TITLE: Mobility and Persistence of Turfgrass Pesticides in a USGA Green

INVESTIGATORS:

John Cisar, Ft. Lauderdale Res. Center, Univ. of Florida
George Snyder, Everglades Res. and Ed. Center, Univ. of Florida

1991 Funding: $ 45,000

CLIMATIC REGION: Warm Humid
USGA REGION: Florida

MOBILITY AND PERSISTENCE OF TURFGRASS PESTICIDES IN A USGA GREEN

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

EXECUTIVE SUMMARY

The first-year project objectives were to construct, install, and test lysimeters for collecting percolate water in a USGA-type green, to evaluate various methodology practices for pesticide analysis, to develop a quality assurance and control (QA/QC) program, and to engage in preliminary data collection. These objectives have been completed.

Stainless-steel lysimeters were installed in a USGA-type green at the University of Florida, IFAS, Ft. Lauderdale Research and Education Center. They were fitted with stainless-steel lines for off-site collection of percolate water. Lysimeter performance was tested in three ways to determine the completeness of sample recovery and to investigate the effect of sample residency time. It was determined that recovery equaled or exceeded 97%. The concentration of fenamiphos (nemacur) remained virtually unchanged after 4 days residency in the collection reservoir, whereas after 1 and 4 days residency, diazinon was only 94 and 0%, respectively, of that injected.

A 19-section, 33-page quality assurance/quality control plan was developed to delineate field and laboratory protocols for such items as sampling, calibration, error determinations, chemical analyses, data reduction and validation, corrective actions, and reporting.

Methods were validated for determining certain organophosphate pesticides in percolate water, thatch, soil, and grass clippings.

In a preliminary field study, fenamiphos applied to bermudagrass (Cynodon sp.) turf was observed primarily in thatch over a 7-day period. Fenamiphos in the underlying soil generally was only 10% that in the thatch, and seven days after application, fenamiphos in thatch was only 10% that observed two days after application.

A. TIMETABLE

Notice of acceptance of the project "Mobility and Persistence of Turfgrass Pesticides in a USGA Green" by the USGA Environmental Research Committee was mailed out on December 20, 1990. A project starting date of February 1, 1991 was assigned by the Committee. The first funding, however, was not mailed out until July 16, 1991, just 3-1/2 months before the Annual Report due date (November 1, 1991). Nevertheless, by using borrowed in-house funds, virtually all of the first-year objectives have been met. Quoting from the project proposal, the first-year objectives were: "It is anticipated that the lysimeters will be constructed, installed, and tested in the first year, that various methodology practices will be evaluated, a quality assurance and control (QA/QC) program will be established, and preliminary data collection will be completed".

B. QUALITY ASSURANCE (QA) QUALITY CONTROL (QC) PLAN

A QA/QC plan was developed and implemented for the study (see attachments, Section G). The nineteen-section plan describes the project scope, methodology, and steps taken to both assure and control the quality of the data generated in the study.

C. TEST SITE SOIL CHARACTERIZATION

The study is being conducted on a USGA-type green built at the University of Florida, IFAS, Ft. Lauderdale Research and Education Center by the Palm Beach and South Florida Chapters of the Florida Golf Course Superintendents Association, in consultation with Mr. John Foy, USGA Green Section Southeastern Region Agronomist for Florida. Prior to installation of lysimeters that will be used for collecting percolate water, "undisturbed" soil was sampled with a specially designed tool that removes soil cores 5.4 cm diameter and 3.0 cm deep encased in brass rings. The cores were centered on the 5 and 15 cm depths in each of the six proposed locations for lysimeter installation. The samples were analyzed for particle size, bulk density, saturated hydraulic conductivity, and for volumetric water content at various matric potentials by the University of Florida Soil Science Department Soil Characterization Laboratory.

