Session 3
Modelling

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EXPERIMENTATION AND MODELING

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ABSTRACT

Because of its probabilistic capabilities some form of probability modeling may very well become the primary tool for assessment of ecological risk. It has become indispensable to DowElanco as a powerful propagator of environmental variability, and continues to undergo development. Currently it makes use of digitized soils databases, weather generators, Geographical Information Systems tools, and parallel computing software. But experience to date indicates serious modeling limitations emanate from present environmental chemistry experimentation that has no focus on natural variability. In anticipation of the future needs of ecological risk assessment, it is suggested that the environmental research community must perhaps begin to think in terms of statistical distribution rather than in terms of single number.

At DowElanco modeling has become indispensable for the conduct of ecological risk assessment. The modeling is of a special nature in that it attempts to report exposure estimates from model output in terms of frequency distribution. This approach is termed "probability modeling" since the modeling results describe the probability that a certain environmental concentration might be encountered in the real world.

First attempts to perform this type of estimation recognized the need to propagate variability of model input to the output. So geographical regions were selected, ranges of values for soil properties and weather patterns were developed to represent the regions, and the ranges were then input into the modeling to generate output frequency distributions. Unfortunately, this created an issue with "nonsense combinations" of input - - - combinations of soil properties and weather that have little chance of co-existing in the real world. The probabilistic modeling approach was subsequently modified to one that made much more sense in reality.

The approach became more specific. A digitized database of all soils in the U.S. was obtained, along with the capability to generate weather patterns for any U.S. location. Both were placed under the umbrella of Arc/Info, a geographical information system (GIS) that allows one to combine layers of data and then express modeling results probabilistically in the form of graphic maps. To minimize the issue of "nonsense combinations", soil series property descriptions from the soils database are kept intact and used directly for model input, along with historical weather associated with an actual soil series location. In this way variability within the modeling has become more controlled. It is restricted to variation in properties within a soil series, and to variation in weather. If the data are available, variation in pesticide properties can also be included. For runoff assessment the assumption is made that an organism's habitat is at the edge of a treated field comprised of the soil series under evaluation. The output is translated into frequency-of-return GIS soil maps that classify the soils in real geography for their likelihood of producing various levels of exposure. Frequency of return with regard to level of risk is defined in the following manner:

Typical Case	1 in 2
Typical Worst Case	1 in 10
Extreme Worst Case	1 in 100

This modeling procedure requires adequate computational power since large numbers of modeling runs are necessary to develop the probabilistic assessment. This was resolved by taking advantage of fairly recent public domain software that allows many computers to be hooked together over a network to form a parallel processing system. Each modeling scenario of weather and soil is portioned out to any computer that is ready to undertake the next run.

We believe that some form of probability modeling will become the dominant mechanism for developing estimates of exposure for purposes of ecological risk assessment. Since risk assessment is essentially a probability-based process, modeling that returns probabilistic information provides exactly the type of information needed to perform an assessment.

Thus critical questions that are asked at this symposium are: Is the environmental chemistry scientific community ready for probabilistic modeling? Is it thinking about whether current experimentation will be relevant to a probabilistic use of its data? What kind of experimental information will be needed to propagate the variability that exists naturally in pesticide properties, soil properties, and weather patterns in order to arrive at probabilistic assessment? Is the information available and, if not, how is it to be generated? Is it time for the environmental community to be thinking in terms of statistical distribution rather than single number?

Preferential flow is a topic that captures considerable attention these days. It is a key topic of this symposium and we are looking forward to finding out the latest in attempts to model the process. But is the community thinking in terms of probability with regard to preferential flow? How will the models deal with variability? Is there some way of expressing current findings in a probabilistic way? Does there appear to be certain fractions of applied material that tend to be associated with preferential flow? For example it would be extremely useful to know that 90 % of the time 5 % or less of applied material participates in preferential flow.

Similar issues apply to soil sorption/desorption phenomena. Ample evidence exists to indicate these processes are kinetic in nature and cannot be captured with a single sorption or desorption number. Therefore, what sorts of experiments are most appropriate to develop the data needed to capture and express this variability in a probabilistic fashion? Is the conduct of soil column leaching experiments or batch equilibrium studies the most appropriate way of obtaining the necessary information? Is there some other way that develops the probabilistic information more effectively?

We think the time is at hand for environmental chemistry to do a paradigm shift with regard to focus of purpose for environmental experimentation. As the use of data from the environmental arena continues to focus directly on the risk assessment process, the awareness of need for experimental support of the tools used to perform this assessment will continue to intensify. We believe these tools will be probabilistic in nature, and future experimentation must be focused to support them.

What might your thoughts be on this matter?

STATISTICAL SIMULATION OF WATER AND PESTICIDE MOVEMENT IN THE UNSATURATED ZONE

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ABSTRACT

The movement of water and pesticides in the unsaturated zone has been investigated numerically. Instead of solving the underlying partial differential equations with conventional methods, we developed a discrete, statistical approach. In a microscopic picture the soil is represented by a lattice of cavities which are connected by channels. Water particles hop between the cavities in discrete time steps, where the statistical weights of the hopping directions depend on the local potential and the permeability of the channels. Averaging over several time steps and mesoscopic spatial areas gives a smooth picture of the water flow. The water dynamics are used as a basis for simulations of pesticide movement. We demonstrate how diffusion, adsorption, degradation, etc. can be described. The model is particularly well suited for the simulation of flow in heterogeneous media. We discuss several applications.

INTRODUCTION

Since the pioneering work of Darcy (1856) it is known that subsoil water flow can adequately be described by partial differential equations. Today these are solved numerically for many different problems. Simulations usually calculate the changes of quantities like density, flux and concentrations, which are represented by *real numbers*. These methods, called *conventional* below, have been developed to a high degree of sophistication. (See Bear and Verruijt, 1987, for an overview). Here we approach Darcy flow with a large number of water particles hopping between the sites of a lattice. The particles do not represent molecules but small amounts of water as compared to the permeability autocorrelation length. Similar *lattice gas* methods have been found to be efficient for free fluid flow (Frisch et al., 1986 and 1987). The collision rules of free fluid lattice gases have been modified by Balasubramanian et al. (1987) and Papatzacos (1988), so as to include friction terms. Our approach (Vollmayr, 1994) is different in that it sets up new rules, which do not conserve momentum. The velocities (directions of motion) of particles leaving a site do not depend on their velocities before the collision.

The movement of chemicals in soil has been simulated with discrete methods by Uffink (1983), Semra et al. (1993) and others. We adopt the technique for our purpose, because it allows simple treatment of various transport phenomena and transformation processes.

WATER MOVEMENT

The algorithm

We use a two-dimensional example for describing the algorithm, which is readily generalized to three dimensions. The soil is represented by a square lattice (see Fig.1). A lattice site can hold up to four water particles. In each timestep the particles hop to nearest neighbours of their current host site. The neighbours receiving particles are selected in a statistical procedure, which we now specify. Assume that site $\mathbf{x}$ holds one particle at time t. One out of four possible directions is *pre*selected at random, i.e. with probability 1/4. Say we chose direction i. Next the probability $P = c^{(1)}k(\mathbf{x})\phi_i$ is calculated from the potential ϕ_i at the preselected target site $(\mathbf{x} + \mathbf{E}_i)$ and the permeability $k(\mathbf{x})$. $c^{(1)}$ is a constant. The potential is due to gravity and capillarity (matrix potential). We accept the preselected direction i with probability $1 - P$ and reject it with probability P. In the latter case a new random selection (probability 1/4 for each direction) is performed. This time the result is accepted in any case. When site $\mathbf{x}$ holds two particles, there are six possible pairs of directions (i, j). So 1/4 is replaced by 1/6 in the above procedure and P is calculated with $(\phi_i + \phi_j)/2$ and the constant $c^{(2)}$. Finally, when we have three particles, the direction *where no particle is sent* is selected in the same way as for one particle but with P and $1 - P$ interchanged. Clearly, for zero or four particles at a node there is no choice of target directions.

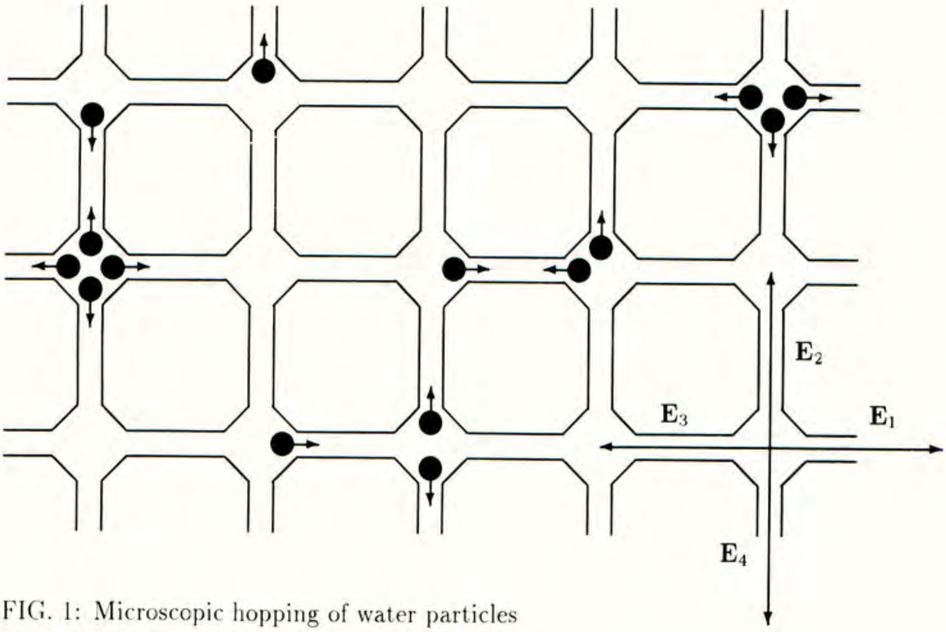

FIG. 1: Microscopic hopping of water particles

We average the particle motion over *cells* with 8 × 8 sites and over 64 timesteps. The water movement on this mesoscopic scale is described by the partial differential equation

$$\mathbf{j} = -\nabla\rho - \kappa\nabla\phi, \tag{1}$$

where $\mathbf{j}$ denotes the flux (density times velocity), ρ is the density (measured in particles per site over four in order to ensure $0 \leq \rho \leq 1$) and

$$\kappa = k_\rho(\rho)k(\mathbf{x}), \tag{2}$$

$$k_\rho(\rho) = 2\left(c^{(1)}\rho(1-\rho)^3 + c^{(2)}\rho^2(1-\rho)^2 + c^{(3)}\rho^3(1-\rho)\right). \tag{3}$$

Discussion of the equation of motion

If $-\nabla\rho$ is disregarded for a moment, eq.(1) represents the Darcy-equation, describing fluid transport in a porous medium. The permeability κ depends on ρ in a way that can be controlled by the constants $c^{(n)}$. One might wish to define $k_\rho(\rho)$ without any constraints (e.g. $k_\rho(\rho) \equiv 1$), however, this turns out to be impossible on theoretical grounds because of the continuity equation. The particle-hopping dynamics defined above take care of mass conservation *per definitionem*, which is reflected in the form of $k_\rho(\rho)$.

The first term in eq.(1) is due to particle diffusion. It is independent of the permeability κ and the potential ϕ. In particular, the diffusion constant is not controlled by an external parameter. This problem can partly be solved by adding a term to the potential $\phi(\mathbf{x})$ which depends on the particle occupation number $n(\mathbf{x})$. If large occupation number corresponds to low potential, e.g. $\phi(\mathbf{x}) \to \phi(\mathbf{x}) - n(\mathbf{x})/4$, the particles move preferably to sites which are already holding many particles, thereby moving "uphill" in a statistical sense and reducing diffusion. Instead of adding $-n(\mathbf{x})/4$ to the potential, it can be added to the probability P. Then the suppression of diffusion is not affected by the permeability. One has to be careful to keep $0 \leq P \leq 1$ (remember that P denotes a probability). This is why we have written $-n(\mathbf{x})/4$. The probability constraint limits the suppression of the diffusion term. It is strongest for $\rho = 1/2$, where the diffusion constant can be reduced to 5/8 of its original value.

Ideally the diffusion term should be proportional to the permeability: $-\kappa\nabla\rho$. Let us try to generate this behaviour by associating the permeability κ with *channels* rather than sites. The underlying idea is that particles should move to neighbouring sites with low potential preferably through channels with high permeability. In the above algorithm $k(\mathbf{x})$ must be replaced by the permeability of the channel connecting site $\mathbf{x}$ to the preselected site $\mathbf{x} + \mathbf{E}_i$. It can be shown that this procedure does not have the desired effect. Instead it leads to eq.(1) plus $(1/2)\phi\nabla\kappa$, which generates flow to the areas with high permeability, not exactly what we want to have.

Other methods to manipulate the diffusion process are conceivable. Here we just note that diffusion can be reduced within limits (density-dependency, minimum diffusion) where the original microscopic algorithm is basically unaltered. The simulation method is mainly intended for problems with small density fluctuations, for which diffusion processes play a minor role.

Discussion of the simulation method

What are the advantages of a lattice gas over conventional simulations (like finite elements)?

Firstly, the lattice gas algorithm is extremely simple on a microscopic level. The simplicity makes it more easily accessible for theoretical investigations. Note that our particles suffer from complete *amnesia*, i.e. after arriving at a site they do not remember from which neighbour they came. In particular momentum cannot be conserved — in contrast to lattice gases for the simulation of free fluids, leading to the Navier-Stokes equations. Physically, momentum is taken up by the soil matrix at any moment, so it can be disregarded in the algorithm. This tells us that Darcy flow is just a caricature of a flow equation, although it originates from Navier-Stokes flow in a tremendously complicated heterogeneous pore-network. It might be compared to the fall of an object in a viscous medium, which has been described correctly by Aristotle (who actually tried to characterize free fall), while it took almost 2000 years until Galilei correctly described free fall (which is less complicated from a microscopic viewpoint but leads to a more difficult equation).

Secondly, the model is very flexible. The basic algorithm can be changed or extended without loosing its feature of being exactly interpretable in terms of a partial differential equation on a macroscopic level. Two examples have been discussed above. In addition, heterogeneous distributions of κ or ϕ do not complicate the model nor slow down the performance of an implementation.

From an information processing point of view lattice gases exhibit very elementary structure. Accordingly they are amenable to direct hardware implementation on highly parallel computer architectures.

The model is certainly not intended to outrun all other simulation methods for Darcy flow. We regard it as an approach from an unconventional starting point, the possible applications of which are worthwhile to be investigated.

PESTICIDE MOVEMENT

The movement of a chemical in soil, which does not affect the dynamics of the water, can again be modelled by continuous or discrete methods. We prefer the discrete, statistical approach, which is known as *particle tracking*.

The pesticide is represented by a cloud of many *particles*, which do not correspond to single molecules but rather to drops small enough that their individual spreading needs not be taken into account. The concentration of the pesticide is given by the number density of particles, so the smallest volume for which a sensible concentration can be given should be large as compared to the typical interparticle distance.

At each timestep all particles follow the water movement at their current position. This models advection. Diffusion of the chemical and dispersion is included by letting the particles perform a random walk, i.e. after an advection jump, the particle performs another jump over a given (small) length to a random direction. In the case of dispersion the probability distribution for the directions is generally anisotropic. For the sake of simplicity and for demonstration purposes we neglect this complication (and others, see Semra et al., 1993).

The consideration of several transformation processes is straight forward in the particle picture. We give two examples. Pesticide is adsorbed at the solid matrix, which is modelled by giving a particle one of two states — adsorbed or free. The adsorbed particles do not change their positions and the actual state changes with a certain rate, e.g. with probability 1/500 per timestep. If we introduce a third state, which is taken with a certain rate, but never left again, we have a model for biodegradation. Further processes like chemical decomposition can be included in the same manner.

NUMERICAL EXAMPLES

The following results of a simulation are intended to illustrate what has been discussed above. At this stage the involved parameters (permeability field, transformation rates, etc.) are not supposed to represent any realistic system, but have been chosen so as to depict the basic behaviour of the model.

