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FINAL REPORT
PROJECT NO. US-1753-89

**Predicting the Effect of Kinetic-Equilibrium Sorption
and Macropore Flow upon Pesticide Movement in
Agricultural Soils**

R.J. Wagenet, U. Mingelgrin

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in co-operation with

THE INSTITUTE FOR SOILS AND WATER
VOLCANI CENTER, ISRAEL

PREDICTING THE EFFECT OF KINETIC-EQUILIBRIUM SORPTION
AND MACROPORE FLOW UPON PESTICIDE MOVEMENT
IN AGRICULTURAL SOILS

BINATIONAL AGRICULTURAL RESEARCH AND DEVELOPMENT FUND
PROJECT NO. US-1753-89
FINAL REPORT

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ABSTRACT

The importance of non-equilibrium phenomena in determining the transport of organic pollutants through the unsaturated zone was demonstrated. Finite kinetics of adsorption and desorption, hysteresis (both real and apparent) of the adsorption-desorption process, especially as affected by the moisture regime, enhanced transport and preferred path flow were all identified as processes which affect transport significantly. Improved predictability of the transport of pesticides was achieved by a set of models, including versions of the LEACHM, LEACHA and TRANSMIT models, developed in line with the findings of the present study.

Carefully controlled laboratory experiments are described and on the basis of these experiments an improved and more realistic representation of pesticide sorption than is presently available was formulated. The development of predictive models for the movement of pesticides based on more accurate and quantitative representations of water and solute flow in both homogeneous and non-homogeneous (macropore) soils is described. The application of the developed models to field data of atrazine and alachlor movement is presented as is a field demonstration of the enhanced transport of atrazine.

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PREDICTING THE EFFECT OF KINETIC EQUILIBRIUM SORPTION AND
MACROPORE FLOW UPON PESTICIDE MOVEMENT IN AGRICULTURAL SOILS

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GENERAL SUMMARY

OBJECTIVES

The objectives of the reported project were:

1. To develop, through carefully controlled laboratory experiments, an improved and more realistic representation of pesticide sorption than is presently available in both surface and subsurface soils.
2. To develop predictive models for the movement of pesticides, based on realistic and quantitative representations of sorption and water flow in both homogeneous and nonhomogeneous (macropore) soils.
3. To apply the models developed in objective 2 to field data of pesticide movement so as to gain insight into the transport of the pesticides in both homogeneous and nonhomogeneous soils.

Synopsis of Report

PART 1. MODEL DEVELOPMENT AND THEIR APPLICATION TO BATCH,
COLUMN AND FIELD LEACHING EXPERIMENTS

Chapter 1: A simulation model describing solute transport through aggregated soils is described. Steady-state water flow is assumed, so the model is applicable to laboratory column studies. A feature of this model is that the effects of a mixture of aggregate sizes can be reflected. Also, biodegradation can be described by any one of six different microbial degradation equations.

chapter 2: A new model, TRANSMIT, is described. TRANSMIT is a multiregion/two-dimensional model which enables soil chemical and physical properties to be varied across regions. This provides the opportunity for reflecting spatial variability, preferential flow and various assumptions regarding soil geometry. This model, applicable to both steady-state and transient water flow, can be used to simulate leaching under furrow and drip irrigation.

Chapter 3: Modifications to the LEACHM models are described. The revised models includes options for two-site kinetic linear sorption and Freundlich sorption isotherms, and an improved

numerical dispersion correction. Soils from two locations in New York were used in a series of batch equilibration studies, using atrazine, alachlor and 2,4-D. Results showed considerable variability, depending largely on equilibration time, the procedure used for equilibration, and, for desorption, whether or not the soil was dried before the desorption step.

Chapter 4: A series of solute breakthrough curves, conducted under steady-state water flux, showed enhanced breakthrough by both tracer and herbicides. Variation between columns of similar soil was high, but the patterns of behavior were similar for each compound. Simulations using the multi-region TRANSMIT model predicted similar enhanced breakthrough. Relatively small ranges of model parameter values can produce a range of curves similar to those observed.

Chapter 5: Field leaching experiments at the two locations are described. Sampling, on four occasions following application, was done at fixed sites in the field. Examining leaching patterns at each of these sites, and expressing results in terms of relative distribution through the profile rather than as absolute concentrations, reduced variability and made the data easier to interpret.

Chapter 6: A two-region (mobile-immobile) capacity version of the LEACHM models is described. This model enables LEACHM to simulate water and solute transport in a manner similar to some other widely used models. This flow option has been incorporated as an option into all versions of LEACHN (nitrogen, pesticide and salinity).

Chapter 7: Simulation models were applied to the field data. All of the convection-dispersion models showed similar results. The capacity mobile-immobile model, LEACHA, generally underpredicted leaching because chemical was bypassed by flowing water. However, this version of the model may be extremely useful for highlighting those periods when preferential flow are likely to occur. A major difference between solute transport in columns subject to steady-state water flow and that under transient field conditions is the absence of convection as a transport mechanism between soil hydraulic regions. Both simulations and measurements suggest that enhanced solute transport in field soils is not as marked as it is in soil columns.

PART 2. AN EXPERIMENTAL TECHNIQUE FOR MEASURING SORPTION KINETICS AND ALTERNATIVE APPROACH TO MODELING PESTICIDE SORPTION.

An important component of the project has been the development and evaluation of a new technique for measuring

sorption kinetics in soil. This research is contained in two manuscripts (Chapters 8 and 9), which form part of a Ph.D. dissertation by Mr. I. Kennedy. One of these manuscripts is now under review in the Soil Science Society of America Journal.

The method uses recirculation of water and chemical flow through a short soil column (Chapter 8). This establishes a condition that mimics a batch study but under conditions of flowing water that preserves the geometry of the soil. This allows the velocity-dependence of sorption to be more accurately studied. Soil solution can be periodically withdrawn for analysis without disturbing the soil. The theoretical basis for the analysis of the data is described in Chapter 9.

Part 3. NON-EQUILIBRIUM PHENOMENA ASSOCIATED WITH TRANSPORT OF PESTICIDES

The inter-related processes of sorption and mass transport with water are two of the most important processes controlling the fate of pesticides in soils. To date, the quantitation of these processes and in particular the interaction between them was not well defined. Most of the past laboratory studies were conducted under water-saturated conditions, an unrealistic approach to the interaction of pesticides with the soil solid phase or in the unsaturated zone in general. There, moisture content is usually below saturation and undergoes periodic variations.

Sorption of pesticides by soils was often inadequately considered as reaching instantaneous equilibrium. The failure of this assumption led to the need to treat sorption by a combination of kinetic and equilibrium phenomena. Furthermore, wetting and drying cycles amplify the often observed differences between adsorption and desorption kinetics. Apparent hysteresis is a common observation in field studies. Finally, the possible enhancement of transport of pesticides by adsorption on suspended colloids and soluble macromolecules or by water flow through macropores or cracks, was often neglected in the classical description of pesticides movement in soils.

Correcting, at least in part, these drawbacks of past attempts to predict transport of pesticides was the main justification for the present study. The part of the project reported below provides data for a more appropriate description of sorption and transport of pesticides in soil than was possible in the past.

