiphos and fenamiphos metabolite adsorption by a stabilized organic polymer (SOP) was investigated in the laboratory and field. The SOP adsorbed relatively non-polar pesticides well, but the more polar pesticides less well. The SOP formulation was modified to improve adsorption of less-polar pesticides. Sufficient reformulated SOP of various sand sizes has been prepared for field studies on the USGA green. The University of Florida has applied for a patent on the SOP as a soil amendment for reducing pesticide leaching without affecting the physical parameters of a USGA green, and for other uses. A private company plans to market the product under the trademarked name "Biosand".

INTRODUCTION

During the current 3-year funding period, studies were conducted on the mobility and persistence of 2,4-D, dicamba, fenamiphos and fenamiphos metabolite in a USGA green. Volatilization of isazofos, chlorpyrifos, and fenamiphos was measured under two climatic conditions. Measurements of the dislodgeability of isazofos, chlorpyrifos, fenamiphos, 2,4-D and dicamba were made by a number of different methods, including several that simulated practices that occur during play. A stabilized organic polymer (SOP) was developed for inclusion in a greens profile to reduce pesticide leaching. Papers were published on the 2,4-D, dicamba, fenamiphos, and fenamiphos metabolite mobility and persistence studies, as well as on work conducted with USGA funding prior to the current funding period. The work on pesticide dislodgeability will be completed by a graduate student. The USGA Research Committee chose to not fund our proposal on amendments for reducing pesticide leaching in golf greens, but the University of Florida is patenting the SOP and they and a private company may fund further studies involving this product.

A. MOBILITY AND PERSISTENCE OF PHENOXY-ACID PESTICIDES

METHODS AND MATERIALS

The phenoxy-acid herbicides 2,4-D and dicamba were applied to a previously described (Cisar and Snyder, 1993) Cynodon dactylon x C. transvaalensis cv. Tifdwarf USGA green at the Ft. Lauderdale Research and Education Center (FLREC) on 3 and 10 August, 1993, and again on 18 and 24 April, 1994 as sprays at the per-application rates of 0.058 and 0.006 g A.I. M^{-2}, for 2,4-D and dicamba, respectively. The area received 9 mm irrigation the day after each application, and was irrigated on subsequent dates to maintain soil moisture. The green was outfitted with six stainless-steel lysimeters for collecting percolate (Cisar and Snyder, 1993).

Soil and thatch samples were taken periodically from the plot area using a 1.9 cm-diameter nickel-plated corer, beginning on the afternoon of the first application date, and including the afternoon of the second application. Three cores were combined in each of 3 replications on each date, and each sample was divided into thatch and soil (0-15 cm soil depth). Samples were frozen prior to analysis (generally immediately after collection).

Water samples were obtained periodically using the lysimeter percolate-collection apparatus installed in the green. Fifty-three g NaCl and 10 ml 2.25 M H_2SO_4 were dissolved in 150 ml portions of each percolate sample. Then 50 ml of 70:30

hexane:ether was added, followed by 15 min shaking on a reciprocal shaker. After phase separation, the upper (organic) phase was transferred by pipeting to a 500 ml round bottom flask. The extraction process was repeated with two 40 ml additions of hexane:ether solvent and the extracts were combined in the round bottom flask. The extract was evaporated to near dryness with a rotoevaporator. The residue was transferred to a 10 ml volumetric flask in 3 aliquots of ether totaling approximately 5 ml, and the volumetric flasks were placed in a 40 C water bath until their contents reached near dryness. The 2,4-D and dicamba in the flasks were derivatized to their methyl esters by addition of 0.25 ml diazomethane-ether solution, which was synthesized in-house from 1-methyl-3-nitro-1-nitrosoguanidine in a Wheton micro-diazomethane generator. After 20 min, the samples were diluted to volume with hexane and analyzed by gas chromatography (GC) using an electron capture detector. Phenoxy-acid herbicide recovery from lysimeter water exceeded 90%.

Turfgrass clipping samples were obtained from each mowing of the treated area. A 20-g (fresh weight) subsample of each harvest was frozen for analysis. The balance of the sample was weighed, oven dried, and re-weighed to determine moisture content.

For herbicide analysis, a blender was used to masticate thatch and tissue for 3 min. in water adjusted to pH 11.6 with NaOH. The resultant slurry was vacuum filtered through Whatman 541 paper, and 150 ml portions were extracted twice with hexane:ether to remove coextractants. The aqueous phase then was extracted and processed in the manner discussed above for the percolate-water samples. Soil samples were processed in a manner analogous to the thatch and tissue, except that a shaker, rather than a blender, was used for the aqueous extractions.

RESULTS AND DISCUSSION

In both studies, peaks for concentrations of dicamba, and especially for 2,4-D, in soil and thatch were clearly observable shortly after each of the two applications in each study (Fig. 1) However, concentrations rapidly declined during the two weeks following each application, but still persisted at detectable levels for approximately two months. From 40 to 90% of the detected dicamba and 2,4-D was found in the thatch (Fig. 2). Although the difference between the two pesticides was not great, a somewhat higher percentage of 2,4-D than dicamba generally resided in the thatch layer. Shortly after each application, the percentage of 2,4-D and dicamba in the thatch was greatest, with somewhat lower thatch percentages, and therefore higher soil percentages, being observed several days after application. These data are in contrast to results presented earlier (Snyder and Cisar, 1995) for organophosphates such as fonofos, isazophos,

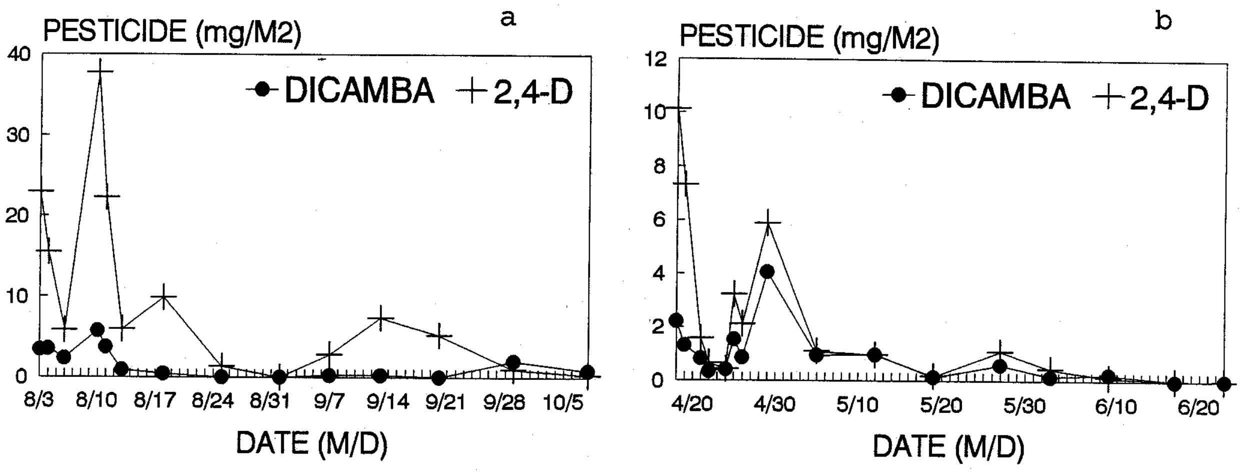

Fig. 1. Dicambа and 2,4-D in thatch and soil combined following a) application on 3 and 10 August, 1993, and b) application on 18 and 24 April, 1994.