Based upon the soil analysis, it appears that the soil mix is somewhat more coarse than was anticipated (Table 1). USGA recommendations call for most of the sand used in the soil mix to be between 0.25 and 0.75 mm (Specifications for a Method of Putting Green Construction, USGA). Most of the sand in the green at Ft. Lauderdale is in the upper end of this range or somewhat above it. For this reason, the 40-cm water retention capacity is lower than the recommended USGA specification of 12 to 18% by weight. On a weight basis, the 45-cm water retention capacity is

5.4 and 4.9% for the 5 and 10-cm depths, respectively (retention by volume divided by bulk density = retention by weight). The bulk density of the soil mix is somewhat higher than the maximum USDA recommended value of 1.60 g cm^{-3}. Judging by the relatively low standard deviations (sd), all measured parameters appear to be fairly uniform among the six lysimeter sites (Table 1).

Table 1. Physical analysis of soil present in the experimental site.

	Sample depth (cm)			
	5		15	
Parameter	Mean	sd	Mean	sd
Sand size (mm)	- - - - - - % - - - - - - -			
Very coarse (2.00-1.00)	17.0	1.7	18.9	2.1
Coarse (1.00-0.50)	59.3	1.4	58.4	1.1
Medium (0.50-0.25)	18.2	1.6	17.7	1.9
Fine (0.25-0.10)	4.6	0.7	4.3	1.2
Very fine (0.10-0.05)	0	-	0	-
	- - - - - - g/cc - - - - - -			
Bulk density	1.72	0.0	1.68	0.0
	- - - - - - cm/hr - - - - - -			
Sat. hydraulic conductivity	114	13	134	20
	- - - - - - - % - - - - - - -			
Volumetric water content				
20 cm pressure	14.3	0.4	12.9	1.7
30 "	11.0	0.3	10.0	0.9
45 "	9.3	0.2	8.2	0.6
60 "	8.2	0.2	7.2	0.5
80 "	7.5	0.1	6.6	0.5
100 "	6.9	0.1	6.2	0.4
150 "	6.1	0.1	5.6	0.4
200 "	5.6	0.2	5.3	0.4
345 "	5.6	0.3	4.4	0.3
15000 "	0.7	0.1	0.8	0.2

D. LYSIMETERS

The stainless-steel lysimeters were installed in August, 1991, in accordance with the QA/QC plan (Sections 6.1.1 and 6.1.2). A videotape record was made of all phases of the lysimeter installation, and a 15-min VHS-format video has been produced for use in presentations on the USGA project. A small metal building with electricity was erected adjacent to the green to house the water-sample collection apparatus and certain other equipment used in the project. The lysimeters were tested as described in the QA/QC plan (Sections 11.1.1, 11.1.2, and 11.1.3).

Lysimeter function was evaluated in three ways. Gross quantitative recovery (QA/QC Section 11.1.1) was determined by adding 1 L of water to each of several lysimeters after the sample lines were in place but before adding the soil. The water in the bottom of the lysimeter was evacuated through the sample line and collected in a 2 L flask inside the building that houses the sampling apparatus. Near quantitative recovery of added sample water was observed (Table 2).

Table 2. Gross quantitative recovery of added water

Lysimeter	Amount added	First addition	Second addition	Third addition
	- - - - - - - - ml - - - - - - - - - -			
A	1000	970	975	965
B	1000	945	1000	987
B	500	508	-	-
C	1000	980	990	990
D	1000	970	1000	1000
E	1000	960	985	1000
E	500	495	-	-
F	1000	975	990	980
Mean recovery (%)		98	99	99

It is probable that some water remains in the lysimeter reservoir and sample line after any given sampling. To examine this matter, water spiked with a green dye was used to determine the carry-over of sample solution between successive additions of sample water (QA/QC Section 11.1.2). One liter of dye-spiked water was added to the empty lysimeter and withdrawn through the sample line. This was followed by 1 L of clear water, which was withdrawn and followed by a third 1 L portion that also was withdrawn. The intensity of green color in the second and third withdrawals, compared to that of the first, provided an

estimation of the amount of sample that is carried over from one sampling to the next. Nearly 1 L of sample was obtained in each sampling (data not presented), in agreement with Table 2. Carry over was found to be slight, averaging less than 3% in the first sampling after the dye addition and 0.1% in the second (Table 3).

