MODELING PESTICIDE TRANSPORT

In

TURFGRASS THATCH AND FOLIAGE

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Executive Summary

Pesticides applied to mature turf move into the soil only after being washed off the foliage and moving through the 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 1996 and 1997 a series of sorption and transport studies were conducted to characterize the movement of 2,4-D acid 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 of 2,4-D to soil was found to be nearly instantaneous. In contrast, 2,4-D adsorption to thatch was dependent on the residence time of the solution containing this pesticide. The adsorption kinetics of the two turfgrass species thatch were similar. The quantity of 2,4-D adsorption to thatch increased 72% as the solution residence time increased from 15 minutes to 24 hours; however, even at a residence time as brief as 15 minutes, 2,4-D adsorption to thatch was three times greater than to soil.

Desorption losses were evaluated by subjecting columns of thatch or soil to three successive leaching events. The leaching events took place after allowing 2,4-D to adsorb to the thatch or soil for 24 hours. The quantity of 2,4-D detected in the leachate was used to determine the proportion of 2,4-D that was desorbed from the sample. The proportion of 2,4-D that was desorbed during the three leaching events was slightly less for thatch than for soil. The difference in proportional losses of 2,4-D, however, was small when compared to the total proportion of 2,4-D that was lost from each media. In a previously conducted desorption study, we found that desorption losses of dicamba were greater from soil than from thatch. Our earlier results suggest that some water soluble pesticides may be more tightly bound to thatch than to soil.

Undisturbed cores of soil and soil plus a surface layer of thatch were used to determine the effect of thatch on the 2,4-D transport in soil. Cores having a surface layer of SOUTHSHORE creeping bentgrass thatch were more effective in reducing 2,4-D transport than cores having a surface layer of MEYER zoyisagrass thatch.

Bromide and 2,4-D breakthrough curves obtained from the transport study were used to evaluate the performance of linear equilibrium (LEM), two-site non-equilibrium (2SNE) and one-site kinetic non-equilibrium models to predict the transport of 2,4-D. The latter two models use non-equilibrium forms of the convection-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. The bromide data did not present strong evidence of significant physical non-equilibrium or two domain flow in any core. In addition, all three models described 2,4-D transport fairly well with slightly improved fits resulting from the 2SNE model.

Research in 1998 will focus on completing sorption and transport studies involving pesticides having low to moderate water solubilities (carbaryl and chlorothalonil). The data collected will be used to further evaluate the predictive capabilities of the three aforementioned models.

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 the convection-dispersion equation to predict pesticide transport through turf containing a surface layer of thatch.

Biographical Briefs:

Dr. Mark Carroll: Mark Carroll joined the Agronomy faculty at the University of Maryland in 1989 after receiving his Ph.D. degree in Turfgrass Science from Cornell University. In 1995 he was promoted to the rank of Associate Professor. Dr. Carroll holds a joint academic appointment in research (75%) and teaching (25%) within the newly formed Department of Natural Resource Sciences and Landscape Architecture. His research efforts have focused on water quality issues in the management of turfgrasses and turfgrass water stress physiology. He is currently investigating the transport of pesticides within turfgrass systems. He also teaches junior and senior level courses in turfgrass management and serves as the undergraduate turfgrass program advisor. He has authored and co-authored more than 45 scientific, technical and popular articles.
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Dr. Robert Hill: Robert Hill received his Ph.D., in Soil Physics from the Iowa State University in 1984. He joined the University of Maryland faculty in 1984 and was promoted to the rank of Associate Professor in 1990. Dr Hill holds a joint academic appointment in research (75%) and teaching (25%) within the Department of Natural Resource Sciences and Landscape Architecture. His primary research efforts have been concentrated in the following areas: 1) *Non-point pollution* - to evaluate the impact of various management practices on surface and subsurface nutrient, pesticide, and microbial losses; 2) *Tillage management systems* - to assess the impact of tillage management systems on soil physical properties as related to plant growth, nutrient loss and utilization, runoff and sediment losses; 3) *Spatial variability* - to examine the distribution of soil and plant property values over time and space. Dr Hill has received more than 1.3 million dollars in external grants to support his research efforts. He currently teaches senior and graduate level courses in soil and water conservation and management, soil physics, and advanced soil physics.
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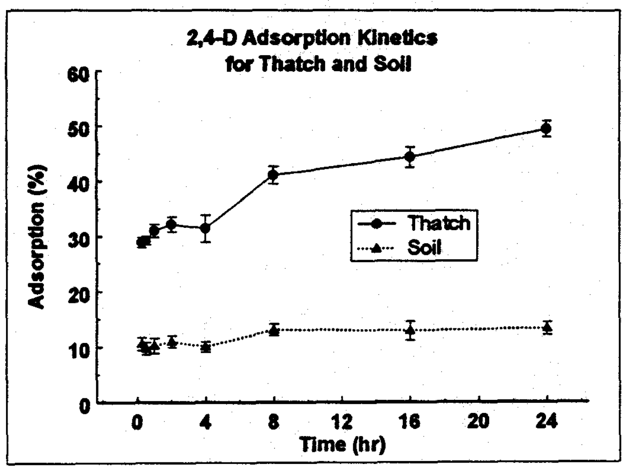