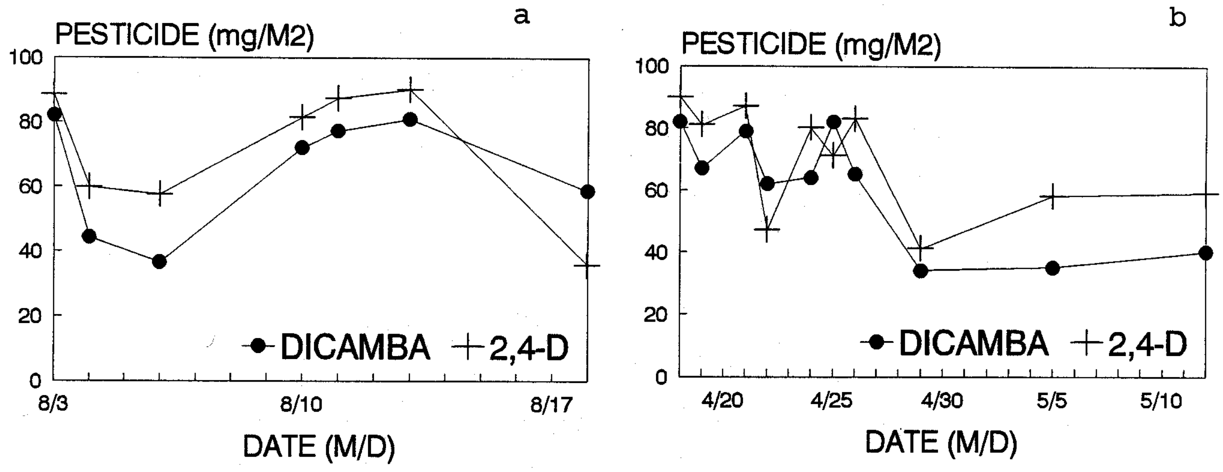

Fig. 2. Portion of dicamba and 2,4-D in thatch following a) application on 3 and 10 August, 1993, and b) application on 18 and 24 April, 1994.

chlorpyrifos, and isofenphos in which over 80% of the pesticide was found in the thatch for long periods after application.

Although only 10% as much dicamba as 2,4-D was applied, nearly 65% as much dicamba as 2,4-D was recovered in the percolate water over a 2-month period following the August 1993 applications, and over twice as much was recovered following the April 1994 applications (Table 1). Clearly, dicamba was much more mobile than 2,4-D in the USGA green. Nevertheless, considering that 508 L percolate M^{-2} was recovered, the average concentration of dicamba in percolate in 1994 was 2.5 $\mu g\ L^{-1}$ (ppb), as compared to 1.7 $\mu g\ L^{-1}$ in the 1993 study. For 2,4-D these values are 2.6 and 1.2 for the first and second study, respectively, which are well below the Maximum Contaminant Level (MCL) of 70 $\mu g\ L^{-1}$ established for 2,4-D (van der Leeden et al., 1990). There are no MCL levels for dicamba, although 70 $\mu g\ L^{-1}$ is the most limiting of several legal standards for dicamba as well (Harrison et al., 1993).

Table 1. Hydrologic data and herbicide leaching for applications on 3 and 10 August, 1993, and on 18 and 25 April, 1994.

	1993		1994	
Item	3 Aug. - 7 Oct.		18 Apr. - 23 June	
Hydrologic data (mm)	Amount	SEM[1]	Amount	SEM
Rainfall	451	-	439	
Percolation	696	50	508	50
2,4-D leaching				
$\mu g\ M^{-2}$	1808	526	611	507
% of applied	1.6	-	0.5	-
Dicamba leaching				
$\mu g\ M^{-2}$	1173	535	1290	569
% of applied	9.7	-	10.8	-

[1] Standard error of the mean

Considerably more dicamba, and especially 2,4-D, was recovered in clippings following application in 1993, than was recovered in the 1994 study (Fig. 3). Nevertheless, in both studies no more than 0.25% of the herbicide applied was recovered in the clippings (Table 2), indicating that clippings are not a major pathway for the removal of these herbicides from treated turfgrass areas.

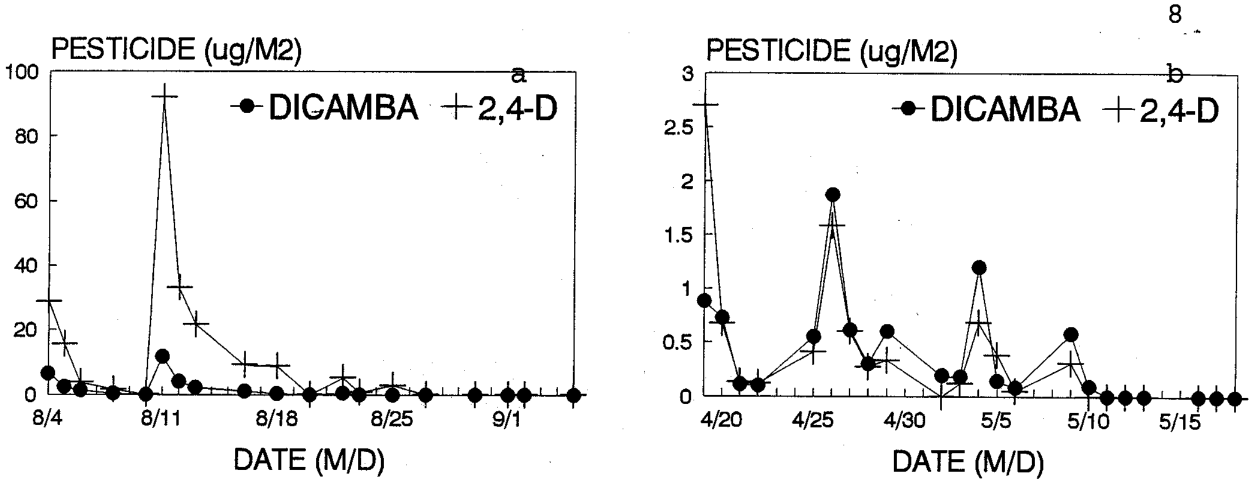

Fig. 3. Dicamba and 2,4-D in turf clipping following application on a) 3 and 10 August, 1993, and b) 18 and 24 April, 1994.

Table 2. Dicamba and 2,4-D recovery in clippings following two applications in 1993 and 1994 studies.

Study dates	Sampling period	Recovery			
		Dicamba		2,4-D	
(D/M/Y)	d	$\mu g\ m^{-2}$	%	$\mu g\ m^{-2}$	%
3/8/93 - 5/9/93	32	29.9	0.25	221.6	0.19
19/4/94 - 24/5/94	35	8.6	0.07	8.6	< 0.01

B. IRRIGATION MANAGEMENT FOR REDUCING FENAMIPHOS LEACHING

METHODS AND MATERIALS

An irrigation management study was undertaken on a previously-described (Cisar and Snyder, 1993) Cynodon dactylon x C. transvaalensis cv. Tifdwarf USGA green fitted with six stainless-steel lysimeters for collecting percolate at the University of Florida Ft. Lauderdale Research and Education Center in south Florida to evaluate the hypothesis that reducing water percolation through prudent irrigation management following fenamiphos application could reduce pesticide leaching.

On June 7, 1995 fenamiphos was applied as a 10G product across the lysimeter area at the rate of 1.12 g A.I. m^{-2}. Fenamiphos had not been applied previously to the green since 27 January, 1992. One-m^{-2} areas centered over three lysimeters received irrigation by hand using a sprinkler can twice weekly at 12.5 mm per application (Low Irrigation), and three areas received the same amount of irrigation on a daily basis (High Irrigation). Thus the Low Irrigation plots were irrigated on 7, 10, and 13 June, and the High Irrigation plots were irrigated each day. For the first 6 days of the study, the plots were covered with plywood at night to prevent irrigation by the system used to irrigate the remainder of the green, and when rain appeared imminent. Thereafter, the differential irrigation treatments and rainfall protection were suspended, with all plots receiving irrigation from the commercial sprinkler system. Percolate was withdrawn from the lysimeters daily for the first week after fenamiphos application, and at 3 to 5 days intervals for the next two weeks. The water was analyzed for fenamiphos and its metabolites (sulfoxide+sulfone) in the manner previously described (Snyder and Cisar, 1993). Thatch and soil (0-5, 5-10, and 10-15 cm depths) were samples several times weekly, and analyzed for fenamiphos and metabolite as previously described (Snyder and Cisar, 1993).