The following will be divided into 4 chapters:

Chapter 10 provides a theoretical treatment of phenomena related to the interaction of small molecules with surfaces. The discussion is based on experimental data which are presented in more detail in the following chapters.

Chapter 11 summarizes the experimental procedures and results of a laboratory study on the interaction of pesticides belonging to three major groups (a triazine, an organophosphate ester, and a carbamate) with soils. Both column and batch runs were made. An

appendix which details all data relevant to the column experiments is made available for future use.

Chapter 12 provides description and analysis of a field study on the enhanced transport of atrazine under irrigation with waters of different qualities.

PROJECT ACHIEVEMENTS AND BENEFIT TO AGRICULTURE

This project improved our understanding of pesticide mobility and applied this improved understanding to soil systems through simulation modeling using a modeling approach that can quantitatively treat macropores and non equilibrium adsorption. As a result of this study, our insight into the availability of pesticides and into their delivery to groundwater as a function of soil properties, water flow velocity and the pesticides' chemical structure has improved. The modeling approach that evolved in this project provided the means to evaluate specific pesticides and management practices with respect to the potential that such chemicals and practices have to contaminate water sources. At the same time, management practices which may lead to the optimization of the chemicals' availability and residence time in the root zone can now be more precisely defined with the aid of the models developed. Optimizing the residence time improves the pesticides' effectiveness while allowing sufficient exposure time to degradation and to volatilization so as to minimize the danger of groundwater contamination by the

pesticides. Both agricultural production and environmental quality should thus be positively impacted by the obtained results. The importance to agriculture of the more effective plant protection which may be achieved through the enhanced capability to predict and control the mobility (and thus the availability) of pesticides in the root zone is obvious. The improved ability to predict and minimize the risk of groundwater contamination may be just as important to agriculture. This is so, since by determining the conditions under which it may be possible to employ some effective but mobile and persistent pesticides without contaminating the groundwater, it may become permissible to use such pesticides, though their use might have otherwise been considered too environmentally hazardous to be permitted.

DESCRIPTION OF COOPERATION

This project was performed throughout in close cooperation. Similar laboratory and field studies were conducted in both the U.S. and Israel. Performing these experiments in two locations allowed both U.S. and Israeli soil conditions to be studied and enabled a cross check of the methodology and results. While more detailed laboratory studies of sorption were performed in Israel, the model-building and testing work was the responsibility of the U.S. investigators. The U.S. and Israeli efforts were combined in a joint evaluation of both groups' laboratory and field work. The laboratory and field data of both groups were incorporated in the model development and testing.

LIST OF PUBLICATIONS BASED ON THE PROJECT

Publications:

Giat, V. 1992. The Interaction of Organic Molecules with the Solid Phase as affected by Soil moisture Regime. M.Sc. Dissertation, The Hebrew university of Jerusalem.

Graber, E.R., Z. Gerstl, E. Fischer and U. Mingelgrin. 1995. Enhanced transport of atrazine under irrigation with effluent. Soil Sci. Soc. Am. J. 59:(in press)

Hutson, J.L. and R.J. Wagenet. 1993. A pragmatic field-scale approach for modeling pesticides. J. Environ. Qual. 22, 494 - 499.

Hutson, J.L. and R.J. Wagenet. 1995. A multi-region model describing water flow and solute transport in heterogeneous soils. Soil Sci. Soc. Am. J. (in press, May-June, 1995 issue).

Hutson, J.L. and R.J. Wagenet. Multi-region water flow and chemical transport in heterogeneous soils: theory and applications. In: Proceedings of British Crop Protection Council Conference on Pesticide Movement to Water, Warwick, England. April 3-5, 1995, pp 171-180.

Kennedy, I. 1995. Measurement of sorption kinetics using recirculated flow. Ph.D Dissertation, Cornell University.

Mingelgrin, U. and Z. Gerstl. 1993. A unified approach to the interaction of small molecules with macromolecules. p. 102-127. In: Organic Substances in Soil and Water: Natural Constituents and their Influence on Contaminant Behavior. Beck, A.J., K.C. Johns, M.H.B. Hayes and U. Mingelgrin, Editors. Royal Society of Chemistry, London.

Wagenet, R.J. and J.L. Hutson. Consequences of scale dependency on application of chemical leaching models: a review of approaches. In: Aly I. El-Kadi (ed), Groundwater models for resources, analysis and management, CRC Lewis Publishers, Boca Raton, FL, Chapter 11, pp. 169-184.

In preparation:

Giat, V., and U. Mingelgrin. 1995. The Interaction of Organic Molecules with the Solid Phase as affected by Soil moisture Regime.

Kennedy, I., et al. 1995. A recirculated flow method for measuring sorption kinetics in soil.

Kennedy, I., et al. 1995. Modeling short-term sorption of pesticides by soil.

Abstracts:

Hutson, J.L. and R.J. Wagenet. Accounting for field variability in a solute leaching model. Agronomy Abstracts, ASA Annual Meeting, 1991, p221.

Beardsworth, F.J., J.L. Hutson and R.J. Wagenet. A multi-region solute leaching models applied to different irrigation regimes. Agronomy Abstracts, ASA Annual Meeting, 1994, p247.

Kennedy, I., W. Chen, R.J. Wagenet, J.L. Hutson and J.-Y. Parlange. Use of recirculated flow in measuring pesticide sorption kinetics. Agronomy Abstracts, ASA Annual Meeting, 1993, p210.

Mingelgin, U., Z., Gerstl and V. Giat. 1993. The role of nonequilibrium phenomena in the mobility of xenobiotics in the unsaturated zone. Proceedings of the IX Pesticide Chemistry symposium . Piacenza, Italy. pp. 335-342.

CHAPTER ONE

SIMULATING BREAKTHROUGH IN AGGREGATED SOILS

Solute flow in aggregated soils is complicated by several factors. Concentration of water flux into the more mobile 'interaggregate' region leads to higher pore water velocities than expected, which in turn can lead to enhanced solute breakthrough. Diffusion of solute into or out of the aggregate may act to retard solute breakthrough and promotes tailing. Diffusion coefficients, tortuosity and sorption may differ from that in the more mobile regions. Microbial degradation rates can also be different within aggregates, depending upon the distribution of organisms and substrates. Interest in these effects has led to the development of analytical and numerical models which reflect some or all of these processes. Rao, et al. (1980), Youngs and Leeds-Harrison (1990); Priesack (1991), Scow and Hutson (1992), Hayot and Lafolie (1993) and Lafolie and Hayot (1993) describe models which explicitly account for the presence of aggregates of defined shape and size, distinct from models which account for an 'immobile' phase of indeterminate geometry. Sardin, et al. (1991) demonstrated that the shapes of solute breakthrough curves can be explained by any of several different conceptual models, and emphasized the importance of residence and transfer time distributions, and characteristic

times for the various chemical and physical processes that influence solute transport. Brusseau (1993) demonstrated the importance of characteristic times for various component processes and their effect on solute breakthrough. Analytical and numerical solutions to solute transport in aggregated systems are complicated (for example, Lafolie and Hayot, 1993). A relatively simple model, based upon basic soil physical properties, could be a useful tool for educational purposes and for evaluating the likely influence of aggregation on solute transport. The model described here may not be as mathematically rigorous as others, but has the advantage that it is easily expanded to include biodegradation, varying properties through the aggregate, and a wide range of initial and boundary conditions. The combination analytical/numerical model for predicting solute transport in aggregated media describe by Hayot (1993) could be useful for comparison purposes.