Figure ? Adsorption kinetics of 2,4-D for thatch and soil.

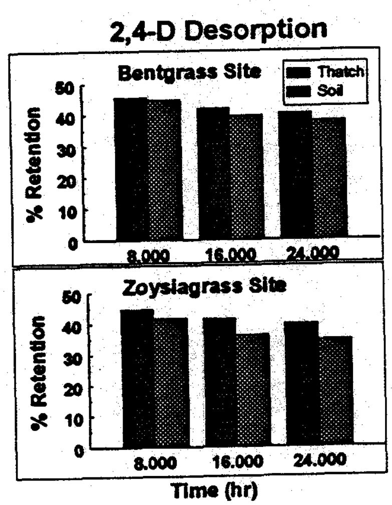

Figure ? Cumulative proportion of 2,4-D retained to thatch following three successive 8 hour leaching events.

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

Washoff: Research evaluating the washoff of chlorothalonil, dicamba and carbaryl from Southshore creeping bentgrass was completed in the fall of 1996. The results were summarized in last years USGA Annual Report. A manuscript tentatively entitled "Washoff of three formulations of chlorothalonil from turfgrass foliage" is currently being prepared for publication. The manuscript will submitted for publication in early 1998. The dicamba and carbaryl washoff data will likely be included as part of a book chapter we have been asked to write for a American Chemical Society and USGA Greens Section research symposium to be held in the summer of 1998.

Sorption: Studies examining the sorptive behavior of 2,4-D acid and carbaryl to bentgrass and zoysiagrass thatch were conducted in 1997. The objectives of these studies are: 1) to determine the equilibrium sorption coefficients for the two turfgrass species thatch and for the soil residing immediately below each turfgrass species thatch, and 2) to characterize the short term adsorptive and desorptive behavior of each pesticide for each of the four aforementioned porous media. With the exception of characterizing the short term adsorptive behavior of carbaryl, all sorption studies involving the carbaryl and 2,4-D have been completed.

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 effect of residence time on 2,4-D acid adsorption to thatch and soil is shown in Figure 1. There was no significant difference in the adsorption kinetics of the two thatch sources or for the two soils underlying each thatch. Hence, a single line was used to characterize the adsorption kinetics of the thatch and soil. The adsorption of 2,4-D to soil was nearly instantaneous whereas the adsorption of 2,4-D to thatch was more time dependent. The adsorption of 2,4-D acid to thatch increased 72% as the solution residence time was increased from 15 minutes to 24 hours. However, even for a solution residence time as brief as 15 minutes, three times as much 2,4-D acid was adsorbed to thatch than to soil. The kinetic data suggest that the use of a thatch equilibrium sorption coefficient in a multi-layered model will under predict 2,4-D leaching losses from thatch whenever a significant rainfall event takes place shortly after applying 2,4-D to turf.

