Measurement and Model Prediction of Pesticide Partitioning in Field-Scale Turfgrass Plots

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INTRODUCTION

Concern over environmental contamination by pesticides has become widespread during the last several years. The United States Environmental Protection Agency has established mandatory standards for several pesticides, including 2,4-D, glyphosate, and atrazine, in drinking water. In addition, several states have established regulations to limit further environmental contamination by pesticides. In California, pesticides that are detected in ground water or have the potential to leach to ground water are regulated by the Department of Pesticide Regulations (DPR). Recently, the California DPR proposed that several pesticides be designated as toxic air contaminants. This list includes several compounds commonly used on turfgrass, including carbaryl (Sevin®), 2,4-D, mancozeb, maneb, and trifluralin (Treflan®).

Previous USGA-funded research at the University of California, Riverside (UCR) indicated that less than 0.1% of the applied carbaryl was lost by volatilization and leaching through the putting green plots. More of the applied 2,4-D could be accounted for: approximately 1% volatilized into the atmosphere, and approximately 5% leached through the soil. However, in both cases, more than 90% of the applied compound was not accounted for. In this project, we are performing a more detailed analysis of the fate of pesticides in the field plots to enable a determination of the mass balance.

A second area of concern after the first three-year cycle of environmental fate research was the need to be able to predict ground-water concentrations of pesticides. It is usually not feasible to monitor ground water for the pesticides of concern, so measurements of pesticide concentrations in the near-surface soil and soil water are made. Mathematical models are then used to predict the concentrations of the pesticides that one might expect at deeper points in the subsurface. Smith and Bridges (1993) attempted to predict pesticide movement through their greenhouse lysimeters using the GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) model (Leonard et al., 1987). They found that the model significantly over-predicted the amount of pesticides that would leach through the soil, even when a thatch layer was included in the model.

There are several possible explanations for the model's predictions failing to match the experimental data. One is that this model is very simple from a hydrologic standpoint: it assumes that when water is applied to the soil surface, it uniformly displaces an equal volume of water from

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the underlying soil (the so-called "tipping bucket" model). It is also a one-dimensional model in that it assumes that the water and pesticides are moving in one dimension. This model is classified as a functional, management-level model because it incorporates certain simplifications in the subsurface processes that reduce the requirement for input data. One advantage of a model such as GLEAMS is that it does not require massive amounts of difficult-to-acquire input data. The difficulties inherent in this and other functional models is that, because they have simplified the subsurface processes, their ability to accurately predict chemical movement may be decreased. There is a need to investigate the ability of other, more sophisticated, albeit more data-intensive models, to predict chemical movement through turfgrass-soil systems.

PURPOSE AND OBJECTIVES

The purpose of this research project is to conduct a mass balance assessment of turfgrass pesticides in field plots and use the data obtained in the assessment to test and modify a pesticide transport model. The specific objectives of the project are to:

a)   determine the partitioning of commonly-used turfgrass pesticides among the components of a turfgrass system including the atmosphere, soil, soil-water, leachate, thatch, verdure, and clippings;

b)   assess the ability of mathematical models, such as CHAIN_2D and PRZM2, to accurately predict pesticide movement in a field-plot-scale turfgrass system;

c)   modify the mathematical model and/or change the data collection protocol
        as necessary to improve the accuracy of model predictions;

d)   test the model using independently-derived data to assess further its predictive capabilities; and

e)   conduct a sensitivity analysis of the mathematical model to determine which input parameters have the greatest effect on the model predictions and therefore should be known to the highest degree of accuracy.

METHODS

Putting Green Preparation

The experiments were performed in lysimeters in the putting green plots located at the Turfgrass Research Facility on the campus of the University of California, Riverside. A profile of one of the putting green plots is shown in Figure 1. In order to obtain results that will be reflective of what would be expected to occur at a golf course, it was essential that the experiments be conducted on a putting green that was representative of one that would be found at a golf course, including all key cultural practices. In the effort to develop a representative putting green, the lysimeter plots were completely renovated prior to the initiation of any experiments. The renovation involved 1) removing the existing sod and any underlying organic material; 2)

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releveling the soil surface (which had settled in an uneven manner during the last few years) using a transit and grade sticks; 3) upgrading the irrigation system, which included replacing all sprinkler heads and mounting them on rebar to ensure verticalness; and 4) changing the irrigation system so that each of the 12 plots is irrigated separately based on the distribution uniformity of that plot. In May, 1995, washed SR 1020 creeping bentgrass sod was installed on the plots. For the next few months, the turf was established and managed in a manner similar to that of a golf course superintendent in southern California. It should be noted that one of the goals was to have the turf established to a point where the mowing height was not more than 3/16" prior to initiating any studies on the plots.

