MODELING PESTICIDE TRANSPORT

In

TURFGRASS THATCH AND FOLIAGE

1998 ANNUAL REPORT

presented to the

UNITED STATES GOLF ASSOCIATION

GREEN SECTION RESEARCH

Dr. Mark Carroll
Dr. Robert L. Hill
University of Maryland
Department of Agronomy

Cooperator
Dr. Albert Herner
USDA:Beltsville
Environmental Chemistry Laboratory

Executive Summary

Pesticides applied to mature turf move into the soil only after being washed off foliage and moving through turfgrass thatch. Any attempt to predict the movement of pesticides applied to turf requires that the retention characteristics of the pesticide to foliage and thatch be known.

In 1997 and 1998 a series of sorption and transport studies were conducted to characterize the movement of carbaryl in soils containing a surface layer of turfgrass thatch. The sorption studies were conducted using a device called a mechanical vacuum extractor. This device precisely controls the rate at which a solution moves through a column of porous media. The adsorption and desorption properties of a 3.5 year old, 2.3 cm thick Southshore creeping bentgrass thatch, and a 6 year old, 3.4 cm thick Meyer zoysiagrass thatch were compared with the soil residing below each thatch layer.

The adsorption kinetics of carbaryl to thatch and soil were similar. Sorption equilibrium was achieved within 4 hours in all media. Both turfgrass species thatch had much higher carbaryl adsorption capacities than the underlying soil. There was, however, no difference in the adsorptive capacities of the two turfgrass species thatch. The normalized sorption coefficients of the four media were similar suggesting that differences in the carbaryl sorptive capacities of thatch and soil were solely due to differences in the organic carbon content of the media.

Desorption losses were evaluated by subjecting columns of thatch or soil to three successive leaching events. The leaching events took place after allowing carbaryl to adsorb to the thatch or soil for 24 hours. The amount of carbaryl detected in the leachate was used to determine the proportion of carbaryl that was desorbed from the sample. Carbaryl retention in soil was much lower than in thatch during the first leaching event. By the end of the third leaching event there was little difference in the proportion of carbaryl retained in the bentgrass thatch and soil. In contrast, zoysiagrass thatch always retained a greater proportion of carbaryl than the underlying soil. This suggests that carbaryl is more tightly bound to zoysiagrass thatch than to the underlying soil.

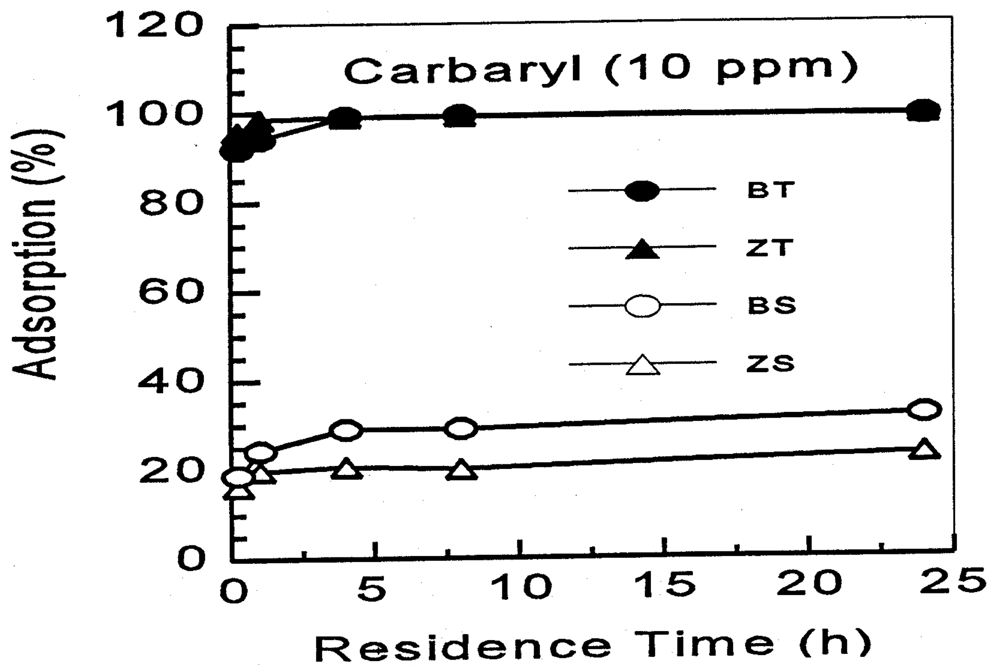
Undisturbed columns of soil or soil plus a surface layer of thatch were used to determine the effect of thatch on the carbaryl transport in soil. Columns having a surface layer of zoysiagrass thatch were more effective in reducing carbaryl transport than columns having a surface layer of creeping bentgrass thatch. Visual examination of the bentgrass site columns revealed extensive earthworm burrowing. The channels present in these columns likely reduced the effectiveness of bentgrass thatch to inhibit carbaryl transport.

Bromide and carbaryl breakthrough curves obtained from the transport study were used to evaluate the performance of the linear equilibrium (LEM) and the two-site non-equilibrium (2SNE) models to predict carbaryl transport. The latter model uses a non-equilibrium form of the convective-dispersion equation to predict solute movement in porous media while the former uses a linear equilibrium form of the equation to predict solute movement. The carbaryl breakthrough curve (BTC) data were also used to compare the use of column retardation factors (R) based on our laboratory measured thatch and soil sorption coefficients with model fitted R's to predict carbaryl transport.