Equilibrium sorption isotherms were constructed using a 24 hour solution residence time. The equilibrium partition coefficients for each media were obtained from the Freundlich sorption isotherms shown in Figures 2 and 3. The organic carbon content of the media were used to calculate the normalized sorption coefficients shown in Table 1.

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

Media	Organic Matter*	Normalized Sorption Coefficient⁺ 2,4-D Acid	Carbaryl
	%	$m^3\ kg^{-1}$	
Bentgrass			
Thatch	11.4	5.29×10^{-2}	7.30×10^{-1}
Soil	1.6	9.70×10^{-2}	4.28×10^{-1}
Zoysia grass			
Thatch	9.1	6.07×10^{-2}	8.98×10^{-1}
Soil	1.1	8.29×10^{-2}	4.43×10^{-1}

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

* % organic carbon = (% organic matter - 0.35)/1.80

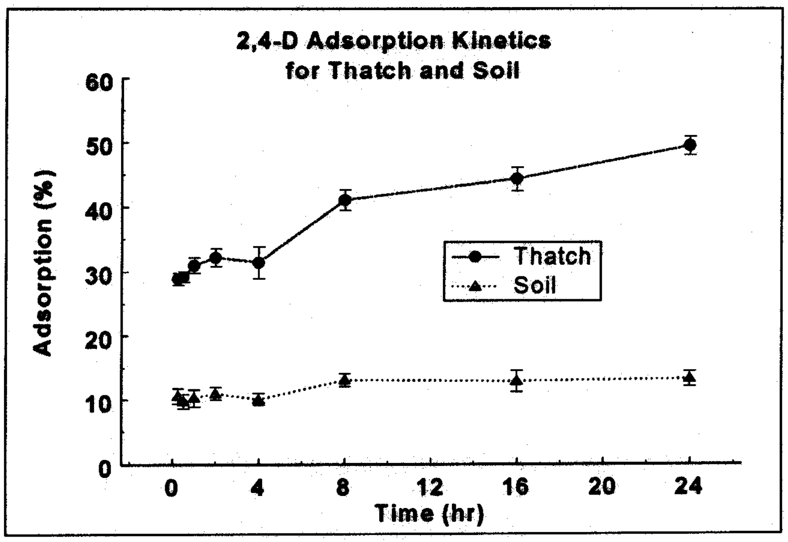

Fig. 1 Adsorption kinetics of 2,4-D acid to thatch and soil.