Figure 1. Green Plot Lysimeter Assembly
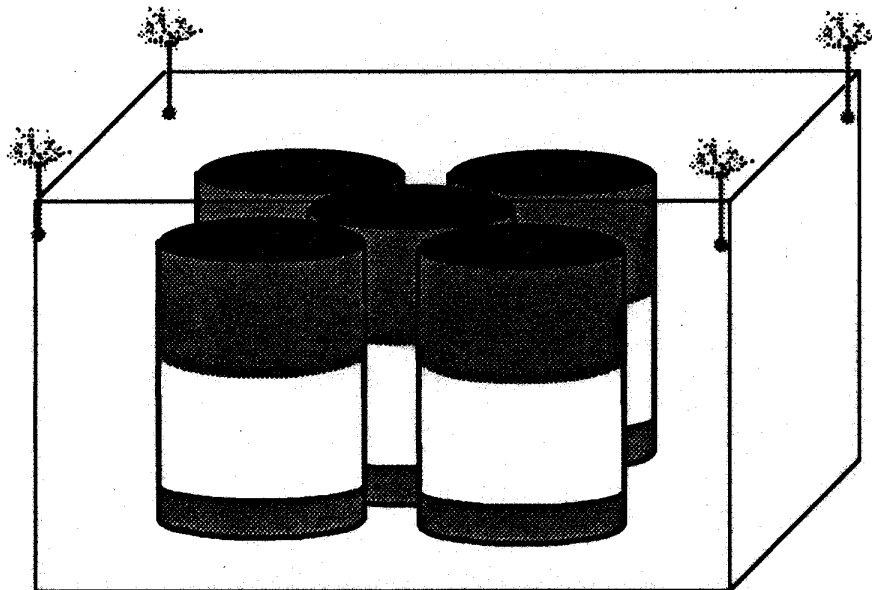
Pesticide Application

The pesticides used in the first experiment were chlorothalonil (Daconil 2787®) and metalaxyl (Subdue®). The environmental fate properties of these pesticides are given in Table 1. The chlorothalonil was applied at a rate of 8 oz/1000 ft^2 (500 g active ingredient per liter). The total mass of chlorothalonil applied to the lysimeter area of each plot (approximately 1.22 m^2) was 1.55 g. The metalaxyl was applied at a rate of 2 oz per 1000 ft^2 (2 lb active ingredient per gallon). The total mass of metalaxyl applied to the lysimeter area of each plot was 0.186 g. The pesticides were applied by a certified pesticide applicator on September 27, 1995 at approximately 8:00a.m.. Four of the plots (plots 1, 3, 7, and 10) were designated experimental plots; all data were collected from these plots (see Figure 2, experimental plots shaded).

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Table 1. Properties of chlorothalonil and metalaxyl

Property	Chlorothalonil	Metalaxyl
degradation half-life (days)	14	28
Henry's constant	3.44×10^{-5}	7.71×10^{-8}
adsorption coefficient (cm^3/g)	60	1.264
water solubility (mg/l)	0.6	7100

Figure 2. Putting Green Plot Map (Location of experimental plots shaded)

1	4	7	10
2	5	8	11
3	6	9	12

Sample Collection and Analysis

Leachate. Samples of drainage water were collected from each of the test plots on a daily basis. Drain volumes were measured and recorded daily, allowing a calculation of the mass of pesticides leaching from the plots. The volume of water applied by irrigation was also recorded for each plot on a daily basis. Drainage samples continue to be taken as this report is written.

Turfgrass clippings. Samples of the turfgrass clippings were taken from each of the experimental plots one day prior to pesticide application to determine any background concentrations. Clippings samples were also taken on days 1, 3, 5, 7, 9, and 12. Sampling of the clippings will continue until concentrations are below detection limits.

Air. The volatilization of the pesticides into the air was measured as follows. Immediately after pesticide application, a volatilization flux chamber was placed directly on the turf in each of the designated plots. The chambers measure approximately 42 cm x 42 cm and have a surface area of approximately 0.16 m^2. The air above the surface of the turfgrass was pulled out of the chamber at a very low rate (approximately 10 liters/minute). As it was removed, the air was passed through a

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polyurethane foam plug (PUF) that adsorbed any pesticides present in the air. Air from outside the chamber was drawn into the chamber to replace the air that is removed. Any pesticides in the outside air were removed as the air was drawn into the chamber. The position of the flux chamber was rotated between two marked spots on the plots to minimize damage to the turfgrass.

Samples were obtained from the chambers beginning 10 minutes after pesticide application and continuing for a period of 8 days. After nine days, pesticide concentrations in the air samples were below the detection limit, so no further samples were collected.

