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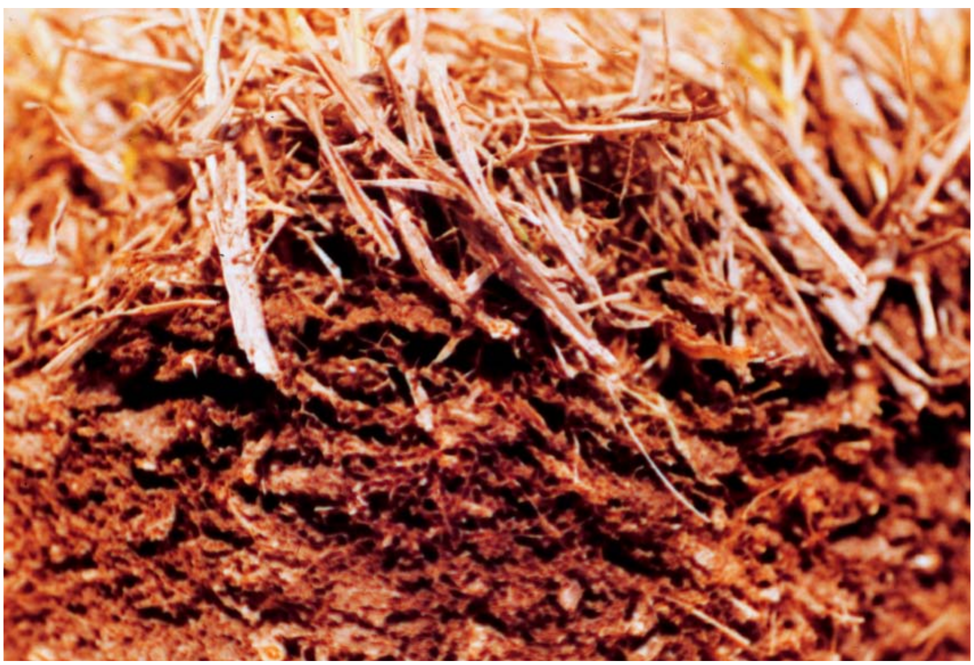


Researchers at the University of Maryland showed that the ability of a pesticide to bind to thatch can be markedly different from that pesticide's ability to bind to the underlying soil.

Volume 2, Number 5
March 1, 2003

PURPOSE

The purpose of *USGA Turfgrass and Environmental Research Online* is to effectively communicate the results of research projects funded under USGA's Turfgrass and Environmental Research Program to all who can benefit from such knowledge. Since 1983, the USGA has funded more than 215 projects at a cost of $21 million. The private, non-profit research program provides funding opportunities to university faculty interested in working on environmental and turf management problems affecting golf courses. The outstanding playing conditions of today's golf courses are a direct result of ***using science to benefit golf***.

Editor

Jeff Nus, Ph.D.
904 Highland Drive
Lawrence, KS 66044
jnus@usga.org
(785) 832-2300
(785) 832-9265 (fax)

Research Director

Michael P. Kenna, Ph.D.
P.O. Box 2227
Stillwater, OK 74076
mkenna@usga.org
(405) 743-3900
(405) 743-3910 (fax)

Does Thatch Complicate Pesticide Leachate Predictions?

