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DEVELOPMENT of a LAYERED MODEL

to

PREDICT PESTICIDE TRANSPORT IN TURFGRASS THATCH

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Executive Summary

Objectives

1. To develop a two phase layered pesticide transport model which considers equilibrium or non-equilibrium transport within each layer and the use of appropriate pesticide adsorption coefficients for each layer.
2. To evaluate the use of the model for two of the pesticides used in the previously funded USGA study.
3. To evaluate the effectiveness of the model to predict pesticide transport in comparison to commonly used pesticide transport models such as PRZM2 or GLEAMS.

Modeling non-equilibrium pesticide transport requires at least two additional transport parameters beyond that needed to estimate pesticide transport using a linear-equilibrium approach. These parameters are usually obtained from curve fitting procedures involving field tracer and pesticide leachate data or from sorption studies specifically designed to investigate non-equilibrium adsorption. When transport parameters are obtained from field data, a least sum-of-squares optimization procedure is generally used to estimate the required transport parameters. From a programming perspective, incorporating sub-routines that estimate non-equilibrium field transport parameters from least sum-of-squares square optimization procedures is complex. In addition, formulating a model that uses this approach inevitably elevates the complexity of model to a level where the end user of the model needs to have considerable expertise in porous media solute transport processes.

The programming complexity and data input requirements of a solute transport model can be simplified by reducing the number of rate-based parameters used in the model. At the most fundamental level, water in porous media moves in response to a hydraulic gradient and at a rate dependent upon the hydraulic conductivity of the soil. The latter is a rate parameter used in mechanistic transport models to calculate instantaneous water movement in soil. A popular approach used to simplify water movement in many models is to predict water movement based on differences in the water content of soil layers. In these models downward water movement in a layer of soil may be specified to occur only when the water content of a soil layer exceeds a specified value such as field capacity. Models that use capacity factors to simplify water and solute transport are called functional models. A primary advantage of these models is that the models require less data input and computer expertise to perform transport simulations than models that use rate-based equations.

We are in the process of constructing a functional transport model that considers non-equilibrium sorption of pesticides to thatch and soil. The model partitions thatch and soil water into mobile and immobile phases and considers time-dependent pesticide sorption using two-site sorption kinetics. A "tipping bucket" methodology will be used to simulate pesticide transport in the thatch and soil layers of the model.

A secondary objective of this project is to compare the predictive transport of pesticides obtained using the PRZM2 and GLEAM's models with predictions obtained from the two-phase model which is being developed. While direct comparison of the three models is not yet possible; a preliminary comparison of the predictive capabilities of PRZM2 and GLEAMS was completed this year. Carbaryl and 2,4-D leachate data collected from previously conducted laboratory column studies were used to evaluate the pesticide transport predictive capabilities of the two models. The columns were 12 to 15 cm in length and contained soil only or soil plus a 2 to 3 cm surface layer of thatch. PRZM2 and GLEAMS model simulations were conducted by evaluating pesticide leaching through a bare-layered soil devoid of a turfgrass canopy. Input parameters for both models were based on actual experimental conditions and on a series of laboratory determinations performed on columns collected from the same location as the columns used in the pesticide leachate study. The columns containing a surface layer of thatch were characterized in model simulations by using the actual measured thatch layer values as the input parameters for the column surface layer.

The GLEAMS model underestimated observed pesticide leachate losses in the columns containing a surface layer of thatch by 82% ($\pm$ 13, n= 4). This difference was slightly higher, but not statistically different, from the amount observed in the soil columns devoid of the thatch layer (69% $\pm$ 17, n= 4). PRZM2 always overestimated pesticide leaching in the soil columns devoid of the thatch layer. The presence of thatch had no consistent effect on PRZM2 model performance. The performance of PRZM2 and GLEAMS will be compared with functional two-phase model currently under development. It is anticipated that development the two-phase model will be completed in the latter half of 2001.

Project Title: Development of a Layered Model to Predict Pesticide Transport in Turfgrass Thatch

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

Progress to Date - The goal of this project is to develop a model that possesses the ability to assign separate equilibrium or non-equilibrium transport parameters to thatch and soil layers. The initial plan was to develop a simple mechanistic model that considered only the effects of equilibrium and non-equilibrium sorption on the transport pesticides within thatch and soil layers. During the first few months of the project, it was decided that a better approach might be to modify an existing widely used linear equilibrium-based model to account for non-equilibrium transport. Using this approach, would allow the utilization of the hydrology and infiltration components of an existing model and, thus, would increase the applicability of the model. PRZM2 was initially studied because of its widespread use by consultants and regulatory agencies. Unfortunately, there were difficulties encountered with obtaining a working version of the source code (these difficulties were discussed in the May 2000 mid-year progress report). Not being able to obtain all the components of the source code necessary to compile and run the PRZM2 model ultimately resulted in a return to the initial model development goals.