The study was repeated beginning January 16, 1996. Fenamiphos was applied to the lysimeter area in the above-described manner, except that lysimeters that were used for the Low Irrigation plots in 1995 were used for the High Irrigation plots in 1996, and lysimeters used for the High Irrigation plots in 1995 were used for the Low Irrigation plots in 1996. The Low Irrigation plots were irrigated at 12.5 mm per application on January 19, 23, and 25, and the High Irrigation plots were irrigated at the same rate, daily. Following the January 25th irrigation, all plots received routine irrigation from the commercial sprinkler system, and 52 mm of rainfall+irrigation on January 29, 1996.

RESULTS AND DISCUSSION

Fenamiphos generally was higher in thatch for Low Irrigation in the 1995 and 1996 studies, although the differences between the two irrigation treatments were not great for the relatively immobile parent compound (Fig. 4). Metabolite also was greater in thatch for Low Irrigation in both years (Fig. 5). In the deeper portion of the soil profile (10 - 15 cm), when differences occurred the metabolite was greater for High Irrigation in both years (Fig. 6). Thus the distribution of the more mobile metabolite in the soil profile suggests that the Low Irrigation treatment reduced movement out of the thatch layer into the deeper portion of the soil profile.

Analysis of the percolate water provides more direct evidence of the effect of irrigation on pesticide movement than do the soil data, although statistically-significant differences are hard to achieve for pesticide leaching-data when only three replications are available (six lysimeters divided between two treatments). For the first two weeks of the first study, before there was any significant rainfall, percolation totaled 96 and 49 mm for the High and Low irrigation treatments, respectively, which were significantly ($P < 0.05$) different (Table 3). During this period, the Low Irrigation treatment clearly reduced fenamiphos leaching during percolation events (Fig. 4a), and total fenamiphos leaching during the period was significantly reduced for Low irrigation (Table 3) However, following a 72 mm rainfall on 20 June, more fenamiphos was observed to leach from the Low Irrigation treatment than in the High Irrigation treatment (Fig. 7b).

The same trend for irrigation occurred for metabolite leaching as for fenamiphos, but with much greater amounts being observed (Fig. 8a, 8b). Note that the units used in Fig. 4 are $\mu g\ M^{-2}$, whereas in Fig. 8 they are mg M^{-2}, with the latter being 1000 times the former. Metabolite leaching was significantly lower (Table 3) for the Low Irrigation treatment for the two week period after pesticide application (Fig. 8a). However, more leaching was observed from the Low Irrigation treatment following the rainfall event on 20 June than was observed in the High Irrigation treatment (Fig. 8b). The same observation was made following a 46 mm rainfall on 23 June, i.e., more metabolite leaching occurred in the Low Irrigation treatment.

The fenamiphos and metabolite leaching data from the 1996 study were similar to that collected in 1995, except both percolation and pesticide leaching were less in 1996 (Table 3),

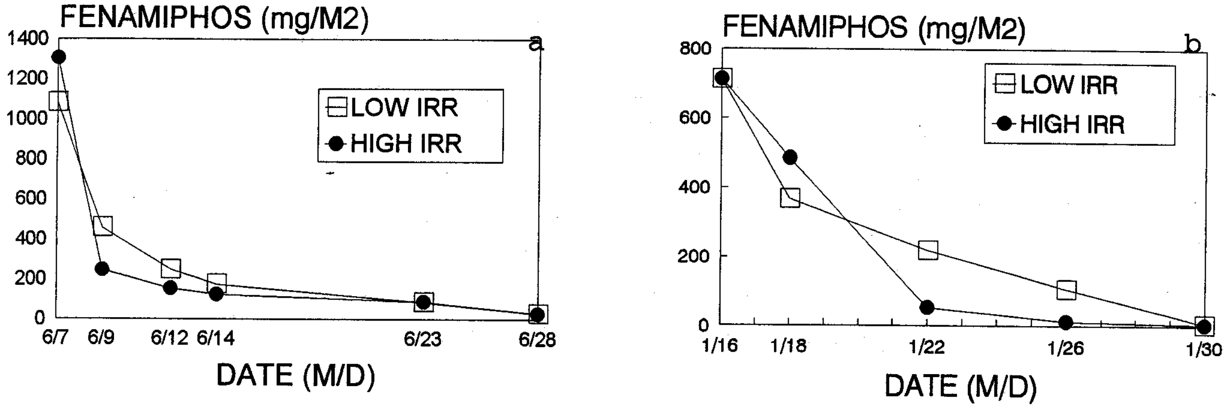

Fig. 4. Effect of irrigation on fenamiphos in thatch following application on a) 7 June 1995 and b) 16 January 1996.

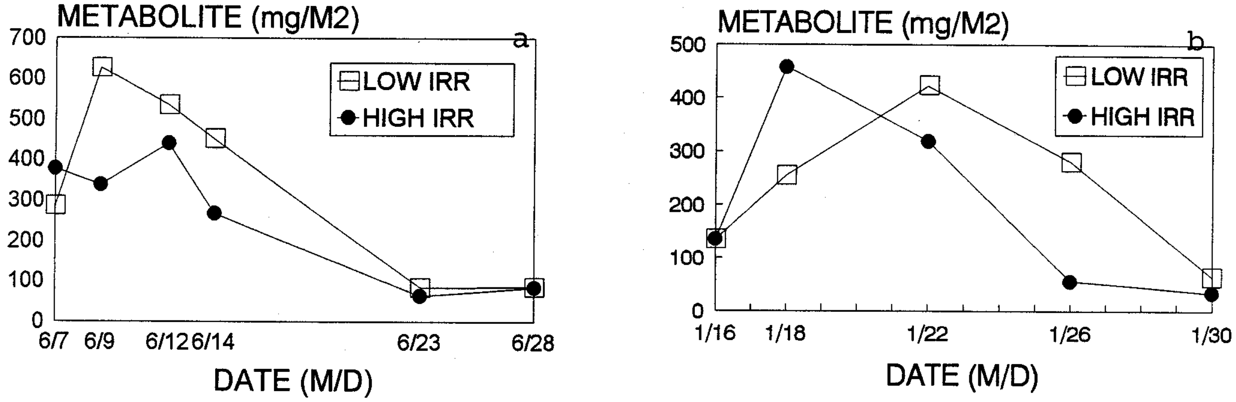

Fig. 5. Effect of irrigation on metabolite in thatch following application of fenamiphos on a) 7 June 1995 and b) 16 January 1996.

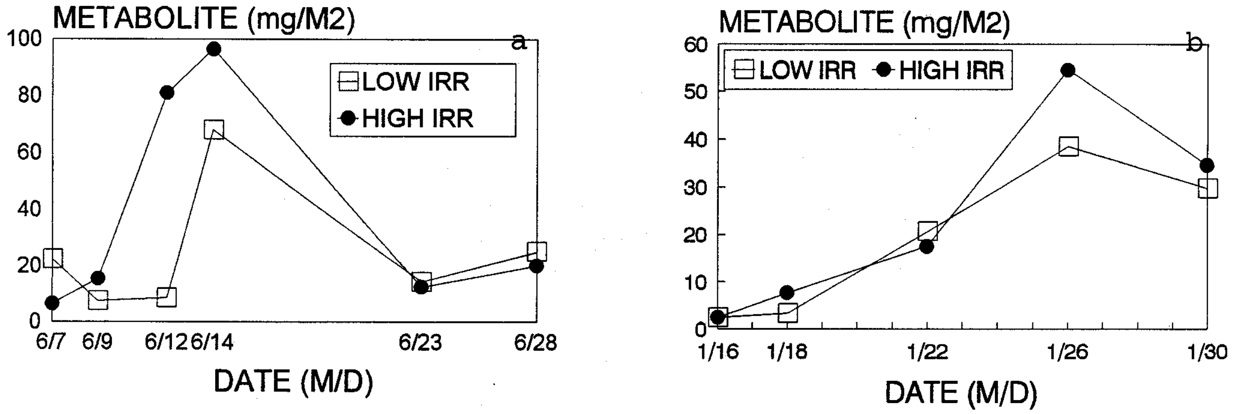

Fig. 6. Effect of irrigation on metabolite in the 10-15 cm layer following fenamiphos application on a) 7 June 1995 and b) 16 January 1996.