Mark Carroll and Robert L. Hill

SUMMARY

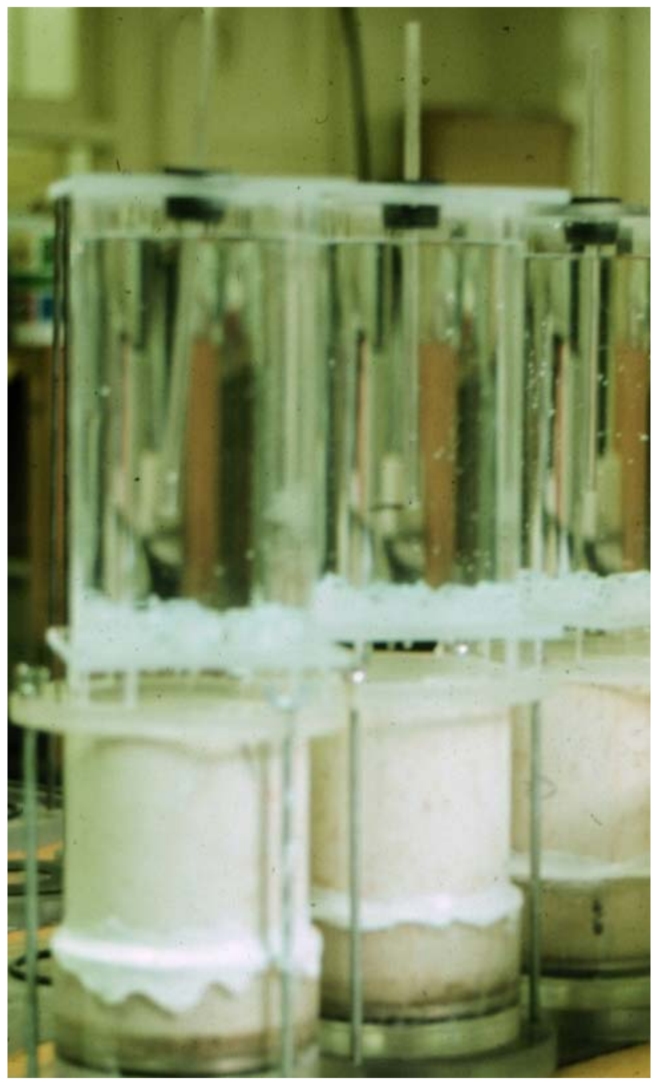
Simulation models used in golf course water quality risk assessment often times assume instantaneous pesticide sorption. Since pesticides must pass through an organic-rich turfgrass thatch layer, this assumption may not be appropriate for modeling the transport of some pesticides. Studies were conducted to examine the sorption behavior of 2,4-D and carbaryl to creeping bentgrass (*Agrostis stolonifera*) and zoysiagrass (*Zoysia japonica*) thatch and to determine the influence of thatch on 2,4-D leaching from columns with a thatch layer and from columns devoid of thatch. Leachate data were used to evaluate the performance of equilibrium (i.e. instantaneous sorption), one-site non-equilibrium (i.e. kinetic sorption) and two-site non-equilibrium (i.e. kinetic and instantaneous sorption) models to predict 2,4-D transport.

- Pesticide mobility often depends on the initial sorptive behavior of a pesticide. Carbaryl reached apparent sorption equilibrium rapidly while sorption of 2,4-D to thatch was highly dependent on solution resident times.
- Bentgrass thatch was more effective in reducing 2,4-D leaching than was zoysiagrass thatch.
- The sorptive behavior of a pesticide to thatch can be markedly different from that of the underlying soil.
- The two-site non-equilibrium model provided more accurate predictions of 2,4-D leaching than when instantaneous equilibrium sorption or one-site kinetic non-equilibrium sorption was assumed. The use of non-equilibrium models should be considered for evaluating "worst-case" turfgrass pesticide leaching loss scenario's.
- Thatch may complicate model predictions of pesticide transport and care should be used in choosing the appropriate model for pesticide transport predictions.
- Studies examining the size of organic constituents and the state of decomposition of the decaying plant material within thatch are needed to better understand turfgrass species' differences in pesticide leaching.

Pesticide transport models are often used in the development of water quality risk assessments for proposed golf course sites. The primary role of simulation modeling in these risk assessments is to provide quantitative estimates of the potential for turf pesticide movement into surface water and groundwater. Model simulation results can lead to revisions in proposed pesticide use and/or revisions in some aspects of the course design to minimize impacts on water quality (3).

There are several computer models that can potentially be used to assess turf pesticide movement into surface water and groundwater.

MARK CARROLL, Associate Professor Turfgrass Science, and ROBERT L. HILL, Professor of Soil Physics, Dept. of Natural Resource Sciences and Landscape Architecture, Univ. of Maryland, College Park, MD. 21742



The sorptive behavior of the two pesticides were examined by packing large syringe tubes with thatch or soil. The syringe tubes were then attached to a machine that controlled the rate at which a known pesticide solution concentration was leached through the packed columns.

Model selection is ultimately decided by several criteria. Those criteria deemed most important include: calibration and validation of the model for the situation of interest, user friendliness of the model, technical support, ability to model several chemicals simultaneously, and regulatory endorsement (3,4, 8). From a purely technical perspective, the first four criteria are the most important. In actual practice, selection is usually based on which model a particular regulatory agency endorses.