In the following Chapter we describe a two-dimensional version of LEACHM, called TRANSMIT, which can simulate flow through aggregated soils, but which has the additional advantage of being applicable to unsaturated, transient conditions. It can also be used to simulate solute transport in situations where two-dimensional processes are important, such as furrow irrigation, row cropping, certain tillage treatments, and band placement of chemicals. However, TRANSMIT can simulate neither

the effects of degradation kinetics other than first-order, nor the effects of a mixture of aggregate sizes.

However, the geometry of the 'aggregates' portrayed in TRANSMIT are not currently comparable to ideal spherical or cubic geometry owing to assumptions that were made regarding the relationships between aggregate volume and surface area. The result of this is that the rate of diffusion into a TRANSMIT 'aggregate' is not the same as that into a spherical aggregate of identical volume and properties. To examine the effect of defined aggregates of defined diameter and porosity on solute transport, the DSB (Degradation and Sorption in Beads) model (Scow and Hutson, 1992) was extended to incorporate both a range of aggregate sizes and solute flow in the interaggregate volume. This extended model is called AGGR. Interpretation of a range of laboratory and field experiments may well require the application of both the AGGR and TRANSMIT models.

MODEL DEVELOPMENT

The Scow and Hutson (1992) program described the degradation of a solute in solution in the presence of spherical porous aggregates. Microorganisms responsible for degrading the solute could not enter the interior of the aggregates, but solute could diffuse into the aggregates. Six microbial growth or substrate

degradation models were defined. The model proved useful for accounting for the observed degradation patterns in experimental systems constructed from ceramic porous beads (Scow and Alexander, 1992). Diffusion of a sorbing solute into and out of the aggregates was simulated using a finite difference form of the radial diffusion equation (Crank, 1975).

The DSB model was extended to simulate solute flow through soil columns subject to steady-state flow. Conceptually, the soil column is divided into a number of segments of equal thickness, each containing soil in the form of spherical aggregates (Fig. 1.1). The interior volume of the aggregates is accessible only through diffusion. Unlike the original DSB model, which considered single-sized aggregates only, the new model (AGGR) reflects a range of aggregate sizes. Solution flow is through the inter-aggregate volume. For simplicity this flow is described by a simple mixing model. Flow can be set to zero to simulate batch equilibration and degradation. Microbial growth and degradation processes occur in the interaggregate volume only, but are not discussed further as degradation was negligible during the time required for our breakthrough curves.

Unlike the DSB model, for which both the number and size of aggregates, as well as the volume of interaggregate volume needed

to be specified, the only parameters required for AGGR are bulk density of the aggregates, bulk density of the whole soil and the radius of each aggregate size class. It is assumed that the total volume of aggregates in each size class are the same and that all of the soil dry mass consists of aggregates. The difference between whole soil bulk density and aggregate bulk density enables the interaggregate volume and total volume of aggregates to be calculated; the aggregate bulk density allows aggregate porosity to be calculated; the number of aggregates within each size class is calculated by dividing the volume of an individual aggregate into the total volume of aggregates per size class.

The soil column is defined in terms of length (l , cm), segment thickness (or volume) (Δz , cm), water flux density (q , cm/day), column bulk density (ρ_{soil} , g/cm³), aggregate bulk density (ρ_{aggr}), column porosity (p), aggregate porosity (p_{aggr}). Density of the solid phase was assumed to be 2.65 g/cm³. Pore volume for the column is

$$P_{\text{vol}} = lp. \quad [1]$$

The volume occupied by aggregates in each segment is

$$V_{\text{aggr}} = \Delta z \rho_{\text{soil}} / \rho_{\text{aggr}}, \quad [2]$$

and the interaggregate volume V_o is

$$V_o = \Delta z - V_{\text{aggr}}. \quad [3]$$

Each of n aggregate size classes are assumed to occupy an equal fraction of the aggregate volume, thus the number of aggregates of each size class i per segment, is

$$N_i = V_{\text{aggr}} / (nV_i) \quad [4]$$

where $V_i = 4\pi r_{i3}^3/3$, the volume of a single aggregate of radius r_i .

The sequence of calculations in the model during each time step is:

a) A time step Δt is calculated according to several criteria. Time steps are shorter at the start of the simulation, increasing gradually to the maximum time step specified in the input data.

b) The water flux (f_w , cm) between segments during one time step (Δt) is calculated as

$$f_w = q\Delta t \quad [5]$$

Water flux during a time step is prevented from exceeding $0.2 \times v_o$ interaggregate water content. If it does, then the time step is reduced.

c) A volume of solution (v_{in}) enters a segment. At the same time, an equal volume (v_{out}) of solution of concentration c_{old} leaves and enters the next segment. The new concentration in the segment (C_{new}) is calculated, assuming complete mixing of the added and remaining resident solute:

$$C_{\text{new}} = [v(C_{\text{new}} - C_{\text{old}}) + v_o C_{\text{old}}] / v_o \quad [6]$$

d) Using the C_{new} as a surface boundary concentration for all aggregate size classes, diffusion into or out of the aggregates is calculated using a finite difference solution of the diffusion equation (Scow and Hutson, 1992). The diffusion coefficient was adjusted for water content and tortuosity within aggregates according to the Millington and Quirk equation,

$$D_m = D_o \theta^{3.33} / p^2. \quad [7]$$

e) Using C_{new} as a substrate concentration, microbial degradation in the inter-aggregate solution during Δt is calculated according to one of six growth models (Simpkins and Alexander, 1984).

f) The inter-aggregate concentration C_{new} is adjusted by the amount diffusing into or out of the aggregates and the amount of solute degraded.

g) The interaggregate concentrations are initialized ($C_{\text{old}} = C_{\text{new}}$; $C_{\text{new}} = 0$), mass balance is checked, and a new flux increment is imposed (step a).

The basic model is easily expanded to allow for sorption in the interaggregate volume, biodegradation within aggregates, and

gradients in sorption capacity within aggregates.

An input data file for this model is shown in Table 1. The mixing procedure in the interaggregate volume introduces numerical dispersion, which depends upon the length of the time step, the water flux density and the segment thickness. According to van Genuchten and Wierenga (1984) the numerical dispersion coefficient used in the convection-dispersion equation (CDE) can be calculated as:

$$D = q(\Delta z - q\Delta t)/2. \quad [8]$$

A desired dispersion effect can be approximated by choosing appropriate time steps and node spacings.

SIMULATIONS OF SOLUTE BREAKTHROUGH

Several scenarios regarding aggregate size distribution, flow velocity and chemical properties were simulated as examples. All combinations of size distribution, flow velocity and chemical properties were simulated (5 aggregate sizes x 2 water flow rates x 2 chemicals = 20 simulations).