Table 3. Percolation and leaching of fenamiphos and metabolite during a differential irrigation/rainfall protected period (1), during a period when rainfall and irrigation were the same on all plots (2), and for the Total of the two periods (Tot).

		1995			1996		
Period	Irr.	Perc.	Fenamiphos	Metabolite	Perc.	Fenamiphos	Metabolite
		mm	ug m^{-2}	mg m^{-2}	mm	ug m^{-2}	mg m^{-2}
1	L	49	3	2	7	1	0
	H	96	78	63	25	8	1
Sig.		*	*	*	+	NS	NS
2	L	138	74	133	62	48	38
	H	167	12	78	63	25	16
Sig.		*	NS	NS	NS	NS	NS
Tot.	L	187	77	135	69	49	38
	H	263	90	141	88	33	17
Sig.		*	NS	NS	NS	NS	NS

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[1] +, *, and NS represent $p < 0.10$, 0.05, and $p > 0.10$, respectively.

which probably contributed to the general lack of statistical significance between treatments in 1996. However the trends observed in 1996 support the 1995 data. Fenamiphos leaching was reduced for Low Irrigation during the week after pesticide application when the differential irrigation treatments were used (Fig. 9a). But when appreciable irrigation and rainfall occurred on all plots, greater leaching was observed in the plots previously receiving low irrigation (Fig. 9b). Metabolite leaching in 1996 generally followed the same pattern observed in the previous year, with metabolite leaching usually being lower for the Low Irrigation treatment during the first week after pesticide application (Fig. 10a), but being greater, or nearly as great, for the Low Irrigation treatment following irrigation and precipitation on all plots (Fig. 10b).

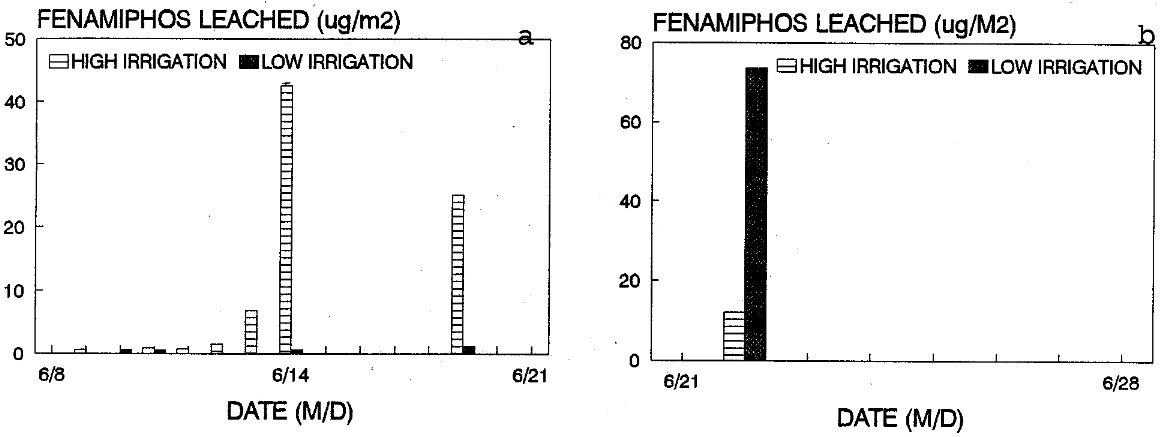

Fig. 7. Effect of irrigation on fenamiphos leaching following fenamiphos application on 7 June 1995 for a) the first two weeks after application, and b) following rainfall on 20 and 23 June.

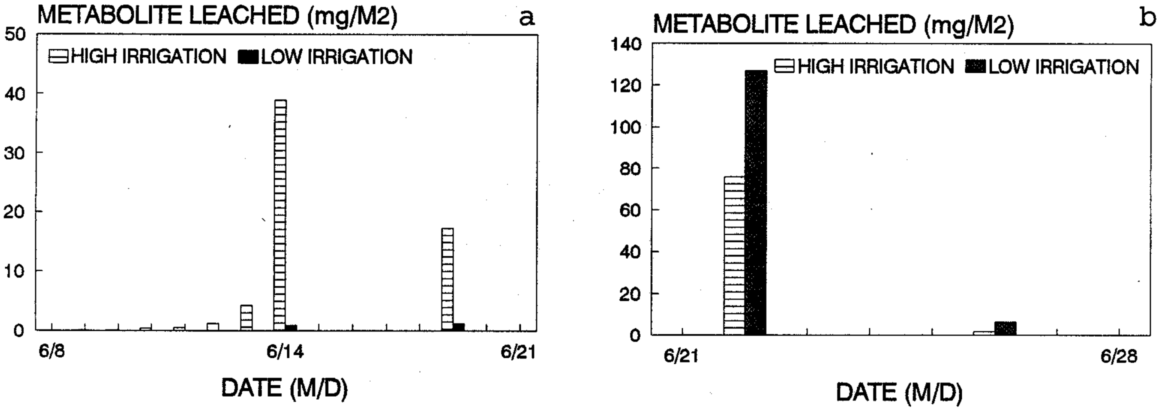

Fig. 8. Effect of irrigation on metabolite leaching following fenamiphos application on 7 June 1995 for a) the first two weeks after application, and b) following rainfall on 20 and 23 June.

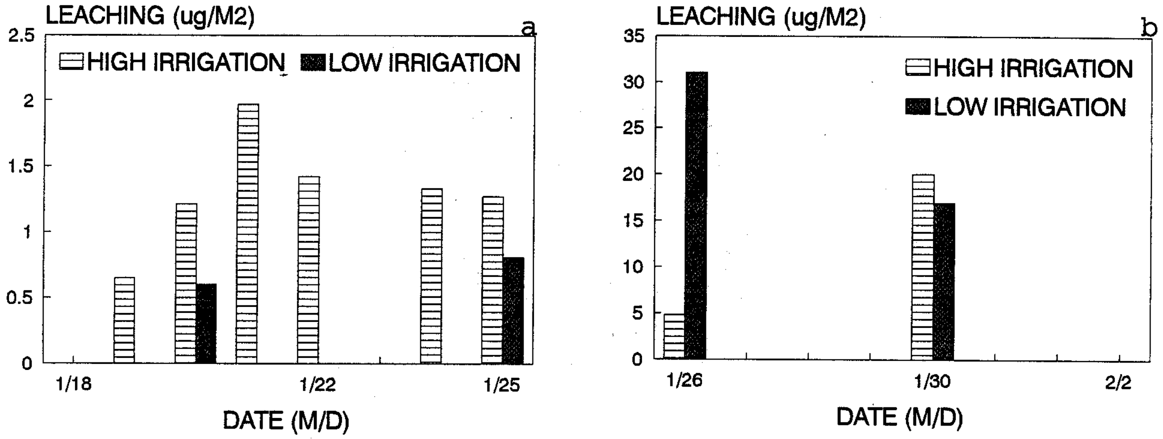

Fig. 9. Effect of irrigation on fenamiphos leaching following fenamiphos application on 16 January 1996 for a) the first week after application, and b) following exposure of all plots to routine irrigation and to rainfall.