Table 3. Color intensity of successive water samples after addition of 1 L of dye-spiked water followed by two 1 L additions of clear water.

Lysimeter	First sample	Second sample	Third sample
	- - - - - - % of First - - - - - -		
A	100	3.4	0.0
B	100	2.2	0.1
B	100	3.4	0.2
B	100	2.1	0.1
Average	100	2.8	0.1

To determine the effect of residency time within the lysimeter reservoir on pesticide recovery, a solution containing Nemacur and Diazinon was injected into each of the six soil-filled lysimeters through the sample line by means of a small water pump (QA/QC Section 11.1.3). Sample was withdrawn from two lysimeters within one hour after injection. Sample was withdrawn from two other lysimeters the following day, and sample was withdrawn from the remaining two lysimeters four days after injection. The samples were extracted with methylene chloride on the day of sampling, as outlined in QA/QC Section 9.1.1 analyzed as outlined in QA/QC Section 9.2.1. From this study it can be concluded that Nemacur samples can remain within the lysimeter reservoir for at least four days before sampling with no loss of pesticide, but substantial loss of Diazinon from the reservoir water occurs after the first day (Table 4).

E. LABORATORY

A 1200 square foot pesticide analysis laboratory has been established at the Everglades Research and Education Center primarily for use on turfgrass studies. A new Hewlett-Packard model 5980A gas chromatograph with autosampler was purchased with non-USGA funds, and additional instrumentation, equipment, and supplies for conducting pesticide analyses have been secured. A chemist and an agricultural technician have been hired for the

project.

F. METHODOLOGY

Methods have been established for collection of percolate water, soil, and thatch samples. A tentative method has been tested to evaluate pesticide dislodgeability and equipment has been obtained for determining airborne residues. Analytical methodology has been developed for measuring organo-phosphate (OP) pesticides in water, soil, thatch, and on cloth. These methods are detailed in the QA/QC report, attached herein.

Table 4. Effect of residency time on Nemacur and Diazinon concentrations in lysimeter reservoir water.

	Time after injection into reservoir (days)		
Pesticide	0	1	4
	- - % of starting concentration- - -		
Nemacur	100	99	108
Diazinon	100	94	0

G. PRELIMINARY DATA COLLECTION

In March, 1991, prior to construction and installation of the lysimeters referred to in Section D of this report, a prototype lysimeter was constructed and installed in the central portion of the green, near the weather station and away from the planned study area. Stainless-steel lines extended from the collection reservoir to the top of the lysimeter, which was at ground level, for collecting percolate and for air return. The turf in the lysimeter was fertilized and received diazinon insecticide application when these materials were applied to the bulk of the USGA green. Specifically, diazinon was applied at 4.0 oz/1000 ft^2 on March 15, and at 2 oz. on April 8 and April 30. Percolate water was withdrawn from the lysimeter periodically throughout this period as necessitated by rainfall and irrigation. The samples were stored at 4C until they were analyzed in September, primarily to serve as a "dry run" of the laboratory procedures. In the absence of a high-purity standard, calibration had to be performed with commercial-grade diazinon. For this reason, along with the extended sample storage period, the fact that the lysimeter soil profile was not matched with the surrounding profile, and the fact that the QA/QC program was not fully implemented during this preliminary trial, results should be viewed primarily as an example of the type of data that can be

obtained with the facilities that have been developed. The observed levels of diazinon in the percolate were low, generally less than 2 parts per billion (PPB), except for the sample (4/4) immediately following a 919 mm (3.62 inch) rainfall (Fig. 1). A much smaller concentration of diazinon was observed following a 19.8 mm (0.78 inch) rainfall on 4/22.

The presence of significant quantities of diazinon degradation products (DP) in the percolate was suspected, but not verified for lack of proper standards. Assuming that the observed products were degradation products, the total quantity of diazinon plus DP was considerably greater than that for diazinon alone (Fig. 2), approaching 300 PPB following the heavy rain on 4/4. The total generally was less than 20 PPB at other times.