Some models used in golf course risk assessments are field-scale process-based models. Process-based models simulate pesticide movement by considering the most fundamentally basic physical and chemical processes known to affect pesticide transport for the resolution level of interest. In theory, a process-based pesticide transport model will correctly predict pesticide movement when all of the model's parameters are correctly represented in the simulation.

There are no field-scale models currently used for golf course risk assessments that are entirely process-based. The multitude of processes that operate at the field scale requires that some processes be simplified while others are simply ignored. This simplification is done so the model will have minimal data requirements and will be relatively easy to use. The simplification also is necessary so that the complexity of processes occurring during pesticide transport can be addressed, and the variability of field-scale processes can be simplified.

A primary challenge in process-based pesticide transport modeling is to identify and adequately represent the processes that operate in a particular field situation. If a process is found to have a substantial impact on pesticide transport, it needs to be considered in the model to insure the model has the capability to correctly predict pesticide transport for the situation of interest. The manner in which the chemical is bound or sorbed to the organic matter and soil particles has a large fundamental impact on the quantities of a chemical that are ultimately leached through the soil profile. Our research addresses the sorption processes for turfgrass thatch and soil and how those sorption processes need to be adequately represented in models predicting the rate of pesticide transport from turf sites.

Thatch Sorption Dynamics

Thatch is represented as a distinct surface layer in most model simulations. The layer is typically treated in a manner analogous to that of the underlying soil. The assignment of thatch chemical and physical properties may sometimes be obtained from direct field measurements, but are more often estimated from values for thatch in the literature. Pesticide movement is modeled by assuming the transport processes operating in thatch are the same as those processes operating in the underlying soil.

Most models used in golf course water quality risk assessments assume that pesticide sorption is an instantaneous process. This assumption is usually valid for homogenous, non-aggregated, low-organic-matter soils not subjected to precipitation events that generate high percolation rates for extended periods of time. In these types of soils, most of the sorption sites are readily accessible because they are located in close proximity or directly on the exterior surfaces of the mineral matter.

In soils that contain high amounts of organic matter, most of the pesticide sorption sites are believed to be located within the interstices of the organic matter (1). Similarly, in well aggregated soils, many sorption sites are believed to be located in cracks and fissures within the aggregates. In both situations, diffusive mass transfer of the pesticide is required for sorption to occur at the interior sites.

The contrasting nature of pesticide sorption to thatch and soil has been clearly seen in our sorption studies. In one study, we examined the sorption kinetics of 2,4-D and carbaryl to thatch and the underlying soil. Thatch and soil were collected from a 3.5 year old stand of ‘Southshore’ creeping bentgrass that had a 0.9 cm thatch layer and from a 6-year-old stand of ‘Meyer’ zoysiagrass that had a 3.3 cm thatch layer. The bentgrass site had a sandy loam surface soil while the