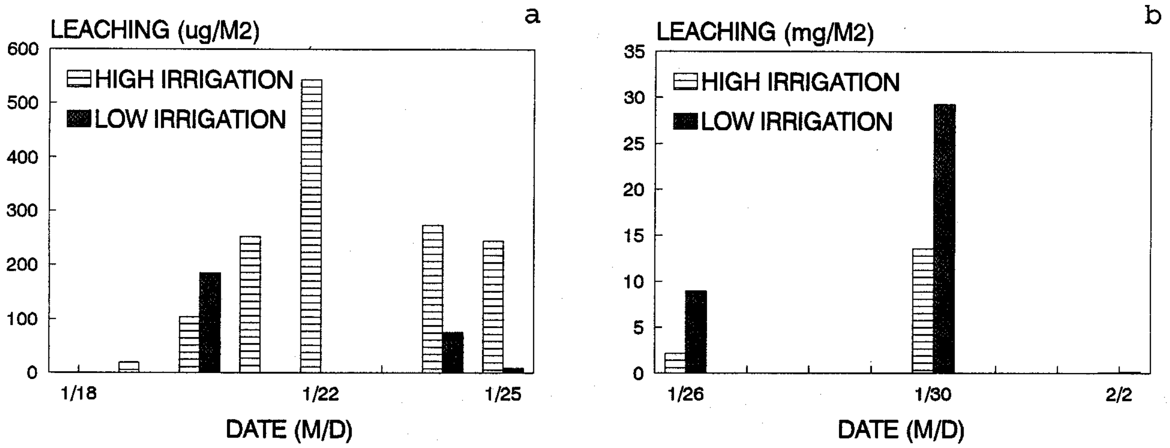

Fig. 10. Effect of irrigation on metabolite leaching following fenamiphos application on 16 January 1996 for a) the first week after application, and b) following exposure of all plots to routine irrigation and to rainfall.

In 1995, total fenamiphos leaching over the three-week period was 90 $\mu g\ m^{-2}$ for the High Irrigation treatment, as compared to 77 $\mu g\ m^{-2}$ for the Low Irrigation treatment (Table 3). In 1996 the comparative values were 33 and 49 $\mu g\ m^{-2}$, respectively. There was no statistically-significant ($p < 0.10$) difference between the treatments in either year. For the metabolites, total leaching amounted to 141 and 135 mg m^{-2} for the High and Low irrigation treatments, respectively, in 1995, and 17 and 38 mg m^{-2}, respectively, in 1996, with no significant differences between treatments in either year.

It is interesting to note that in the first study, which was conducted on a portion of the green that had not been treated with fenamiphos for 3 1/2 years, metabolite leaching averaged 12.3% of the fenamiphos applied. In 1996, it averaged only 2.1% of the applied rate of fenamiphos. The observation of considerably less leaching of metabolite following a second, closely-spaced, fenamiphos application, is consistent with the observation that fenamiphos and, presumably, fenamiphos-metabolite degrading microorganism populations increase following a fenamiphos application (Ou, 1991). The observation also is consistent with the authors' previously-published experience with fenamiphos (Snyder and Cisar, 1993), in which metabolite leaching following an initial application of fenamiphos amounted to 17.7% of the parent compound applied, whereas following the second application metabolite leaching amounted to only 1.1% of the applied rate of fenamiphos.

CONCLUSION

Both studies suggest that fenamiphos, and its more mobile metabolites, remained in the soil under the Low Irrigation treatment, but were subject to leaching when major percolation events occurred, resulting in statistically similar total leaching for the two irrigation treatments over the full length of each study. Thus it is questionable whether irrigation control alone can provide assurance against leaching of fenamiphos/metabolites in south Florida where abundant rainfall can occur at any time of the year, or in similar climates. Irrigation management might be more effective for reducing leaching of both parent and metabolite compounds in arid climates, as is evidenced by the reduced leaching observed during the period when the Low Irrigation plots were not exposed to rainfall. This theory awaits verification.

C. PESTICIDE VOLATILIZATION

While the lysimeter system was being repaired, two studies of pesticide volatilization were conducted using the Theoretical Profile Shape technique described by Jenkins et al. (1993).

Isazofos, chlorpyrifos, and fenamiphos were applied at 0.229, 0.229, and 1.125 g AI m^{-2}, respectively, to a bermudagrass green at the FLREC. Fenamiphos was applied as a granular material in the first study, and the other pesticides were applied as emulsifiable concentrates (EC). In the second study, EC materials were used for all three pesticides. Following Jenkins et al., pesticides were applied over a 20 m radius circle. Airborne residues were collected with a Staplex TF1A high volume air sampler containing Amberlite XAD-4 polymeric resin set in the center of the circle at a height of 73 cm. Wind speed was measured with a standard anemometer. In the first study, which was conducted on a cloudy, rainy day, the pesticide applications were completed by 10 AM on October 4, 1996. Resin was changed at 2 h intervals for the first six hours, and then at 18 and 24 hours. Irrigation following pesticide application totaled 0.6 cm, but 1.25 cm rainfall occurred several hours later, and another 2.69 cm fell during the evening and night of the same day. In the second study, which was conducted on a clear day, pesticides were applied by 10:30 AM on October 10, and resin was changed hourly for the first six hours, after one-half hour of exposure, and then left in place overnight for an additional 14 hours. Irrigation totaling 0.6 cm followed application of the pesticides, and there was no rainfall. Pesticides were extracted from the resin with methylene chloride and analyzed by GC.

RESULTS AND DISCUSSION

Volatilization of all three pesticides decreased rapidly with time after application, (Fig. 11 and 12). Total volatilization was considerably greater in the second study, which was conducted on a clear day, than on the first (Table 4).

Table 4. Volatilization of isazofos, chlorpyrifos, and fenamiphos following application to a bermudagrass green on two dates.

	Application date			
Pesticide	October 4[a]		October 10[b]	
	mg m^{-2}	% of applied	mg m^{-2}	% of applied
Isazofos	2.38	1.04	20.93	9.14
Chlorpyrifos	6.13	2.66	26.54	11.59
Fenamiphos	0.40	0.04	2.8	0.25

[a] Collected over a 48 hour period on a cloudy, rainy day.
[b] Collected over a 22 hour period on a clear day.

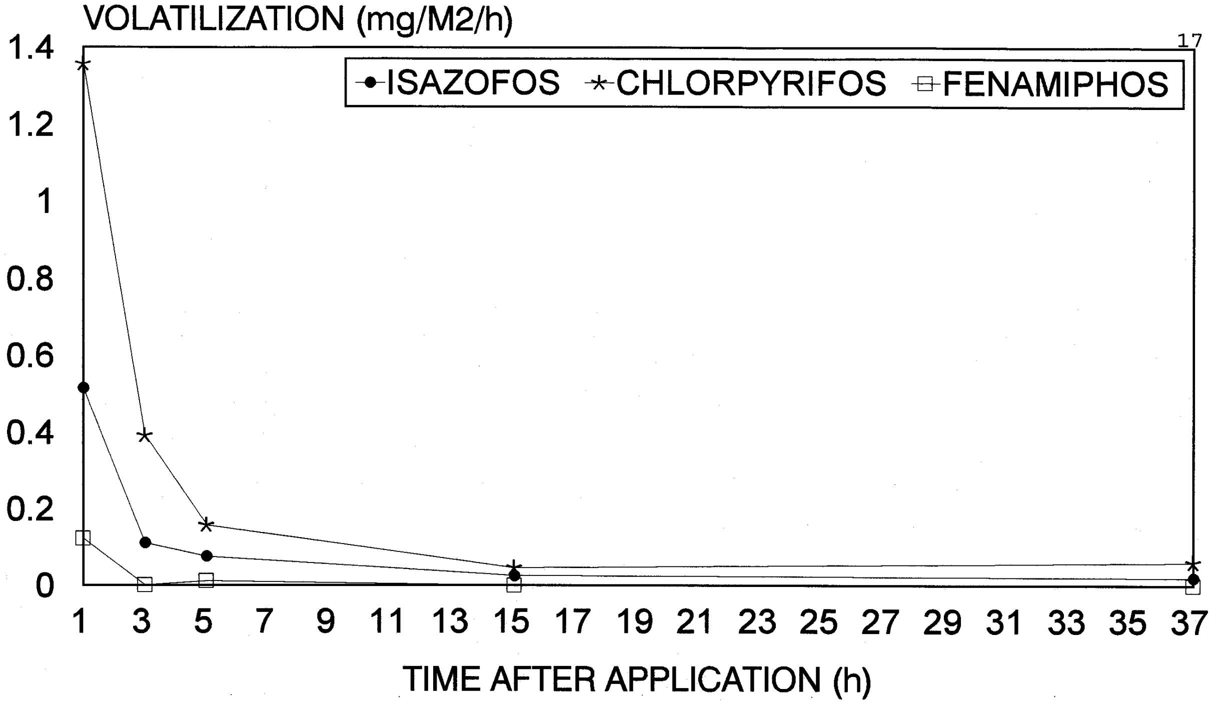

Fig. 11. Volatilization of isazofos, chlorpyrifos, and fenamiphos during a rainy, cloudy period.