All other parameters corresponded approximately to the experimental apparatus used in the breakthrough curve experiments

described in a later chapter, i.e. column length of 21.4 cm, soil bulk density of 1.4 kg/dm³, chemical applied during the initial 92 mm infiltration, followed by solute-free water.

Biodegradation was assumed negligible.

RESULTS AND DISCUSSION

Breakthrough curves for fast and slow water flux, for each of the two chemicals are shown in Fig. 1.2 (Cl⁻) and Fig. 1.3 (atrazine). Each set of breakthrough curves is compared with a breakthrough curve simulated using a single-region CDE model. The breakthrough curves show the expected response to changes in water flux density and aggregate size distribution. As the aggregates become larger, their surface area decreases, reducing the amount of diffusion into the aggregates and promoting earlier breakthrough. Faster water flux accentuates this since solute residence times are decreased and diffusion is decreased further. Atrazine, being a sorbing chemical, shows a far greater spread of breakthrough curves than does Cl⁻. Diffusion of atrazine from the interaggregate solution into the aggregates is faster since sorption from the intra-aggregate solution maintains lower solution concentrations and hence higher concentration gradients. Once atrazine enters the aggregate, subsequent diffusion is slower, since atrazine has a smaller diffusion coefficient than Cl⁻ and much of the chemical is in the sorbed phase. Thus for

large aggregates, when diffusion from the flowing water into the aggregates is limited by the surface area of the aggregates, atrazine behaves similarly to Cl^- ; when aggregates are smaller and diffusion from solution is greater then breakthrough is retarded owing to sorption and slow release of chemical from the aggregates. Breakthrough curves simulated using a mixture of aggregate sizes did not correspond to any single aggregate size. For the size distribution used, it would not be possible to use single-sized aggregates as being representative of the mixture.

Columns of aggregates of 1 mm radius produce breakthrough curves almost identical in shape to the CDE, displaced slightly owing to the forward differencing approximation used in calculating solute flow through the interaggregate volume. If the number of segments are increased (i.e. their thickness decreased), the breakthrough curve approaches that simulated by the CDE. Further reduction of the aggregate size had a negligible effect on the breakthrough curve. This implies that aggregates of this size and smaller will not impact solute breakthrough. However, measured breakthrough in columns of soil which had been passed through a 2 mm mesh sieve (Chapter 4) show enhanced breakthrough of both chloride and atrazine. This implies that physical non-equilibrium played a role. A possible explanation for the fact that simulations of flow through small aggregates did not show the effects of physical non-equilibrium

is that the calculated diffusion coefficients in the aggregate were too high. In the simulations diffusion coefficients are reduced based on the basis of simple assumptions regarding tortuosity and water content. In soils, diffusion contents within and across organic matter volumes may be considerably lower than those in solution. Also the tortuosity correction is the same regardless of pore size distribution, accounting for increased path length, but not for phenomena such as dead-end pores, stagnant areas and negative adsorption.

The AGGR model uses parameters which are easily comprehended, the code is relatively simple and short, and lends itself to further expansion. It does not provide solutions to solute flow through aggregated media as do some of the more rigorous models referred to. However, owing to its relative simplicity and ease of expansion, the AGGR model could prove a useful tool for examining the effects of aggregation and biodegradation on solute flow in a semi-quantitative way.

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Table 1. Input data file for AGGR.

Concentration units: Soln (1) or mass (2) basis	:	1
If (1): Initial solute concentration (mass/ml)	:	0.000E+02
If (2): Initial solute concentration (mass/g)	:	0.100E+02
Initial conc in solution outside beads (mass/ml)	:	0.000E+00
Number of aggregate size classes	:	5
Radius of size class 1 (cm)	:	0.040E-00
Radius of size class 2 (cm)	:	0.080E-00
Radius of size class 3 (cm)	:	0.160E-00
Radius of size class 4 (cm)	:	0.320E-00
Radius of size class 5 (cm)	:	0.640E-00
Number of concentric segments in aggregates	:	10
Maximum time step (day)	:	6.944E-04
Total time (days)	:	1.000E+00
Diffusion coefficient in water (cm ² /day)	:	0.460E-00
Whole soil bulk density (kg/dm ³)	:	1.400E+00
Bulk density of aggregates (kg/dm ³)	:	1.550E+00
Partition coefficient (dm ³ /kg)	:	0.000E+00
Time print interval (day). If zero, uses	:	0.000E+00
pore volume print interval (fraction)	:	0.050E+00
Water flux density (cm/day)	:	1.174E+02
Length of column (cm)	:	0.214E+02
Segment thickness (cm)	:	0.214E+01
Starting concentration of inflow (mass/ml),	:	1.000E+00
ending at time (day)	:	0.778E-01
and changing to concentration (mass/ml)	:	0.000E+00
Microbial degradation model*	:	3
1) Zero-order (k ₁ , per day)	:	0.000E+00
2) Michaelis-Menton (k ₂ , per day)	:	0.000E+00
3) First-order (k ₃ , per day)	:	0.000E+00
4) Logistic (k ₄ , per day)	:	0.000E-00
5) Maximum growth rate (μ, per day)	:	0.000E-00
4,5,6) Initial population density (X ₀)	:	0.000E-00
2,5) Half saturation (k _s , mass/ml)	:	0.000E+00
1-6) Incorporation fraction (ζ)	:	0.000E+00

* 1: Zero-order; 2: Michaelis-Menton; 3: First-order; 4: Logistic; 5: Monod (growth); 6: Logarithmic. Defined in Simpkins and Alexander (1985).

Table 2. Aggregate size, water flow and chemical property combinations used in the suite of simulations.

Aggregate radius:	0.1 mm	0.2 mm	0.4 mm	0.8 mm	Equal volumes of each
Flow velocity:	1174 mm/day		117 mm/day		
Chemical properties:	<u>Atrazine</u>		<u>Chloride</u>		
Diffusion coefficient	46 mm/day		160 mm/day		
Kd value	3 dm ³ /kg		0 dm ³ /kg

Fig. 1.1. Conceptual structure of the aggregate column.

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Chloride breakthrough, fast flow $K_d = 0 \text{ dm}^3/\text{kg}$

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Chloride breakthrough, slow flow $K_d = 0 \text{ dm}^3/\text{kg}$

Fig. 1.2. Chloride breakthrough curves simulated for a range of aggregate sizes. The solute was applied as a pulse, and subjected to steady state water flow of 1174 mm/d or 117 mm/d.

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Fig. 1.3. Atrazine breakthrough curves simulated for a range of aggregate sizes. The solute was applied as a pulse, and subjected to steady state water flow of 1174 mm/d or 117 mm/d.