A second preliminary trial was initiated on 18 September 1991, when granular fenamiphos (nemacur) was applied to a portion of the green away from the planned project study area at the rate of 22.4 kg a.i. ha^{-1} (20 pounds per acre). Soil and thatch samples were taken immediately prior to nemacur application, one hour after application, and again 2 and 7 days later. The samples were frozen (-20C), transported to the lab, and analyzed for nemacur.

Throughout the sample period, most of the nemacur was recovered in the thatch (Table 5), and there was a 10-fold reduction in nemacur in the thatch between the second and seventh days after application. Generally, the soil layers contained <10% of the nemacur observed in the overlying thatch.

The oxidation products of nemacur (sulfone and sulfoxide) also were detected (Fig. 6). They generally were <10% that of the parent compound, except on the last sampling date when the metabolites equaled or somewhat exceeded the parent compound.

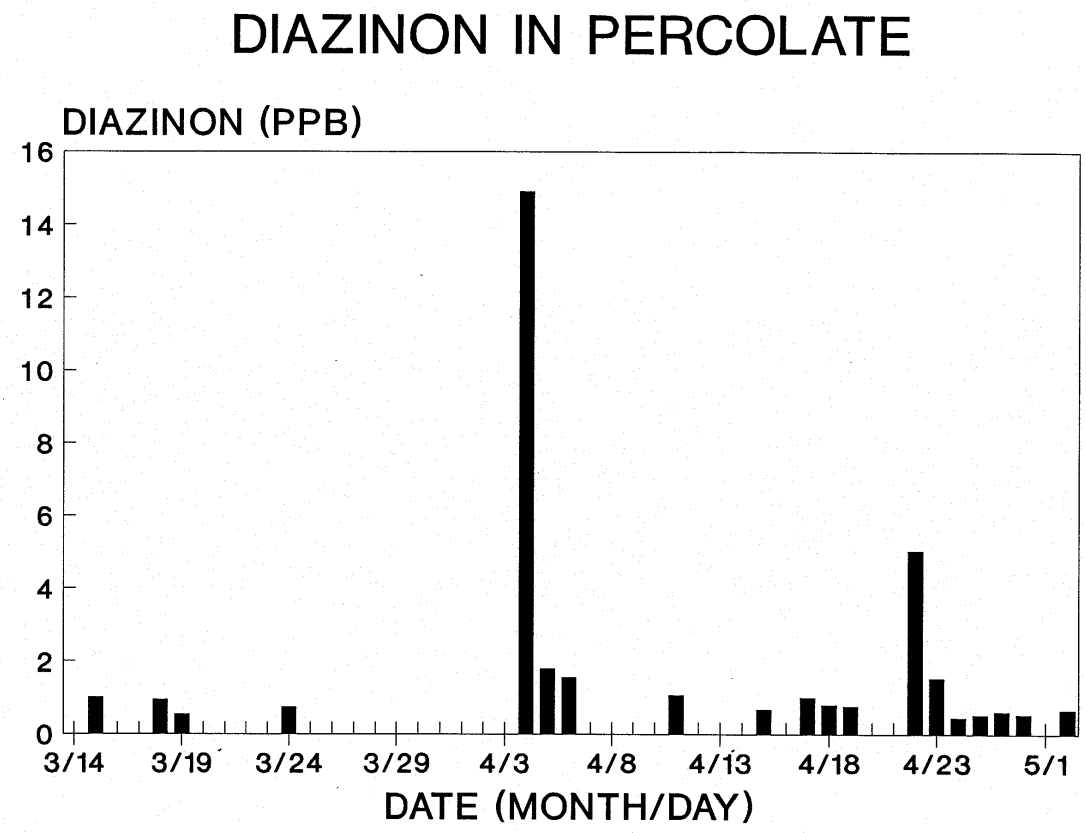
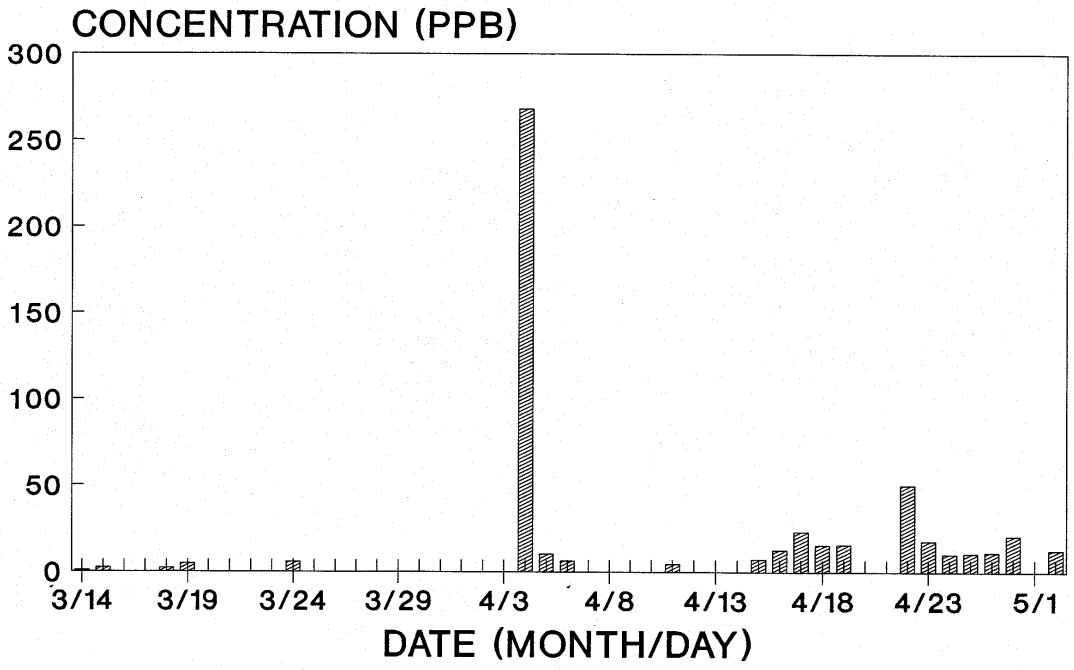