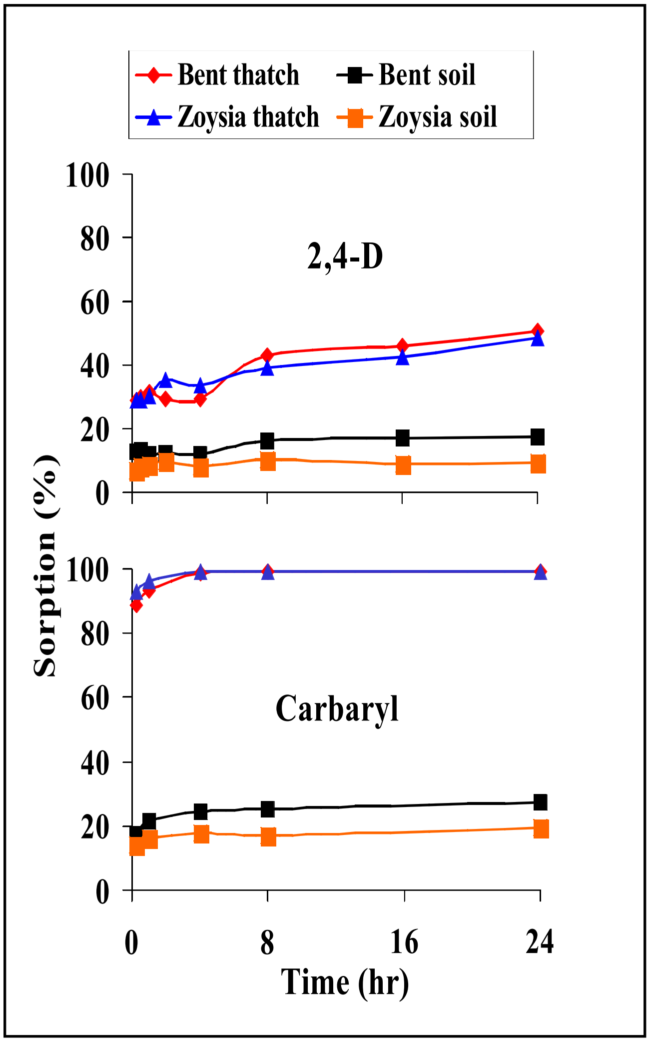


Figure 1. Sorption of 2,4-D and carbaryl to thatch and soil.

zoysiagrass site had a loamy sand surface soil.

The sorptive behavior of the two pesticides were examined by packing large syringe tubes with thatch or soil. The syringe tubes were then attached to a machine that controlled the rate at which a known pesticide solution concentration was leached through the packed columns. By varying the rate at which the solutions were leached through the columns, we were able to examine the effect of pesticide solution residence time on the sorption of each pesticide to thatch and soil.

The data from this study showed that the sorption kinetics of 2,4-D and carbaryl differed for the two turfgrass species thatch, but were pretty much the same for the two soils (Fig. 1). The quantity of the two pesticides sorbed to the soil did not increase very much with increasing solution residence time for soils from either site. Similarly, the sorption of carbaryl to thatch only slightly increased with increasing solution residence time, indicating that the carbaryl rapidly reached sorption equilibrium. Sorption of 2,4-D to thatch, however, was highly dependent on solution residence time.

The relatively rapid rate at which carbaryl seemed to achieve sorption equilibrium in both thatch and soil is likely due to the low water solubility of carbaryl. Sorption of hydrophobic compounds to organic matter is believed to be mechanistically similar to the action of surfactant micelles (2, 6). Many scientists believe that hydrophobic pesticides like carbaryl quickly partition into the non-polar humic and fulvic acid fractions of soil organic matter much like the way an oil droplet dissolves into a laundry detergent surfactant micelle.

The herbicide 2,4-D, on the other hand, is a polar compound. It forms strong bonds with water, but will also readily sorb to many of the functional groups found in organic matter. The sorption kinetics of this pesticide are slower because time is needed for 2,4-D to diffuse to the various sorption sites located within organic matter. Competition with other polar compounds for soil and organic matter bonding sites is also believed to be factor contributing to the more time-dependent nature of 2,4-D sorption compared with carbaryl.

The results of our sorption studies suggest that precipitation events that occur shortly after pesticide application will have a greater impact on 2,4-D mobility in thatch than on carbaryl mobility in thatch because of differences in sorption equilibrium behavior between the two pesticides.

Different Types of Transport Models to Address Sorption Behavior

Process-based transport models that assume instantaneous pesticide sorption are usually referred to as equilibrium transport models. Transport models that assume time-dependent sorption or kinetic sorption are categorized as non-equilibrium transport models. A non-equilibrium transport model that characterizes all pesticide sorption using a single kinetic rate coefficient is often referred to as a one-site non-equilibrium model.

An alternative modeling approach is to assume that different soil constituents (ie., soil mineral, oxides, and organic matter) react with pesticides at different rates (7). Pesticide sorption in this case is modeled by dividing the sorption sites into two fractions; sorption to one fraction is assumed to be instantaneous, while sorption to the other fraction is assumed to be time-dependent (5). This later type of model is often called a two-site non-equilibrium model.

A specialized form of the two-site non-equilibrium model is used to predict pesticide transport when physical non-equilibrium flow conditions exist (e.g. preferential flow, macropore flow, etc.). When both chemical and physical non-equilibrium exist during the transport process, the two site non-equilibrium model may perform well in describing pesticide transport, but it is not possible to separate the physical and chemical components contributing to the non-equilibrium transport conditions.