Modeling of bromide transport presented strong evidence of significant two domain flow in all columns except the zoysiagrass site soil columns. In columns exhibiting two domain flow use of retardation factors based on laboratory measured adsorption coefficients accounted for 74 to 94% of the variability in carbaryl transport. Slightly improved estimates of carbaryl transport were obtained when R was kept as a fitting parameter. In columns where two domain flow was not apparent, the LEM model could satisfactorily describe carbaryl transport only when R was curve-fitted. Use of R's based on laboratory derived adsorption coefficients resulted in poor LEM estimates of carbaryl transport. The 2SNE model gave reasonable estimates of carbaryl transport when R was calculated using the adsorption coefficients we determined in our sorption studies.

Goals:

- To quantify the washoff of pesticides from bentgrass foliage as a function of time after application and pesticide formulation.
- To determine the effect of solution residence time on the sorption of pesticides to turfgrass thatch.
- To compare the use of linear equilibrium, two-site non-equilibrium and one-site kinetic non-equilibrium forms of convection/dispersion equation to predict pesticide transport through turf containing a surface layer of thatch.



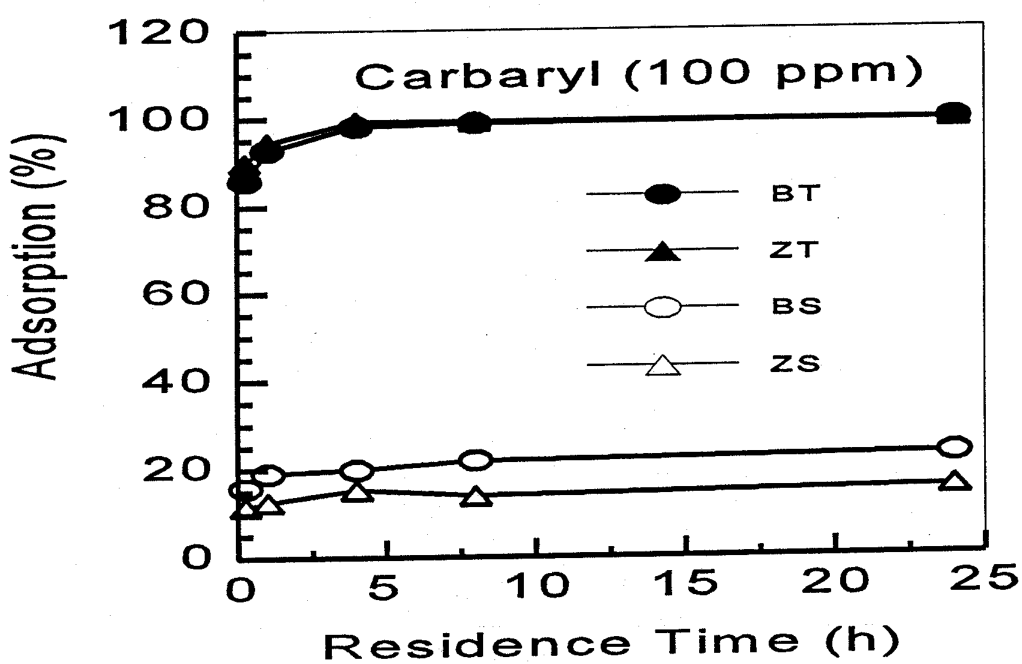


Figure x. Adsorption kinetics of bentgrass thatch (BT), zoysiagrass thatch (ZT) and the soil residing below each thatch layer.

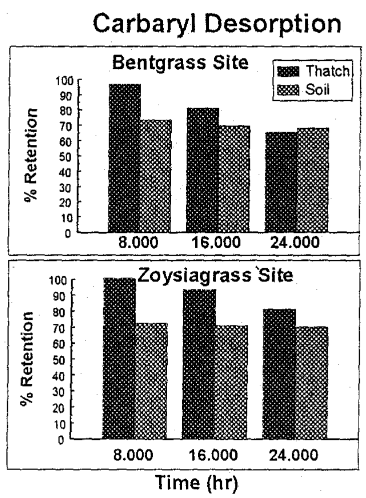


Figure x. Cumulative proportion of carbaryl retained to thatch and soil following three successive 8 hour leaching events.

Project Title: Modeling Pesticide Transport in Turfgrass Thatch and Foliage

Principal Investigators: Mark J. Carroll and Robert L. Hill

Project Overview- Pesticides applied to mature turf move into the soil only after being washed off foliage and moving through turfgrass thatch. Any attempt to predict the movement of pesticides applied to turf requires that the retention characteristics of the pesticide to foliage and thatch be known.

Many pesticide transport models, such as PRZM and LEACHM, use the linear equilibrium form of the convection-dispersion equation to predict pesticide movement in porus media. A major assumption inherent in use of this form of the convection-dispersion equation is that the residence time of solution containing the pesticide is of sufficient duration that sorption equilbium between the solution and porus media is achieved. It has been hypothesized that turfgrass thatch differs from soil in that it exhibits non-equilibrium pesticide sorption. In such cases, pesticide movement within the media may be predicted with greater accuracy when a non-equilibrium form of the convection-dispersion equation is used to model pesticide transport. The primary objectives of this project are to determine the pesticide sorption characteristics of turfgrass thatch, and to use that information to evaluate linear equilibrium and non-equilibrium forms of the convection-dispersion equation to predict pesticide transport in soils containing a turfgrass thatch surface layer.