Fig.2a shows the permeability $k(\mathbf{x})$ of a soil profile with 16×16 cells. Dark areas have high

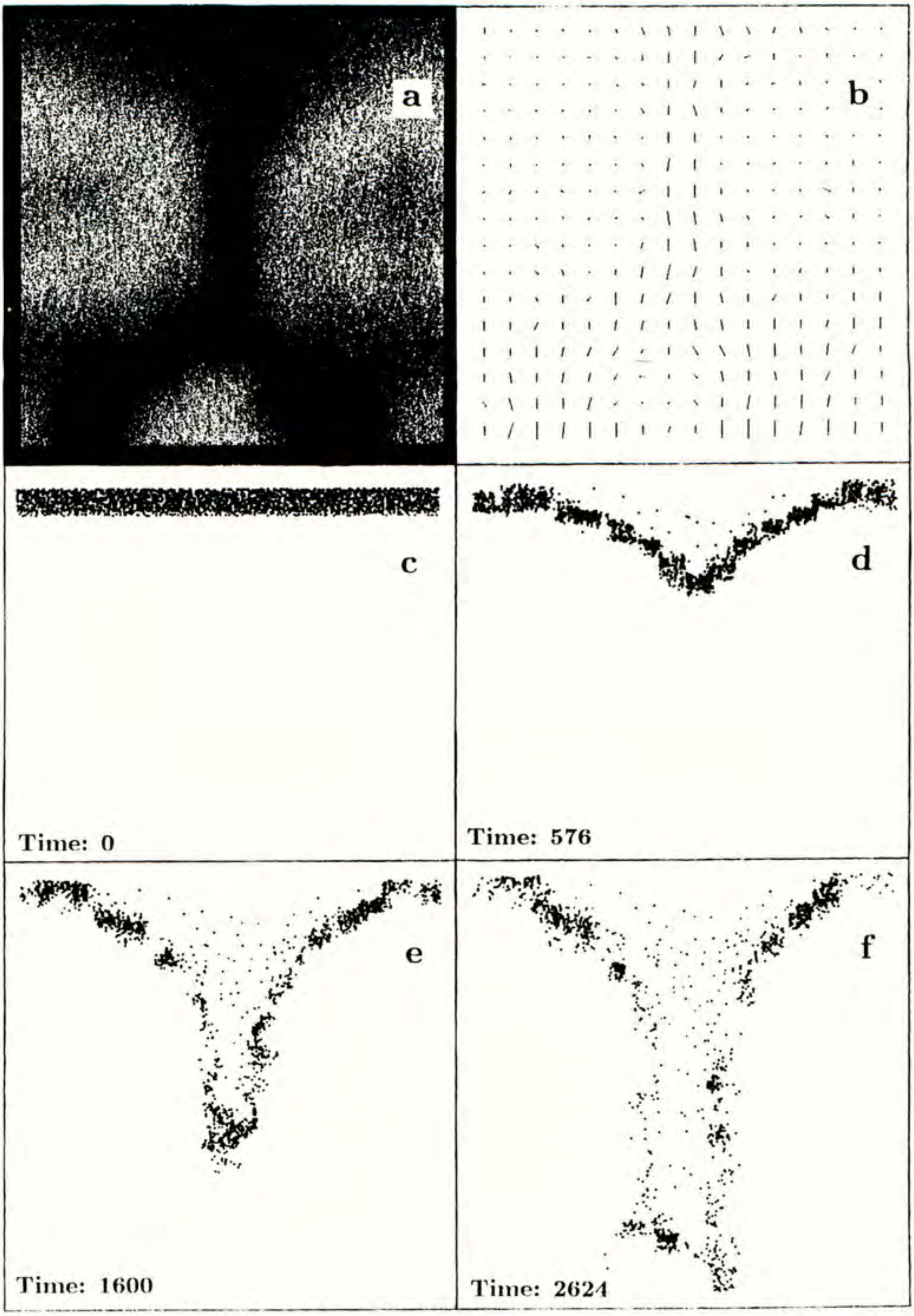

FIG.2: Pesticide movement through a heterogeneous soil profile

permeability. Gravity points downwards and the top is kept at a fixed humidity. The water flow (averaged over 8×8 sites = 1 cell and 64 time steps, see Fig.2b) is steady apart from statistical fluctuations, which are caused by the random elements of the algorithm. Figs.2c-f depict the evolution of a chemical applied to the top layer. Time is measured in microscopic timesteps, i.e. the time intervals during which water particles hop to a neighbouring site. Each pesticide particle moves every 64 timesteps: first it follows the local water flow, next it makes a small step in a random direction (step length $\approx (1/6) \times$ cell length). With probability $(1/256)$ it becomes immobile. If the particle is immobile, it becomes mobile again with probability $(1/256)$. Note that the pesticide roughly follows the main flow through areas with high permeability but slowly enters dense regions after some time.

QUESTIONS

Our aim is to model spatio-temporal distributions of pesticides. The model must be calibrated to represent realistic soil types and chemicals. One-dimensional *cascade*-models are suitable to determine parameters like the total amount of pesticide reaching a certain depth, e.g. an aquifer. Some of these aspects might be improvable by two- or three-dimensional modelling (horizontal heterogeneities, crop on ridges, etc.). In order to simulate the dynamics of populations of microorganisms, it is sometimes necessary to understand the typical spatio-temporal pattern of chemical exposure. Our work in the near future will be orientated along these lines.

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THE FATE AND MOBILITY OF PESTICIDES AT LABORATORY, LYSIMETER AND FIELD SCALE: A EUROPEAN PROJECT

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ABSTRACT

We report on the current status of a European project dealing with the identification of critical parameters governing the fate and mobility of pesticides in soil-aquifer systems. Emphasis is on a coherent interpretation of transport parameters and physical-chemical characteristics measured at multiple scales, using both experiments and modelling activities on each of the scales examined. The first objective is to quantify the effect of important parameters on the vertical and lateral flux of selected pesticides and tracer substances in the vadose zone and the underlying aquifer. The second objective is to model the effect of these parameters at laboratory, lysimeter and field scale. The aims of the project are the establishment of a comprehensive, detailed and high quality experimental data set of an integrated soil/aquifer system, offering relevant information on the value and the spatial variability of important model parameters. This should result in an improved understanding of the mechanisms controlling the sorption, transformation and transport of selected pesticides in a soil/aquifer system.

INTRODUCTION

Mathematical models are increasingly being used to describe the fate and mobility of pesticides in soil and groundwater and to perform risk assessments of pesticide use. The quality of these models in describing important processes such as transport, degradation and sorption are usually tested by comparing calculated values with measured ones obtained from laboratory measurements (e.g. breakthrough curves), lysimeter studies (e.g. leachate) or field measurements (e.g. pesticide concentrations in soil and groundwater).

Although a number of field data sets exist, practically no information is available on the variability of important model parameters. Spatial variation of soil and aquifer properties is known from literature to cause considerable fluctuations in solute concentrations and leachate amounts (Dagan, 1989; Russo, 1991). Prediction of the field behaviour of pesticides both in the saturated and unsaturated zone therefore requires a characterisation of spatial variability and the quantification of its influence. Neglecting the effect of spatial variability makes it difficult to compare model calculations with measured values obtained from the field. When discrepancies occur between measured and calculated values, no distinction can be made between a bad parameter description (e.g. by neglecting variability or incorrect measurement) and an incorrect process description. When a unique parameter set is used to describe the behaviour of a pesticide at the field scale, over- or under estimation of e.g. leachate fluxes might occur. One way of solving the problem is to make a clear distinction between process scale and system scale.

Much of the present information on pesticide behaviour is constrained either to the top soil layer or aquifers. Application of mathematical models for the purpose of predicting net fluxes to the groundwater requires the characterisation of the complete vadose zone and often also from the saturated zone in the case of a shallow groundwater table. There exists therefore a need to have complete datasets of soil-aquifer systems in order to obtain a full picture of the behaviour of a pesticide. This requires an interdisciplinary approach.

Increasing evidence is found both in literature and in reports of national and international authorities that pesticides are found in groundwater at various locations throughout Europe. A higher risk of groundwater pollution may exist in areas with shallow groundwater table. These shallow groundwaters are still an important source of drinking water supply. Protection and management of these water resources is one of the future challenges. This can only be done when processes both in soil (unsaturated zone) and aquifers (saturated zone) are understood. This requires an approach in which both systems are integrated.

Within the framework of an European project, an attempt is made to describe and understand such an integrated soil-aquifer system by studying at various scales the fate and mobility of pesticides, reactive and non-reactive tracer substances. The major objective is to identify and quantify parameters governing the vertical and lateral fluxes of selected agrochemicals in the vadose zone and the aquifer system, and to model the effect of these parameters on the transport of these compounds at different scales (laboratory, lysimeter, field and regional scale).

To meet this objective both experimental research and modelling activities are needed at the process and system level. The process level encompasses laboratory scale (often coined the Darcy scale) and the lysimeter scale, focusing on the identification of mechanism and processes involved in describing the behaviour of pesticides. This scale is assumed to be of the order of magnitude of 0.1 to 1 m and is usually assumed to be uniform in its properties. The system level includes both the field and regional scale and will provide information on the validity of the processes identified at the process level, the spatial structure of important properties and allow for the identification of effective parameters. This implies that all experimental studies are performed at one experimental field site.

THE FIELD SITE KRAUTHAUSEN

A one hectare field site has been chosen near Jülich at the village of Krauthausen. The soil is classified as gleyic planosol with five distinct horizons: an Ap horizon (0-33 cm), an eluvial horizon Eg (30-40 cm) a textural B horizon with gleyic properties (60-100 cm) and a C2 horizon (> 100 cm). The soil texture is loamy with clay percentages ranging between 20-30%. The aquifer consists of fluvial sands and gravel deposited during the quaternary period. It has a thickness of 10-12 meter; and is underlain by thin clay layers and several metres of silty fine sands. While the layer between 1 and 5 meter is built by a rather coarse gravel, the lower 5 to 7 meter consist of a medium to fine gravel with some interlayers of sands and coarse gravel. The water table fluctuates between 0.8 m below the soil surface during the winter and 3 m in the late summer. Within the test site the hydraulic gradient varies between 0.0024 and 0.0016, but remains relatively constant throughout the year. The average permeability of 3.10^{-3} m/s was determined by a large scale pumping test, the average flow velocity during the first tracer test (eosine) was about 1m/d.

During 1993 and 1994 62 wells were drilled within the plot each equipped with 24 Multi-level-samplers. 189 metre of soil cores were drilled for characterisation of the field site and to determine the spatial variability of basic soil and aquifer properties. 90 meter of core was obtained on a depth between 6 and 8 meter. 9 drillings of 11 m length were fully cored.

In total, 500 samples will be analysed for texture, organic carbon content, CEC, and specific surface. Sampling is done in such a way that a 3D picture of soil-aquifer heterogeneity can be realised. 28 wells are fully screened in order to determine the hydraulic conductivity using flow meter measurements. The primary objective of the 62 wells is to follow the plume development of eosine, uranine and LiCl in space and time and to relate it to the heterogeneity of basic aquifer properties. Unfortunately permission to inject pesticides was not given. It was therefore decided to compare the behaviour of two pesticides and the above mentioned tracers at the process level; and to scale-up this information.

In addition to the installation of wells, two undisturbed lysimeters were taken to examine the behaviour of atrazine and benazoline-ethyl with special emphasis on determining the mass balance of water and the two compounds.

To determine the influence of spatially variable soil properties on solute transport ($CaCl_2$) a small scale tracer experiment was conducted using 140 time domain reflectometry (TDR) probes to determine the transport of Cl^- on a 12 meter long transect up to a depth of one meter.

STUDIES AT THE PROCESS LEVEL

Laboratory studies were done on the transport and sorptive behaviour of atrazine, benazolin-ethyl and chlorobenzene. For atrazine, breakthrough curves are measured at each soil layer (to 1 meter depth) at three different locations in such a way that a spatially nested variance analysis may be used to obtain information at what scale variation occurs. Break through curves (BTC) give information both on transport as well as on the reactivity of a compound (sorption - decay). Using inverse optimisation techniques estimates of important parameters such as dispersion, Kd or rate constants for decay may be derived.

Two larger soil columns were sampled and used for determination of BTC of $CaCl_2$. Fig(1) shows the BTC in resident concentrations obtained on one of the columns using a pulse application (duration 1 day, initial concentration 82.8 g/l) under a flux of 2.5 cm/day. One day after application, substantial concentrations were found at a depth of 90 cm indicating that preferential flow or macropore flow played an important role in the downward movement of solute.

Biodegradation studies with the herbicides [benzene-U-^{14}C]benazoline-ethyl and [triazine-U-^{14}C]atrazine were carried out in Erlenmeyer flasks under different soil moisture (20, 40, 60 % WHC) and temperatures (6, 15, 25 °C). The laboratory study was conducted to describe metabolism of benazolin-ethyl and atrazine in the plough layer of two different soil types. The applied concentration of benazolin-ethyl was 1 mg/kg soil and for atrazine 4.8 mg/kg. Soil sampling at day 0, 2, 6, 11, 25, 39 and 91 allows model calculations to determine half life time of each compound under different environmental conditions. Results of the laboratory study will be compared to degradation processes taking place occuring outdoors.

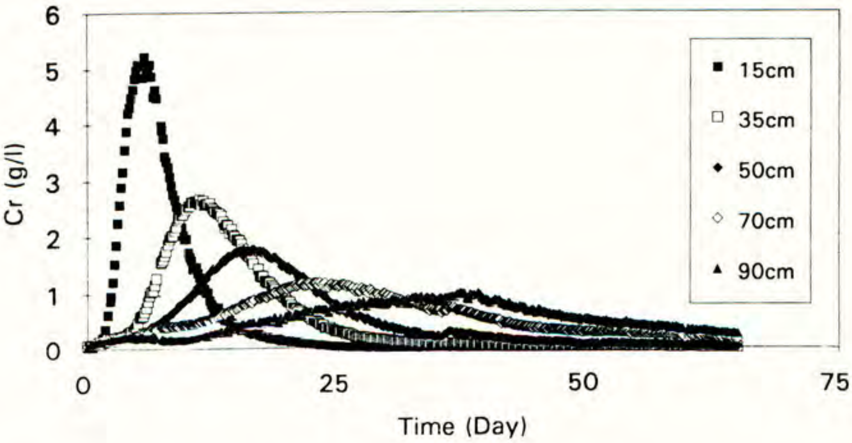

Fig. 1 Breakthrough curves of $CaCl_2$ in resident concentrations obtained at various depth using a flux type boundary condition.

Batch experiments were performed to obtain information on the spatial distribution of sorption parameters both in soil and aquifer material. To compare the behaviour of the three compounds, analyses were done on the same samples from three drillings (five samples up to one meter, five samples between 6-8 meter) . First results indicate that atrazine is hardly sorbed in the aquifer because of the low levels of clay minerals and organic matter. Amounts sorbed are usually less than 3% of the applied dose.

For the top (0-33m) and bottom layer (80-100) sorption of atrazine was found using concentrations between 1 and 1000 µg/l (Fig.2). Adsorption could be described by a Freundlich isotherm with the n value ranging between 0.95 and 1 (linear isotherm).

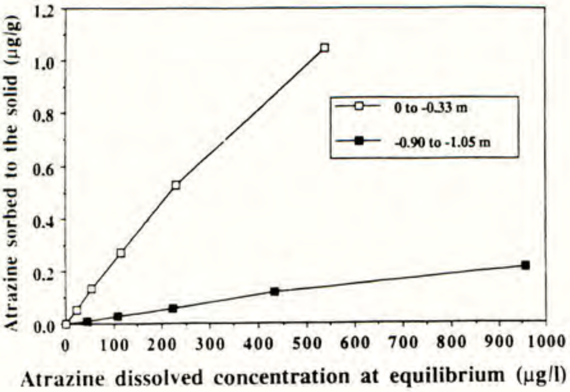

Fig. 2 Adsorption isotherms for atrazine in the plough layer (0-33 cm) and the C horizon (90-105 cm)

In February 1994 an outdoor lysimeter study with ^{14}C-benazolin-ethyl and atrazine was started. In total four undisturbed lysimeters ($1\ m^2$, 1.1 m height) received both ^{14}C-benazolin at an average rate of 0.945 kg a.i./ha and atrazine at 4.8 kg a.i./ha. To monitor water flow in the lysimeters, deuterated water, potassium bromide and methyl blue were applied as tracers. Two lysimeters contained an orthic luvisol from a nearby sidt, the other two a gleyic planosol from the Krauthausen experimental site. From March 1994 to August 1994 the plough layer was sampled in two lysimeters to elucidate the degradation of benazolin and atrazine outdoors. Soil samples were taken at 0-2.5, 2.5-5, 5-7.5, 7.5-10, 10-15, 15-20 and 20-30 cm depth and analysed separately for herbicide residues and tracers. The other two lysimeters were equipped with suction candles at depths of 20, 40 and 80 cm to collect soil solution, an access tube for neutron probe measurements; and time domain reflectrometry probes (depths of 15, 30, 45, 65, 80, 105 cm). Soil temperature sensors were installed at depths of 5, 10, 20, 30 and 60 cm. About 18 % of the total precipitation of 561 mm from February until September 1994 could be recovered as drainage water. The contents of radioactivity in the drainage water was determined to be less than 1 % of the applied radioactivity of benazoline-ethyl. The experimental data will be used for model calculations in the vadose zone.