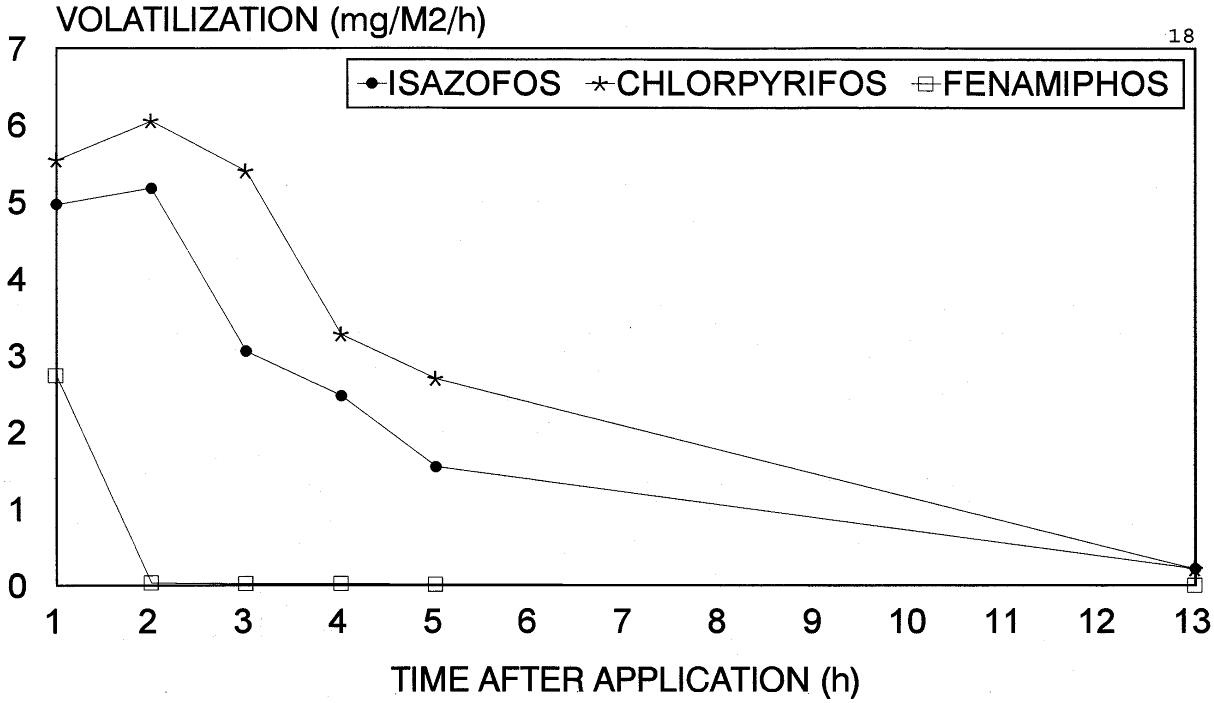

Fig. 12. Volatilization of isazofos, chloropyrifos, and fenamiphos during a clear, dry period.

The differences in rainfall and sunshine between the two studies easily account for the differences in volatilization that were observed. Using the same application rate and sampling technique, Cooper et al. (1955) reported isazofos volatile loss of 5.8% during the first day after application. Since their study was conducted in August and their irrigation was greater (1.25 cm) than ours in the second study, but less than the irrigation+rainfall that occurred in our first study, the values obtained for isazofos in our studies appear to agree well with that obtained by Cooper et al. Nevertheless, we feel that our application of the technique requires further verification, particularly in regards to concerns we have about possible incomplete trapping of the pesticides by the resin. Then, additional volatilization studies will be conducted.

D. PESTICIDE DISLODGEABILITY STUDIES

We are collaborating with an M.S. graduate student, Raymond Snyder, who received the G. C. Horn Memorial Scholarship from the Florida Turfgrass Association. Dr. Cisar is his major professor. The M.S. project concerns pesticide dislodgeability studies related to golf turf that will include risk assessment analyses. The initial study was conducted on the 'Tifdwarf' bermudagrass USGA green at the Ft. Lauderdale REC that was overseeded with Poa trivialis to provide five replications of randomized, paired plots that were either overseeded or not overseeded. As soon as possible after application of dicamba and 2,4-D, the following dislodgeability treatments were initiated: cheesecloth rubbed on each of the treated turf surfaces, cotton and leather pressed on the turf, a golf ball putted over the turf, and a club grip rolled on the turf. The pesticides also were sprayed on the fringe of the green, and cheese cloth was rubbed on the head of a club that was swung through the turf to simulate a chipping stroke. These treatments were repeated at the end of the day, and again the next morning. The various materials and objects exposed to the pesticide-treated grasses will be analyzed for dicamba and 2,4-D.

A similar study that involved organophosphate pesticides (isazofos, chlorpyrifos, and fenamiphos) applied to the bermudagrass green without overseeding was conducted in June, 1997, with a follow-up study in October.

The 2,4-D and dicamba analyses have been delayed because of concerns by our University of Florida Safety Office over our use of ether. This situation has been resolved, and the analyses are being performed at the time of this writing. Some data are available for the first organophosphate pesticide study. These data demonstrate rapid decreases in dislodgeable pesticides with time after application, and particularly after irrigation. For example, cheesecloth wiped vigorously on turf at one-minute intervals following application dislodged 295, 236, 200, 182, and 55 ug isazofos per sample, respectively (each wipe occurred on a portion of the turf that was not wiped before). One hour after an irrigation an average of 11 ug/sample was obtained, and only 3 ug was obtained the next morning. Other methods of dislodging pesticides produced less pesticide, except that some relatively high values were found on cotton cloth used to wipe the head of a club that had been used to simulate chipping a ball out of high grass. Additional analyses and the risk assessment based on the analyses will be complete by the graduate student as part of his MS program.

E. LYSIMETER SYSTEM REPAIR AND EXPANSION

During the spring and early summer of 1996, problems developed with the lysimeters on the USGA green at the FLREC such that percolate extraction from some lysimeters became irregular, and in some cases the water samples were clouded with soil and organic matter. A number of attempts were made to correct the problem in situ, without success, so the lysimeters had to be excavated to locate the problem. It was discovered that silver-soldered joints in certain extraction lines had developed leaks. The fittings were replaced with stainless-steel compression fittings. While the lysimeter system was under repair, an additional six lysimeters were installed. One lysimeter was added to the west side of each of the three existing east-west rows, and a new row of three lysimeters was added to the north side of the existing rows. There now are twelve lysimeters in all, making it possible to conduct experiments with six replications of two treatments or four replications of three treatments, where before there could be only three replications of two treatments, which really are not enough for pesticide studies. Specially-modified switching valves were purchased so that the six stations for collecting percolate within the shed on the edge of the green could accommodate twelve lysimeters.