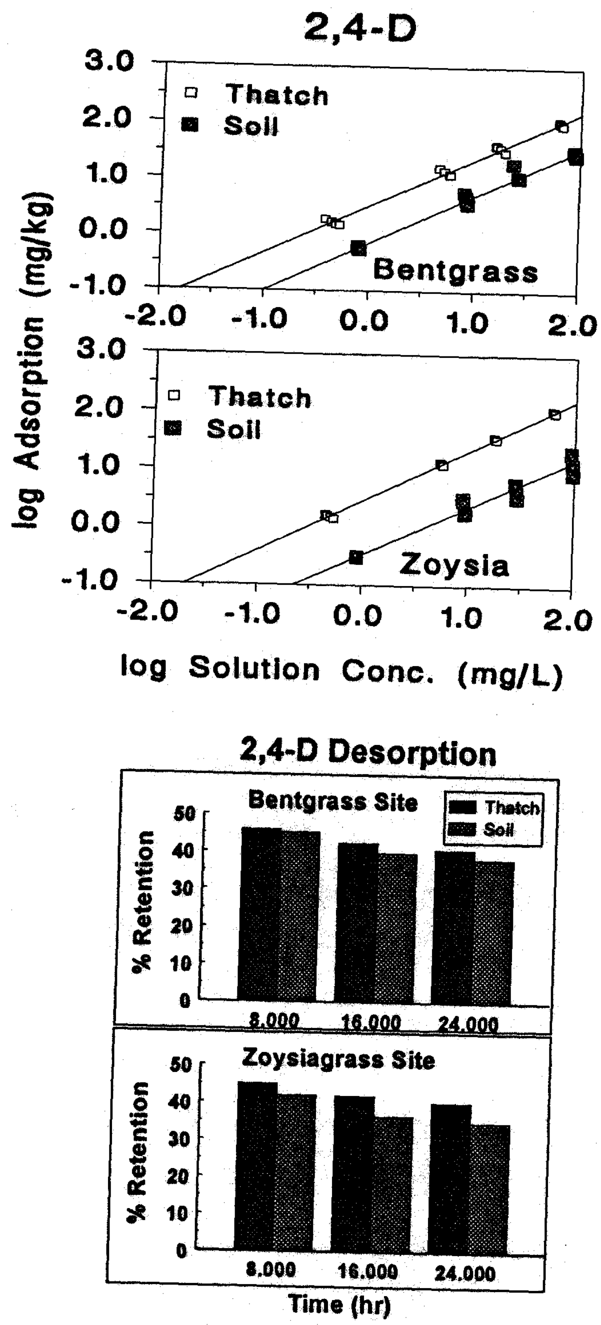

Fig. 2 Adsorption of 2,4-D acid to thatch and soil using a 24 hour solution residence time and the cumulative proportion of 2,4-D acid retained to thatch and soil following three successive 8 hour leaching events.

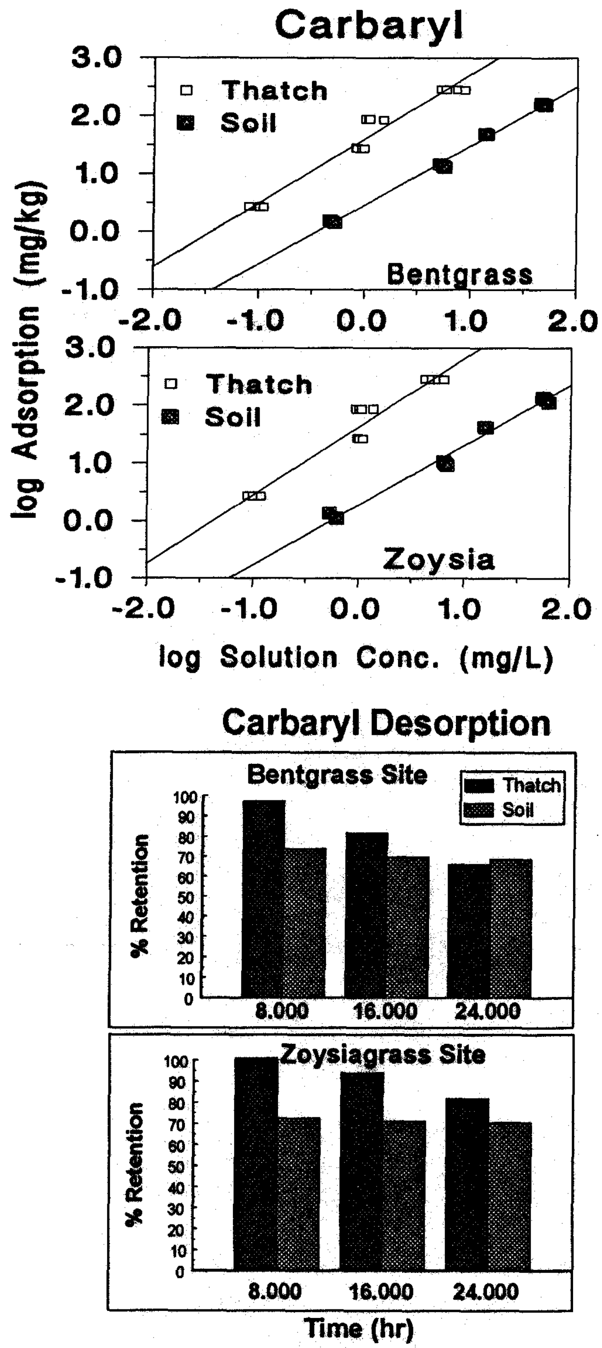

Fig. 3 Carbaryl adsorption to thatch and soil using a 24 hour solution residence time and the cumulative proportion of carbaryl retained to thatch and soil following three successive 8 hour leaching events.