The volatilization flux chambers used for this experiment have been newly designed to correct for some of the deficiencies of the old system. The new chambers are constructed of galvanized metal, which has been painted white on the outside. This ensures that the temperature inside the chamber is approximately the same as the temperature of the outside air. In addition, the chambers have baffles at the inlet and outlet ends to force the air to travel as uniformly as possible over the ground surface. In other volatilization studies conducted by our research group, it was found that the volatilization measured using the new flux chambers was comparable to that measured using large-scale volatilization flux methods (see Table 2).

Table 2. Comparison of Flux Chambers with Other Volatilization Methods

Method Used	Experiment 1		Experiment 2	
	% Volatilized	Mass Balance (%)	% Volatilized	Mass Balance (%)
Aerodynamic, discrete	62.2	100.8	3.8	83
Aerodynamic, profile	67.3	105.9	2.8	82
Flux chamber	57.8	96.4	4.9	84
Theoretical Profile Shape	60.1	98.6		
Integrated Horizontal Flux	69.8	108.3	1.9	81
AVERAGE	63.0	101.5	3.4	82

Soil. Soil samples were obtained from the entire soil profile (47 cm) using a handheld coring device. The diameter of the core obtained was approximately 1.5 in. The soil was divided into five increments as shown in Figure 3 prior to analysis to permit a determination of the depth distribution of the pesticides in the profile.

Soil samples were taken prior to the pesticide application, and on days 0, 2, 7, 15, and 30 after pesticide application. Soil samples will continue to be taken on days 60, 90, and 120 after application. Four core samples were obtained from each of the four plots on each of the sampling days. Soil samples were taken from the plot area outside of the lysimeters so that the integrity of the lysimeters themselves was not compromised. The locations from which the samples were taken from each of the four plots are shown on the sampling grid in Figure 4. A summary of the soil samples taken is given in Table 3.

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Figure 3. Soil Sample Depth Profile

Clippings

0-2 cm

2-7 cm

7-17 cm

17-32 cm

32-47 cm
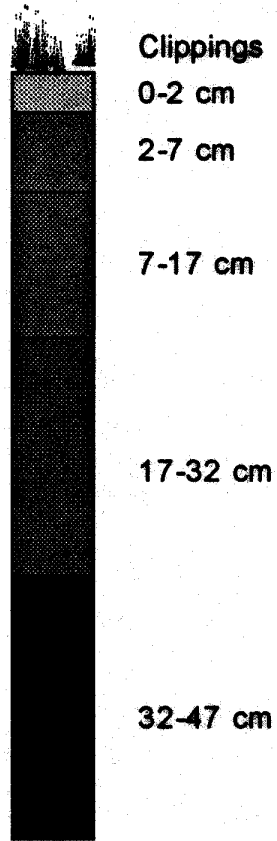
Figure 4. Locations of Soil Samples Collected from Plots 1, 3, &, and 10.

	A	B	C	D	E	F	G	H	I	J	K	L
1												
2			B		Day 30			Day 30		B		
3		Day 0	Day 7	Day 2					Day 2	Day 7	Day 0	
4												
5		Day 16									Day 16	
6					LYSIMETER AREA							
7												
8		Day 16									Day 16	
9												
10		Day 0	Day 7	Day 2					Day 2	Day 7	Day 0	
11			B		Day 30			Day 30		B		
12												

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Table 3. Summary of Soil Samples Obtained from Plots 1, 3, 7, and 10.

Depth	0-2 cm	2-7 cm	7-17 cm	17-32 cm	32-47 cm
Background	Quad 2C	Quad 2C	Quad 2C	Quad 2C	Quad 2C
	Quad 11C	Quad 11C	Quad 11C	Quad 11C	Quad 11C
	Quad 2J	Quad 2J	Quad 2J	Quad 2J	Quad 2J
	Quad 11J	Quad 11J	Quad 11J	Quad 11J	Quad 11J
Day 0	Quad 3B	Quad 3B			
	Quad 10B	Quad 10B			
	Quad 3K	Quad 3K			
	Quad 10K	Quad 10K			
Day 2	Quad 3D	Quad 3D	Quad 3D	Quad 3D	Quad 3D
	Quad 10D	Quad 10D	Quad 10D	Quad 10D	Quad 10D
	Quad 3I	Quad 3I	Quad 3I	Quad 3I	Quad 3I
	Quad 10I	Quad 10I	Quad 10I	Quad 10I	Quad 10I
Day 7	Quad 3C	Quad 3C	Quad 3C	Quad 3C	Quad 3C
	Quad 10C	Quad 10C	Quad 10C	Quad 10C	Quad 10C
	Quad 3J	Quad 3J	Quad 3J	Quad 3J	Quad 3J
	Quad 10J	Quad 10J	Quad 10J	Quad 10J	Quad 10J
Day 15	Quad 5B	Quad 5B	Quad 5B	Quad 5B	Quad 5B
	Quad 8B	Quad 8B	Quad 8B	Quad 8B	Quad 8B
	Quad 5K	Quad 5K	Quad 5K	Quad 5K	Quad 5K
	Quad 8K	Quad 8K	Quad 8K	Quad 8K	Quad 8K
Day 30	Quad 2E	Quad 2E	Quad 2E	Quad 2E	Quad 2E
	Quad 11E	Quad 11E	Quad 11E	Quad 11E	Quad 11E
	Quad 2H	Quad 2H	Quad 2H	Quad 2H	Quad 2H
	Quad 11H	Quad 11H	Quad 11H	Quad 11H	Quad 11H