CHAPTER TWO

A MULTI-REGION/TWO-DIMENSIONAL MODEL DESCRIBING
WATER FLOW AND SOLUTE TRANSPORT
IN HETEROGENEOUS SOILS

INTRODUCTION

Many computer simulation models used to simulate the movement of chemicals in soil use a one-dimensional form of the convection-dispersion equation (CDE), for example, LEACHM (Wagenet and Hutson, 1986; Wagenet, et al. 1989; Hutson and Wagenet, 1992). This form of the CDE and other simplifying assumptions, such as uniform distribution of both infiltration and chemical fluxes across the soil surface are not always valid (Pignatello, 1989). Many early soil column studies of pesticide transport showed substantial deviation between measured effluent curves and those calculated using the classical assumptions (Kay and Elrick, 1967; Davidson et al., 1968; Davidson and McDougal, 1973; Jardine et al., 1988). 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 both spatial variability in soil properties, and non-equilibrium flow and sorption processes. This paper describes such a model.

Physical non-equilibrium processes affect both sorptive and nonsorptive chemicals. For a sorptive chemical such as pesticide to substantially interact with all of the solid phase, sorbate molecules have been heretofore represented as moving between two regions: from the relatively fast flowing mobile region (inter-aggregate porosity) to the relatively immobile region (intra-aggregate porosity). Both a first-order transfer process (van Genuchten and Dalton, 1986; van Genuchten and Wagenet, 1989), and diffusion in uniform spheres or cubes (Passioura, 1971; Rao et al., 1980a; 1980b) have been used to characterize this process. Heterogeneity in shape and size of aggregates (or the rate coefficient in the first-order kinetic model) was simplified by using an equivalent shape such as spheres, a weighted mean aggregate size, or a unique value for the first-order rate coefficient.

This simple two-region model has been a popular approach to non-equilibrium cases of both transport and sorption. It assumes that the porous medium is composed of two interactive regions superimposed over the same volume. Vertical convective transport occurs in a mobile region, while diffusion is the main transport mechanism in a stagnant or 'immobile region' (van Genuchten and Wierenga, 1976; van Genuchten and Wagenet, 1989; Brusseau et al., 1989). Heterogeneity in chemical properties is reflected by

defining two or more classes of sorption sites having different sorption kinetic properties (Selim et al., 1976; Cameron and Klute, 1977; van Genuchten and Wagenet, 1989). Analytical solutions for two-site and two-region models are available (Parker and van Genuchten, 1984; van Genuchten and Dalton, 1986; van Genuchten and Wagenet, 1989), based on assumptions of uniform water content and steady-state flow.

Alternatives to the two-region approach have been developed based upon different mechanistic processes prevailing in each region. Water flow in a mobile region composed of fractures, macropores, fissures, and other non-capillary preferential pathways, is not necessarily described by the conventional Darcy-Richards equation (Wagenet and Germann, 1989; Germann, 1990). A kinematic wave equation may be appropriate for the macropore region (Germann, 1990; Germann and Beven, 1985). 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 Richards' equation but with different coefficients (Gerke and van Genuchten, 1993). One region may be described by other flow mechanisms (Chen and Wagenet, 1992a,b). Recent studies of long-term leaching of atrazine under slow water flow conditions (Chen, 1994) showed that the two-site approach was not sufficient to describe the

enhanced leaching tail over long time scales, but that a generalized distributed sorption-site model, which uses a continuum of sorption sites, described long-term leaching data more successfully. Similar results by Karickhoff and Morris (1985) and Connaughton et al., (1993) suggest that the two-site approach fails to describe desorption over long time periods. 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 and Riemsdijk, 1987; Steenhuis and Parlange, 1991).

Solute transfer under natural conditions is complicated further by variable soil properties and antecedent water and chemical distributions. The complex geometry of the soil solid phase leads 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.

Currently, there is no simulation model which enables the

effects of these factors to be assessed. The TRANSMIT (Transport And Non-equilibrium Soil Multi-region Interpretive Tool) model described in this paper is an extension of the LEACHM model (Hutson and Wagenet, 1992), in which a heterogeneous soil hydraulic regime is subdivided into finite, multiple, hydraulically interacting regions. Heterogeneities in sorption, degradation, root distribution and surface boundary conditions are also considered in this model, which can be applied to both steady-state and transient flow conditions.

MODELING APPROACH

Conceptually, the soil profile is divided into horizontal segments of thickness Δz (mm), further subdivided into m regions (Fig. 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_i , mm) used for calculating concentration and potential gradients. Each region occupies a relative area a_i , so that for m regions

$$\sum_1^m a_i = 1. \quad [1]$$

Water retention and hydraulic conductivity relationships are

represented by Campbell's (1974) equations, as modified by Hutson and Cass (1987). Volume fraction of water (θ , $\text{m}^3 \text{m}^{-3}$) and matric potential (ψ , Pa) are related by

$$\begin{aligned}\psi &= \alpha \left(\frac{\theta}{\theta_s} \right)^{-\beta} & \theta \leq \theta_c \\ \psi &= \alpha \frac{(1-\theta/\theta_s)^{1/2} (\theta_c/\theta_s)^{-\beta}}{(1-\theta_c/\theta_s)^{1/2}} & \theta \geq \theta_c\end{aligned}\quad [2]$$

$$s_c = \frac{2\beta}{1+2\beta}$$

where θ_s ($\text{m}^3 \text{m}^{-3}$) is water content at saturation, θ_c is water content at the point of coincidence of the two functions, and α (Pa) and β are constants for a particular soil segment and region.

Hydraulic conductivity is described by

$$K(\theta) = K_s \left(\frac{\theta}{\theta_s} \right)^{2\beta \cdot p + 2} \quad [3]$$

where $K(\theta)$ is hydraulic conductivity (mm d^{-1}), K_s is conductivity at saturation, and p is a pore interaction parameter for further adjustment of the $K(\theta)$ curve. The parameters α , β , θ_s and p can

be varied with depth and across regions. In addition, there is a maximum infiltration rate defined for each region, representing the effects of surface sealing. This value can easily be made a function of cumulative rainfall, soil water content or any factors likely to influence surface sealing.

The mean water content for each depth segment is thus

$$\bar{\theta} = \sum_1^m \theta_i a_i \quad [4]$$

and mean hydraulic conductivity, applicable when matric potentials in all regions are equal, is

$$\bar{K}(\psi) = \sum_1^m K_i(\psi) a_i \quad [5]$$

Similarly, if C_i (g m^{-3}) is the concentration of solute in region i , and K_{di} ($\text{m}^3 \text{kg}^{-1}$) is a linear sorption partition coefficient, then the mean concentration in a depth segment is

$$\bar{C} = \sum_1^m a_i C_i (\theta_i + \rho_i K_{di}) \quad [6]$$

Fluxes in the system are calculated according to the schematic algorithm shown in Fig. 2. Vertical fluxes are calculated for each region in turn, in order of increasing surface permeability, for a time period t_{max} (d). The component time steps used for the simulations for each region depend upon water flux densities in a region, but sum to t_{max} for each region. If the water application during a time step exceeds the

infiltration capacity of a region, then the excess water is allocated to the regions of higher permeability which have yet to be simulated. Thus infiltration is weighted to the more permeable regions as the water application rate increases.