STUDIES AT THE SYSTEM LEVEL

The research activities at the system level focus on the effect of heterogeneity of soil-aquifer properties on solute transport at the field scale. To study the governing solute transport mechanism and the effect of heterogeneity on solute transport, a small scale tracer experiment was performed in a plot of 4.5 by 12 m. TDR probes (120) were installed horizontally at 24 locations and at 5 different depth in the middle of the plot (1.25 x 8 m).

A greenhouse was installed to prevent the contribution of rainfall. A steady state flux was achieved after the application of water at 1.5 cm/day for 3 weeks. A pulse of solute ($CaCl_2.H_2O$, 80 g/l) was applied for a duration of 8 hours. The movement of the solute front was monitored from bulk electrical conductivity automatically for 2 months. The mean resident concentrations obtained for different depths are given in Figure 3.

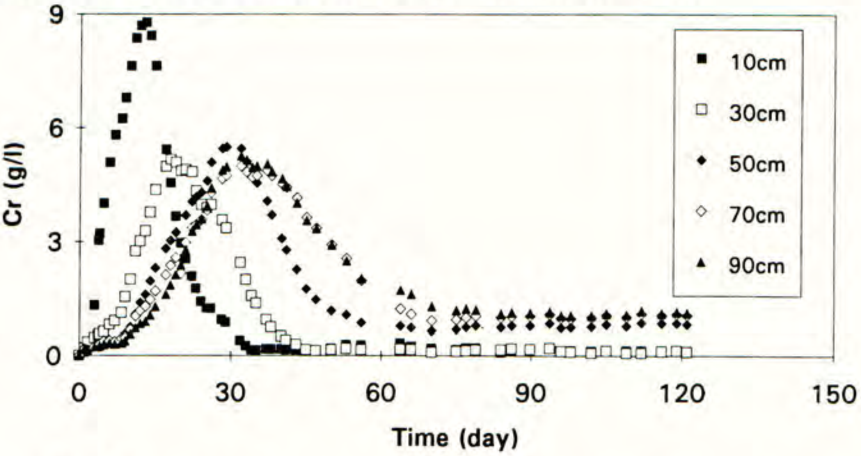

Fig.3 The mean resident concentrations of $CaCl_2$ versus time at various depth in the soil column

Large scale tracer experiments in the aquifer.

To study the effect of heterogeneity on solute transport, eosine, uranine and lithium chloride (LiCl) were directly injected in the underlying aquifer. Eosine was used as a pre-tracer to determine the flow velocity and flow direction of the groundwater in order to optimise the layout of the drilling locations. On August 30 1994, uranine and LiCl were injected in three wells to a depth between 7 and 8 m.

At various wells, breakthrough curves were monitored at 24 depths. First results are shown in Fig.(4) for well B52. Although uranine is known to be a conservative tracer it seems to retarded somewhat stronger than Li. This tendency increases with depth. In the deeper part of the well (9-10 meter) there is a substantial loss of uranine which presently cannot be explained. Batch sorption experiments are on their way combined with a characterisation of the aquifer material to clarify this behaviour.

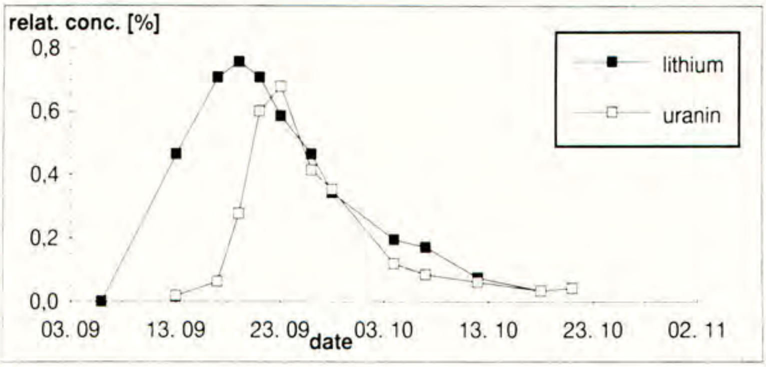

Fig. 4 Breakthrough curve of lithium and uranine for the upper part (4-5 m below soil surface) of well B52

The estimated dispersivity is in the order of about of 0.5 m and increases with distance. This is known as the scale effect in literature. At monthly intervals, all multi-level-samplers were sampled in order to calculate the spatial moments of the two plumes. This allows quantification of the time dependent behaviour of macrodispersion and its relation to the heterogeneity of aquifer properties (e.g. hydraulic conductivity, sorption)

MODELLING

The WAVE model (Vanclooster et al., 1995) isused to study the behaviour of atrazine and benazolin-ethyl in the soil. This model is an extended and revised version of the SWATNIT (Vereecken et al., 1991) model originally developed to describe the behaviour of nitrogen in soils. This model was tested against data obtained from the two lysimeters and to six lysimeters treated with radioactivity labelled methabenzthiazuron (MBT). Figure 5 shows the results obtained for one of the lysimeters with MBT application.The simulation of drainage is in good agreement with the data but the model was not able to predict the loss of MBT by leaching. This might be caused by the presence of macropores. A description of macropore flow will be incorporated in future versions of the model.

TRACE (Vereecken et al., 1994) was developed within the project to describe the behaviour of pesticides in heterogeneous soil-aquifer systems. TRACE is a 3D model for water flow and solute transport in saturated-unsaturated systems. Finite elements and finite difference methods are used to solve the generalised Richards' equation and the convective-dispersive equation. Heterogeneity of soil and aquifer parameters at the experimental site may result in numerical grids with more than one million unknowns. This faces the limits of sequential solution algorithms even for powerful computer systems. A domain decomposition method (Vereecken et al., 1994) was therefore implemented to allow the use of parallel based computer systems such as a massively parallel computersystem or a workstation cluster. Objectives of these activities are to understand the impact of the heterogeneity of basic soil and aquifer properties on solute transport.

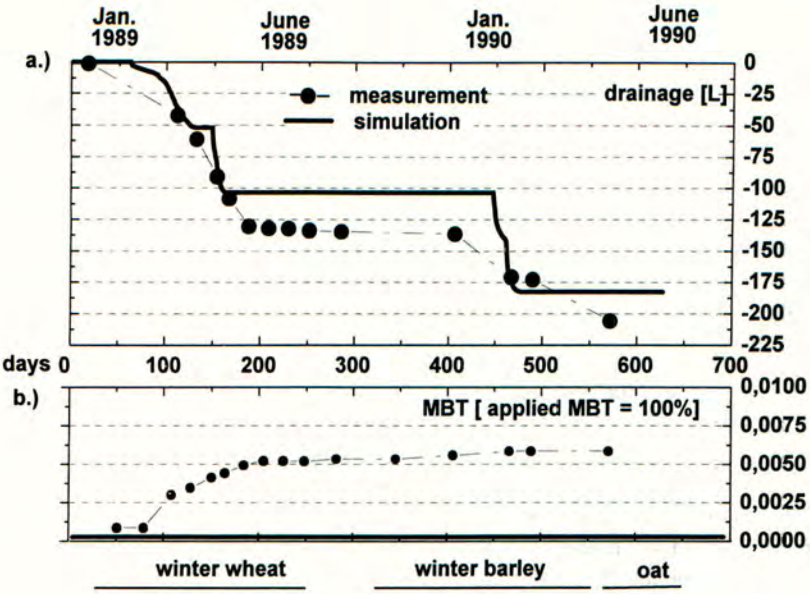

Fig.5 Time course of measured and simulated accumulated drainage flux at the lower boundary of the lysimeter (a.)) and the accumulated amount of MBT in the leachate [applied MBT = 100 %] (b.)).

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COMPARISON OF DIFFERENT MODELS TO SIMULATE THE LEACHING BEHAVIOUR OF QUINMERAC PREDICTIVELY

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ABSTRACT

Results of simulation models for the prediction of pesticide leaching (VARLEACH 2.0, PELMO 1.5, PESTLA 2.3, LEACHP 3.1, MACRO 3.1) were compared with experimental results of a lysimeter study with the herbicide quinmerac.
The models differ widely in their basic concepts of water and pesticide dynamics. The model parameters were determined *a priori* from available data and with pedotransfer functions. None of the models described pesticide behaviour (transformation, vertical distribution) and water percolation to a completely satisfying degree. The models differed considerably in the simulation of the herbicide amount in soil profile (1.5 - 32.9 % of initial simulated vs. 1.4 % measured) and vertical distribution in the lysimeter (most in 0-10 cm vs. evenly distributed in 0-30 cm). With the exception of MACRO herbicide amount was considerably overestimated by the models. Good agreement of the relative vertical distribution of residues (i.e. most in top 0-10cm) was simulated only by VARLEACH and PELMO which consider increasing K_d-values with time. MACRO, PELMO and PESTLA could simulate the development of percolate to a sufficient degree.

INTRODUCTION

Lysimeters are useful tools to study the behaviour of pesticides in agroecosystems under natural conditions. They provide the opportunity to describe exactly the boundaries of soil compartments and to monitor fluxes in and out of the soil system. Therefore lysimeters are prerequisites to calibrate and validate simulation models.

The objectives of the study were the comparison and the predictive use of widely applied simulation models with different conceptual bases to describe the leaching behaviour of the herbicide quinmerac. The experimental results of a lysimeter study (Mittelstaedt *et al.*, 1994) with a gleyic cambisol and of laboratory studies from literature (Nörtersheuser, 1993) as well as pedotransfer functions (PTFs) were used to provide parameter values for quinmerac and to validate the simulation models. In addition to graphs, statistical criteria according to Loague & Green (1990) are given.

MATERIAL AND METHODS

The experimental results of a lysimeter study (Mittelstaedt *et al.*, 1994) with a gleyic cambisol (plow layer(0-35 cm): organic carbon = 0.95 [%], sand/silt/clay = 73.0 / 22.1 / 4.9 [%]; $pH_{(CaCl2)}$ = 6.55) and of laboratory studies from different soils (Nörtersheuser, 1993) were used to provide parameter values for quinmerac.

The simulation models VARLEACH 2.0 (Walker, 1987), PELMO 1.5 (Klein, 1993), PESTLA 2.3 (Boesten, 1993), LEACHP 3.1 (Hutson & Wagenet, 1992) and MACRO 3.1 (Jarvis, 1994) were used. These models differ substantially in their basic concepts for calculating water flow (capacity concept vs. Richard's-Equation), solute transport (displacement vs. convection dispersion) and the degradation and sorption behaviour of pesticides (linear distribution coefficients (K_d) vs. Freundlich-isotherm; constant K_d vs. variable K_d) (Table 1). The model parameters were determined *a priori* independently. The simulation models were not calibrated with the data of the lysimeter study, a necessary procedure if the models are to be used as assessment tools.

To characterise the sorption behaviour of quinmerac in the lysimeter soil a sorption coefficient (K_{oc}-value) of 44 was estimated using an empirical formula (**1**) proposed by Nörtersheuser (1993).

$$K_d\left(C_{org}, pH\right) = \frac{a * C_{org}}{b + C_{org}} * \left(c + e^{-\left(\frac{pH}{pH_{crit}}\right)^{d}} \right) \qquad \mathbf{1}$$

with $a = 28.84;\ b = 3.36;\ c = 0.06;\ d = 3.92;\ pH_{CRIT} = 4.41$

The Freundlich-exponent (n) of quinmerac determined in sorption studies by Nörtersheuser (1993) with a similar soil (low organic carbon) was $n = 0.85$. The data of Nörtersheuser (1993) show an increase of sorption of quinmerac with time and an assumed linear rate of 9.9 (year^{-1}) was calculated. Parameters for the degradation behaviour of quinmerac were estimated from laboratory studies of Nörtersheuser (1993) (sandy loam soil 'Bruch-West') at different moisture and temperature regimes, assuming first-order kinetics. Only data from an incubation period of < 100 days were used because of the danger of microbial exhaustion in the laboratory studies. At reference temperature conditions (T_{ref}) of 20 (°C) and a reference volumetric soil moisture (Θ_{ref}) of 0.30 (cm^3 cm^{-3}, = 50 % of maximum water holding capacity) a reference half-life of 50 (days) was calculated. Parameters for temperature and moisture dependance of the degradation rate as described by Walker (1987) were $E_a = 29.4$ (kJ Mol^{-1}), $A = 859$, $b = 0.847$ (days Θ^{-1}). From the data of Nörtersheuser (1993) a Q_{10}-value (linear increase rate of degradation with increase of temperature of 10 °C) of 3.3 for the characterisation of the temperature dependance of degradation in PELMO 1.5 and LEACHP 3.1 was calculated.

The soil physical parameters of the $K_{(\Theta)}$-relation (hydraulic conductivity - soil moisture) and $\Theta_{(\Psi)}$-relation (soil moisture - hydraulic head) according to Van Genuchten (1980) for the models solving the common equation for soil water flow (Richard's-equation) were estimated using pedotransfer functions (PTFs) from Vereecken *et al.* (1989) for PESTLA and MACRO and for LEACHP with the internal implemented PTFs of Rawls & Brakensiek (1985). For the top soil the estimated Mualem-Van Genuchten-parameter (residual soil moisture [Θ_r], saturated soil moisture [Θ_s], saturated hydraulic conductvity K_s) with the PTFs of Vereecken *et al.* (1989) were Θ_r=0.00 (cm^3 cm^{-3}), Θ_s=0.37 (cm^3 cm^{-3}), K_s = 15.2 (cm d^{-1}), α= 0.480E-2, n= 0.571, m= 1.14, L= 0.120 and combined with the PTFs of Rawls & Brakensiek (1985) the parameters for Campbell's-water retention equation were $\Theta_s = 0.379$ (cm^3 cm^{-3}), K_s = 15.2 (cm d^{-1}), a = -0.455 (kPa), b = 4.67, p = 1.0.

The formulae for the description of degradation by the different models and the parameter values were

for **VARLEACH 2.0** $$K_{el}(T,\Theta) = e^{-\frac{E_a}{RT}} A\,\Theta^{-b} * f_z \tag{2}$$

$E_a = 29$ [kJ mol^{-1}], $A = 859$, $b = 0.847$; $f_z = 1$, $K_{dt} = 0.44 + 0{,}04 * \sqrt{\text{days}}$,

for **PELMO 1.5** $$K_{el}(T,\Theta) = K_{el}\,(T_{ref},\Theta_{ref}) * \left(\frac{\Theta}{\Theta_{ref}}\right)^{-b} * Q_{10}^{\frac{T-T_{ref}}{10}}\; f_z \tag{3}$$

$\Theta_{ref} = 0.3$ [cm^3 cm^{-3}], $T_{ref} = 20$ [°C], $b = 0.847$; $f_z = 1$, $Q_{10} = 3.3$ [10 °C^{-1}],
$K_{dt} = 0.44 + 9.9/365$; $1/n = 0.85$,

for **PESTLA 2.3** $$K_{el}(T,\Theta) = e^{[\gamma(T-T_{ref})]} * \min\left[1,\left(\frac{\Theta}{\Theta_{ref}}\right)^{b}\right] * f_z \tag{4}$$

$\gamma = 0.004$, $T_{ref} = 20$ [°C], $\Theta_{ref} = 0.3$ [cm^3 cm^{-3}], $b = 0.847$; $f_z = 1$, $K_{om} = 26$; $1/n = 0.85$,

for **LEACHP 3.1** $$K_{el}(T,\Theta) = K_{el}(\Theta_{ref},T_{ref}) * \frac{\max(\Theta,\Theta_{wp}) - \Theta_{wp}}{\Theta_{min} - \Theta_{wp}} * Q_{10}^{\frac{T-T_{ref}}{10}} \tag{5}$$

$\Theta_{min} = 0.05$ [cm^3 cm^{-3}], $\Theta_{wp} = 0.02$ [cm^3 cm^{-3}], $Q_{10} = 3.3$ [10 °C^{-1}], $K_{oc} = 44$; $1/n = 0.85$,

for **MACRO 1.3** $$K_{el}(T,\Theta) = e^{[\gamma(T-T_{ref})]} * \min\left[1,\left(\frac{\Theta}{\Theta_{ref}}\right)^{b}\right] f_z \tag{6}$$

γ fixed at 0.008, $T_{ref} = 20$ [°C], $\Theta_{ref} = 0.3$ [cm^3 cm^{-3}] $b = 0.847$, $f_z = 1$, $K_{oc} = 44$; $1/n = 0.85$,

with Θ_{FC} = field capacity; Θ_{WC} = water content; Θ_{WP} = wilting point; E_a= Arrhenius' activation energy, K_{el} = elimination rate; Θ_{ref} = reference moisture content; T_{ref} = reference temperature; γ, b, f_z = correction factor for temperature, moisture and depth dependence of transformation; K_{dt} = K_d-value at day t; Q_{10} = linear increase of degradation rate with a rise of temperature of 10°C

On May, 16th 1990 [^{14}C]quinmerac was applied onto sugar beet in the lysimeter. Soil from the plough layer was sampled 155 days after application and residues were analysed. The percolate was collected and analysed for residues. No significant residues of quinmerac could be detected in the leachate (Mittelstaedt *et al.* 1994) which agree with model results (data not presented). Pesticide residues in undisturbed soil samples and amount and time course of percolate were chosen for the comparison of simulated and experimental results.The study was simulated until end of 1991.