Analysis. All samples are placed in glass containers and stored at 4 C until analyzed. After processing the samples are analyzed using a gas chromatograph. For chlorothalonil, and electron capture detector (ECD) is used ; while detection of metalaxyl requires the use of a nitrogen-phosphorus detector (NPD). Details of the sample processing are given in the following sections.

Water. 100 ml of the water sample is poured into a 1-L separatory funnel. #0 ml of methylene chloride is added, and the mixture shaken vigorously for 30 seconds. The organic and water phases are allowed to separate completely, then the organic phase is decanted off into a 300-ml flat-bottomed flask. Another 30 ml of methylene chloride is added to the separatory funnel, and the process is repeated. The same organic extraction process is repeated for a third time. Sodium sulfate is added to the extracted organic material to remove any residual water, then the extract is concentrated to a small volume on a RotoVap. The final sample is brought to a volume of 5 ml prior to analysis by gas chromatography.

Tissue.   Ten grams of tissue is weighed into a blender jar, and 150 ml of a 35% water/acetone mixture added. The sample is blended for 2 min at high speed. The mixture is filtered through a buchner funnel, collected in a 500-ml suction flask, and then transferred to a separatory funnel which contains 50 ml methylene chloride. 50 ml of petroleum ether is added to the separatory funnel, which is then shaken for 1 minute. The aqueous layer is transferred to a second separatory funnel, and the organic extract is transferred to a 300-ml flat-bottomed flask. Four g sodium chloride is added to the aqueous phase in the second separator, which is shaken vigorously until the NaCl is dissolved. The methylene chloride extraction procedure is repeated two more times. The organic extract is dried by passing it through a sodium sulfate column, then concentrated to a small volume. The final sample is analyzed by gas chromatography.

Soil.   125 ml of hexane are put into a 300-ml flat-bottomed flask and boiling chips are added. A soil thimble containing 30 g soil sample is loaded into the extraction flask, and 125 ml acetone are poured onto the soil sample. The entire Soxhlet extraction set is placed onto a hot plate (60C) and extracted for 8 h. The extracts are stored in the freezer until analysis by gas chromatography.

Air. Air samples are processed in the same manner as previously described for the soil samples except that the extraction time is 2 hours rather than 8 hours.

MODELING

The mathematical contaminant transport model used to simulate the environmental fate of chlorothalonil and metalaxyl was CHAIN_2D (Simunek and vanGenuchten, 1995). This model simulates the movement of water, heat, and contaminants in unsaturated, partially saturated, or fully saturated media. The program includes provisions for partitioning between soil and liquid components and between liquid and gaseous components. It also includes water uptake by plant roots, changes due to atmospheric conditions, and first-order degradation processes.

Testing

Prior to pesticide application, CHAIN_2D was used to predict the behavior of the two compounds in the putting green lysimeters. The model predictions of the partitioning of the pesticides into the various environmental compartments (soil, water, air, and tissue) were used to design the sampling protocol for the experiment.

Tables 4 and 5 list the data used as input for the model. Values were obtained from literature when possible; for some values, extrapolation had to be made using best judgment. For example, vales for the degradation rate of the pesticides in the coarse gravel were not found in the published literature, therefore estimates were made. The Henry's constant for chlorothalonil is 3.44 x 10^{-6} and for metalaxyl is 7.71 x 10^{-6}. The diffusion rates for both compounds were assumed to be 1.0 cm^2/day in free water and 4320 cm^2/day in the gas phase.

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Table 4. Soil Properties used in Simulation of Chlorothalonil and Metalaxyl Fate and Transport

Soil Region	Bulk Density (cm^3/cm^3)	Initial Moisture Content (cm^3/cm^3)	Alpha (1/cm)	n
tissue	0.4	0.004	0.4	3.01
thatch	0.9	0.068	0.2	2.01
sand	1.55	0.173	0.05	2.01
pea gravel	1.66	0.047	0.08	4.01
coarse gravel	1.66	0.037	0.08	4.01

Table 5. Environmental Fate Properties of Pesticides used in Simulation

	Adsorption Rate		Degradation Half-Life	
Soil Region	Daconil	Subdue	Daconil	Subdue
tissue	30	0.633	14	28
thatch	120	2.529	11.6	20
sand	60	1.264	14	28
pea gravel	6.9	0.145	17.5	47
coarse gravel	2.5	0.0525	23.5	145

RESULTS

Water

Leachate volumes collected and measured daily for each of the experimental plots are shown in Table 6. The volumes of water applied by irrigation to each of the plots are also shown in Table 6.