Both turfgrass species thatch had much higher 2,4-D acid and carbaryl absorption capacities than the underlying soil. Conflicting results, however, arose when the data were normalized for the presence of organic carbon. In the case of 2,4-D, the two soil Koc's were greater than the thatch Koc's whereas the opposite was true for carbaryl. When averaged over the two turfgrass site locations, the 2,4-D Koc for thatch was 63% lower than for soil. 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 the opposite may true for the thatch and soil we examined. The Koc values we obtained for 2,4-D acid and carbaryl were near the upper limits reported by other researchers (Balogh and Walker 1992).

As expected, 2,4-D retention to thatch and soil were much less than carbaryl. Desorption losses of both pesticides were greatest during the first leaching event and declined with subsequent leaching. There was little difference in the proportion of 2,4-D retained in thatch and soil. Carbaryl retention in soil, however, 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 indicates that carbaryl is more tightly bound to zoysiagrass thatch than to the underlying soil.

Transport: The transport of 2,4-D through undisturbed cores of soil or soil plus a surface layer of thatch were examined in 1996. Each core contained 10 to 11 cm of soil. The bentgrass site cores had a sandy loam texture while the zoysiagrass site cores had a loamy sand soil texture. The average thatch depth of the cores containing a surface layer of thatch was 2.3 cm for the bentgrass thatch cores and 3.4 cm for the zoysiagrass thatch cores. A constant rate of simulated rainfall (1 cm/hr) was applied to the cores using a specially designed emitter. Once steady state flow conditions were achieved in each core, a pulse of bromide was added and leachate samples collected for the next 12 hours. The bromide leachate data was used to derive the convective dispersive parameters needed to model 2,4-D transport. Analytical grade 2,4-D acid was added to the surface of each core 12 hours after adding the pulse of bromide. The emitters were removed from the cores at this time and the 2,4-D allowed to sorb to the thatch and soil for 24 hours. Simulated rainfall was then re-initiated and leachate samples collected at regular intervals until the concentration 2,4-D in the leachate approached the lower limits detection.

At the end of the leaching event a portion of each core was used to determine the soil physical properties of the core. The remainder of the core was placed into a freezer. The frozen portion of the core was thawed in early 1997 to determine the amount of 2,4-D that remained in the core at the end of the leaching event. The thawed sample was placed in a 50:50, methanol:water, solution and the sample shaken for 2 hours. The resulting slurry was then subjected to vacuum filtration and filtrate analyzed for 2,4-D. The amount of 2,4-D remaining in the sample was then determined by combusting the slurry and measuring the amount of ^{14}C, 2,4-D evolved using liquid scintillation methods. The amount of 2,4-D removed by the methanol/water solution is considered to be the potentially leachable fraction of 2,4-D whereas the remaining amount removed by combustion is considered to be the non-leachable or irreversibly bound fraction of 2,4-D present in the sample.

In our primary analysis of the 2,4-D data we reported that no more than 7% of the applied 2,4-D could be leached from any core. During our modeling efforts it became apparent that we had incorrectly used the cumulative number of pore volumes to calculate the total amount of 2,4-D leached from each core. This calculation should have been based on the total volume of solution leached through each core. The correct leachate losses from each core treatment along with potentially leachable and non-leachable fraction of 2,4-D present in the cores at the end of the transport study are shown in Table 2. The leachate losses of 2,4-D while being considerably higher than 7% continue to shown the positive effect thatch has on reducing 2,4-D transport. This is especially true in the case of bentgrass thatch which reduced 2,4-D leaching by 59%. Visual comparison of the two thatch sources revealed that the thinner diameter of the creeping bentgrass stolons resulted in this thatch being much finer than zoysiagrass thatch. The lower amount of 2,4-D leaching observed in the cores containing bentgrass thatch, may be the result of more organic matter surface area, (ie., more exchange sites) being available for sorption in the bentgrass thatch than in the zoysiagrass thatch.