RESULTS AND DISCUSSION

Low residues of quinmerac (1.4 % of applied amount) were detected in the 0-20 cm layer after 155 days (Figure 1a) which contrasts to simulation results (Figure 1b-1e). The models differed considerably in the simulation of the herbicide amount (1.5 - 34.0 % of initial) and vertical distribution in the lysimeter (most in 0-20 cm vs. distributed in 0- >30 cm). With the exception of MACRO the herbicide amount was considerably overestimated by the models.

This overestimation of residues is due to the reference half life of 50 (days) and the degradation parameters determined by Nörtersheuser (1993). The preliminary version of MACRO 3.1, that was used, did not allow to vary the internal fixation of temperature dependancy which was set at $\gamma = 0.008$ (= 50 kJ Mol^{-1}).

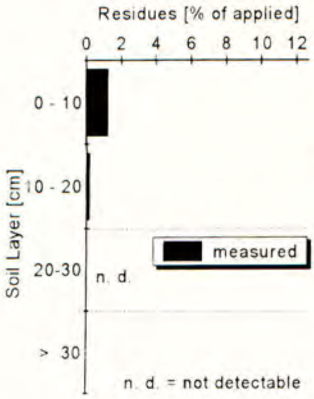

Figure 1a: Measured distribution of quinmerac (Σ= 1.4 % of applied)

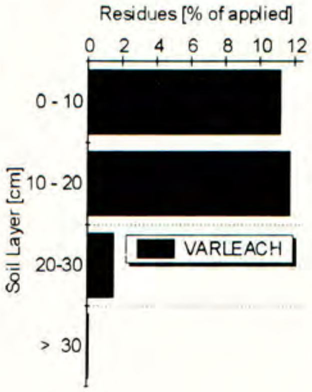

Figure 1b: Simulated distribution of quinmerac (Σ=24.7 % of applied)

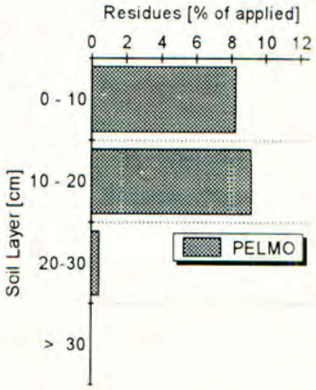

Figure 1c: Simulated distribution of quinmerac (Σ=17.9 % of applied)

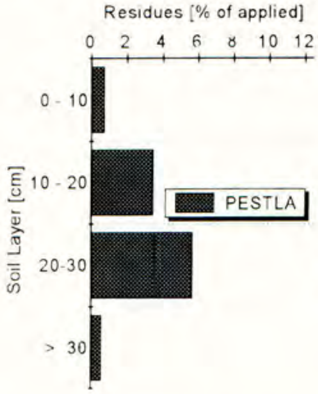

Figure 1d: Simulated distribution of quinmerac (Σ=10.4 % of applied)

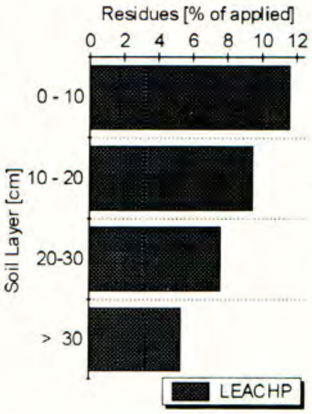

Figure 1e: Simulated distribution of quinmerac (Σ=34.0 % of applied)

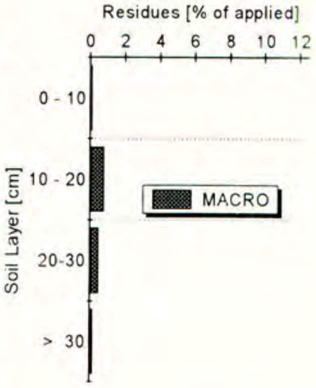

Figure 1f: Simulated distribution of quinmerac (Σ=1.5 % of applied)

Good agreement of the <u>relative</u> vertical distribution of residues (i.e. most in top 0-20 cm) was simulated only by VARLEACH and PELMO. These models consider variable (= increasing) K_d-values with time. But their simulation of pesticide amount and by VARLEACH also water percolation (Figure 2) was insufficient. Statistical terms show that MACRO produced the lowest root mean square error and had the best model efficiency (nearest to 0) (Table 1) thus supporting the differences between the model results shown graphically.

Table 1: Simulated residues of quinmerac 155 days after application and statistical criteria for the comparison with measured values (measured =1.41 %) (Loague & Green 1990)

	VARLEACH	*PELMO*	*PESTLA*	*LEACHP*	*MACRO*
Residues [% of applied]	24.6	17.9	10.4	34.0	1.5
$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum(P_i - O_i)^2} * \frac{100}{\overline{O}}$	129.59	96.26	55.50	141.13	11.81
$\mathrm{EF} = \frac{\sum_{i=1}^{n}(O_i - \overline{O})^2 - \sum_{i=1}^{n}(P_i - O_i)^2}{\sum_{i=1}^{n}(O_i - \overline{O})^2}$	-220.42	-121.16	-39.61	-261.58	-0.84
$\mathrm{CRM} = \frac{\sum_{i=1}^{n} O_i - \sum_{i=1}^{n} P_i}{\sum_{i=1}^{n} O_i}$	-16.49	-11.71	-6.38	-23.14	-0.08

O = observed values, P = predicted values; EF = Model efficiency;
RMSE = Root mean square error; CRM = Coefficient of residual mass

Figure 2 show that PELMO could simulate the development of percolate to a sufficient degree. MACRO and PESTLA calculated the accumulated percolate at the end of the simulation period.

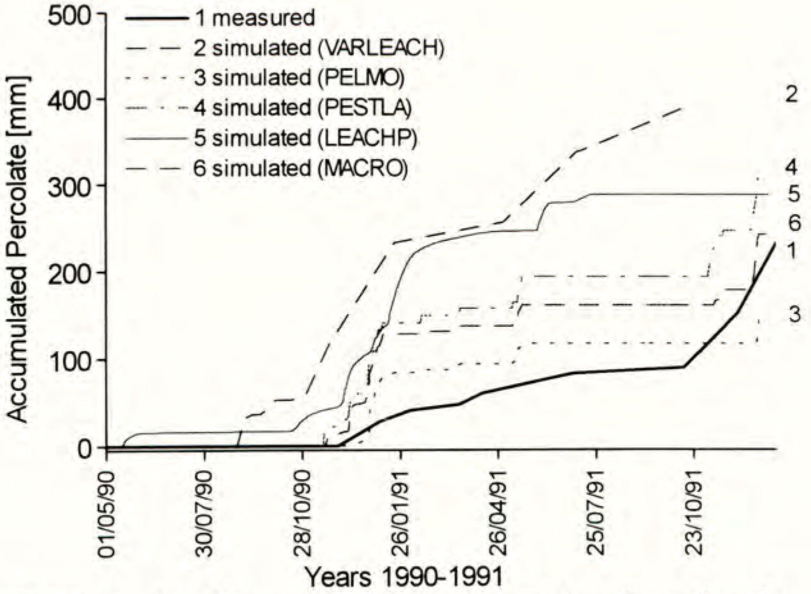

Figure 2: Comparison of measured and simulated percolation of water from the lysimeter

None of the models described pesticide behaviour (transformation, vertical distribution) and water percolation to a completely satisfying degree. Comparing the different models PELMO and MACRO showed the best description of the percolation of water during the lysimeter study. MACRO was the only one yielding the correct total residues. However even in this case the depth profile was wrongly described. The relatively good results of PELMO illustrate that the implementation of an important chemical process (i. e. increase of sorption with time as confirmed by e. g. Walker, 1987, Gottesbüren *et al.*, 1994) could override the disadvantage of a very simplified concept of water flow. Unfortunately the complete climatic water balance of the models could not be compared to experimental data as those shown by Printz *et al.* (1994) because the soil moisture in different horizons of the lysimeter soil core was not recorded. Parameter values taken from the literature should be used carefully if used for different scenarios.

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VALIDATION OF THE DUAL-POROSITY MODEL 'MACRO' FOR ASSESSING PESTICIDE FATE AND MOBILITY IN SOILS

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ABSTRACT

This paper assesses the predictive accuracy of the dual-porosity model MACRO. Model simulations are compared with the observed behaviour of alachlor in lysimeter and field experiments in two sandy loams and one clay loam. The results suggest that preferential flow occurred at all three sites. Discrepancies between model predictions and measurements were attributed to inappropriate estimates of parameters describing the macropore domain, and in the sandy soils, to an inability of the model to account for by-pass flow in the soil matrix ('fingering'). The development of improved estimation procedures for macropore flow parameters will lead to a more robust and accurate model suitable for management purposes.

INTRODUCTION

Pesticide leaching models are now being used as potentially effective and inexpensive management and decision-support tools. With this increasing use of simulation models, it is vital that confidence can be placed in model outputs. This implies the need for rigorous model validation and quantitative assessments of model predictive accuracy. It is important that models incorporate treatments of all processes that are known to significantly affect pesticide fate and mobility. Preferential flow is perhaps one of the more important processes which, until recently, has largely been neglected. Preferential flow is a generic term used to describe a range of physical non-equilibrium flow processes. In fine-textured soils, macropores (e.g. shrinkage cracks, earthworm channels, root holes) dominate the soil hydrology, operating as high-conductivity flow pathways by-passing the denser soil matrix (Beven & Germann, 1982). Preferential flow has also been observed in unstructured coarse sandy soils (Hillel, 1987), caused by large-scale profile heterogeneities such as horizon interfaces, textural variations, or by water repellency. Preferential flow is critical for pesticide leaching, since the biologically and chemically active topsoil may be by-passed. Preferential movement of pesticides has been demonstrated by, among others, Kladivko *et al.* (1991), Ghodrati & Jury (1992) and Harris *et al.* (1994). Preferential flow may be the rule rather than the exception. From dye tracing experiments conducted at fourteen sites, Flury *et al.* (1994) concluded that preferential flow was to be expected in most Swiss agricultural soils.

The dual-porosity MACRO model (Jarvis, 1994) is a physically-based model accounting for macropore flow. The soil porosity is divided into macropore and micropore domains, each characterized by a flow rate and solute concentration. Richards' equation and the convection-dispersion equation are used to model soil water flow and solute transport in the micropores, while a simplified capacity-type approach is used to calculate fluxes in the macropores. Mass exchange between the flow domains is calculated using approximate, but physically-based, expressions based on an effective aggregate half-width. Additional model assumptions include first-order kinetics for degradation in each of four 'pools' of pesticide in the soil (micro- and macropores, solid/liquid phases), together with an instantaneous sorption equilibrium and a linear sorption isotherm in each pore domain. This paper assesses the performance of the dual-porosity model MACRO (v. 3.1, Jarvis, 1994), run predictively without calibration of model parameters. This assessment is based on comparisons of model predictions with measurements of concentrations of the herbicide alachlor in three soils (one clay loam and two sandy loams).

EXPERIMENTAL MEASUREMENTS

Full details of the experimental methods and measurement techniques can be found in Moon & Walker (1991) and Williamson & Carter (1991). Therefore, only brief details are presented here. In the lysimeter experiment, seven replicate PVC columns, 11.5 cm in diameter and 30 cm in height, containing undisturbed sandy loam soil, were collected in July 1990. Alachlor was applied on 5 November 1990 at 8 kg ha^{-1}. The soil was bare throughout the experiment. At *c*. 28 day intervals, individual columns were removed and dissected into successive 2 cm segments, and soil extracts analysed for alachlor. Leachate was also collected following significant rainfall events. Sampling continued until 22 April 1991.

The field experiments were located at Temple Balsall (near Birmingham). Alachlor was applied at a rate of 1.92 kg ha^{-1} on two fields representing contrasting soils (Brockhurst series clay loam, Hall series sandy loam), three days after drilling fodder maize in May 1993. Alachlor residues were measured by sequential core sampling at approximately 10 day intervals from the soil surface to 10 cm depth. Alachlor concentrations in soil water were measured in suction cup samplers located at 3 depths (25, 40 and 80 cm depth in Brockhurst clay loam; 25, 50 and 150 cm depth in Hall sandy loam). The suction cups were installed vertically in auger holes backfilled with bentonite to the base of the topsoil. Water was extracted under a tension of 700 cm H_2O for a minimum of 2 h, allowing samples of *c*. 1 l to be collected. Sampling was triggered by significant rainfall events and continued until August 1993.

MODEL APPLICATION

Soil profile

Simulations were performed for soil profiles 1.3 and 1.65 m deep in the Brockhurst and Hall soils respectively. Drain tiles at 0.7 m depth and 5 m spacing were specified for the Brockurst series clay loam, based on field observations.

Hydraulic properties

Soil water retention curve parameters were estimated using pedo-transfer functions developed on a subset (*c.* 180 soil horizons) of the SSLRC soil water retention database. These functions predict Brooks-Corey parameters (Brooks & Corey, 1964) from soil particle size distribution, organic carbon content and bulk density. The derived parameter values are shown in Table 1. The residual water content was set 'a priori' to zero. The saturated hydraulic conductivity values shown in Table 1 were estimated from the predicted soil-air capacity or effective porosity (defined as the soil porosity minus the water content at a pressure head of -50 cm H_2O) using the functions described by Hollis & Woods (1989). Saturated micropore hydraulic conductivity (K_b, Table 1) was calculated from the estimated water retention curve parameters using the approach outlined by Jarvis (1995). All remaining soil hydraulic parameters in MACRO were set to the default values supplied with the model. Thus, the effective aggregate half-width was fixed at 20 mm.

Pesticide properties

Degradation rate constants for alachlor were directly measured on soil samples taken from the lysimeter sandy loam (Moon & Walker, 1991) and from each identified horizon in both the Brockhurst clay loam and Hall sandy loam (A. Walker, pers. comm.). These data are shown in Table 2. Sorption constants (K_d values, Table 2) were also measured in batch experiments in the laboratory on soil samples from the lysimeter sandy loam and Brockhurst clay loam. Sorption was not measured for Hall series sandy loam. Thus, the K_d values for Hall series soil shown in Table 2 were calculated assuming an organic carbon partition coefficient K_{oc} of 95 $cm^3\ g^{-1}$, derived from the measurements on the lysimeter sandy loam.

The exponent in the degradation soil water content response function (Jarvis, 1994) was set to 0.6, based on laboratory measurements made across a range of soil water contents using the sandy loam soil (Moon & Walker, 1991). Similarly, the exponent in the modified Arrhenius equation accounting for temperature effects on degradation was set to 0.1, based on the results of laboratory experiments described by Moon & Walker (1991). The fraction of sorption sites in the macropores was set to the default value in the model (= 0.1). Degradation was assumed to occur at the same rate in solution and sorbed phases and in macropores and micropores. Herbicide uptake by maize was assumed to be zero.

Crop parameters

Parameters related to root-water uptake in the field experiments on Hall and Brockhurst series soils were set to default values supplied with the model. Dates of emergence, maximum crop development and harvest were set according to field observations of the fodder maize crops at the two sites.