Experimental Methods for Leaching Study

We conducted a laboratory column study to examine the effect of thatch on 2,4-D leaching. The leaching data from the study were then used to compare the performance of the equilibrium, one-site non-equilibrium, and two-site non-equilibrium models to predict 2,4-D leaching in the columns.

The study was conducted by extracting undisturbed columns of soil and soil+thatch from the two turfgrass sites mentioned previously. The columns containing soil only were extracted after removing all above ground thatch and foliage. The columns were 10.2 cm in diameter and approximately 10.7 cm in length. A water-saturated porous stainless steel plate was fitted to the base of each column after which each column was placed in one port of a multi-port vacuum chamber. Steady-state water flow was established in each column by placing a specially designed rainfall emitter over the top of each column, and subjecting the base of the column to a constant suction of -10 kPa (i.e., field capacity). Ten small diameter tubes located at the base of each rainfall emitter uniformly delivered 0.33 inch/hr (0.83 cm/hr) of simulated rainfall to the surface of the columns. Leachate samples were collected in sterile plastic cups located within vacuum chambers at the base of each column.

Leaching of 2,4-D in the columns was examined in the following manner. Once steady-state water flow had been achieved in all columns, stimulated rainfall was terminated and the suction applied to the base of column was discontinued. A field rate of 2,4-D was then uniformly surface applied to the columns and the 2,4-D allowed to sorb to thatch and soil for 24 hours. The columns were covered to reduce any potential pesticide volatilization.

At the end of the 24-hour sorption period, stimulated rainfall and suction at the base of the column were reinitiated. Leachate samples were then collected every 30 minutes and leachate volume measured for the next 18 hours. After collecting the last leachate sample, columns were removed from the vacuum chamber and the physical properties (lengths, moisture contents, organic matter contents, and bulk densities) of the thatch (if present) and soil layers were determined. The concentration of 2,4-D in each leachate sample was measured.

Additional information needed to model

Column Type	2,4-D leached
	%
Bentgrass site soil only	43.1 ($\pm$ 1.10)
Bentgrass site soil + thatch	17.4 ($\pm$ 1.83)
Zoysia site soil only	34.3 ($\pm$ 2.04)
Zoysia site soil + thatch	29.0 ($\pm$ 3.01)

Table 1. Percent of 2,4-D leached from bentgrass and zoysiagrass thatch+soil columns and soil columns devoid of thatch. The mean and standard error are based on four replicates of each column type.

2,4-D transport in the columns was obtained from previously conducted sorption isotherm experiments and from the analysis of bromide tracer leaching data collected from each column prior to the 2,4-D leaching phase of the study.

Leaching Study Results

The experimental procedures used in this study simulated a near "worst case" scenario leaching event. The columns were at field capacity when 2,4-D was applied, and over 5.5 inches (14 cm) of simulated rainfall was leached through the columns over an 18-hour period. In addition, the leaching event was initiated 24 hours after the application of 2,4-D. The short time duration of the experimental study severely limited the role of microbial degradation in reducing the amount of 2,4-D in the columns.

As a result, substantial 2,4-D leaching losses were observed from all columns. Even under such unfavorable conditions, the presence of a bentgrass thatch layer reduced 2,4-D leaching by 60% when compared to columns from the same site that were devoid of thatch (Table 1). Conversely, the presence of a zoysiagrass thatch layer had little impact ($P < 0.162$) on the amount of 2,4-D that was leached from the zoysiagrass site columns.

The zoysiagrass results were somewhat surprising given that the two turfgrass species thatch had similar 2,4-D sorptive capacities. Visual inspection of the two turfgrass species' thatch revealed that the zoysiagrass thatch had a substantial quantity of partially decomposed lateral stems whereas the bentgrass thatch was more finely granulated and had little coarse undecomposed stem material. Since the 2,4-D was uniformly applied to the surface of each column in a drop wise fashion using a pipette, we felt that uniform distribution of the pesticide and, therefore, the opportunity to be sorbed was not a problem.

We believe the coarse nature of the zoysiagrass thatch organic matter may have permitted substantial quantities of the applied 2,4-D solution to rapidly redistribute to the bottom of the thatch layer at the time of application. If this occurred, many of the potential sorption sites within the thatch layer would have been by-passed.