Table 2. Mass balance of 2,4-D recovery following transport studies for bentgrass and zoysia grass thatch and soil

	2,4-D Recovery			
Column ID	Easily Extractable	Tightly Bound	Leached	Total Recovery
	%			
ZT+	5.18 (±0.98)§	46.97 (±5.32)	29.03 (±3.01)	81.18 (±2.35)
ZS*	11.36 (±2.66)	26.55 (±4.35)	34.35 (±2.04)	72.26 (±3.02)
BT#	9.89 (±1.71)	57.58 (±7.88)	17.45 (±1.83)	84.91 (±8.17)
BS##	12.29 (±1.28)	35.46 (±17.08)	43.11 (±1.10)	90.86 (±7.03)

+ 3.4 cm surface layer zoysia grass thatch + 7.6 cm soil
* 10.5 cm soil only (zoysia grass site)
# 2.3 cm surface layer of bentgrass thatch + 9.8 cm soil
10.9 cm soil only (bentgrass site)
§ Values in parentheses indicate standard errors of estimates

The experimental conditions of this study represent a near "worst case scenario" for 2,4-D leaching from turf. Limited recovery of 2,4-D by the 50:50 methanol:water extraction indicate that little additional 2,4-D leaching would have occurred had the study been extended. The higher percentages of tightly bound 2,4-D found in the cores containing thatch can be attributed to the higher overall 2,4-D adsorption capacities of the two turfgrass species thatch.

Bromide and 2,4-D breakthrough curves obtained from each of the cores were used to evaluate the performance of linear equilibrium (LEM), two-site non-equilibrium (2SNE) and one-site kinetic non-equilibrium models to predict the transport of 2,4-D. The latter two models use non-equilibrium forms of the convective-dispersion equation to predict solute movement in porus media while the former model uses a linear equilibrium form of the equation to predict solute movement. Graphical comparisons of a representative soil or thatch plus soil core are shown in Figures 4 and 5 for each of the four porus media combinations. The data presented are the actual measurements for a individual core and the corresponding model estimations for that core.

If model evaluation is based on the coefficient of determination, modeling of bromide transport did not present strong evidence of significant non-equilibrium or two domain flow (Fig. 4). Similarly, all three models described 2,4-D transport fairly well with slightly improved fits resulting from the 2SNE model. The coefficients of determination for the cores containing a surface layer of bentgrass thatch were lower than the other cores using all three models. There was also greater variability in leachate 2,4-D concentrations present in all cores containing bentgrass thatch that was not observed for any other porus media combinations. The reasons for this variability must be attributable to some unique unknown properties of bentgrass thatch.

A study investigating the transport of chlorothalonil through undisturbed cores of soil or soil plus a surface layer of thatch was initiated in the summer of 1997. Chlorothalonil is a relatively immobile pesticide. Hence, compared to a pesticide like 2,4-D much more water must be leached through a core before the pesticide will appear in leachate. In this study, we applied 336 cm (11 feet) of water to 10-11 cm deep undisturbed cores of soil or thatch plus soil. At the beginning of the study, each core received a single surface application of 6 ounces Daconil 2787 Ultrex WDG per 1000 square feet. The simulated rainfall was applied in even increments every day for 80 days using the same emitters that were used in the 2,4-D transport study. Leachate from the cores was collected daily. As in the 2,4-D transport study, a pulse of bromide was added to the cores to permit determination of the transport parameters needed to model chlorothalonil movement in the cores. The leachate samples are currently being analyzed for chlorothalonil.

Work Planned for Dec. 1 1997 - Nov. 1 1998 Period

A transport study involving carbaryl will be conducted in December of 1997. The data collected from this study will be used to evaluate the use of linear equilibrium, two-site non-equilibrium and one-site kinetic non-equilibrium models to predict the transport of a moderately water soluble pesticide through soils containing surface layer of thatch. The procedures used in this study will be similar to those described previously for 2,4-D. We anticipate that all laboratory work involving each of the three transport studies will be completed by the end of March 1997. After that time we will concentrate our efforts on completing the modeling evaluations.