Progress to date

Sorption: The thatch used in the sorption studies was collected from a 3.5 year old stand of Southshore creeping bentgrass and a 6 year old stand of Meyer zoysiagrass. The thatch from each site was collected by first removing all verdure using a walk behind greens mowing. A sod cutter was then used to remove a roll of the thatch from each site by setting the blade of the sod cutter at the terminal depth of the thatch. The bentgrass and zoysiagrass thatch rolls were approximately 1 and 3 centimeters thick, respectively. The thatch rolls were shredded using a modified wood chipper and then hand sieved to pass through a 4 mm screen. The sieved thatch material was placed into zip lock plastic bags for storage. The soil immediately below the thatch was also hand sieved to pass through a 4 mm screen before being placed into zip lock plastic bags. The thatch and soil were stored in a refrigerator maintained at 4 °C.

All sorption studies were conducted using a modified batch/flow technique, the details of which can be found in Raturi et al., (1997). Briefly, this procedure involves placing a known amount of thatch or soil in a syringe tube barrel. The sample is hand packed into the barrel creating 2 to 3 cm deep column of thatch or soil . A given volume of solution, containing a know amount of pesticide, is passed through the column and the pesticide concentration of the resulting leachate is measured. The difference in the pesticide concentration of the solution added to the column, and the pesticide concentration of the leachate represents the amount of pesticide that is retained or adsorbed to the thatch or soil sample. A device called a mechanical vacuum extractor is used to precisely control the rate at which the solution moves through the thatch or soil column.

The initial intent of this project was to examine the sorptive and transport behavior of 2,4-D, carbaryl and chlorothalonil to two turfgrass species thatch and to the soil residing immediately below each turfgrass species thatch. When it became apparent that chlorothalonil movement through thatch and soil was almost non-existent we decided to examine the sorption and transport of triclopyr in place of chlorothalonil. (see the *transport* section for additional details on our work with chlorothalonil).

With the exception of the short term adsorptive behavior of carbaryl, all sorption studies involving carbaryl and 2,4-D were summarized in our 1997 report. Figure 1 of this report summarizes the adsorptive kinetics of carbaryl to thatch and to the underlying soil. Carbaryl adsorption to thatch and soil was measured for residence times as brief as 15 minutes and as long as 48 hours. Two carbaryl solution concentrations (10 and 100 mg L^{-1}) were examined. There was no significant difference in the adsorption kinetics of the two turfgrass species thatch at either carbaryl concentration. Equilibrium sorption of carbaryl to thatch and to soil was achieved within 4 hours. The adsorption kinetics of carbaryl and 2,4-D are markedly different for thatch. In the 2,4-D adsorption kinetic study we completed last year, we found that 2,4-D acid adsorption to thatch increased 72% in a nearly linear manner as the solution residence time increased from 15 minutes to 24 hours.

Sorption studies involving triclopyr were more problematic. Our triclopyr sorption data exhibited high variability with several instances of increasing triclopyr adsorption being observed during the desorption phases of our experiments. Much of the variability can be attributed to the lowl amounts of triclopyr that were adsorbed. The triclopyr equilibrium isotherm data, while also being more variable than we would like, did provide Freundlich sorption isotherm coefficients that were similar to the values others have reported in the literature. The triclopyr 24 hour sorption isotherm data is presented in figure 2. The soil isotherm data was more variable than the thatch isotherm data. The Freundlich sorption isotherm coefficient of determination (r^2) ranged from 0.84 for the zoysiagrass soil to 0.98 for the bentgrass thatch. There was no significant difference in the Freundlich sorption isotherm coefficients for the two thatch sources or for the soils underlying each thatch. Hence, a single line was used to characterize triclopyr sorption to thatch and soil.

Table 1 provides the normalized sorption coefficients (Koc) for thatch and soil for each of the three pesticides examined. The Koc values were calculated using the Freundlich sorption isotherm equilibrium partition coefficients obtained from our sorption experiments and the measured organic carbon content of each media. In last years report we calculated the individual media Koc's for 2,4-D and carbaryl indirectly. We used the loss on ignition organic matter content of each media to indirectly calculate the organic carbon content present in each media. The formula we used was: % organic carbon = [(% organic matter - 0.35)/1.80]. This past year we directly measured the organic carbon content of each media using a LECO analyzer (Leco Corp., St Joseph, MI). We feel the Koc's presented in this report, because they were calculated using organic carbon contents that were directly measured, better represent the actual media Koc.