During the excavation process, it was noted that the soil surface was approximately 7 cm higher than at the time of the original lysimeter installation, presumably due to frequent topdressing of the green. The accumulated layer was noticeable because it was darker in color and appeared to contain more moisture than the underlying soil. The organic matter content and particle size distribution were determined for the accumulated layer and for the topdressing material that has been used consistently for the past several years, and compared with the original rootzone mix (Table 5). Although the total of the MS and CS fractions does not vary greatly among the three

Table 5. Organic matter content and particle size distribution of the FLREC USGA green original rooting media, topdressing sand, and accumulated topdressing layer.

Particle size		Original	Topdressing	Accumulation
Designation	mm		%	
Gravel	>2.0	0	0.3	0
VCS	1.0-2.0	17.0	9.6	6.9
CS	0.5-1.0	59.3	48.0	44.6
MS	0.25-0.5	18.2	34.1	32.6
FS	0.10-0.25	4.6	7.9	14.9
VFS	0.05-0.10	0	0	0.6
Silt	<0.05	0	0	0.6
Total CS+MS		77.5	82.1	77.2
Organic matter		0.7	0.9	4.7

materials, the topdressing has roughly half the VCS, less CS, and approximately and twice the MS and FS as the original soil, making it finer textured and more conducive to water retention. The accumulated layer reflects this shift in particle size distribution which, along with the accumulated organic matter, may account for the darker color and apparent greater water-holding capacity of the accumulated layer. When the sod above the old and new lysimeters was removed, the accumulated layer was removed with the grass. The combination will be replaced, thereby maintaining the character of the entire green above the lysimeters.

During lysimeter excavation, it also was noted that there was no visible migration of rootzone mix into the coarse sand (choker) layer, or of coarse sand into the gravel layer. The boundaries were clean and sharp, indicating that the layers were properly sized and stable in this green.

F. PESTICIDE ADSORPTION WITH SOP - LABORATORY STUDIES

A stabilized organic polymer (SOP) was made from sugarcane filter-cake stabilized with a phenol-formaldehyde polymer. The resulting material was crushed and graded into particles corresponding to very coarse sand (1.0-2.0 mm), coarse sand (0.5-1.0 mm), and medium sand (0.25-0.50 mm).

Due to the unavailability of fenamiphos metabolite (sulfone), a protocol was developed for synthesizing sulfone in a pure crystalline form from fenamiphos. Fenamiphos was oxidized with aqueous potassium permanganate and the resultant sulfone was extracted into methylene chloride. After evaporation of the solvent, the crude sulfone was solubilized in ethanol:water (65:35). This solution was extracted with hexane:ether (50:50) to remove coextractants, the sulfone remaining in the ethanol:water phase. Pure (92%) sulfone crystals created by enrichment of the ethanol:water with water were isolated by filtration.

The adsorption capacity of various size grades of SOP for fenamiphos and fenamiphos metabolite was determined in 1.25 cm diameter glass columns containing 10-cm sections of 15% (v/v) SOP mixed in a USGA-sand. An excess of fenamiphos (11 mg) and metabolite (12 mg) was applied at the top of separate columns (4 replications for each organophosphate) and leached into the profile with small increments of water. Then the columns were flushed with two, 50 ml portions of water. Each resultant leachate was analyzed for fenamiphos or metabolite by placing 200 μl of leachate into 10 ml methylene chloride. After adding anhydrous sodium sulfate and shaking, the methylene chloride:organophosphate mixes were decanted into vials for analysis by gas chromatography. Adsorption was calculated as the difference between organophosphate applied minus that obtained in the total leachate. A similar adsorption capacity experiment was conducted for coarse-sand size activated charcoal and for the inorganic soil amendment "Profile".

The charcoal and inorganic amendment displayed little pesticide-retention capacity (Table 6). The finer sizes of SOP retained appreciable quantities of fenamiphos and sulfone. If a layer of 0.5 mm diameter SOP particles two particles deep were contained within the profile, the total volume of the SOP would be approximately 1 liter m^{-2}. Since the recommended rate of fenamiphos is 1125 mg m^{-2}, it appears that the 2-particle layer could absorb an entire application rate of fenamiphos or metabolite (Table 6). However, in previous studies, less than 1% of the applied fenamiphos and no more than 18% of the metabolite leached (Snyder and Cisar, 1995), which indicates that even a small amount of SOP could absorb leachate from numerous applications of fenamiphos.

It is not proposed that SOP be placed in a single layer within the rootzone, but rather it be mixed into the lower portion of the rootzone mix, below the probable location of target organisms. It is statistically improbable that percolation water carrying pesticide would encounter two SOP granules when mixed at the rate of 1 liter m^{-2} (1% by volume in a 10 cm layer). A column study was conducted to determine the effect of SOP concentration in a 10 cm layer of USGA-sand on the adsorption of fenamiphos metabolite (sulfone). The study was conducted in a manner analogous to the study described above for determining the adsorption capacity of the SOP, except that an application rate of 1.125 g AI m^{-2} was used instead of an "excess". Based on this study, it appeared that SOP needs to be incorporated at a rate of 15% (v/v) to adsorb an amount of sulfone nearly equal to the normal application rate of fenamiphos (Fig. 13). The indication that this higher rate is required to assure contact between the SOP and the percolate, and is not due to poor adsorption of the metabolite by the SOP, was confirmed when an amount of SOP equivalent to a 1% rate was placed directly on the top of a soil column and treated directly with a solution of metabolite at the 1.125 g AI m^{-2} rate. During subsequent percolation events, no metabolite was recovered in the percolate (data not presented).

Table 6. Adsorption capacity for fenamiphos and fenamiphos sulfone of various SOP grades, charcoal, and Profile.

Material*	Fenamiphos	Sulfone	Fenamiphos	Sulfone
	mg g^{-1}		mg L^{-1}	
SOP-VCS	2.39	0.69	1434	414
SOP-CS	2.30	1.97	1380	1182
SOP-MS	2.39	2.27	1434	1362
CS-Charcoal	0	0	0	0
Profile	0	0	0	0

* VCS = 1-2 mm, CS = 0.5-1.0 mm, and MS = 0.25-0.50 mm.