Modeling non-equilibrium pesticide transport requires at least two additional transport parameters beyond that needed to estimate pesticide transport using a linear-equilibrium approach. These parameters are usually obtained from curve fitting procedures involving field tracer and pesticide leachate data or from sorption studies specifically designed to investigate non-equilibrium adsorption. When transport parameters are obtained from field data, a least sum-of-squares optimization procedure is generally used to estimate the required transport parameters. From a programming perspective, incorporating sub-routines that estimate non-equilibrium field transport parameters from least sum-of-squares square optimization procedures is complex. In addition, formulating a model that uses this approach inevitably elevates the complexity of model to a level where the end user of the model needs to have considerable expertise in porous media solute transport processes.

The programming complexity and data input requirements of a solute transport model can be simplified by reducing the number of rate-based parameters used in the model. At the most fundamental level, water in porous media moves in response to a hydraulic gradient and at a rate dependent upon the hydraulic conductivity of the soil. The latter is a rate parameter used in mechanistic transport models to calculate instantaneous water movement in soil. A popular approach used to simplify water movement in many models is to predict water movement based on differences in the water content of soil layers. In these models downward water movement in a layer of soil may be specified to occur only when the water content of a soil layer exceeds a specified value such as field capacity. Models that use capacity factors to simplify water and solute transport are called functional models. A primary advantage of these models is that the models require less data input and computer expertise to perform transport simulations than models that use rate-based equations.

A functional modeling approach similar to that described above was first proposed by T.M Addiscott (1979). A later version of this functional model partitioned soil water into mobile and immobile phases. This approach to describing water movement to some extent mimics physical non-equilibrium transport. Partitioning of the mobile/immobile solution phases is based on specific soil water contents and can be modified by the user if another soil moisture content is deemed more appropriate to describe water movement in the soil. This functional approach to modeling water movement can also be extended to solute transport and has been crudely described as a "tipping bucket" methodology. It is interesting to note that the Root Zone Water Quality Model (RZWQM), which was released earlier this year, utilizes some very complex algorithms to simulate water movement in soil, but the authors chose to simulate non-equilibrium pesticide transport utilizing a functional "tipping bucket" methodology. Although the model developers had tremendous resources at their disposal and could have chosen any methodology during the 12 year development of the RZMQM model, the "tipping bucket" methodology was considered to give the best results for model applicability.

Once it was realized that there was little likelihood of obtaining a working version of the PRZM2 source code, study began on developing a functional model that would consider non-equilibrium sorption of pesticides to thatch and soil. Dr. Sanju Raturi, who was hired to spearhead development of the proposed model, began working on the model by attempting to create the functional water movement routines. Because of complications preceding the impending birth of her second child, Dr. Raturi was unable to complete coding of the water movement routines prior to leaving the project in September of this year. With the loss of Dr. Raturi from the project, it will be necessary for the project investigators (Drs. Carroll and Hill) to assume responsibility for coding of the functional model.

A secondary objective of this project is to compare the predictive transport of pesticides obtained using the PRZM2 and GLEAM's models with predictions obtained from the two-phase model which is being developed. While direct comparison of the three models is not yet possible; a preliminary comparison of the predictive capabilities of PRZM2 and GLEAMS was completed by Dr. Raturi prior to her departure.

Pesticide leachate data collected from previously conducted laboratory column studies were used to evaluate the pesticide transport predictive capabilities of PRZM2 and GLEAMS. In these studies, undisturbed columns of soil or soil plus a surface layer of thatch were removed from the field and attached to an specially designed vacuum apparatus. The apparatus maintained steady state flow conditions within the columns during the leaching phase of the experiment. The columns were approximately 12 to 15 centimeters (cm) in length; with the taller columns possessing a 2 to 3 cm surface layer of thatch. A constant rate of simulated rainfall (1 cm hr^{-1}) was applied to the columns using a specially designed emitter. Once steady state flow conditions were achieved in the columns, a pulse of bromide was surfaced-applied to each column and leachate samples collected for 12 hours. Pesticides were then added to the surface of the columns and allowed to adsorb to thatch and soil for 24 hours. After the 24 hour adsorption period, simulated rainfall was re-initiated. A second series of leachate samples were then collected at regular intervals until the concentration of pesticide approached the lower limits of detection. At the end of the leaching event, the columns were cut into thatch (if present) and soil sections and the organic carbon content, bulk density and moisture content of the respective layers determined. Additional model input parameters such as soil and thatch adsorption coefficients, hydraulic conductivity, and soil moisture release properties were obtained from a series of laboratory determinations performed on other columns collected from the same location as the columns used in the pesticide leachate study.