Vertical water flow within each region is described by Richards' equation

$$\frac{\partial \psi}{\partial t} C_w(\psi) - \frac{\partial}{\partial z} \left(K(\psi) \frac{\partial (\psi + z)}{\partial z} \right) + U, \quad [7]$$

where t is time (d), z is vertical distance (mm), $C_w(\psi)$ is differential water capacity ($d\theta/d\psi$, Pa^{-1}), $K(\psi)$ is hydraulic conductivity and U is uptake of water by plant roots (d^{-1}).

Vertical solute flux is calculated from the convection-dispersion equation:

$$\frac{\partial C}{\partial t} (\theta \cdot \rho K_d) - \frac{\partial}{\partial z} [\theta D(\theta, q) \left(\frac{\partial C}{\partial z} \right) - qC] \quad [8]$$

where ρ is bulk density (kg dm^{-3}), C is solute concentration in the aqueous phase, q (mm d^{-1}) is vertical water flux density (from solution of Eq. 7), and $D(\theta, q)$ ($\text{mm}^2 \text{d}^{-1}$) is the sum of molecular diffusion and hydrodynamic dispersion coefficients. The molecular diffusion coefficient (D_e) in soil is estimated by adjusting the aqueous diffusion coefficient (D_o) for the effects

of water content and tortuosity (Jury, et al. 1983):

$$D_c = D_o \theta^{3.33} / \theta_s^2. \quad [9]$$

The hydrodynamic dispersion coefficient (D_m) is calculated as

$$D_m = \lambda \theta / q \quad [10]$$

where λ is dispersivity (mm).

Equations [7] and [9] are solved numerically using the finite difference procedures described in Hutson and Wagenet (1992).

After simulating vertical flow in each region for a time period t_{max} , horizontal equilibration between segments is simulated for an equal period of time. Again, time steps Δt within t_{max} are determined by water flux densities.

The multi-region concept

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, and the fractional areas of each of m regions are $a_1, a_2, a_3, \dots, a_m$, then the most probable area of contact between any pair of regions a_i and a_k across the contact plane, as a fraction of total contact area, is $2a_i a_k$ (for $i \neq k$).

An example will demonstrate the assumptions and equations for lateral flow. Assume three regions, occupying 0.5, 0.3 and 0.2 of the total volume of soil. Assume also that the effective diffusion distance is largest for region 1 and smallest for region 3. There are thus nine possible combinations of regions across the contact plane. Assume further assume that 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. The relative contact areas and direction of flow across a contact plane of area $\Delta y \Delta z$ are illustrated conceptually in Fig. 3. The volume of each region is $a_i \Delta x \Delta y \Delta z$, where Δz is the segment thickness, Δx is a characteristic region width, and Δy is unit length. The length of the arrows reflect effective diffusion distances, which are not necessarily related to Δx ; smaller diffusion distances

result in larger hydraulic gradients and hence higher flow rates.

Thus the change in water content in region 2, for example, is the sum of the flux between 1 and 2, and between 3 and 2. The water flux density q_{ik} between any pair of regions i and k , across a vertical contact plane of area $2a_i a_k \Delta y \Delta z$, is

$$q_{ik} = K_{ik} \frac{\bar{\psi}_i - \bar{\psi}_k}{d_{ik}} \quad [11]$$

where d_{ik} is the distance over which the hydraulic gradient is calculated, currently calculated in TRANSMIT as the geometric mean of the diffusion distances of the two regions, ψ is the matric potential, averaged over a time step Δt , and $2a_i a_k$ is the fractional area of contact between regions i and k . Flux into region i is positive, and away from i is negative. Mass balance of region i is

$$\Delta \theta_i a_i \Delta x \Delta y \Delta z = 2 q_{ik} a_i a_k \Delta y \Delta z \Delta t. \quad [12]$$

Thus the change in water content of region i , during the time step Δt is

$$\Delta \theta_i = 2 q_{ik} a_k \Delta t / \Delta x \quad [13]$$

or, recognizing that $\Delta \theta_i = \Delta \psi C_{wi}$,

$$\Delta \psi_i C_{wi} / \Delta t = 2 q_{ik} a_k / \Delta x. \quad [14]$$

The functional dependence of C_w and K on ψ , and of D on both q and ψ , is assumed in this and following equations. 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,

$$\frac{\Delta \psi_i}{\Delta t} C_{w_i} = \sum_{k=1}^{k=m} \frac{2a_k K_{ik}}{\Delta x} \frac{(\bar{\psi}_i - \bar{\psi}_k)}{d_{ik}}. \quad [15]$$

$\bar{\psi}_i$ is defined as

$$\bar{\psi}_i = (\psi_i^{j+1} + \psi_i^j) / 2, \quad [16]$$

where the superscript j refers to the beginning and $j+1$ the end of the time step. By substituting Eq. [16] into Eq. [15], a difference equation can be written for each region,

$$\frac{\psi_i^{j+1} - \psi_i^j}{\Delta t} C_{w_i} = \sum_{k=1}^{k=m} \frac{a_k K_{ik}}{\Delta x} \frac{(\psi_i^j + \psi_i^{j+1} - \psi_k^j - \psi_k^{j+1})}{d_{ik}} \quad [17]$$

forming 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} , $\text{g m}^{-2} \text{d}^{-1}$) between two regions i and k , across their contact plane, is

$$J_{ik} = D_{ik} \left(\frac{\bar{C}_k - \bar{C}_i}{d_{ik}} \right) + \beta_1 q_{ik} \bar{C}_i + \beta_2 q_{ik} \bar{C}_k, \quad [18]$$

where $\bar{C}_i$ and $\bar{C}_k$ are mean solute concentrations in regions i and k during the time step Δt . 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 $\beta_2 = 1$.

Recognizing that solute concentration is the sum of sorbed and solution concentrations ($C(\theta + \rho K_d)$), and following the mass balance approach used above, the change of concentration ($C_i^{j+1} - C_i^j$) during Δt in region i is

$$\frac{(\theta_i^{j+1} C_i^{j+1} - \theta_i^j C_i^j) + \rho_i K_{di} (C_i^{j+1} - C_i^j)}{\Delta t} = \sum_{k=1}^{k=m} \frac{2a_k J_{ik}}{\Delta x} \quad [19]$$

Writing Eq. [19] for each region, substituting Eq. [18] for J , and using θ and q values arising from the solution of Eq. [17], creates a matrix which can be solved for the m unknown values of C^{j+1} .

Three parameters (a , Δx , and d) define the geometry of the regions. These parameters do have some physical significance: a is the fractional area occupied by each region, Δx is 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 is an effective diffusion distance. The 'size' or 'scale' parameter (Δx) is constant for all regions, while d , a 'shape' parameter, is specified for each

region. Smaller d values are used if the shape of the region suggests faster equilibration. For example, a cubic ped would have a larger d value than a narrow, elongated preferential flow region. In practice, we combine Δx and d into a single geometry parameter d' . The mean value of d' for any two regions determines the relative rate at which matric potentials and solute concentrations approach equilibrium.