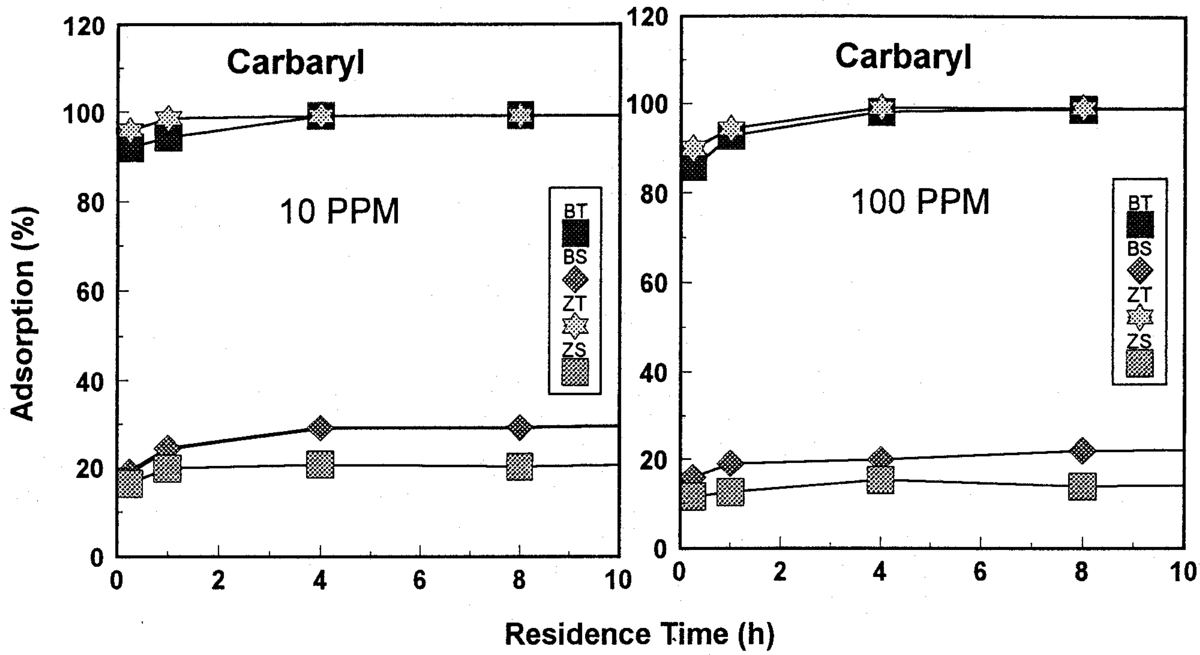


Figure 1. Adsorption kinetics of carbaryl to thatch and soil.

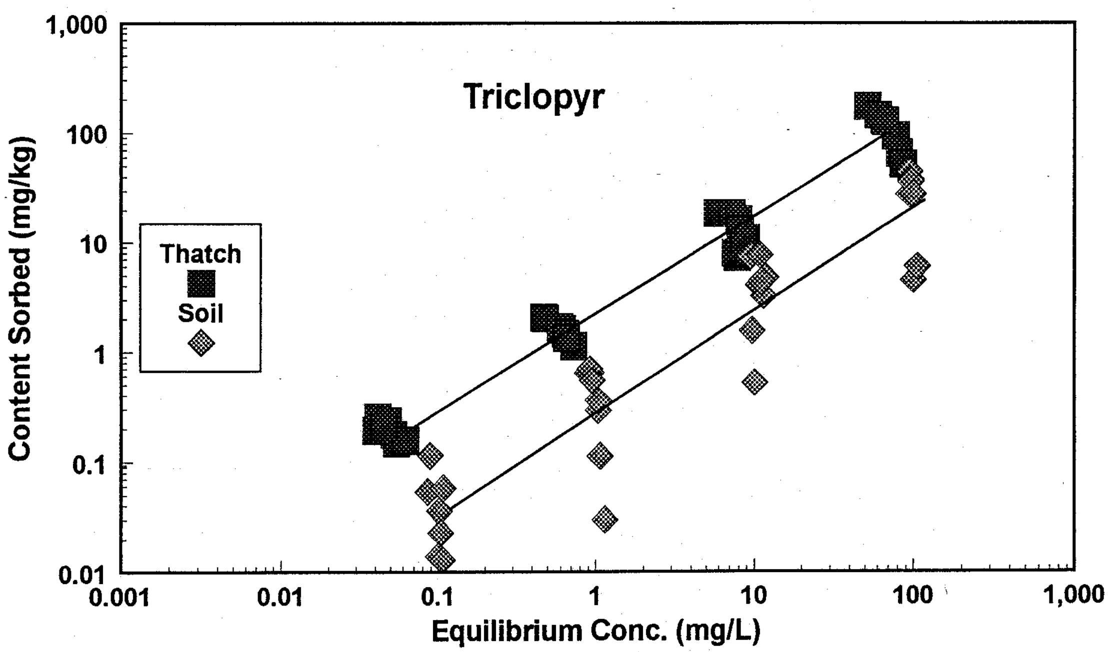


Figure 2. Adsorption of triclopyr to thatch and soil using a 24 hour solution residence time.

Table 1. Carbaryl, 2,4-D and triclopyr normalized sorption coefficients for thatch and soil.