PRZM2 and GLEAMS model simulations were conducted by evaluating pesticide leaching through a bare-layered soil devoid of a turfgrass canopy. Input parameters for both models were based on actual experimental conditions and the laboratory measured values described in the preceding paragraph. The columns containing a surface layer of thatch were characterized in model simulations by using the actual measured thatch layer values as the input parameters for the column surface layer. One value that was not actually measured, but was required for simulating pesticide movement in PRZM2 was the wilting point moisture content of the thatch. The value was subsequently determined via sensitivity analysis so that this input parameter did not influence the performance of PRZM2 when the simulation was restricted to the experimental conditions of the leachate study. Both PRZM2 and GLEAMS simulation runs were conducted using a daily time step iteration. Because the pesticide leachate studies were short term (lasting no more than 7 days) and involved relativity high leachate fluxes, the rainfall inputs for both models were adjusted to provide 1/24 of the experimental daily rainfall amount to the surface of the column each day. This procedure resulted in each model simulation day being equal to one hour of the actual experiment. All other time dependent input variables that may have influenced daily simulated pesticide leachate viability such as pesticide volatilization, soil pesticide degradation and evaporation were assigned a value of zero.

Table 1 shows the actual and predicted amounts of 2,4-D or carbaryl lost from individual columns. The table also includes the coefficient of determination values (R^2) that were obtained when the column bromide tracer data was fit to the CXTFIT one and two domain flow models. The CXTFIT data indicated preferential flow within three of the columns; the bentgrass thatch+soil 2,4-D column, the zoysiagrass +soil carbaryl column and the bentgrass soil carbaryl column. Preferential flow is frequently observed in undistributed soils, however neither PRZM or GLEAMS were designed to evaluate pesticide leaching in media exhibiting preferential flow. PRZM2 provides two options to solve the model transport equations: (1) a backwards-difference implicit scheme that may be affected by excessive numerical dispersion at high Peclet numbers or (2) a method of characteristics algorithm. The later methods minimizes numerical dispersion, but requires the user to know the effective dispersion coefficient of the soil. Since our bromide data allowed us to determine the average dispersion coefficient (D_{mes}) for the columns, it was decided to run the PRZM2 simulations using both model transport options.

Table 1. Actual and model predicted leachate losses of 2,4-D and carbaryl.

	CXTFIT R^2		Percent of applied pesticide leached			
Column ID	One domain	Two domain	Observed	PRZM2 (D_{mes})	PRZM2 (D_{Pre})	GLEAMS
2,4-D						
Zoysiagrass thatch + soil	99	99	36	82	94	7
Zoysiagrasss soil	98	99	41	85	55	23
Bentgrass thatch + soil	93	96	22	72	61	8
Bentgrass soil	99	99	43	66	47	11
Carbaryl						
Zoysiagrass thatch + soil	88	98	64	11*	29	7
Zoysiagrasss soil	99	99	80	99	99	21
Bentgrass thatch + soil	96	97	71	65	43	3.5
Bentgrass soil	94	99	66	81	85	11

*Mass balance error obtained in simulation.

A clear trend seen in Table 1 is that GLEAMS underestimated pesticide leaching in every column examined. The GLEAMS model generally underestimated pesticide leachate losses in the columns containing a surface layer of thatch by 82% ($\pm$ 13). This difference was slightly higher, but not statistically different, from the amount observed in the soil columns devoid of the thatch layer (69% $\pm$ 17). PRZM2 always overestimated pesticide leaching in the soil columns devoid of the thatch layer. This same result was obtained regardless of the transport option used to predict the PRZM model solute transport. The presence of thatch had no consistent effect on PRZM2 model performance.

Work Plan - Because of the complications involved in an unexpected pregnancy which occurred during the middle stages of this project Dr. Raturi was unable to complete the development of a water transport routine prior to leaving this project. The source code provided to us by Dr. Raturi was archaic in design, lacked proper documentation of the source code variables and is something that can not be easily modifyed to allow incorporation of non-equilibrium pesticide sorption within the individual thatch and soil layers of the model. It has been decided that it would be easier and more time efficient to write entirely new simulation codes rather than trying to work with the code Dr. Raturi provided.

The complications surrounding Dr. Raturi's health were an unexpected development in this project. The project investigators are currently modifying their professional schudules to free up the substantial blocks of time that will be required to code and debug the proposed model. It is our belief that 9 to 12 months of time will be required to completely achieve the objectives as stated in the original project proposal.