The two-dimensional version

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

In the two-dimensional linear model, regions are arranged adjacently and all have the same diffusion diameter. By specifying appropriate volumes for adjacent regions, different geometries can be simulated. If volumes are equal, then lateral flow is linear (case A, Fig. 4). For radial flow, the volumes of the concentric cylinders must increase in proportion to $i^2 - (i-1)^2$, where i is the region number and region $i = 1$ is at the center (case B, Fig. 4). To represent spherical aggregates, vertical flow is not allowed for regions which are part of the aggregate. Volumes of concentric shells are proportional to $i^3 -$

$(i-1)^3$ for $i = 1$ at the center of the aggregate (case C, Fig. 4). The outside vertical boundaries of the end columns are assumed to be planes of zero water and solute flux. Lateral flow is simulated for the period t_{max} using the horizontal flow form of the Richards equation for water, and the convection-dispersion equation for solute. Currently, simulations obtained with the radial and spherical versions of TRANSMIT are not strictly correct, since the the areas across which the solute diffuses do not change in the same proportion as the volumes of the regions, a problem which should soon be resolved.

APPLICATIONS

TRANSMIT is demonstrated by simulating solute breakthrough curves for several hypothetical soil and flow scenarios, assuming a non-interacting conservative tracer. These simulations were designed to complement an experimental program not reported in detail here. Column length (210 mm), initial soil solution concentration ($C_i = 0$ at $t = t_0$), and influx concentration ($C_0 = 1$ for $0 < q(t-t_0) \leq 91.3$ mm, $C_i = 0$ for $t-t_0 > 91.3$ mm) were used for all simulations. 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 accuracy. Time steps within Δt_{max} are determined by prevailing maximum water flux densities within each

region.

Soil hydraulic parameters

For a single-region model, neglecting hysteresis, mean $K(\psi)$ and $\theta(\psi)$ curves are defined for the entire soil volume. For these demonstrations the soil was assumed to have a bulk density of 1.27 Mg m^{-3} , a porosity of $0.5208 \text{ m}^3 \text{ m}^{-3}$, $\theta(\psi)$ described by Eq. [2] ($\alpha = -2 \text{ kPa}$ and $\beta = 8$), and $K(\psi)$ defined by Eq. [3] ($K_s = 1176 \text{ mm d}^{-1}$ and $p = 1$).

Using TRANSMIT, departures from this uniform soil were considered which reflect possible variations in soil structure. An immobile region was defined as only accessible by lateral diffusion and convection, and by prohibiting vertical water flow through it. If desired, different $\theta(\psi)$ and $K(\psi)$ relationships can be defined for each mobile and immobile region. Hydraulic conductivities of the mobile regions were increased by a factor $1/F$, where F is the mobile fractional area, in order to maintain the infiltration capacity of the bulk soil (Table 1).

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. For simplicity, different $K(\psi)$ and $\theta(\psi)$ curves

were defined by modifying the α and K_s parameters only.

Following scaling theory, if the water retention parameter α was decreased by a factor S_f then K_s was increased by S_f^2 . A three-region soil (Table 1) was created by adding a preferential-flow region to a two-region mobile-immobile soil. The preferential region ($S_f = 64$) had an α value of -0.03 kPa, leading to lower water retention and a much higher saturated conductivity than the mobile matrix, but because it occupied only 2% of the soil volume, had a small influence on overall water retention and unsaturated hydraulic conductivity (Figs. 5 and 6).

A five-region soil (Table 1) was defined by applying log-normally distributed scaling factors ($\bar{S}_f = 1$, $SD = 0.25$) to the bulk soil $\theta(\psi)$ and $K(\psi)$ curves, creating an ensemble of five different hydraulic regions of equal area. Values for α ranged from -1.50 to -5.63 kPa (Table 1). The mean $\theta(\psi)$ and $K(\psi)$ curves were similar to those for the single region soil (Figs. 7 and 8).

Mean K_s values for both the three- and five-region soils were calculated so that, after adjustment by the scaling factors, the mean conductivity at -3 kPa was 433 mm d^{-1} , to allow comparative simulations of steady-state water flow at this potential. Specifying steady-state water flow at a defined mean

water content (Eq. [4]) causes TRANSMIT to calculate the corresponding matric potential, which will be the same across the regions, and allocate infiltrating water to each region in proportion to the hydraulic conductivity values at that potential. Thus relative hydraulic conductivity values at a defined potential determine steady-state water flux distributions, and the vertical water flow subroutine, which solves Richards' equation, is bypassed. However, if transient flow is specified, water flux into a region will be determined primarily by the specified infiltration flux density, but may be reduced by prevailing conductivity values and matric potential gradients in the region, or increased by overflow from less permeable regions.

Within certain bounds, the simulations are sensitive to the value of d , the effective diffusion distance 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. For sieved soil, the regions may represent aggregates of different sizes and properties, inter-aggregate volume and packing heterogeneities. Aqueous diffusion coefficients were assumed to be $160 \text{ mm}^2 \text{ d}^{-1}$, while dispersivity was set at 15 mm.

SIMULATIONS

Solute breakthrough curves were simulated for saturated, steady-state water flow conditions for all soils (Table 2). The effects of reducing water flux density and matric potential (to -3 kPa) were examined for some of the soils.

Solute breakthrough simulations under steady-state flow in single- and two-region soils were compared to those generated by analytical solutions of the CDE, using the CXTFIT (single-region) and CXT4 (two-region) programs of Parker and van Genuchten (1984). Although transfer of chemical between mobile and immobile phases is first-order in both TRANSMIT and CXT4, it is difficult to equate the value of the phase transfer coefficient used in CXT4 to the combined influence of region volumes, molecular diffusion coefficient and effective diffusion distance used in TRANSMIT. The phase transfer coefficient in CXT4 was optimized, but all other parameters in both CXTFIT and CXT4 corresponded to those used in TRANSMIT.

Water and solute transport in initially dry (-30 MPa) three-region soil was simulated at each of three water influx rates: equivalent to the mean saturated conductivity of the soil matrix (K_{matrix}) (regions 1 and 2 only), $1.5 \times K_{\text{matrix}}$, and $4 \times K_{\text{matrix}}$. In

these simulations the matric potential at the lower boundary had to increase to -0.2 kPa before drainage occurred.

RESULTS AND DISCUSSION

Comparison to analytical solutions

When configured as a single- or two-region system, confining vertical flow to one region only, TRANSMIT simulated breakthrough curves almost identical to those predicted by the analytical solutions of Parker and van Genuchten (Figs. 9 and 10). The CXTFIT and CXT4 simulations were obtained by specifying the values of pore water velocity, retardation factor, column length, dispersion coefficient, fraction of mobile water, pulse length and input solution concentration corresponding exactly to those used in the TRANSMIT model. Only the phase transfer coefficient was fitted to the TRANSMIT breakthrough curves. Constant molecular diffusion coefficient and diffusion length should lead to constant best-fit values for the phase transfer coefficient which was approximately true. Simulations using a wide range of flow and soil parameters have shown that TRANSMIT behaves in conformance with results of classical theory: constant ratios of D/d_{ik} produce similar breakthrough curves; the fitted phase transfer coefficient is inversely proportional to D/d_{ik} ; and changing the water flux density has a negligible effect on the

phase transfer coefficient.