Irrigation times were determined by the needs of the bentgrass, rather than a strict adherence to an evapotranspiration rate calculation. The percent of applied water that leached through the plots ranged from 55.3% to 78.3%, with an average of 66.7%.

Using the volume of leachate obtained from each plot on a daily basis and the pesticide concentration measured in each of the water samples, a calculation of the total mass of pesticide that leached through the plots will be made. However, at the time this report was written, the results of leachate analysis for pesticides were not available.

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Table 6. Water Applied to and Leached from Experimental Plots

	Plot 1		Plot 3		Plot 7		Plot 10	
	Applied	Leached	Applied	Leached	Applied	Leached	Applied	Leached
Day	(liters)	(liters)	(liters)	(liters)	(liters)	(liters)	(liters)	(liters)
0	7.91		8.13		6.73		6.79	
1	7.91	5.25	8.13	7.80	6.73	5.75	6.79	6.05
2	6.79	3.75	6.98	4.10	5.76	3.55	5.82	3.90
3	6.79	3.80	6.98	3.55	5.76	4.00	5.82	3.45
4	6.79	4.50	6.98	4.25	5.76	3.80	5.82	3.55
5	6.79	4.90	6.98	6.00	5.76	5.00	5.82	4.10
6	6.79	3.10	6.98	5.00	5.76	3.60	5.82	2.90
7	6.79	3.25	6.98	5.25	5.76	4.90	5.82	2.50
8	6.79	2.50	6.98	3.80	5.76	3.90	5.82	2.00
9	6.79	2.25	6.98	3.90	5.76	3.00	5.82	2.00
10	6.79	2.43	6.98	3.34	5.76	3.02	5.82	2.05
11	6.79	3.92	6.98	4.40	5.76	6.11	5.82	2.63
12	13.58	3.84	13.95	4.25	11.52	4.75	11.65	3.44
13	10.18	7.25	10.46	10.00	8.63	10.90	8.75	8.95
14	6.79	6.30	6.98	8.06	5.76	7.95	5.82	7.00
15		4.50		8.05		4.25		4.30
16	6.79	3.95	6.98	5.75	5.76	4.98	5.82	4.50
17								
18	6.79		6.98		5.76		5.82	
19	6.79	8.95	6.98	10.30	5.76	10.00	5.82	9.10
TOTAL	134.62	74.44	138.32	97.80	114.25	89.46	115.50	72.42

Tissue

The results of the pesticide analyses for the tissue samples are shown in Table 7. Analyses of these data to determine the mass of pesticides that partitioned into the tissue has not yet been completed.

Table 7. Pesticide Residues in Turfgrass Clippings

Day	Plot 1	Plot 3	Plot 7	Plot 10
	Metalaxyl (ppm dry weight)			
1	46.6	46.98	58.86	43.37
3	8.36	5.96	8.69	12.65
5	13.81	14.46	11.78	14.56
7	10.87	8.94	0.31	11.93
9	6.37	6	0.73	9.95
12	2.45	1.53	0.17	1.89

	Chlorothalonil (ppm dry weight)			
1	221.9	245.04	269.21	75.32
3	215.66	48.6	66.71	99.18
5	260.37	294.96	68.13	64.75
7	103.85	75.31	213.89	76.09
9	14.01	37.99	55.47	49.47
12	16.53	7	17.27	9.13

Air

All air samples obtained during the volatilization experiment have been analyzed. The results of these analyses are presented in Table 8. Note that the concentrations are given as ng per sample. In order to put these results into a form in which they can be interpreted, it is necessary to convert the raw data. In Figures 4 and 5, the rate at which the compounds volatilized into the air per m^2 of surface area are shown. In these figures, day 1 is midnight of the day after pesticide application. It can be seen that the flux is the lowest at midnight and peaks at mid-day.

Table 8. Concentrations of Pesticides Volatilized from Putting Green Plots

Day	Start Time	Stop Time	Plot 1 (ng/sample)	Plot 3 (ng/sample)	Plot 7 (ng/sample)	Plot 10 (ng/sample)
0	800	1000	197.8	355.1	421.5	314.3
0	1000	1200	219.7	274.9	1128.6	382.4
0	1200	1400	130.7	450.4	404.6	97.6
0	1400	1600	262.2	336.7	790.3	108.6
0	1600	1800	305.2	592.8	923.9	695.2
0	1800	2000	265.5	298.1	740.6	565.8
0	2000	700	771.9	962.8	2552.4	3554.9
1	1000	1500	239.7	2451	403.5	178.8
1	1500	1900	239.4	611.03	5740.9	1353.4
1	1900	700	2651.6	1690.5	4873.8	827.3
1	830	1230	1481.9	316.7	321	399.7
2	1230	1645	290.1	567.4	507.1	858.9
2	1645	2030	625.12	733.63	2591.5	664.4
2	2030	3100	562.6	310.5	2181.7	1067.6
3	945	1600	1384	1132	1072	1568
3	1600	2130	2234	1796	1919.8	1684
3	2130	3100	863.2	267.7	672.8	584.6
4	815	1400	178.42	154.5	99.8	22.75
4	1400	2030	702	1586	5902	2142
4	2030	3100	940	1130	2220	996