Media	Organic Carbon	Normalized Sorption Coefficient[+] 2,4-D Acid	Carbaryl	Triclopyr
	%	$m^3\ kg^{-1}$		
Bentgrass				
Thatch	15.3	2.12×10^{-2}	3.37×10^{-1}	1.49×10^{-2}
Soil	0.9	7.98×10^{-2}	3.31×10^{-1}	3.92×10^{-2}
Zoysiagrass				
Thatch	10.6	2.78×10^{-2}	3.37×10^{-1}	2.53×10^{-2}
Soil	0.5	7.00×10^{-2}	3.72×10^{-1}	4.44×10^{-2}

[+] The normalized sorption coefficient was calculated by dividing the Freundlich adsorption coefficient of the media by the organic carbon content of the media.

Both turfgrass species thatch had much higher absorption capacities than the underlying soil for all three pesticides examined. Conflicting results, however, arose when the data were normalized for the presence of organic carbon. In the case of 2,4-D and triclopyr, the two soil Koc's were greater than the thatch Koc's whereas there was no difference in the thatch and soil Koc's for carbaryl. Dell (et al. 1994) found that the Koc's of three fungicides were less for thatch than for the underlying soil. Lickfield and Branham (1995) reported a similar trend when determining the Koc's of several non-ionic compounds. The later researcher's believed that the organic matter in soil was a more hydrophobic sorbent that the organic matter in thatch. Our results suggest that this may not be true for the thatch and soil we examined. The Koc values we obtained for 2,4-D acid and carbaryl were slightly greater than the average value reported by other researchers (Balogh and Walker 1992). Our triclopyr Koc's were similar to that reported by other researchers (Balogh and Walker 1992).

Transport: In our semi-annual report we indicated that we decided to examine the transport of triclopyr in place of chlorothalonil. The reason for this substitution is that it would take us over a year of continuously applying water and collecting leachate samples to obtain enough data to construct the breakthrough curves necessary to evaluate the transport of chlorothalonil. Leaching the 50 plus feet of water our model runs indicated would necessary to obtain a complete breakthrough curve for chlorothalonil was cost and labor prohibitive given the limitations of our current transport experimental apparatus. In addition, maintaining the thatch and soils cores above field capacity for a year or more is unrealistic for just about any real world situation imaginable. The results obtained from such a study would not be applicable to any "real world" pesticide transport situation.

To further illustrate the point above, a comparison of the breakthrough curves obtained from our 2,4-D, carbaryl and chlorothalonil transport studies, for soil columns collected from zoysiagrass site, is shown in figure 3. Note the amount of rainfall that was applied to each of the columns and the absence of a peak in the breakthrough curve for the column that received a single application of chlorothalonil.