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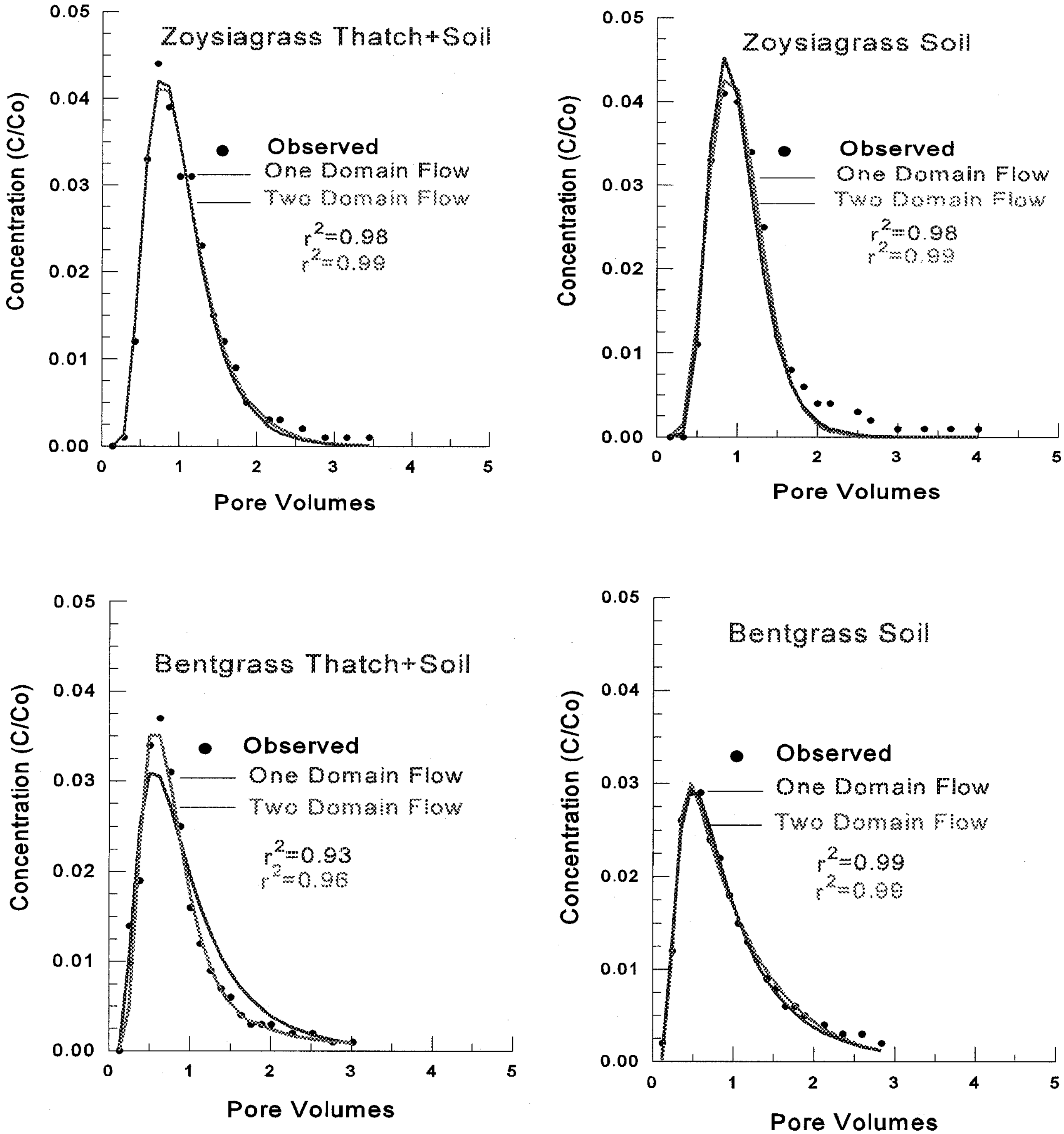

Fig. 4 Bromide breakthrough curves for one and two domain flow models for soil columns containing a surface layer of thatch and soil columns devoid of thatch.