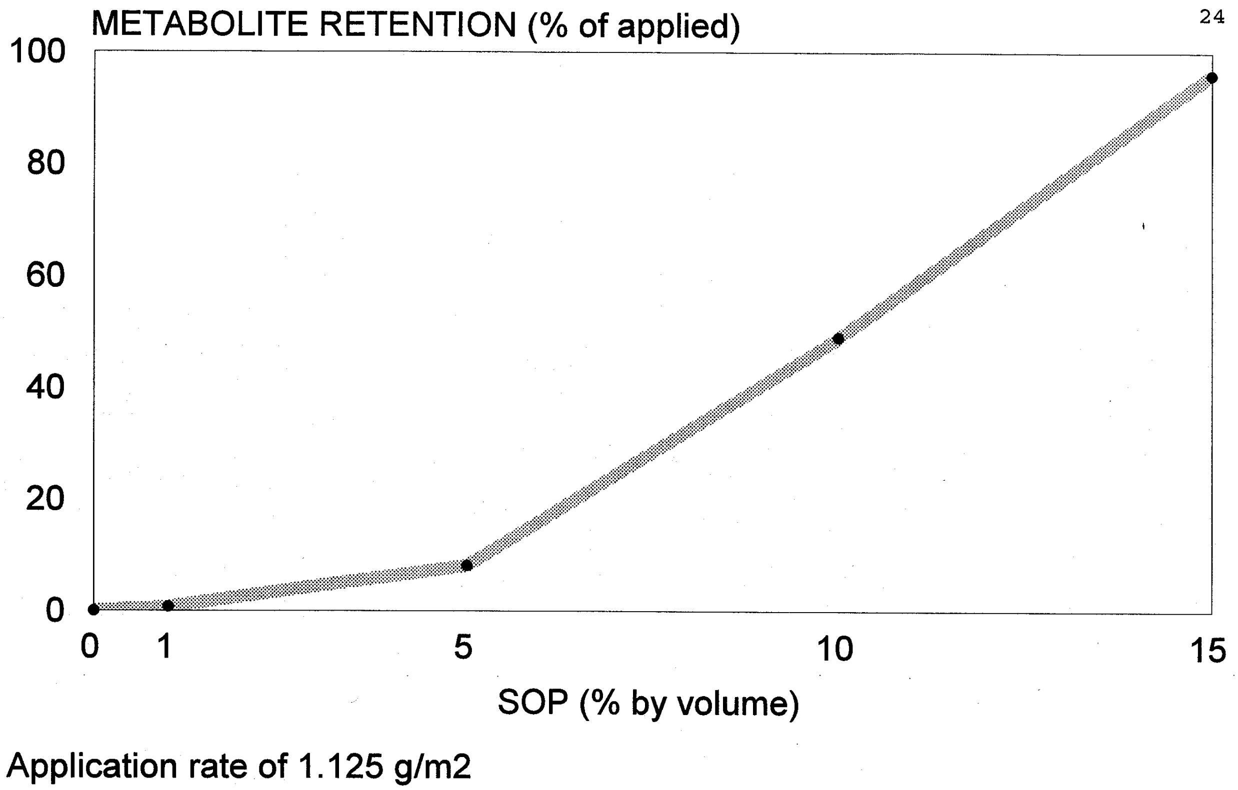

Fig. 13. Effect of SOP on retention of fenamiphos metabolite applied at 1.125 g AI m^{-2}.

G. PESTICIDE ADSORPTION WITH SOP - FIELD STUDIES

The percolate collection system in the USGA green at the Ft. Lauderdale Research and Education Center was expanded during the summer of 1995 to include twelve lysimeters. A stabilized organic polymer (SOP) was made from sugarcane filter-cake (FC) stabilized with a phenol-formaldehyde polymer and polyvinyl chloride (PVC). The resulting material was crushed and graded into batches of particles corresponding to very coarse sand (1.0-2.0 mm), coarse sand (0.5-1.0 mm), and medium sand (0.25-0.50 mm). From these batches, a mix was made to correspond to the particle size distribution found in the USGA green at the Ft. Lauderdale-REC.

In November, 1996, gravel, coarse (choker) sand, and rooting mix were added to six of the twelve lysimeters on the green to reproduce the soil profile in the vicinity of each lysimeter. Soil profiles in the other six lysimeters were similarly constructed, except that the graded SOP was mixed 15% by volume in the lower 10 cm of the rooting mix. Lysimeters were arranged in random fashion to provide six blocks of paired profile treatments (± SOP).

After the sod over the lysimeters became established, fenamiphos was applied as a liquid to the lysimeter area at the label rate of 1.12 g A.I. m^{-2}. The area was irrigated following application, and maintained as a golf green. Percolate was collected from the lysimeters four times during the ensuing 28 days, and analyzed for both fenamiphos and fenamiphos metabolite (sulfoxide + sulfone).

The SOP had no effect on the amount of percolate collected during the study (Table 7). As we have observed previously, considerably more metabolite than parent fenamiphos was found in the percolate. Only 11% as much fenamiphos leached in the SOP treatment as leached in the unamended soil profile. Considerably more metabolite leached in the unamended soil than was observed in previous studies (Snyder and Cisar, 1993). Nevertheless, SOP significantly ($p < 0.05$) reduced metabolite leaching 66%. We have some concern that the lysimeters were not fully drained before the start of the study, resulting in at least a portion of the soil profile being saturated with water. This may have contributed to the very high pesticide leaching that was observed.

Table 7. Effect of a stabilized organic polymer (SOP) on percolation and leaching of fenamiphos and fenamiphos metabolite.

SOP	Percolate	Fenamiphos		Metabolite	
	cm	ug M^{-2}	% of applied	ug M^{-2}	% of applied
+	35.3	5,900	0.49	167,300	13.9
-	34.6	52,500	4.37	495,400	41.3

The herbicides dicamba and 2,4-D were sprayed on the lysimeter area two times, one week apart, at the label rates of 6 and 58 mg A.I. m^{-2}, respectively. The plots were first irrigated one day after application, and were maintained as a golf green thereafter. Percolate water in the lysimeters was collected five times over a 37-day period and analyzed for dicamba and 2,4-D.

As was found in the fenamiphos study, SOP had no effect on the amount of percolation (Table 8). The percolation results in both studies are consistent with the expectation that if the SOP were sized to match the sand sizes in the rooting mix, it would not alter the hydrological characteristics of the green. In agreement with our previous studies (Snyder and Cisar, 1997), although the application rate of dicamba was only one tenth that of 2,4-D, nearly as much dicamba as 2,4-D was found in the percolate (Table 8). SOP did not reduce leaching of either pesticide.

Table 8. Effect of a stabilized organic polymer (SOP) on percolation and leaching of dicamba and 2,4-D.

SOP	Percolate	Dicamba		2,4-D	
	cm	ug M^{-2}	% of applied	ug M^{-2}	% of applied
+	22.6	2301	19.2	5427	4.7
-	24.8	2409	20.1	3006	2.6

The data clearly illustrate that pesticide retention by the SOP, as constituted, varied with the polarity of the pesticides (polar molecules are more soluble in water, which is a polar molecule itself, than are non-polar molecules). Adsorption was greatest for fenamiphos, which the least polar of the pesticides tested. Less adsorption was found for the fenamiphos metabolites, which are more polar than the parent compound, and the most polar pesticides, dicamba and 2,4-D, were not adsorbed by the SOP. It should be noted that fenamiphos, dicamba, and 2,4-D were chosen for study because a) in previous experiments they have been observed to leach in a USGA green, b) they represent a range of polarities, and c) we are experienced in their analysis. Other pesticides that may be of interest in turfgrass management have polarity characteristics similar to or comparable with one of the pesticides used in our studies.

H. IMPROVING ADSORPTION OF HIGHER-POLARITY PESTICIDES

The revision in the formulation of SOP has involved two phases of work: 1) Development of an adsorbent, and 2) development of a granular delivery system.

A series of adsorbent-formulation experiments were conducted with dicamba, 2,4-D, and fenamiphos sulfone (FS). In order to simplify the chemistry of adsorption to better understand the underlying mechanisms, studies were conducted with silica sand coated with various polymers in addition to modifications of the sugarcane filter-cake (FC) based SOP.

Two methods were used for determining the effect of various treatments on pesticide adsorption: batch and column. By the batch method, 10 g of candidate adsorbent along with 40 ml water and pesticide was placed in a 50 ml glass tube. After shaking for 1 hr, the filtrate was collected. Pesticide in the extract of the filtrate was analyzed by gas chromatography (GC). For the column method, glass tubes 6 x 30 cm were packed 10 cm deep with medium-size silica sand amended 15% (v/v) with candidate adsorbent. Pesticide was placed on the surface, followed by 10 ml water. After 1 hr, six 50-ml aliquots of water were added to the tubes to leach pesticide. Pesticide in the combined leachate was extracted and analyzed by GC.

The SOP used in the field was formulated with polymers synthesized in-house. In contrast, one set of lab experiments was conducted with SOP formulated with commercially-available polymers. Both polymer type and polymer concentration were investigated. It was determined that the PVC added to increase the mechanical strength of the SOP used in the field was unnecessary when using commercially-available phenol-formaldehyde resin (PFR), and actually decreased adsorption. By the batch method in the lab, SOP formulated with commercially-available PFR adsorbed dicamba and 2,4-D, and significantly more so in the absence of added PVC. The optimal PFR concentration, maximum FC moisture content, maximum pH, and proper curing temperature were determined. Furthermore,in the field, it was noted that for some time after SOP was incorporated into the lysimeter soil, percolate water was brownish in appearance. Phenol was detected