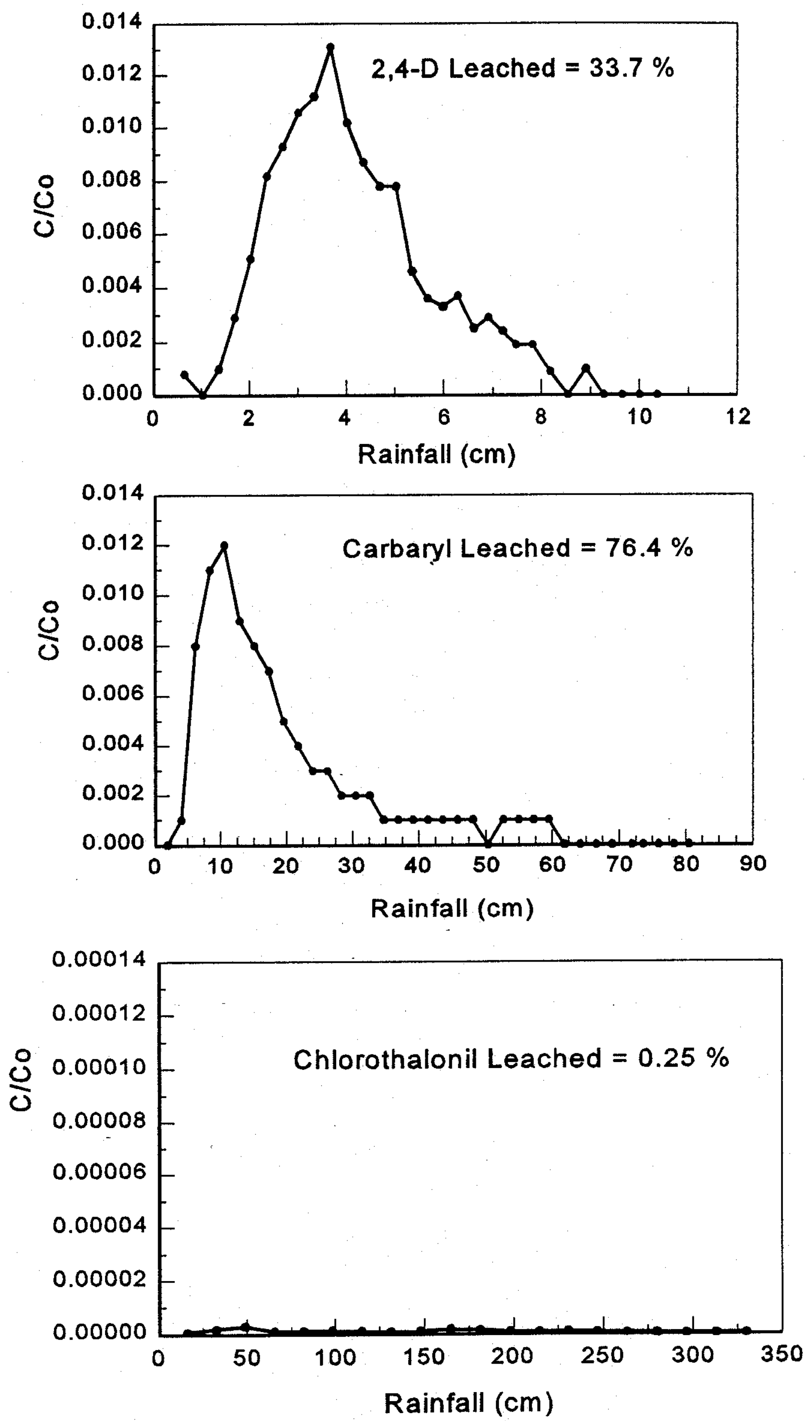


Figure 3. Zoysiagrass site soil column breakthrough curves for 2,4-D, carbaryl and chlorothalonil.

In last years annual reported we provided a comprehensive summary of our 2,4-D transport study and the modeling effort related to this study. This past year we completed our carbaryl and triclopyr transport studies and most of our modeling efforts with carbaryl. We are currently evaluating the use of equilibrium and non-equilibrium convection-dispersion equation based models to predict triclopyr transport through soils containing a surface layer of turfgrass thatch.

A summary of the percent of applied pesticide that was leached from the columns used in the 2,4-D, triclopyr and carbaryl transport studies is presented in table 2.The experimental conditions of our transport studies represent a near "worst case scenario" for pesticide leaching from turf. Each pesticide was applied to columns that were nearly saturated and the surface applied pesticide allowed to sorb to the thatch and soil (or soil only in the columns that were devoid of a thatch layer) for only 24 hours. After the 24 hour sorption period, the columns received 0.8 to 1 cm hr^{-1} simulated rainfall continuously until a complete breakthrough curve (BTC) for the pesticide of interest was obtained from the column. The depth of soil in each column was only 10 to 11 cm.

Table 2. Percent of 2,4-D, triclopyr and carbaryl leached from columns containing a surface layer of thatch and columns devoid of thatch, and the associated contrasts of interest..

Column ID	2,4-D	Triclopyr	Carbaryl
	--------------------	% leached	--------------------
Bentgrass thatch + soil (BT)	17.5	59.7	52.9
Bentgrass soil (BS)	43.1	70.5	65.7
Zoysiagrass thatch + soil (ZT)	29.0	81.2	60.8
Zoysiagrass soil (ZS)	34.3	87.9	78.2
Contrasts of interest			
	-------------	significance probability	-------------
BT vs BS	0.001	0.224	0.305
ZT vs ZS	0.162	0.042	0.001
BT vs ZT	0.008	0.669	0.041

Pesticide leachate losses were greatest for triclopyr and least for 2,4-D. Carbaryl leachate losses were slightly less than triclopyr, however, approximately 8 times more rainfall (10 cm verses 80 cm) was required to leach carbaryl from the soil and thatch+soil columns. Similar amounts of rainfall were required to leach 2,4-D and triclopyr from the columns. When compared to columns devoid of thatch, the presence of a bentgrass thatch layer reduced 2,4-D transport but not triclopyr or carbaryl transport. As we mentioned in our earlier mid-year progress report, the presence of earthworm channels within the triclopyr and carbaryl columns collected from the bentgrass site resulted in preferential flow within these columns. The presence of preferential flow likely reduced the effectiveness of bentgrass thatch to inhibit triclopyr and carbaryl transport.

The presence of a zoysiagrass thatch layer reduced triclopyr and carbaryl transport but not 2,4-D transport. The columns used in the carbaryl and triclopyr study were removed from the field in February of 1998 while the columns used in the 2,4-D study were removed from the same field in June of 1996. No thatch control measures were used between the two collection periods. Thus, the zoysiagrass thatch columns collected in 1998 likely had a greater total amount of organic matter than the columns collected in 1996. Furthermore, it is possible the time of the year in which the columns were collected may have influenced the relative proportion of the thatch organic matter that was partially or highly decomposed. It is generally believed that highly degraded organic matter is a more effective sorbant than partially decomposed organic matter.

Bromide and carbaryl breakthrough curves obtained from several of the columns used in the carbaryl transport study were used to evaluate the performance of linear equilibrium (LEM), and two-site non-equilibrium (2SNE) models to predict the transport of carbaryl. The latter model uses a non-equilibrium form of the convective-dispersion equation to predict solute movement in porous media while the former model uses a linear equilibrium form of the equation to predict solute movement. A key parameter in convective-dispersion based models is the retardation factor. The retardation factor (R) can be calculated directly if the bulk density, soil moisture content and adsorption properties of the column for the pesticide of interest are known. Alternatively, the model can determine R using a least squares approach. A second objective of our modeling work was to compare the use of retardation factors (R) based on our laboratory measured sorption coefficients (ie., measured or calculated R) with model fitted R's to predict carbaryl transport. Graphical comparisons of representative soil or thatch plus soil columns are shown in figures 4 and 5 for each of the four porous media combinations. The data presented in figures 4 and 5 are the actual measurements for individual columns and the corresponding model estimations for the column.