5	1000	1600	498	135	135	460
5	1600	2145	2544	1818	5320	2500
5	2145	3100	852.6	251.3	417.8	60.5
6	820	1400	852	804	774	996
6	1400	1945	1566	2922	1636	2748
6	1945	3100	2748	1674	4752	2730
7	945	1530	194.9	177.7	1466	46.5
7	1530	2150	584.8	885.4	2962.9	1819.1
7	2150	700	588.2	586.4	1204.5	644.7
8	830	1430	10.2	27.9	412.7	452.5
8	1430	2045	465.2	49.1	1845.6	1029.7
8	2045	700	405.9	69.8	1316.4	315.3

The cumulative mass of chlorothalonil and metalaxyl that volatilized from the plots during the experiment is shown in Figures 6 and 7, respectively. The portion of the total applied mass that volatilized from the putting green plots was 0.017% for the chlorothalonil and 0.083% for the metalaxyl.

Modeling

CHAIN_2D was used to calculate the proportions of the pesticides that would partition into the soil, water, air, and tissue compartments. The results of the model predictions are shown in Tables 9 and 10 for chlorothalonil and metalaxyl, respectively.

Table 9. Model Predictions of Chlorothalonil Fate On Putting Green Plots

Days	Percent of Applied			
	Degraded	Leached	Volatilized	Remaining
0.1	0.0	0.0	0.0	100
7	35.0	0.0	0.6	64.4
15	62.0	0.0	0.6	37.4
30	88.1	0.0	0.6	11.3
90	99.4	0.0	0.6	0

Table 10. Model Predictions of Metalaxyl Fate On Putting Green Plots

Days	Percent of Applied			
	Degraded	Leached	Volatilized	Remaining
0.1	0.0	0.0	0.0	100
7	18.5	0.0	0.0	81.5
15	33.8	0.0	0.0	66.2
30	54.5	0.0	0.0	45.5
90	88.4	0.0027	0.0	11.6