Driving variables

Driving variables for the simulations consisted of daily potential evapotranspiration, rainfall, and maximum and minimum air temperatures. Rainfall duration was calculated from measured daily rainfall totals assuming a constant rain intensity of 2 mm h^{-1}.

TABLE 1 Parameter input values : soil hydraulic properties.

Soil	Depth interval (cm)	Parameter						
		K_s (mm h^{-1})	K_b (mm h^{-1})	ψ_b (cm)	θ_s (m^3 m^{-3})	θ_b (m^3 m^{-3})	θ_w (m^3 m^{-3})	λ
Brockhurst	0-24	50.0	0.11	-16	0.43	0.39	0.18	0.113
	24-48	8.0	0.15	-12	0.39	0.36	0.17	0.107
	48-89	4.0	0.02	-30	0.36	0.35	0.22	0.086
	89-130	4.0	0.06	-17	0.31	0.30	0.19	0.087
Lysimeter	0-30	49.0	0.85	-9	0.49	0.36	-	0.150
Hall	0-33	47.0	0.12	-16	0.45	0.39	0.16	0.126
	33-51	47.0	1.06	-7	0.44	0.35	0.06	0.229
	51-80	68.0	2.50	-5	0.43	0.34	0.02	0.358
	80-165	1080.0	3.67	-5	0.56	0.38	0.01	0.436

K_s	total saturated hydraulic conductivity.
K_b	saturated micropore hydraulic conductivity.
ψ_b	boundary pressure head between macropores and micropores.
θ_s	saturated water content.
θ_b	water content corresponding to ψ_b.
θ_w	wilting point water content.
λ	pore size distribution index.

TABLE 2 Parameter input values : pesticide properties.

Soil	Depth interval (cm)	Property	
		Sorption constant (K_d, cm^3 g^{-1})	Reference half-life ($t_{1/2}$, d)
Brockhurst	0-24	2.60	21
	24-48	0.33	138
	48-89	0.27	230
	89-130	0.53	493
Lysimeter	0-30	1.07	29
Hall	0-33	3.04	23
	33-51	0.57	56
	51-80	0.19	102
	80-165	0.10	178

Initial and boundary conditions

The simulations were started assuming drainage equilibrium in the soil profile. A unit hydraulic gradient was assumed as the bottom boundary condition in the Hall series sandy loam. No flow was assumed at the base of the profile in Brockhurst clay loam. A boundary condition suitable for gravity-drained soil columns was used in the lysimeter experiment.

RESULTS AND DISCUSSION

Field experiments

Figure 1 shows a comparison of model predictions and the measurements of alachlor residues and soil water concentrations in Hall series sandy loam. The model performance

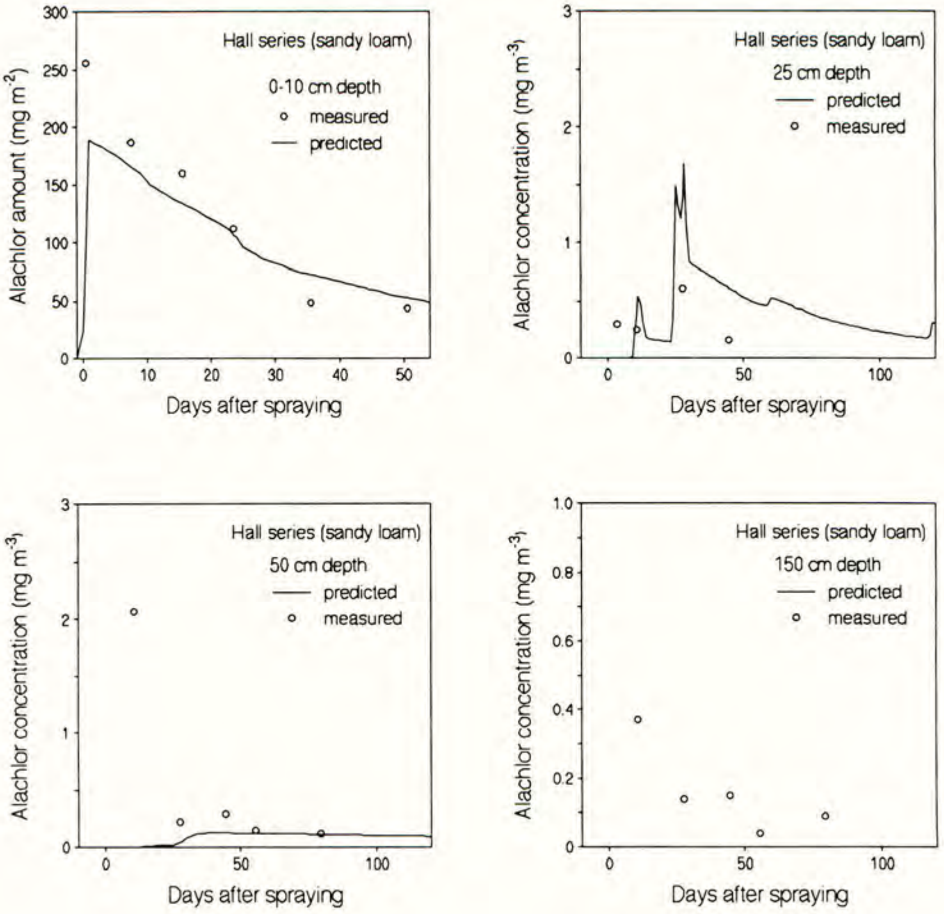

Figure 1 Model predictions and measurements of alachlor soil residues and soil water concentrations (Hall series sandy loam)(note different scales on y-axes).

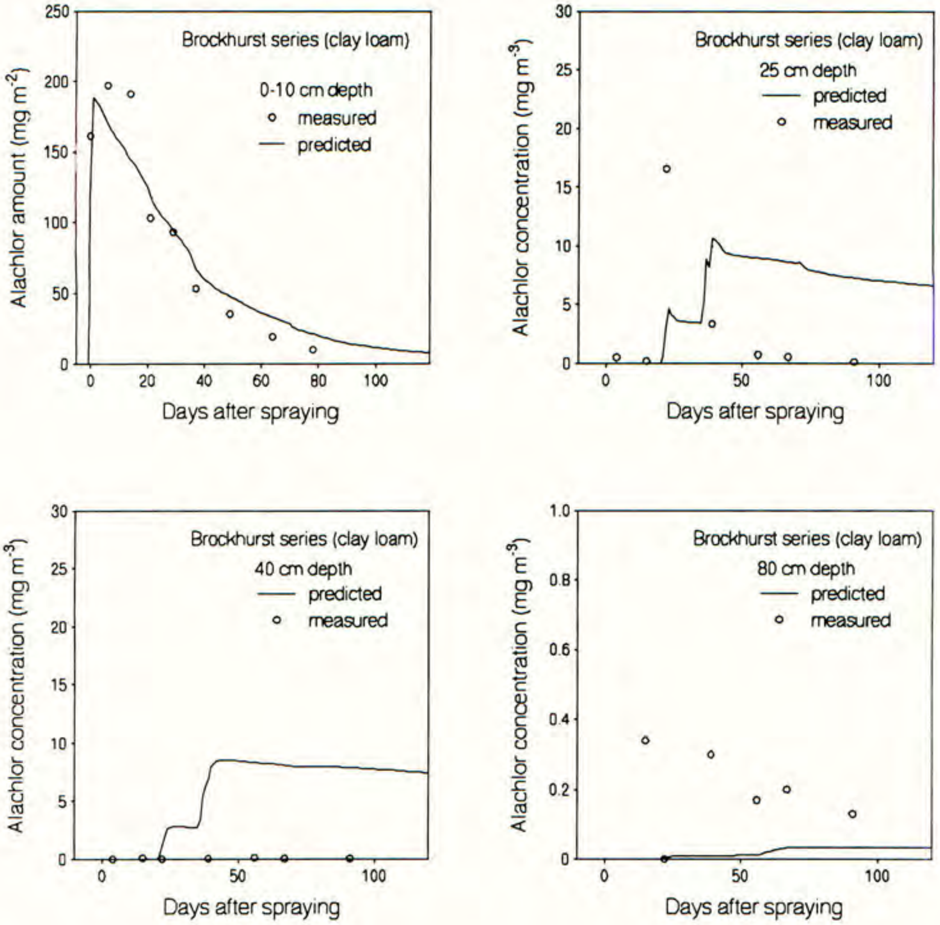

Figure 2 Model predictions and measurements of alachlor soil residues and soil water concentrations (Brockhurst series clay loam)(note different scales on y-axes).

must be considered satisfactory, given that no model calibration was carried out. The actual amount of alachlor applied to the plot appeared somewhat larger than that assumed (192 mg m^{-2}), perhaps due to non-uniformity and variability in the application rate across the field. Despite this, the course of soil dissipation of alachlor is reasonably well predicted by the model using the half-lives measured in the laboratory. At 25 cm depth, MACRO predicted maximum concentrations of *c.* 1.7 µg l^{-1}, while a maximum concentration of *c.* 0.6 µg l^{-1} was observed (see Fig. 1). The timing of the peak concentration at 25 cm depth, observed 27 days after spraying, was well matched by the model, although an early breakthrough (*c.* 0.3 µg l^{-1}, 3 days after spraying) was slightly delayed in MACRO. This rapid transport to the base of the plough layer was presumably caused by 14 mm of rain which fell only two days after application. With the exception of the initial breakthrough, the model accurately matched the observed concentrations of 0.1 to 0.3 µg l^{-1} at 50 cm depth, during the summer following application (Figure 1). The suction cup samplers detected a mean concentration of 2.1 µg l^{-1} at 50 cm depth, 10 days after application. The model could not match such an

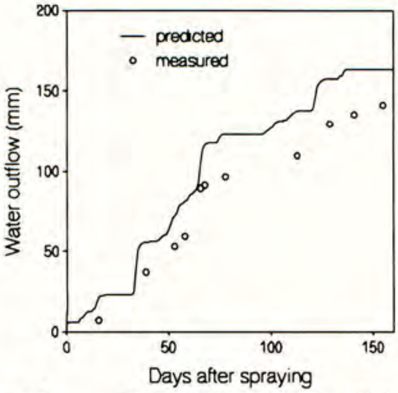

Figure 3 Comparison of model predictions and measurements of water outflow from the lysimeters

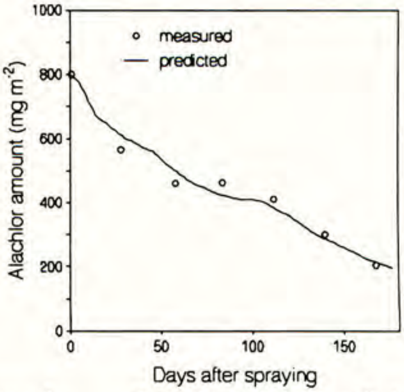

Figure 4 Comparison of model predictions and measurements of the total Alachlor residues in the lysimeters

early breakthrough, which was presumably caused by 47 mm of rain which fell during the three days immediately prior to sampling. This heavy rain also resulted in breakthrough to 150 cm depth, with concentrations of *c*. 0.4 μg l^{-1} detected 10 days after application (see Fig. 1). This rapid response, which can only be explained by preferential flow, was not predicted by MACRO. This is because the subsoil micropore conductivities (Table 1) were sufficiently large to prevent generation of macropore flow. The preferential flow in Hall series sandy loam may have resulted from 'finger' flow, which MACRO cannot simulate. Fingering may occur when conductivities increase with depth in the soil. This is likely to be the case in Hall series (Table 1), where the subsoil is coarser-textured than the topsoil.

Figure 2 compares predicted and measured alachlor concentrations at the Brockhurst clay loam site. Dissipation of alachlor was reasonably well predicted by the model using the half-lives measured in the laboratory, together with the corrections for water and temperature response. The model predicted a maximum concentration of *c*. 10 μg l^{-1} at 25 cm depth, compared to the observed peak concentration of *c*. 16 μg l^{-1}. The model overestimated concentrations for the remainder of the summer at 25 cm depth, and also for the entire experimental period at 40 cm depth, where observed cocnentrations were always smaller than 0.1 μg l^{-1} (Fig. 2). In contrast, at 80 cm depth, concentrations of up to 0.4 μg l^{-1} were detected, while those predicted by the model remained below 0.05 μg l^{-1}. Taken together, these discrepancies suggest that the strength of interaction between the two pore domains was overestimated in the model using the default value for aggregate half-width (20 mm), and that a larger value for this parameter would be appropriate for Brockhurst clay loam. It should be remembered, however, that the suction cup technique itself may not be reliable in structured clayey soils, yielding unrepresentative and/or highly variable results. It is possible that the suction cups at 40 cm depth did not contact active flow pathways and that this may explain why only small concentrations of alachlor were detected at this depth.

Lysimeter experiment

Figure 3 compares model predictions and measurements of water outflow from the lysimeters. The model overestimated outflow by *c*. 25 mm during the 160 day experiment.

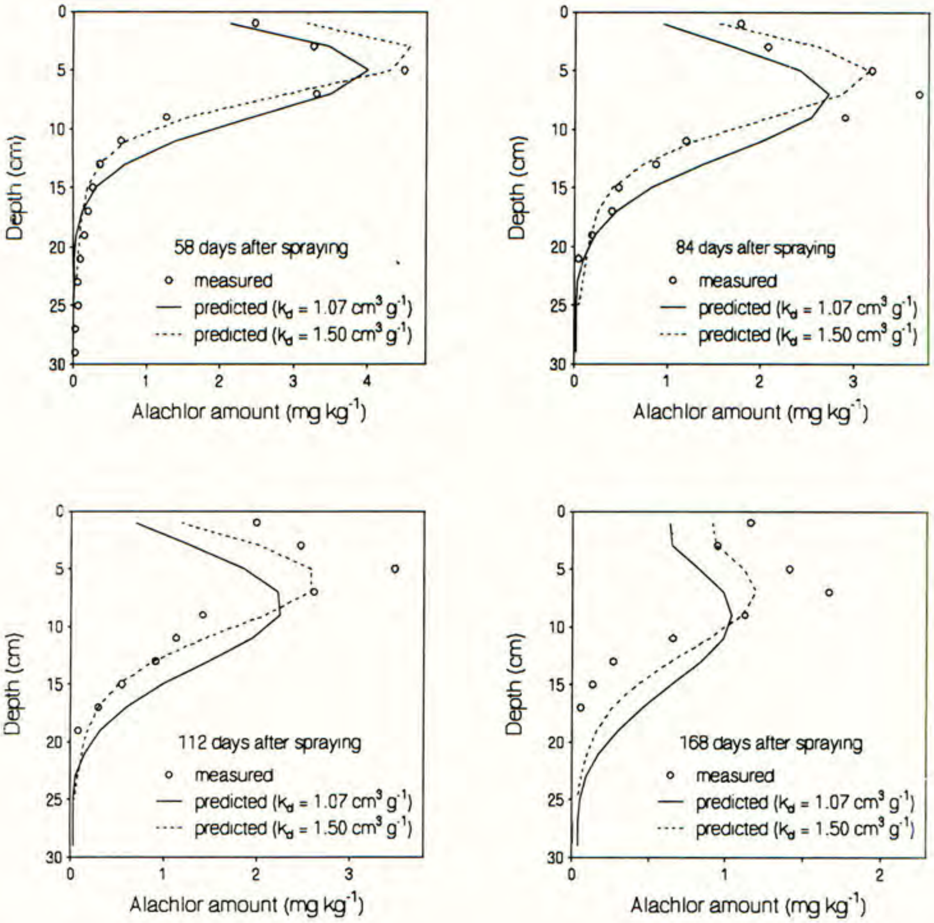

Figure 5 Model predictions and measurements of the distribution of alachlor in lysimeters.

This appears largely due to the initial condition assumed (drainage equilibrium), rather than to model errors in predicting either soil evaporation or soil water flow. Figure 4 compares measurements and predictions of total alachlor residues in the columns. It demonstrates that the model closely reproduced the dissipation observed in the lysimeters, with *c*. 25% of the applied amount remaining in the soil at the end of the experiment.