Fig. 1. Diazinon in percolate.

DIAZINON PLUS DEGREDATION PRODUCTS IN PERCOLATE



1991

Fig. 2. Diazinon plus degradation products in percolate.

Fig. 5. Fenamiphos recovered in thatch and soil following application to provide 1914 ug total sample^{-1}.

Layer	Pre-application	Post-application	2 days	7 days
	ug sample^{-1}			
Thatch	7.6	1653.5	2364.6	226.0
Soil 0-5 cm	0	241.0	272.5	10.2
5-10	0	-	13.0	7.6
10-15	0	38.6	15.4	2.8
Total	7.6	1933.1	2665.5	246.6
% Recovery	-	101	139	13

Fig. 6. Fenamiphos oxidation products recovered in thatch and following application to provide 1914 ug total sample^{-1}.

Layer	Pre-application	Post-application	2 days	7 days
	ug sample^{-1}			
Thatch	33.0	121.6	394.0	127.4
Soil 0-5 cm	5.1	15.8	61.1	61.7
5-10	0	-	0	115.2
10-15	0	0	1.4	83.6
Total	38.1	137.4	456.5	387.9
% Recovery	-	7	24	20

H. EXPENDITURES

To date, $ 22,500 has been released by the USGA for the project. Expenditures from this money have been $ 9,790 for salaries (Chemist, Agricultural Technician), $ 2,276 for expendable supplies, and $ 1,403 for University overhead, making a total of $13,469. Other monies spent on the project include salaries for the principal investigators and their state-supported staff whose time on the project is estimated as:

Name	Position	Full-time equivalent
Snyder	Professor	0.6
Cisar	Assist. Prof.	0.4
Williams	Biologist	0.7
Figueiras	Chemist	0.2

and items purchased from non-USGA funds, including the following:

Item	Cost
Metal building	$ 490
Prototype lysimeter	171
Batteries	250
Start-up lab supplies	600
Refrigerator	850
Gas Chromatograph	36,000

I. ATTACHMENTS

Quality assurance/quality control plan