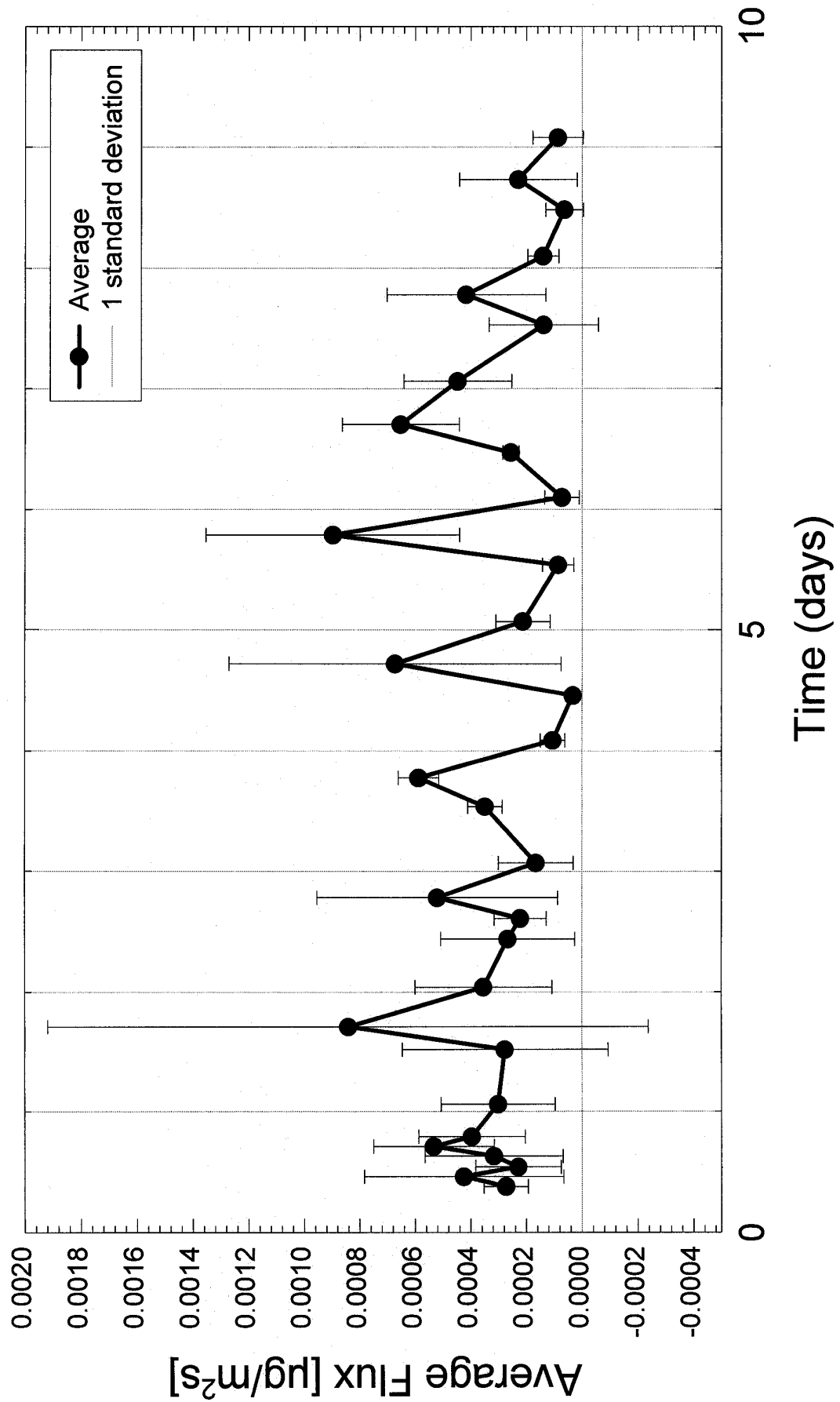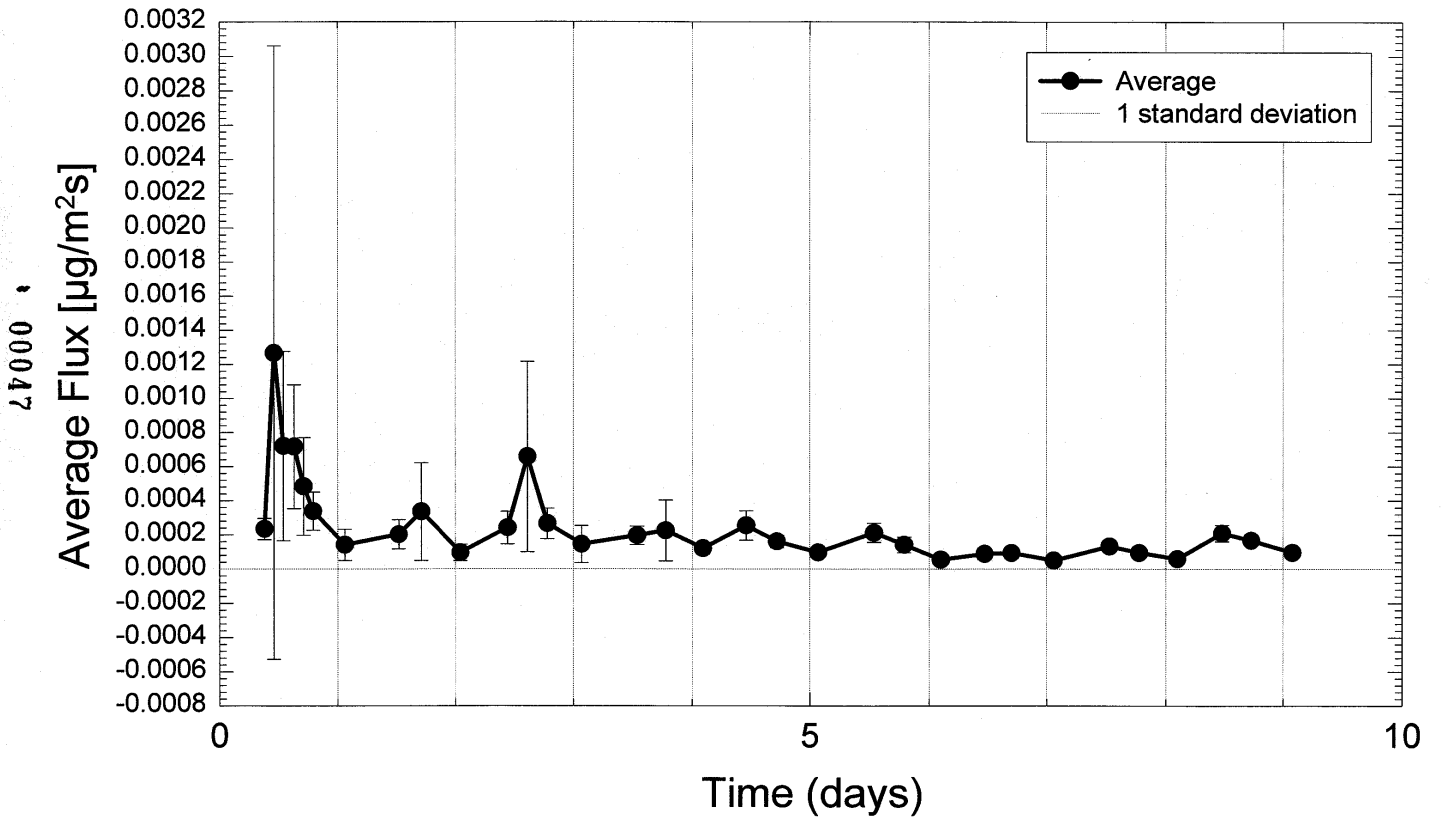# Figure 4. Chlorothalonil Flux