Figure 5 compares model predictions of concentration-depth profiles with measurements made in four of the seven lysimeters. The model overestimated downward displacement by *c*. 2 to 3 cm during the course of the experiment. It is possible that the K_d value measured in laboratory experiments on slurried soil was not representative of undisturbed soil in the lysimeters, perhaps due to sorption hysteresis. Assuming a K_d value of 1.5 cm^3 g^{-1} improved model performance (Fig. 5). However, an underestimate of sorption is not the only possible reason for the results presented in Figure 5. Another likely explanation is the occurrence of preferential flow, not in soil macropores, but in the soil matrix as 'finger flow'. If significant amounts of water move through the soil matrix in preferred flow paths, without interacting

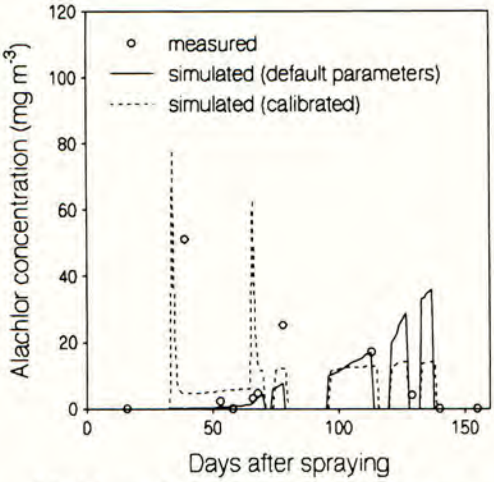

Figure 6 Model predictions and measurements of Alachlor concentrations in lysimeter leachate

with the bulk of the pesticide stored in relatively immobile water, then the downward movement of the peak will be overpredicted.

Figure 6 shows model predictions and measurements of concentrations in the lysimeter leachate. The data indicate preferential transport of Alachlor, with maximum concentrations of *c*. 50 μg l^{-1} found in the first significant outflow event. MACRO did not predict this early breakthrough using default parameters to describe the macropore domain (Fig. 6). Instead, maximum concentrations approaching 40 μg l^{-1} were only predicted to occur at the end of the experiment. Figure 6 shows that an early breakthrough of alachlor can be simulated following model calibration, in this case by reducing the fraction of sorption sites in the macropores from 0.1 to 0.02 and by increasing the aggregate half-width from 20 to 60 mm.

CONCLUDING REMARKS

The results of this model validation excercise must be considered encouraging, given the extensive use of simple parameter estimation methods (pedotransfer functions) to derive soil hydraulic properties and model default values. Soil dissipation of alachlor was adequately predicted from laboratory measurements in all three experiments. In the field experiments, concentrations measured in suction cups at 25 and 50 cm depth in the sandy loam soil, and at 25 cm depth in the clay loam soil, were reasonably well matched by the model.

Preferential flow apparently occurred in both sandy loam soils. The model did not adequately predict this phenomena, either because default parameter values describing the macropore system were inappropriate, or because soil macropores were not the underlying cause. The model may need some modification before it can be used to predict rapid transport processes ('fingering') in sandy soils. A three-domain model, including immobile water in the micropores, may be a promising approach.

In the clay loam soil, discrepancies between model predictions and measurements were partly attributed to inappropriate estimation of parameters describing the macropore domain, especially the effective aggregate size and the fraction of sorption sites in the macropores. More research effort is required to establish improved estimation methods for these critical model parameters.

ACKNOWLEDGEMENTS

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MULTI-REGION WATER FLOW AND CHEMICAL TRANSPORT IN HETEROGENEOUS SOILS: THEORY AND APPLICATIONS.

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ABSTRACT

Many different processes influence chemical leaching patterns, including chemical kinetics, diffusion, matrix geometry and flow heterogeneity. TRANSMIT, a multi-region model which reflects many of these features, is described. Simulations of chloride and atrazine breakthrough from soil columns which have immobile and mobile matrix regions as well as a preferential flow region, and leaching of atrazine in a similar field soil, are demonstrated. TRANSMIT can describe a wide range of multi-region and two-dimensional geometries, and is applicable to transient and steady-state flow typical of both laboratory experiments and field situations. Sorption and degradation parameters can be varied, and non-uniform surface boundary conditions, resulting from irrigation methods and banded chemical placement, can be described.

INTRODUCTION

Many models used to simulate chemical movement in soil use a one-dimensional form of the Darcy-Richards equation for water flow and the convection-dispersion equation (CDE) for solute transport, for example, LEACHM (Hutson & Wagenet, 1992). This, and other simplifying assumptions such as uniform distribution of both infiltration and chemical fluxes across the soil surface, are not always valid (Brusseau *et al.*, 1989; Pignatello, 1989). In field applications, spatial variation in soil properties is common (Nielsen *et al.*, 1986). There is a need for a model which can reflect the influences of non-equilibrium flow and sorption processes, and spatial variability in both soil properties and surface boundary conditions. This paper describes such a model.

Various two-region models, incorporating a transfer process between mobile and immobile regions, have been used to characterize physical non-equilibrium (Passioura, 1971; Addiscott, 1977; Rao *et al.*, 1980a,b; van Genuchten & Dalton, 1986; van Genuchten & Wagenet, 1989;). Analytical solutions for steady-state, CDE-based, single- and two-region models are available (Parker & van Genuchten, 1984; van Genuchten & Dalton, 1986; van Genuchten & Wagenet, 1989).

Alternatives to the two-region approach are based upon water flow in a mobile region composed of fractures, macropores, fissures, and other non-capillary preferential pathways not necessarily described by the Darcy-Richards equation (Germann & Beven, 1985; Wagenet & Germann, 1989; Germann, 1990). In other studies the stagnant region was replaced with a slowly-permeable porous system, resulting in a dual-porosity model in which both regions are mobile and can be described by the Richards equation, but with different coefficients (Gerke & van Genuchten, 1993). For field conditions where water flow is transient, slow, and unsaturated, models considering a wider range of sorption site and physical heterogeneity become necessary. This need has promoted the development of multi-region models intended to more closely represent the high heterogeneity of field soils (van der Zee & Riemsdijk, 1987; Steenhuis & Parlange, 1991).

Solute transfer under natural conditions is complicated further by variable soil properties and geometry, leading to a wide range of diffusion distances and variable access to sorption sites. In addition, surface relief, irrigation method, banded chemical placement, row cropping, and non-uniform root distribution influence water and chemical distribution, while chemical degradation and transformation rates may vary over short distances.

The TRANSMIT (TRansport And Non-equilibrium Soil Multi-region Interpretive Tool) model (Hutson & Wagenet, 1995) was developed in an attempt to reflect many of the sources of variability which influence solute transport in heterogeneous soils. It is an extension of the LEACHM model (Hutson & Wagenet, 1992), in which a heterogeneous soil hydraulic regime is subdivided into multiple hydraulically-interacting regions.

MODELING APPROACH

The theoretical basis of the model is described in detail in Hutson & Wagenet, 1995. The soil profile is divided into horizontal segments of thickness Δz (mm), further subdivided into m regions (Figure 1). Water and solute can move vertically within a region and horizontally between regions. All transport of water and solute is based upon Darcy's law and the convection-dispersion equation. Two parameters define the geometry of the regions: relative cross-sectional area and an effective distance (d, mm) used for calculating concentration and potential gradients. Each region occupies a fractional area a_i. Mean water and solute contents for each depth segment are calculated from the values for each region, weighted according to a_i.

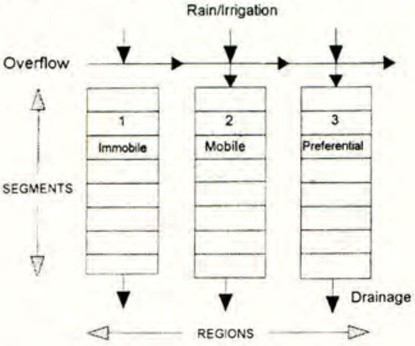

Figure 1. Division of the soil profile into segments and regions, showing infiltration and overflow pathways at the soil surface.

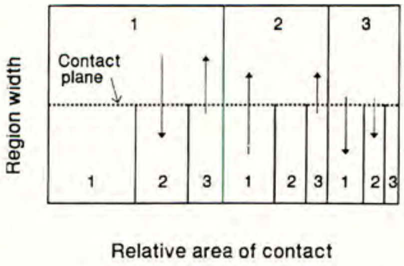

Figure 2. Areas of contact and direction of water flow across a contact plane for a three-region soil, assuming lowest matric potential in region 2 and highest in region 3.

Vertical fluxes are calculated for each region in turn, in order of increasing surface permeability, for a time period t_{max}, usually set between 0.005 and 0.1 day. Vertical water flow within each region is described by Richards' equation and vertical solute flux is calculated from the convection-dispersion equation (CDE). The subdivisions of t_{max} used in the simulations within each region depend upon water flux densities in the region, but sum to t_{max}. If the water application during a time step exceeds the infiltration capacity of a region, then the excess water is allocated to regions of higher permeability. Thus infiltration is weighted to the more permeable regions as the water application rate increases.

After simulating vertical flow in each region for a time period t_{max}, horizontal equilibration between segments is simulated for an equivalent period of time. Again, time steps within t_{max} are determined by water flux densities. Horizontal flow can reflect either multi-region or two-dimensional soil geometry.

The multi-region conceptual model considers simultaneous lateral transport between all possible pairs of segments at the same depth. Although 'vertical flow' is simulated as if the regions were simply vertical columns, they are conceived as having a complex, linked geometry which allows for the lateral interactions described in the model. All regions are assumed to have some contact with each other, the area of contact being proportional to their relative area or volume fraction. Conceptually, if the soil volume is broken at a cross-sectional plane, and rejoined randomly then the most probable area of contact between any pair of regions i and k across the contact plane, as a fraction of total contact area, is $2a_ia_k$ (for $i \neq k$).

In the three-region example (Figure 2) there are nine possible combinations of regions across the contact plane. The effective diffusion distance is largest for region 1 and smallest for region 3. If the current matric potential is lowest in region 2, intermediate in region 1 and highest in region 3, then water will flow from region 1 to region 2, and from region 3 to both regions 1 and 2. No flow occurs between pairs of similar regions because no matric potential gradient exists. Thus the change in water content in region 2, for example, is the sum of the flux between regions 1 and 2, and between 3 and 2. For m regions, the change in water content in region i is the sum of the area-weighted fluxes between i and all other regions, which can be written as a difference equation,

$$\frac{\psi_i^{j+1} - \psi_i^j}{\Delta t} C_{w_i} = \sum_{k=1}^{k=m} \frac{a_k K_{ik}}{\Delta x} \frac{(\psi_i^j + \psi_i^{j+1} - \psi_k^j - \psi_k^{j+1})}{d_{ik}} \tag{1}$$

where ψ is matric potential, Δt is the time step (j to j+1), C_{wi} is the mean differential water capacity during the time step, K_{ik} is the mean hydraulic conductivity between regions i and k, d_{ik} is the distance over which the hydraulic gradient is calculated and Δx is a size parameter, discussed below. Eq. 1, written for each region, forms a matrix which can be solved for the m unknown values of ψ^{j+1}.

Solute transport between regions is calculated in the same way. The mass flux density (J_{ik}) between two regions i and k across their contact plane, is

$$J_{ik} = D_{ik}\left(\frac{\overline{C}_k - \overline{C}_i}{d_{ik}}\right) + \beta_1 q_{ik}\overline{C}_i + \beta_2 q_{ik}\overline{C}_k, \qquad [2]$$

where C_i and C_k are mean solute concentrations in regions i and k during the time step Δt, D_{ik} is the effective dispersion coefficient (the sum of molecular diffusion and hydrodynamic dispersion) and q_{ik} is water flux density between regions i and k. The direction of water flow determines the values of β_1 and β_2; when q is negative (from i to k) then $\beta_1 = 1$ and $\beta_2 = 0$, when q is positive (from k to i) $\beta_1 = 0$ and $\beta_2 = 1$.

Assuming a linear sorption isotherm having a partition coefficient K_d, the total solute concentration is the sum of sorbed and solution concentrations ($C(\theta + \rho K_d)$). The change of concentration during Δt in region i is

$$\frac{(\theta_i^{j+1} C_i^{j+1} - \theta_i^j C_i^j) + \rho_i K_{di}(C_i^{j+1} - C_i^j)}{\Delta t} = \Sigma_{k=1}^{k=m} \frac{2 a_k J_{ik}}{\Delta x}. \qquad [3]$$

Writing Eq. [3] for each region, substituting Eq. [2] for J, and using θ and q values arising from the solution of Eq. [1], creates a matrix which can be solved for the m unknown values of C^{j+1}.

TABLE 1. Spatial scaling and weighting options in the TRANSMIT model (extract from input data file).

	3		[Number of soil columns: 1 or greater]
	2		[Geometry: 2-dimensional (1), multi-region (2)]
	1		[Overflow at the surface: yes (1), no (0)]
	1		[Lateral equilibration during infiltration: yes(1), no(0)]
	Region		
1	2	3	
0	1	1	[Vertical transport: yes (1), no (2)]
1	1	64	[Geometric scaling factor for hydraulic properties]
1	1	1	[Bulk density adjustment]
0.25	0.73	0.02	[Relative area]
1000	1000	1000	[Depth of scaling, mm]
1	1	1	[Irrigation weighting, does not apply to rain]
1	1	1	[Chemical application weighting]
1	1	1	[Partition coefficient adjustment]
100	10	1	[Diffusion geometry parameter d' (= $d\Delta x$), mm^2]
0	50	10000	[Surface seal limit mm d^{-1}, not used for steady-state]
1	1	1	[Degradation rate constant adjustment]
10	10	10	[Distance for root:soil gradient, mm]
1	1	1	[Fraction of equilibrium sites, for two-site sorption]
1	1	1	[Phase transfer coefficient d^{-1}]

The three parameters (*a*, Δx, and *d*) which define the geometry of the regions do have some physical significance: *a* is the fractional area occupied by each region, Δx is a 'size' parameter, the width of a slice of soil encompassing all of the structural heterogeneity (a first estimate, for example, may be based on the diameter of the largest peds), and *d* (different between regions) is an effective diffusion distance or 'shape' parameter. In practice, Δx and *d* are combined into a single parameter (d') reflecting soil diffusion geometry.

TRANSMIT can also be configured as a two-dimensional model. Linear, radial and spherical geometries can be represented, enabling simulation of the effects of furrow and drip irrigation, row crops and banded chemical placement.

Table 1 lists a section of the input data file showing soil chemical and physical properties which can be varied across regions. The data are those used in the example described below.

APPLICATIONS

TRANSMIT is demonstrated by simulating solute breakthrough curves and field leaching behaviour for hypothetical single- and three-region soils. TRANSMIT can use more than three regions if desired. Examples in Wagenet and Hutson (1995), for example, show the consequences of distributing water retention and hydraulic parameters log-normally across five regions.

Soil hydraulic parameters

For a single-region soil (which can be simulated with LEACHM or TRANSMIT), mean $K(\psi)$ and $\theta(\psi)$ curves are defined for the entire soil volume. The soil was assumed to have a bulk density of 1.27 Mg m^{-3}, a porosity of 0.5208 m^3 m^{-3}, and $\theta(\psi)$ and $K(\psi)$ curves shown in Figures 3 and 4. More complex spatial variation of hydraulic properties, structural units, and preferential flow paths can be represented in TRANSMIT, in which each region may have different $K(\psi)$ and $\theta(\psi)$ functions. A three-region soil was created by dividing the soil into an immobile matrix (25% by volume), a mobile matrix (73%) and a non-sorbing, preferential flow region (2%). The immobile region was defined as only accessible by lateral diffusion and convection, and by prohibiting vertical water flow through it. The preferential region had a lower water retention and much higher saturated conductivity than the mobile matrix, but because it occupied only 2% of the soil volume, it had a small influence on overall water retention (Figure 3) and unsaturated hydraulic conductivity (Figure 4).

Mean K_s values for the single- and three-region soils were 433 mm d^{-1} at a matric potential of -3 kPa, to allow comparative simulations of steady-state water flow at this potential.

The simulations are sensitive to the value of d', the diffusion geometry parameter for each region. In these simulations the value of d_i was fixed at 100 mm for immobile regions, 10 mm for mobile matrix and 1 mm for the preferential flow region. Aqueous diffusion coefficients were assumed to be 160 mm^2 d^{-1}, while dispersivity was set at 15 mm.

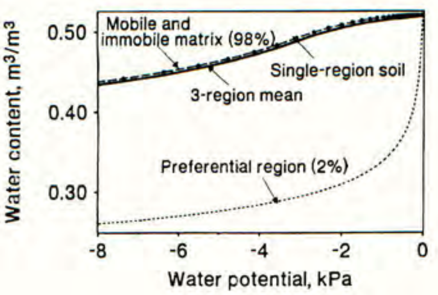

Figure 3. Water retention curves for single- and three-region soils.