Modeling of bromide transport presented strong evidence of significant two domain flow in all columns except the zoysiagrass site soil columns (fig 4.). Visual examination of the bentgrass site columns revealed extensive earthworm burrowing which it is felt contributed to the preferential flow behavior observed. In the presence of two domain flow, only the 2SNE model could be used for the bentgrass site columns and the zoysiagrass site thatch plus soil columns. The curve-fits of the 2SNE model explained 74 to 94% of the variability when laboratory measured sorption coefficients were used to calculate R. Allowing the 2SNE model to estimate R improved the amount of variability the model could account for (93 to 97%) but resulted in substantial lower R's when compared to the measured R's.

In the zoysiagrass soil columns, the predicted BTC's based on the LEM did not adequately describe the observed BTC's when calculated retardation factors were used. The LEM gave acceptable estimates when R was fit, although fitted values of R were substantially lower than the measured R. The 2SNE model gave reasonable estimates using calculated R's indicating that two site adsorption may have occurred in the zoysiagrass soil columns. When R was fitted for the 2SNE model the estimated R's were also substantially lowed than measured R's. Estimating R resulted in fits with the 2SNE model that explained 99% of the variability from measured observations in the zoysiagrass soil columns.

Work Planned for Nov. 1 1998 - Nov. 1 1999 Period

Most of this project constitutes the Ph.D. dissertation research of Ms. Sanju Raturi. Sanju is currently finishing up her modeling efforts with triclopyr. She is also currently writing her Ph. D. dissertation, which should be completed in early 1999. Once her dissertation is accepted by the University of Maryland Graduate School she will begin her USGA sponsored post doctorate project. In her post doctorate studies she will use the 2,4-D carbaryl and triclopyr data from her

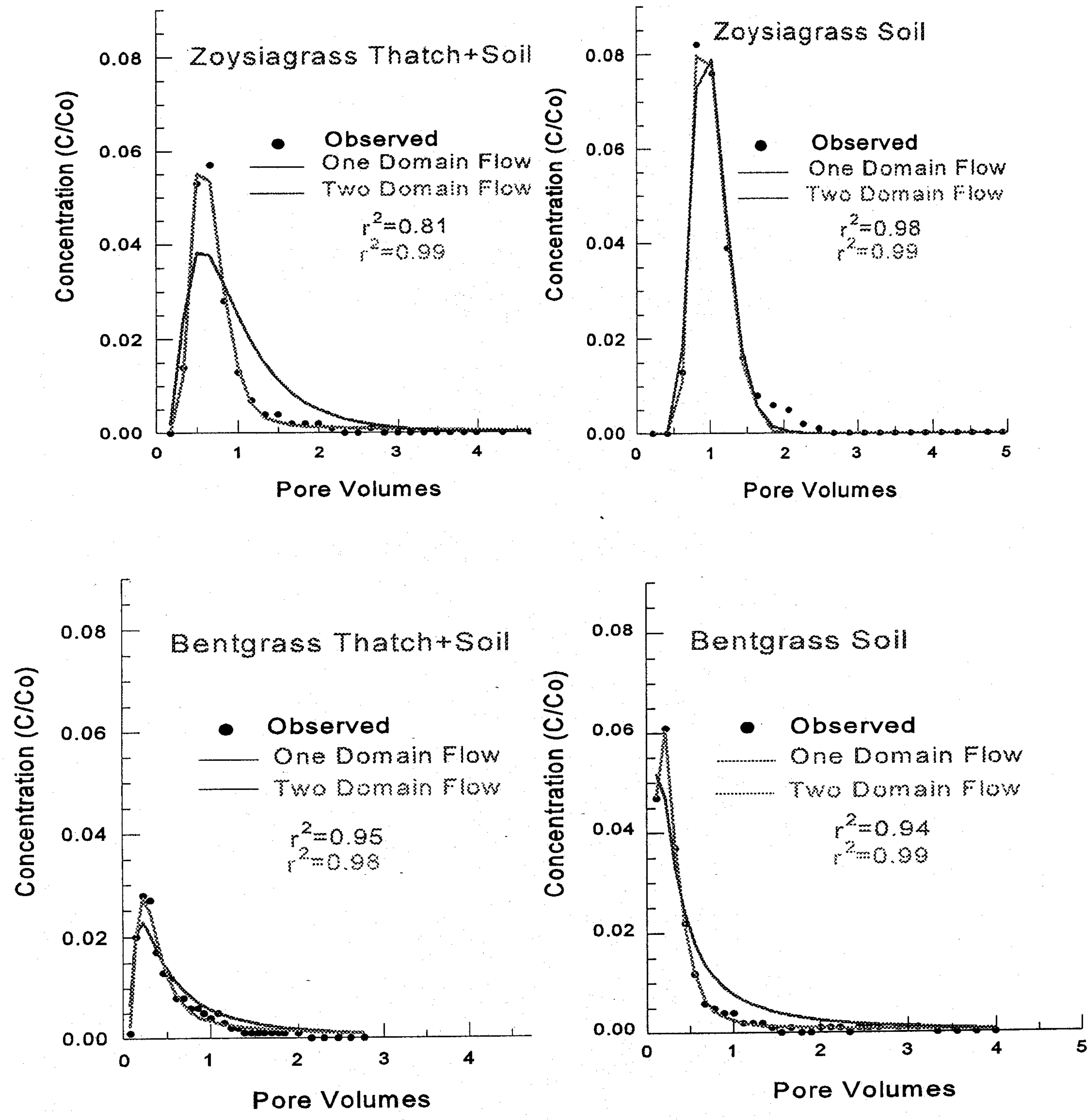


Figure 4. Bromide breakthrough curves for one and two domain flow models for soil columns containing a surface layer of thatch and soil columns devoid of thatch.