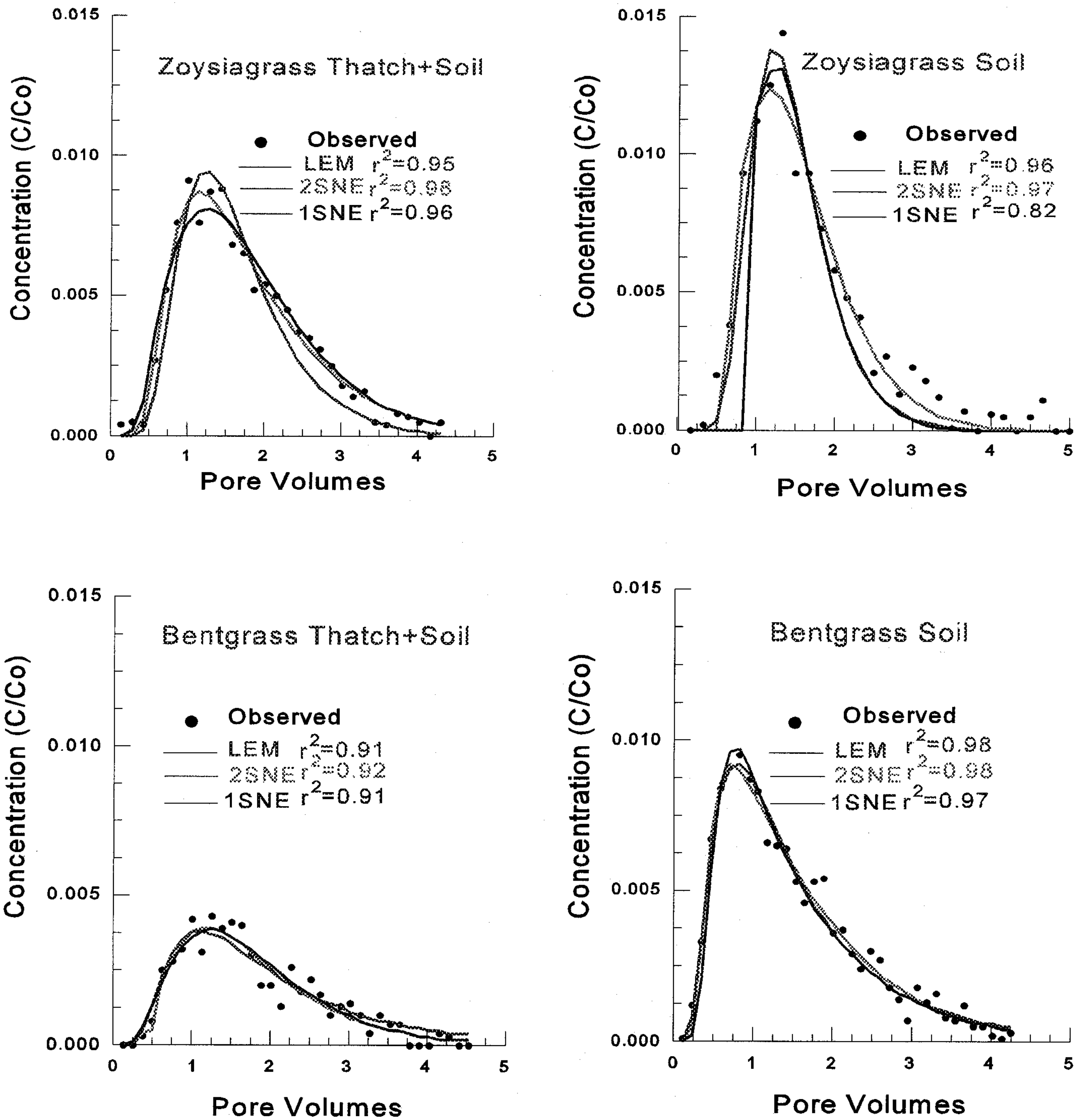

Fig. 5 2,4-D breakthrough curves for linear equilibrium model (LEM), two site nonequilibrium model (2SNE) and one site kinetic nonequilibrium model (1SNE) for soil columns containing a surface layer of thatch and soil columns devoid of thatch.