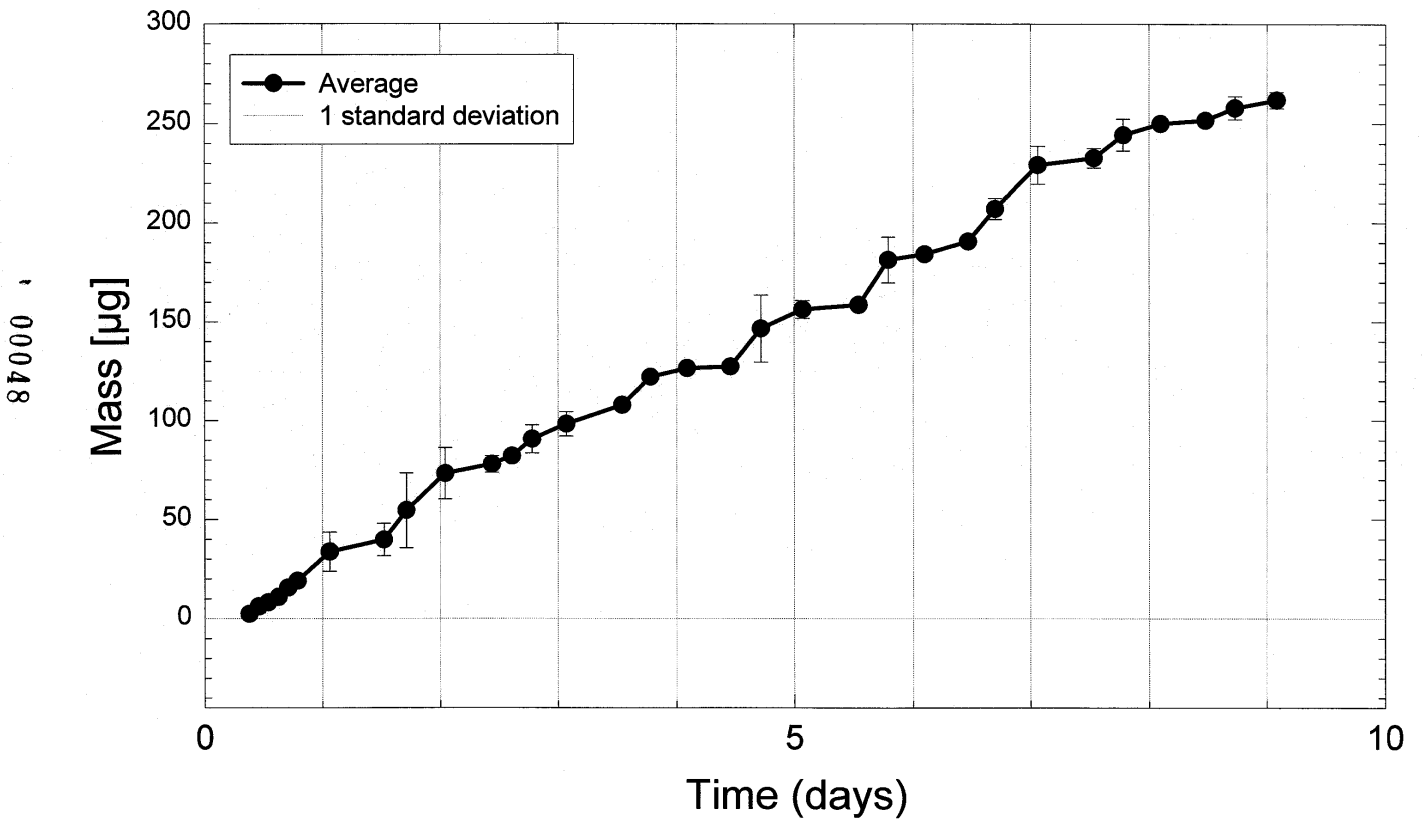**Figure 5. Metalaxyl Flux**

Figure 6. Chlorothalonil - Cumulative Mass Volatilized

Figure 7. Metalaxyl - Cumulative Mass Volatilized