Model Comparisons

Model performance was evaluated by determining how well the predicted breakthrough curves agreed with the actual column breakthrough curve data. Model assessment was based on a comparison of coefficient of determination values (ie., R^2) for the three model types and for the soil only and thatch+soil columns. In pesticide breakthrough curves, the ratio of the relative concentration of pesticide exiting the soil column (C) over the input concentration (C_o) is calculated and plotted against the number of pore volumes that have exited from the column. Pore volume

Column Type	Coefficient of determination: Equilibrium model	One-site model	Two-site model
Bentgrass site soil only	0.35	0.49	0.89
Bentgrass site soil + thatch	0.09	0.27	0.78
Zoysia site soil only	0.05	0.66	0.92
Zoysia site soil + thatch	0.15	0.31	0.93

Table 2. Proportion of variation in 2,4-D transport explained by three pesticide transport models. All values in table are based on four replicates of each column type.

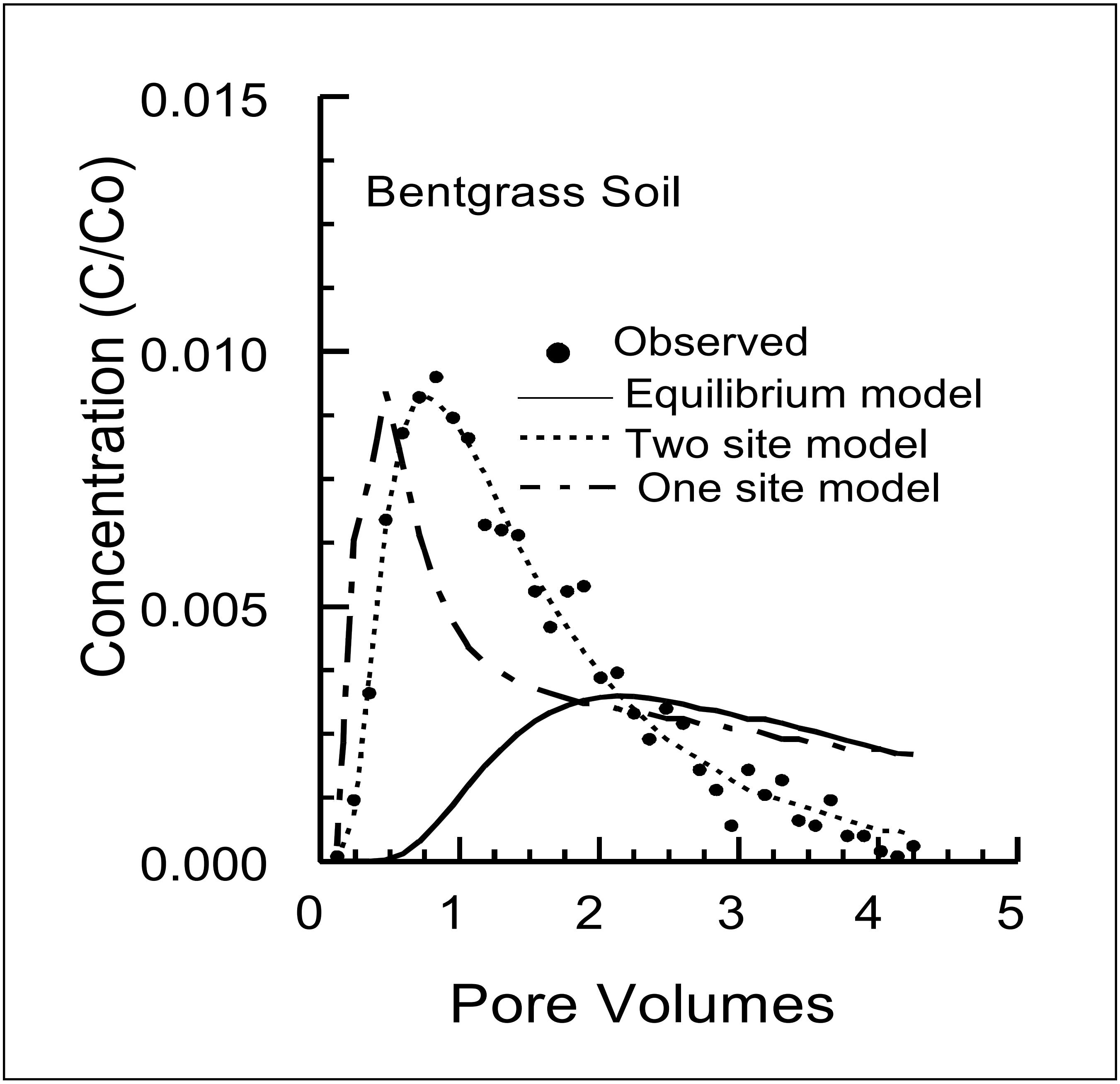


Figure 2. Breakthrough curves of 2,4-D applied to columns of bentgrass soil comparing observed versus an equilibrium model, and both one- and two-site non-equilibrium models. In pesticide breakthrough curves, the ratio of the relative concentration of pesticide exiting the soil column (C) over the input concentration (C_o) is calculated and plotted against the number of pore volumes that have exited the column.

expresses the quantity of liquid exiting the column in terms of the volume of water that is in the column at the ambient soil water content. In this study, one pore volume was approximately equivalent to amount of water in the column at field capacity.

The equilibrium and one-site non-equilibrium models did a poor job of describing 2,4-D transport (Table 2) Both model types failed to accurately predict the peak concentrations of 2,4-D in the leachate and over-predicted the amount of 2,4-D in the leachate in the latter stages of the study (Figs. 2 and 3). It is likely that the relatively high rate of simulated rainfall used in this study enhanced the contribution that any preferential flow may have had on 2,4-D transport. The