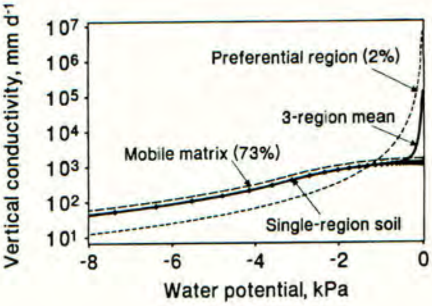

Figure 4. Vertical hydraulic conductivity for single- and three-region soils.

Solute breakthrough curves

Solute breakthrough curves were simulated for steady-state water flow at saturation and at -3 kPa. Values for column length (210 mm), initial soil solution concentration ($C_i = 0$ at $t = t_0$), and influx concentration ($C_0 = 1$ for the initial 91 mm infiltration, $C_1 = 0$ thereafter) were used for all simulations. A non-interacting solute (Cl$^-$) and a sorbing solute (atrazine, $K_d = 3$) were compared at two water flow rates and matric potentials: 1176 mm d^{-1} at 0 kPa, and 443 mm d^{-1} at -3 kPa. Prior sensitivity studies showed that 10 depth nodes ($\Delta z = 21$ mm) and a time step t_{max} which allowed 1 mm of influx provided adequate numerical accuracy.

Field leaching simulations

Soil properties, chemical applications and boundary conditions represent those of a herbicide leaching experiment conducted at Cornell University during the period July to October, 1992. Soil properties were varied to represent the A and B horizons of the soil, but the three-region representation extended throughout the profile.

RESULTS AND DISCUSSION

Solute breakthrough curves

For the three-region soil, differences in hydraulic conductivity between regions are largest at saturation (Figure 4), leading to large differences in pore water and solute velocities between the regions. Flow through the preferential flow region, occupying only

2% of the soil volume, leads to early solute breakthrough (Figure 5) and there is little opportunity for equilibration between regions. However, some of the solute diffused into the matrix; the chloride peak is lower than that of atrazine because the diffusion coefficient of chloride is about four times higher. Following the pulse, solute diffused from the matrix into the preferential region, creating an elongated low-concentration tail.

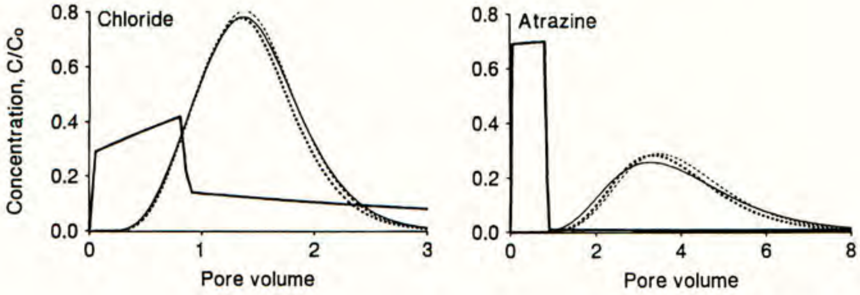

Figure 5. Breakthrough of atrazine and chloride from single-region and three-region soils at two matric potentials and flow velocities [1176 mm d^{-1}, 0 kPa: ——(1-region), ---- (3-region); 443 mm d^{-1}, -3 kPa: —— (1-region), ---- (3-region)].

When the water content was reduced to a matric potential of -3 kPa the preferential flow region no longer conducted most of the flow, and the breakthrough curve was typical of a two-region, mobile-immobile system. These curves matched those predicted by analytical solutions to the two-region CDE (the CXTFIT and CXT4 models of Parker and van Genuchten, 1984).

In a multi-region soil, under steady-state flow, breakthrough curves depart from the classic single-region pattern because pore water and solute velocities differ across the regions. Differences in the vertical distribution of solute create lateral concentration gradients which cause molecular diffusion between the regions. During steady-state flow there are no matric potential gradients to drive lateral convective flux between regions. Depending upon equilibrium matric potential and hence relative conductivities across the regions, vertical convective flux densities may range from zero in immobile regions to several thousand times the application flux density in preferential flow regions.

Field leaching of atrazine

Chemical application and field sampling dates in relation to rainfall are shown in Figure 6. Cumulative soil water flux at four depths, simulated by LEACHM (Figure 7) suggest that water movement in a single-region soil diminishes with depth. Variability of the measured chemical data was too high to allow firm conclusions as to which model was most applicable.

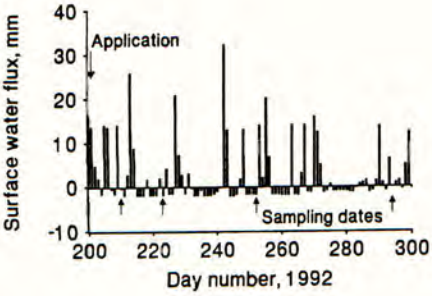

Figure 6. Chemical application and sampling in relation to rainfall, Ithaca, 1992.

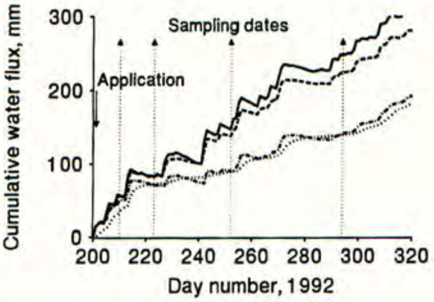

Figure 7. Cumulative water fluxes simulated for four depths in the profile: ▬▬ surface; ---- 100 mm ▬·▬ 300 mm; ·····600 mm.

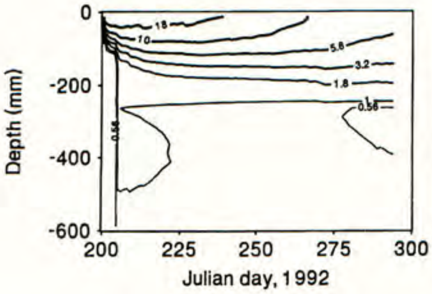

Figure 8. TRANSMIT simulations of atrazine concentrations in a three-region soil. Concentrations are in units of relative mass per volume of soil.

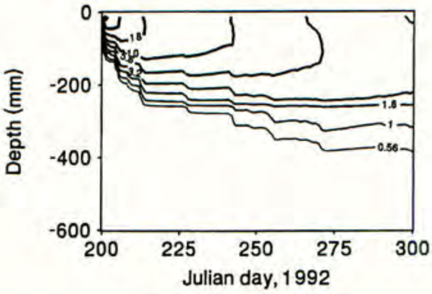

Figure 9. LEACHM simulations of atrazine leaching in a single-region soil.

Simulations using TRANSMIT (Figure 8) were not very different to those using the single-region CDE model (Figure 9). Unlike the steady-state column leaching simulations, water flux through the regions was controlled largely by rainfall flux, and did not differ across regions to the same extent. If rainfall flux densities were to increase (or surface sealing increase), then overflow from less permeable to more permeable regions would be accentuated. However some chemical, present in the preferential region after the initial infiltration, was leached to the B horizon (Figure 8). A major difference between transient and steady-state simulations is that under transient flow, matric potential differences can lead to convective flux between regions. If water is removed from all regions by transpiration, infiltrating water will move from more- to less-mobile regions, suppressing chemical leaching.

Most of the parameters used in the model are identical to those used in one-dimensional models. The difficulty of quantitatively measuring input data values for the different regions means that the model should presently be considered primarily as an educational and demonstration tool, aiding our understanding of how various interacting factors can impact solute fate in heterogeneous soils. Characterization of the regions are inevitably somewhat subjective at this point, based on conceptual models of soil structure and variability. However, the model provides a research opportunity to relate such phenomena as aggregate size distributions, spatial water retention and hydraulic conductivity relationships, pedological profile descriptions (which indicate soil structure), root distribution, and presence of cracks and wormholes to transport of water and chemicals.

The TRANSMIT model has several advantages over simpler two-region models. A wider range of soil geometries can be described, and the model is applicable to steady-state and transient flow in both laboratory and field situations. Although only some of the soil physical options were described in this paper, analogous simulations could examine the effects of variability in soil chemical properties, degradation rates, and boundary conditions. Two-dimensional options enable the effects of row cropping, irrigation method and banded chemical placement to be reflected. Because the model makes provision for a wide range of both physical and chemical variation in the profile, it could be useful for predicting the relative effects of water content at the time of application, explaining the slow release of chemical over long periods of time, and predicting the effects of microbial distributions on chemical degradation, to name but a few applications.

ACKNOWLEDGEMENTS

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MECHANISTIC MODELLING OF PESTICIDE LEACHING FROM CRACKING CLAY SOILS

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ABSTRACT

Detailed mechanistic modelling of pesticide movement in cracking clay soils requires the explicit consideration of water movement in macropores. The use of the CRACK-P model to predict the movement of isoproturon on the Brimstone Farm experiment is described. Issues of model verification are discussed, and independent verification of hydrological components of leaching models is suggested.

INTRODUCTION

Prediction of pesticide leaching presents a particular challenge to the modeller, requiring considerations of hydrology and plant behaviour as well as of pesticide behaviour. The need to evaluate new pesticides and to inform policy decisions and pesticide management strategies has led to the development of a number of models. Leaching models can be created for various purposes, which in turn define the approach to the modelling. Distributed models aimed at the catchment scale need to be simple, and are thus often empirically derived. These need not understand the processes, but offer usable predictions from simple inputs. At the other end of the modelling scale are detailed mechanistic models, which attempt to use the basic principles of physics and chemistry to predict the behaviour of pesticides. These models frequently require large parameter sets to describe the processes operating within them, and are computationally expensive. The work reported in this paper is of the detailed mechanistic type. Its aim is to understand and predict the movement of pesticides in cracking clay soils. When it is complete and validated, it may be possible to use it to derive a simplified intermediate level model, but that stage is still some way off.

FIELD CONTEXT

The modelling reported in this paper used results from the Brimstone Farm Experiment, in particular the pesticide leaching results described by Harris *et al.*, 1994. This site has been used for many experimental investigations into the movement of water and solutes in cracking soils (e.g. Cannell *et al.*, 1984; Harris *et al.*, 1993a). The soil of the site is Denchworth series, which typically has 55-60% clay and extensive macropores. Effective drainage is required for the utilisation of this soil for arable agriculture and is achieved by the use of mole drainage which both introduces close-spaced drainage channels and increases the macroporosity. The soil is typical of many cereal growing areàs of central England. The Brimstone Farm site has been intensively monitored since its establishment in 1978, and offers a unique facility of 20 field-scale plot lysimeters. The combination of detailed soil physical information, a complete description of the site hydrology and detailed cropping information makes this an ideal context for modelling studies. The modelling effort concentrated on the fate of the herbicide, isoproturon, through the winter of 1990/91. The herbicide was applied on 8 October 1990, and its subsequent fate and appearance in drainage water were reported by Harris *et al.* (1994).

PESTICIDE LEACHING MODELLING

The choice of a model suitable for predicting the leaching of pesticides from cracking clay soils is not easy. Application of standard models, such as PRZM (Carsel *et al.*, 1984) or CALF (Walker, 1987) which do not include any allowance for macroporosity, fail to reproduce the hydrology of the site, and so fail to reproduce the leaching patterns (Harris *et al.*, 1993b). Although the PRZM model may represent a reasonable approximation to water flow in a sandy soil, it is inappropriate for use in fine textured soils (Wagenet & Rao, 1990).

Two models were identified for application to this site: CRACK (Jarvis & Leeds-Harrison, 1987), and MACRO (Jarvis, 1991). Both were developed explicitly for macroporous soils, but differ in the way they conceptualise the water movement in the soil matrix. In both models, soil porosity is divided into two components, macro- and micro-pores. Both models assume that water flow into the macropores is generated at the surface by an infiltration excess and that, once in the macropores, water moves rapidly downwards. Both models allow for drainage of water from the macropores, and so give the opportunity to model the mole-drainage system that is installed at Brimstone Farm. In CRACK, the macropores are identified with the inter-ped boundaries, and the movement of water and solute into the micropores is described by infiltration theory; water moves into the peds by sorption only and out of them by crop extraction. The problem of estimating the sorptivity of peds unmodified by macropore flow, required by this model, has been resolved by the technique of Leeds-Harrison *et al.* (1994). By contrast, MACRO describes water movement in the micropores using unsaturated soil physical theory by solving the Richards' equation for movement of water to depth under gravity drainage. In practice, the major difference between the two models is that CRACK conceptualises the soil as layers of aggregates, into which water and solute moves, whereas MACRO conceptualises the soil as two linked and interacting columns, We chose to work with CRACK because its description of soil water movement is more appropriate to the Brimstone Farm soil, and also because the important term describing the rate of interaction between the macropores and the peds is derived from observable physical data in CRACK, whereas in MACRO this was originally replaced by an empirical calibration coefficient (though this has now been corrected in the most recent release of MACRO, Jarvis 1994).

The CRACK model includes a description of the movement of a conserved solute (Jarvis, 1989), which has already been shown to offer a good description of both the hydrology and the short term behaviour of nitrate at the Brimstone Farm site (Armstrong *et al.*, 1995). A pesticide module was added to the CRACK model, based on the descriptions contained in the CALF model of Nicholls *et al.* (1982), as modified by Walker (1987). The combined model is now called CRACK-P. Degradation is modelled as an exponential function, with coefficients dependent on temperature and moisture content, so requiring the estimation of soil temperatures from air temperatures using the techniques of Walker & Barnes (1981).

RESULTS

The CRACK-P model was applied to data from the Brimstone Farm site for two periods: the whole of the winter period of 1990-91, and a six-day period in January 1991 for which detailed data were available. The model was thus evaluated for its ability to predict both the behaviour of pesticides over the whole winter, and over short periods of time. The first test indicates whether the overall fate of the pesticide is modelled correctly, the second indicates whether the detailed mechanisms of pesticide movement are correctly predicted. The model attempted to predict the fate of a single dose of isoproturon applied to the soil on 8 October, and concentrated on the data from Plot 6 (Harris *et al.*, 1994, Figures 3 and 6), which was considered to be the most representative of the drainage treatments. The over-winter fate is shown in Figure 1, and the detailed behaviour of the model in Figure 2.

For the whole winter (Figure 1) the CRACK-P model reproduced well the general pattern of behaviour of the site. It showed the site returning to field capacity in the beginning of December, with the watertable remaining close to mole drainage depth for the rest of the winter. The model, however, failed to reproduce the drying out of the site in the following summer, and thus over-predicted drain flows in the late spring. This reflects the lack of a deep-drainage routine in the model. The pesticide behaviour was predicted well, with most of the pesticide lost being moved at high concentrations in the first few major flows. The predicted soil concentrations indicate that most of the pesticide was restricted to the top layers of the soil, in agreement with the data reported by Harris *et al.* (1994, Figure 7). These data indicate that higher concentrations of pesticides in drainage water originate close to the soil surface, and that they are transported without any major re-sorption through the macropore system to the drains. Figure 2 shows the short-term behaviour of the model for the period when frequent measurements of pesticide concentration in drainage water allowed comparison with model results. The agreement is remarkably good, in both representing the concentrations and in reproducing the dilution effect of large flows.