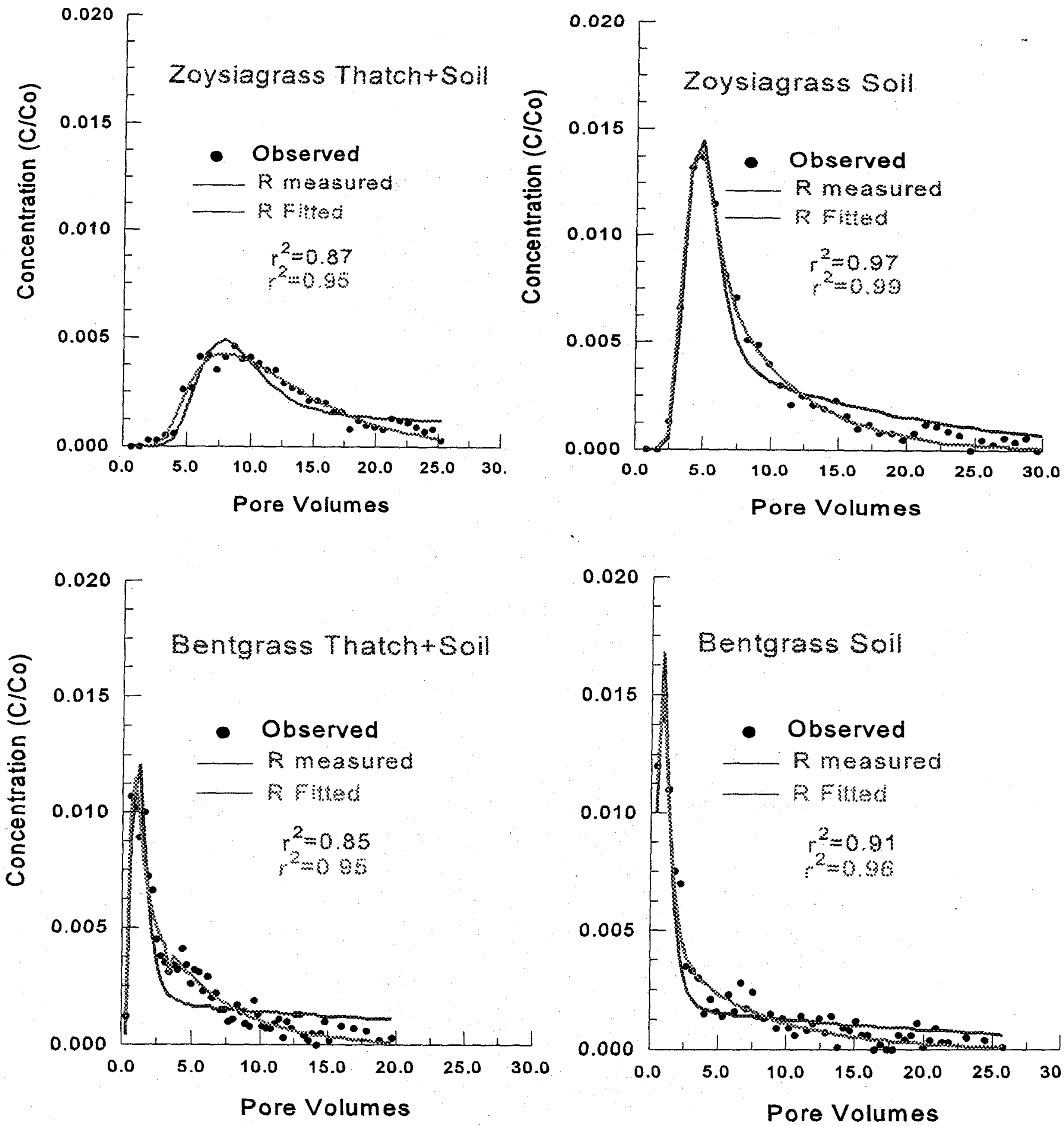


Figure 5. Carbaryl breakthrough curves from two site nonequilibrium model using measured and fitted retardation factors for soil columns containing a surface layer of thatch and soil columns devoid of thatch.

Ph.D. research to create a model that considers the presence of thatch in turfgrass. We anticipate that the development and validation of model will require approximately 9 months to complete.

LITERATURE CITED

Balogh J.C. and W.J. Walker. 1992. Golf Course Management & Construction: Environmental Issues. 951 pp. Lewis Publishers, Boca Raton, FL

Dell, C.J., C.S. Throssell, M. Bischoff and R.F. Turco. 1994. J. Environ. Qual. 23:92-96.

Lickfield, D.W. and B.E. Branham. 1995. J. Environ. Qual. 24:980-985.

Raturi, S., M.J. Carroll, R.L. Hill. E. Pheil, A.E. Herner. 1997. Inter. Turf. Soc. Res. J. 8:187-196.