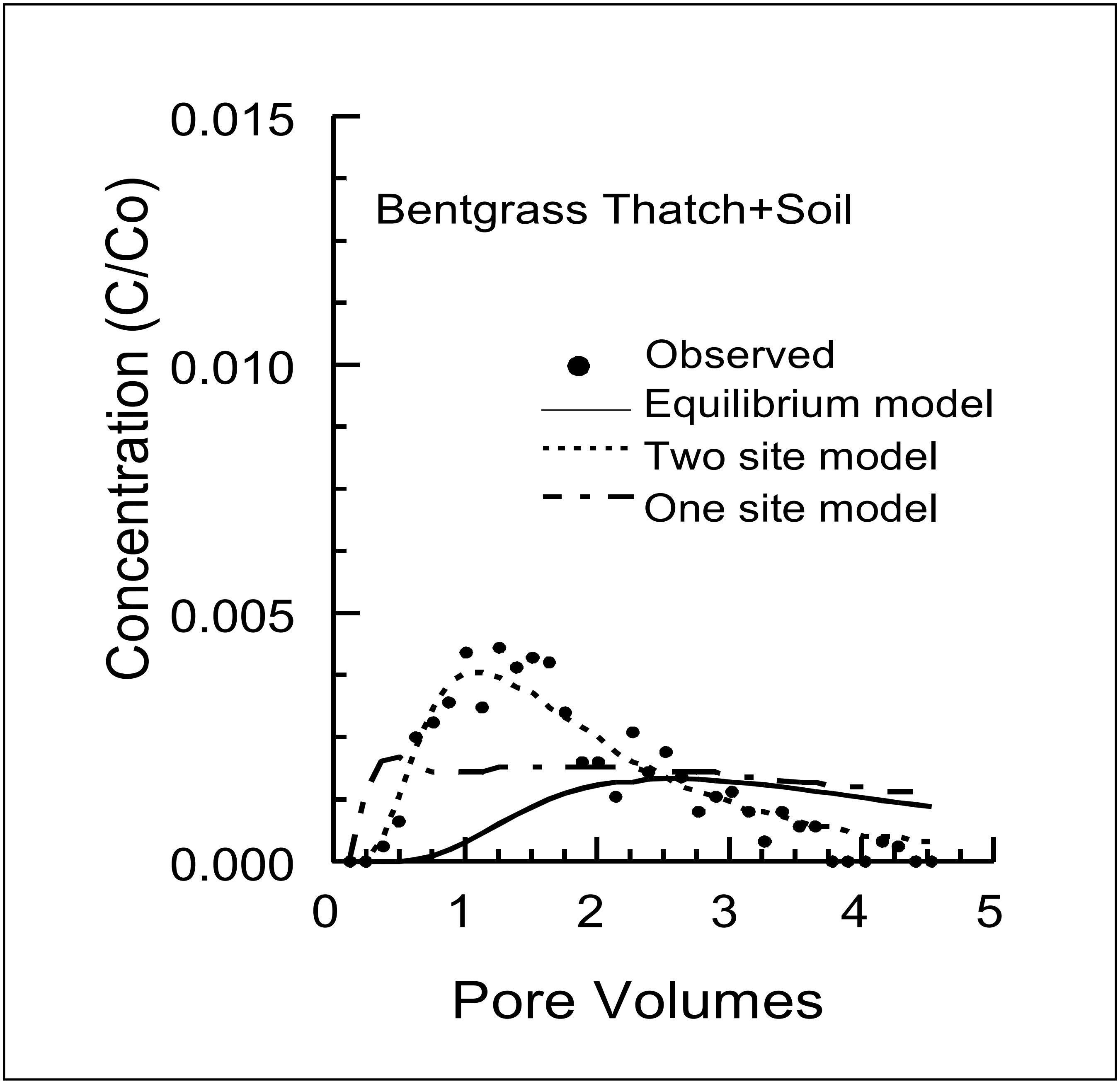


Figure 3. Breakthrough curves of 2,4-D applied to columns of soil and bentgrass thatch comparing observed, equilibrium model, and both one- and two-site non-equilibrium models. In pesticide breakthrough curves, the ratio of the relative concentration of pesticide exiting the soil column (C) over the input concentration (C_o) is calculated and plotted against the number of pore volumes that have exited the column.

inability of the one-site non-equilibrium model to provide a reasonable estimate of 2,4-D transport also suggests that more than one process was contributing to the non-equilibrium transport of 2,4-D.

The two-site non-equilibrium model provided very good estimates of 2,4-D transport. The bentgrass site, thatch+soil columns had lower coefficient of determination values than the bentgrass site, soil only columns. Overall, the presence of a surface layer of thatch had little impact on the predicted transport of 2,4-D. The two-site model accurately predicted the peak concentration and tailing behavior of 2,4-D in both the thatch+soil and soil only columns (Figs. 2 and 3). The weaker fits observed in the columns containing thatch at the bentgrass site can be attributed to the lower amplitude of the 2,4-D breakthrough curves in these columns. The lower levels of 2,4-D in the leachate of these columns magnified the sampling errors associated with analytical techniques used to measure 2,4-D.

Conclusions

This study is one of the first to examine pesticide transport through different turfgrass species' thatch. We found that even though zoysiagrass and bentgrass thatch had similar sorption properties, bentgrass thatch was more effective in reducing 2,4-D leaching. We believe the size of organic constituents and the state of decomposition of the decaying plant material within thatch may play a role in the amount of pesticide that is initially intercepted by the thatch. More detailed sorption investigations involving undisturbed samples of thatch are needed to examine this hypothesis.

Model evaluation of the column leachate data revealed that the two-site non-equilibrium model provided more accurate predictions of 2,4-D leaching than when instantaneous equilibrium sorption or one-site kinetic non-equilibrium sorption was assumed. Our results demonstrated that when the proper model is selected, the presence of thatch did not substantially impact model performance.

Our modeling effort was somewhat unique in that we obtained measurements for almost every model input parameter needed to model 2,4-D transport in the thatch and soil layers. Having experimentally-based input parameters rarely occurs in most golf course risk assessment modeling efforts. For example, we directly measured the 2,4-D sorption capacity of the thatch and soil at both study sites.

In most proposed golf course risk assessment models, evaluations of the pesticide sorption capacity of thatch is not actually determined, but is instead based on a best guess estimate of the future organic matter content of the thatch. Given that most risk assessments are performed prior to the actual establishment of turf at a site, the use of this type of approach is unavoidable. This study illustrates, however, that thatch may complicate model predictions of pesticide transport and care should be used in choosing the appropriate type of model for pesticide transport predictions.

Acknowledgments

The research presented in this paper represents a portion of Ph.D., research of Ms. Sanju Raturi. Funding support for this research was received from the United States Golf Association Greens Section.

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