The results demonstrate that models designed specifically for cracking clay soils are capable of predicting the behaviour of pesticides in those soils, whereas standard models such as PRZM perform poorly in this respect (Harris *et al.*, 1993b). A similar result for nitrate leaching at the same site was observed by Armstrong *et al.* (1995). Movement in cracking clay soils cannot be modelled using conventional soil models, but need models that explicitly

Figure 1. Results of CRACK-P for the winter 1990-91

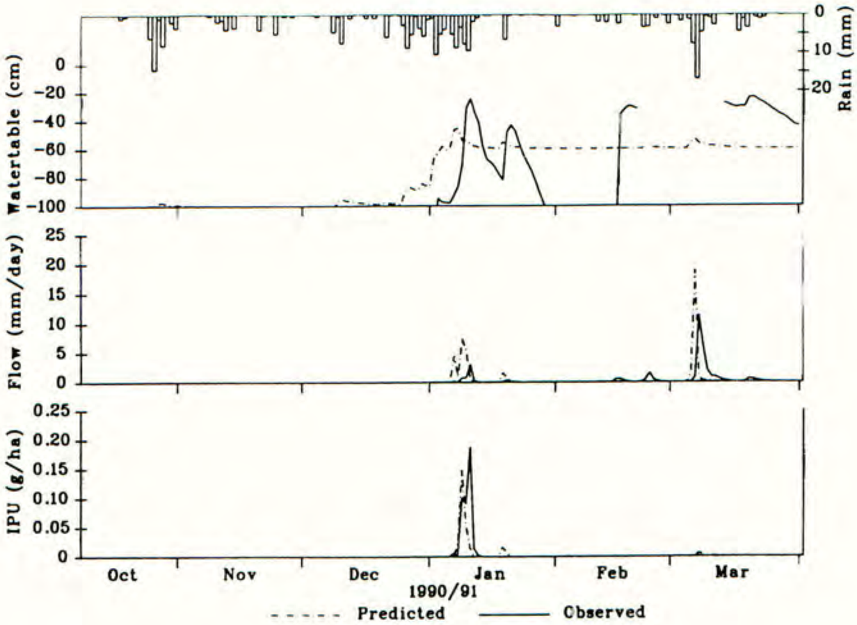
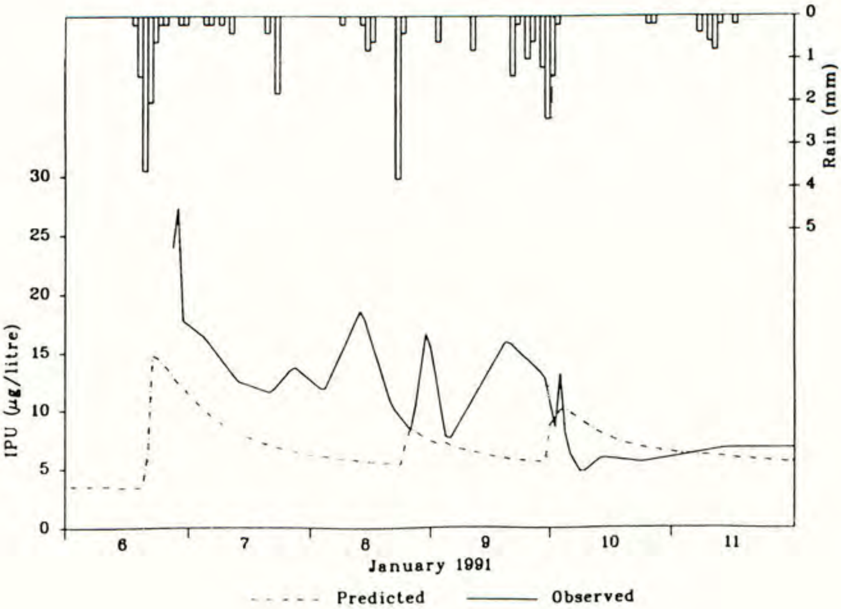


Figure 2. Results of Crack-P for a 10 day period in January 1991



consider the macropores. This identifies a potential difficulty for any regulatory use of models: for either screening or registration purposes, evaluation of a potential product for a range of soils scenarios will require the use of different models.

DISCUSSION: MODEL VALIDATION

Detailed mechanistic models of the complexity of CRACK require many parameters. Only sites of the complexity of Brimstone Farm allow many of these to be collected, and even for this exercise some parameters are less securely based on field observation than is ideal. An alternative approach (adopted by the earlier versions of the MACRO model) is to calibrate empirical parameters from observation, but this procedure is impossible to apply to a new site. CRACK-P offers, in principle, the opportunity to measure all the relevant parameters independently. The most important parameter, the size of the structural units, which gives the frequency of macropores in each soil layer, can be established by field inspection. Nevertheless, the use of detailed mechanistic models does raise the issue of the spatial variability of input parameters. Sensitivity analyses, such as that carried out by Jarvis and Leeds-Harrison (1987) for the CRACK model, may indicate those parameters which are most likely to lead to problems, but there are few data to indicate the likely magnitude of the spatial variability.

Validation of such models presents a particular set of problems. Because these models predict many output variables, there is a need to validate the model for several of the output series. Loague & Green (1991) identify some statistics that can be used to describe the goodness of fit, using differences between the observed values and model predictions. Pesticide models generally have the added problem that the number of observations varies dramatically between variables. At Brimstone Farm drain flows are recorded every half hour, but pesticide concentrations are available for no more than 20 to 30 samples per plot-year. Although the pesticide data may be the most sparse, they are also the most important, and any model validation must take note of the relative importance of these sparse data points.

A more robust validation procedure might then be to evaluate each model component separately. A successful pesticide leaching model would then be expected to predict the water balance, water discharge from the profile, and water table depth, all verified independently of the solute performance. Equally, it would be expected that the model should then make acceptable predictions of the overall degradation of the pesticide throughout the year. The combined model must also be tested for its predictions of short term behaviour. We suggest that the ability to mimic short term behaviour within a longer term simulation is probably an "acid test" for most models.

ACKNOWLEDGEMENTS

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USE OF THE PESTICIDE LEACHING MODEL (PLM) TO SIMULATE PESTICIDE MOVEMENT THROUGH MACROPOROUS SOILS

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ABSTRACT

Models that assume equilibration of sorption should only be used to assess risk of leaching of pesticides in soils that exhibit chromatographic flow. A macropore model is required for the majority of soils. The macropore model PLM is able to mimic accurately the trace concentrations of compounds found in leachates. The ability of macropore models to make predictive simulations is still uncertain because simulated concentrations are extremely sensitive to the parameters that describe macropores. The PLM model is easy to use and is probably most useful for simulating lysimeter experiments for which difficult-to-obtain soil physical data are not readily available.

SIMULATIONS AND MACROPOROUS SOILS

The models CALF (VARLEACH), LEACHM-P, PESTLA and PRZM (PELMO) (Nicholls *et al* 1982; Wagenet & Hutson 1992; Boesten *et al* 1991; Carsel *et al* 1985) are used to simulate leaching and degradation of pesticides in soils. The models do not simulate preferential or bypass flow of trace concentrations of pesticides through soils because they assume that sorption is always at equilibrium during leaching. The models are therefore useful to predict the distribution of the predominant proportion of the applied compound in the cultivated layer but should only be used to predict leaching to drains and surface waters for soils that are known to exhibit chromatographic flow. Of 14 soils investigated by Flury *et al* (1994) using a dye tracer, only one soil exhibited chromatographic flow with all others showing preferential or bypass flow. After simulating concentrations of herbicides in leachate from lysimeters containing Swedish soils, Hall (1994a) and Jarvis *et al* (1994) concluded that preferential flow occurred in all five soil types tested, including two sandy soils as well as three structured soils.

In lysimeters, preferential flow is indicated when pesticide is observed in the first leachate collected after application of the compound. In the Swedish study (Hall 1994a), dichlorprop, which was completely degraded within 11 days in laboratory incubations of topsoil, was found in leachate more than 300 days after application. The presence of dichlorprop in leachate was only simulated by moving the compound by preferential flow

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down to a depth where rates of degradation were assumed to be slow. It is concluded that a macropore model is required to predict risks of leaching for the majority of soils.

HYDRODYNAMIC DISPERSION

In tracer experiments, a band of chemical spreads as it moves through a porous bed. A small degree of spreading results from simple thermal diffusion because this continues after elution has stopped. In soils, most spreading is due to hydrodynamic dispersion caused by different solute molecules being carried along different pathways through the porous matrix. In a well packed bed of small particles, the band shape of the chemical subject to dispersion is similar to that which results from diffusion but the band is much broader. In structured soils, there is a variety of pore sizes, and so spreading bands are even broader and also skewed because a small proportion of chemical moves close to the water front whilst some chemical is immobilised in pores remote from the main channels of downward flow. It is important to understand and simulate dispersion because a quantitative knowledge of the small proportion of chemical moving in the channels of fast flow is a *sine qua non* for the prediction of the risk of the chemical reaching ground and surface waters. Dispersion increases with the velocity in soil pores the greatest spreading occurring at high flow rates. However, hydraulic conductivity, used in some models, is only an average value of water flux and does not directly give rates of flow in the largest pores in which fluxes are greatest. It was thus important to check the ability of PLM to simulate dispersion by comparing simulations with measurements of non-sorbed tracers such as bromide and chloride ions (Hall, 1993; Hall & Webster, 1993). Non-adsorbed tracers applied to the surface of a soil can occur in leachate in a pulse of relatively high concentration because of preferential flow in macropores. Concentrations of tracers that are spread evenly down the soil profile, such as nitrate, sharply decrease in concentration in leachate during a drainage event due to bypass-flow of water from the surface. At Brimstone Farm, the decrease in nitrate concentration starts with the onset of the drainage event and levels out when flow (the hydrograph) reaches its maximum (Armstrong & Burt, 1993).

Models such as PLM and CALF (VARLEACH) use the idea of mobile and immobile water categories to simulate dispersion by allowing chemical to move in mobile water but not in immobile water. This approach reduces the requirement for difficult-to-obtain soil physical data such as dispersion, soil-water pressure and hydraulic conductivity functions. The simulation of dispersion in field soils will probably always be rather inaccurate because movement of trace amounts of chemicals to great depths is quantitatively very sensitive to the size, variability and continuity of the largest pores and fissures. Such precise data may never become widely available and so accurate prediction of trace concentrations of organic compounds reaching ground and surface waters may never be achieved using readily available input data.

NON-EQUILIBRIUM SORPTION

In liquid chromatography, a band of sorbing chemical spreads as it moves through a porous bed partly due to hydrodynamic dispersion and partly due to adsorption. Adsorption retains some molecules whilst others move. It is observed that, for a column of given length, eluted bands of the more strongly retained compounds are broader than those of the more mobile compounds. If sorption is at equilibrium during elution bands are relatively narrow and symmetrical. In soils, when flow in macropores is too rapid for equilibration of sorption to be maintained, trace amounts of a compound can spread rapidly down the soil profile. Therefore a leaching model must simulate both the broad and skewed dispersion, described above, and non-equilibrium sorption for solute associated with water in the macropores.

DESCRIPTION OF THE PLM MODEL

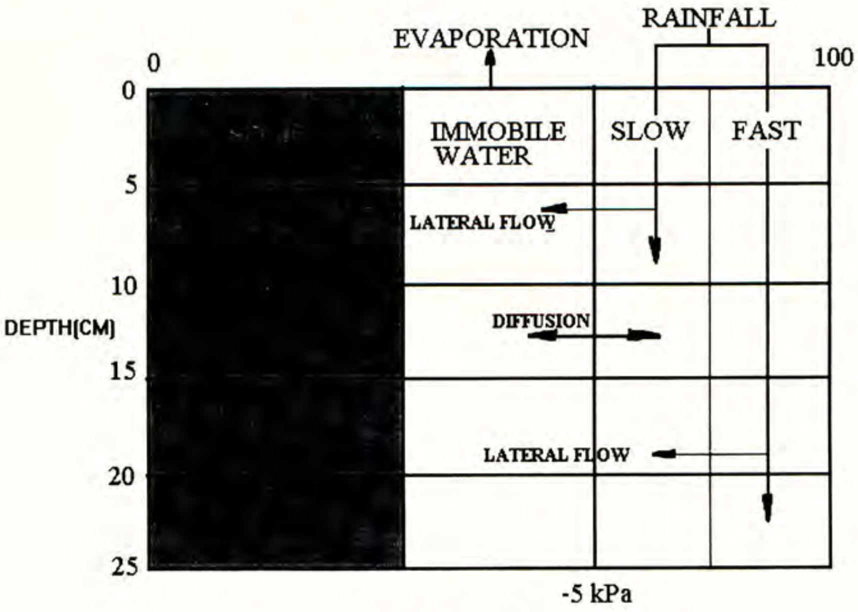

Figure 1. Diagram of the PLM model

PLM is fully described and documented by Hall (1993,1994a,1994b). PLM is a layer model with the layer thickness set at 5 cm, and calculations are done for intervals of one day. Within each layer (Figure 1), soil solution is divided into mobile and immobile categories, with the division set at -5 kPa (field capacity) and with only mobile water being displaced during drainage. The broad dispersion and non-equilibrium sorption that occurs in macroporous soils is modelled by subdividing the mobile water into 'slow' and 'fast' categories. Solute in the top layer equilibrates with any 'slow', 'fast' and immobile water present and with the soil-solid phase for sorption. In lower layers, lateral equilibration of solute is only among 'slow' mobile and immobile water and with soil-solid phase for sorption. Below the top layer, solute in the 'fast' mobile water only interacts with other categories if lateral flow of water occurs. Thus solute can penetrate deeply into the soil profile by moving with the 'fast' mobile water. Lateral flow occurs when water reaches lower layers in which immobile or 'slow' mobile water categories are unfilled. Then, water moves into immobile pores before mobile and into 'slow' before 'fast' pores. Preferential flow will only occur when rainfall intensity is sufficient to allow water into 'fast' mobile pores.

Processes such as evaporation of water and transpiration by crops are described by Hall (1994a). Sorption is calculated from linear isotherms as a function of soil depth and time. Degradation of parent compound is calculated as a function of soil depth, temperature and soil-water content. A number of soil parameters, *viz* α (fraction of mobile water moving from one layer to the next during flow), β (hold-back factor restricting equalization of solute concentrations during diffusion), n_s and n_f (number of layers passed through during 'slow' and 'fast' drainage), can be given default values ($\alpha = 0.9, \beta = 0.1$, $n_s = 7$, $n_f = 15$). Thus the model can often be calibrated by adjusting only one sensitive soil parameter *viz* P_f (% of 'fast' pores in the mobile phase). However, it is necessary to ensure that the rate of degradation of the pesticide in the lower layers of the soil profile has a realistic value.

SIMULATION RESULTS

Results for a weakly sorbed pesticide applied in spring to a fallow lysimeter (0.8 m diameter; 1 m depth) at Rothamsted are given in Figure 2. The soil was a sandy loam containing up to 29% clay in the lowest layer. The lysimeter was exposed to natural rainfall up to day 260, after which some irrigation was applied to maintain average rainfall. The PLM simulation was made using measured data where possible but the output was optimised by adjusting the P_f parameter (% of 'fast' pores in the mobile phase) and rate of degradation in soil layers where data from laboratory incubations was not available. The observed early appearance of pesticide in leachate indicates that macropore flow occurred in this soil. Optimisation allows close fitting of simulated to measured data. In later work the model was calibrated using a mobile compound in three different soil types and simulations were subsequently made of leaching of a less mobile compound without changing soil parameters in the model. Again, simulations showed useful agreement with measured concentrations in leachate, albeit not as close as that in Figure 2.

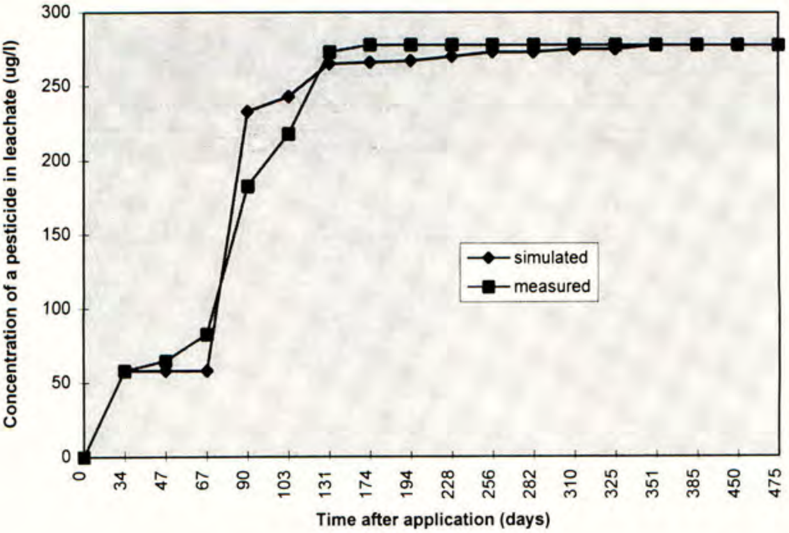

Figure 2. Measured and simulated concentrations of a pesticide in lysimeter leachate.

CONCLUSIONS

Models that assume equilibration of sorption should only be used to assess risk of leaching of pesticides in soils that exhibit chromatographic flow. Models incorporating macropore leaching are able to mimic accurately the trace concentrations of compounds found in leachates. The ability of macropore models to make predictive simulations is still uncertain because simulated concentrations are extremely sensitive to the parameters that describe macropores. The PLM model is easy to use and hence is probably most useful for simulating lysimeter experiments for which difficult-to-obtain soil physical data, such as solute dispersion coefficients and hydraulic conductivity functions, are not readily available.

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