Effect of soil geometry on saturated steady-state breakthrough curves

The main mechanisms causing breakthrough curves to depart from the classic single-region pattern during steady-state flow are, i) pore water and solute velocities may be different across the regions, and ii) the resulting 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.

For the soil geometries defined (Table 1), differences in hydraulic conductivity are large at saturation (Fig. 7), leading to large differences in pore water and solute velocities between the regions. The two-region geometry advances breakthrough in comparison to the single-region soil and increases the peak concentration, because convective flow is restricted to 75% of the soil volume, while diffusion between the mobile and immobile

regions is restricted to the area of contact between the two regions. Inclusion of a preferential flow region, occupying only 2% of the soil volume, drastically alters the nature of the breakthrough curve. At saturation most of the flow occurs through this region, and at the high flow rates used, there is little opportunity for equilibration between the regions.

The five-region soil (Table 1) had no immobile region. Scaling factors determining water retention and hydraulic conductivity were distributed log-normally. Convective flow rates were proportional to the saturated conductivity. These differences in water flux density between the regions act both to advance and to smear the mean breakthrough curve (Fig. 9). Slight tailing is apparent, caused by solute moving in the less permeable regions. If the differences in hydraulic properties between the regions were greater, then advance of the breakthrough curve would be increased still further.

Effects of flow velocity and water content

Figure 10 shows the effect of slower flow velocities and slightly lower water contents (all at -3 kPa) on solute breakthrough. Breakthrough from the three-region soil was similar to that from the two-region soil, because conductivity in the preferential region had dropped, and this region was no

longer conducting a disproportionate fraction of the water flow. The two-region breakthrough curves moved towards the single-region breakthrough curve as water flux density decreased from 433 mm d⁻¹ to 118 mm d⁻¹. These two breakthrough curves demonstrate the interaction between increased pore water velocity in the mobile region, which promotes advanced breakthrough and increases peak concentration, and diffusion into and out of the immobile region, which has an effect similar to an increase in dispersivity, lowering the peak concentration and broadening the breakthrough curve.

At -3 kPa, breakthrough from the five-region soil (Fig. 10) was almost identical to that from the single-region soil, because at -3 kPa, differences in hydraulic conductivity, and hence flux densities, between the regions were small.

Leaching from initially unsaturated soil

Figure 11 shows breakthrough curves from initially unsaturated soil columns (matric potential -30 MPa) subject to infiltration fluxes equivalent to the mean saturated conductivity of the soil matrix (K_{matrix}), $1.5 \times K_{\text{matrix}}$ and $4 \times K_{\text{matrix}}$. Drainage occurred once the lower boundary potential of any region reached a maximum value of -0.2 kPa.

Solute concentration (C/C_0) in the effluent was initially about 0.3 (Fig. 11), water initially resident in the column having diluted the percolating solution.

When the infiltration flux density equalled K_{matrix} , transport processes of both water and solute were similar to those of a two-region soil. Water and solute infiltrated into the mobile matrix. Lateral water flow, driven by matric potential gradients, and convective solute transport, increased the water and solute content of the immobile region. There was no additional overflow to the preferential region. The soil matrix could accommodate an infiltration flux density equivalent to K_{matrix} without additional overflow to the preferential flow region. Most vertical solute transport occurred in the mobile matrix, leading to a BTC similar to that for a single-region soil. Once the solute input ended, however, solute from the immobile region continued to diffuse to the mobile matrix and preferential regions, maintaining a low concentration (about 0.0035 for the third pore volume) for a long period of time. After 0.6 d, about 9% of the solute applied was still retained in the immobile region.

Increasing the infiltration flux density to 1.5x and 4x K_{matrix} eventually caused overflow from the matrix to the

preferential flow region as hydraulic gradients decreased (Fig. 11). The breakthrough curves reflect the rapid movement of solute through the preferential region, the abrupt drop in concentration once the solute pulse ended, and the tailing concentration caused by slow diffusion from the matrix into the preferential region and continued breakthrough from the mobile matrix. The saturated conductivity ($6.6 \times 10^5 \text{ mm d}^{-1}$) of the preferential region was sufficient to accommodate this overflow. Water and solute moved rapidly through the preferential region, from where water and solute moved laterally into the matrix and immobile regions. Although infiltration into the mobile matrix continued, it was slow in comparison to flow into the preferential region. Once water flow reached steady-state throughout the column, matric potentials in all regions were the same, and solute transport between regions was by molecular diffusion only. At this stage, the infiltrating water was free of solute, the concentration in the preferential region was low, and solute transport from the immobile and mobile regions to the preferential region was slow, since molecular diffusion in response to concentration gradients was the only lateral transport mechanism.

The apparent early breakthrough when the infiltration flux was $4 \times K_{\text{matrix}}$ is misleading, since it totalled only 0.3 mm.

Water moved through the preferential region faster than it could be absorbed by the matrix; the lower boundary matric potential of -0.2 kPa required for drainage was established earlier in the preferential region than in the soil matrix, leading to the small effluent volumes. The breakthrough curve reflects the rapid movement of solute through the preferential region, the abrupt drop in concentration once the solute pulse ended, and the tailing concentration caused by slow diffusion from the matrix into the preferential region and continued breakthrough from the mobile matrix. Concentrations in the tail increase slightly as the peak concentration in the matrix reaches the end of the column. Resident solute concentrations in each of the regions at several times (Fig. 12) demonstrates how solute may be rapidly absorbed and retained for long periods in structured soils, if convection is the mechanism for entry into less mobile regions and slow diffusion is the only exit mechanism. This effect will be accentuated if sorption occurs primarily in these less mobile volumes. These processes can explain why soil surface conditions and water content, and amount and timing of subsequent rainfall, have large effects on 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 different interacting factors 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.

Breakthrough in relation to macropore geometry

The two-dimensional form of TRANSMIT was used to simulate flow through a soil column having a linear crack, a cylindrical crack, a central hole, and a preferential region surrounding spherical aggregates (Table 2). The shape of the breakthrough curves are shown in Fig. 13. Breakthrough of the peak Cl^- concentration is faster when the preferential volume is a smaller fraction of the total volume. The preferential fraction ranges from 0.02 in the case of the central hole, to 0.265 for the cylindrical crack (Table 2). Tailing increases as the preferential volume becomes smaller, since a greater proportion

of the solute enters the matrix at the column surface. This solute continues to move slowly downwards in the mobile matrix and also diffuses into the preferential volume, supporting a low concentration in the preferential region for a long period of time. The breakthrough curves become more angular as the preferential fraction decreases since the pore water velocity in that region increases. The breakthrough curve thus reflects surface boundary concentration changes very quickly.

In natural soils the preferential geometry is difficult to assess

CONCLUSIONS

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 will be valuable 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.

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Table 1. Soil parameters for simulations using the multi-region version of TRANSMIT.

Soil geometry	Region	Relative area	d' mm	α kPa	K _s [*] mm d ⁻¹	Vertical flow
1-region	mobile	1.00	-	-2.00	1176	Yes
2-region	immobile	0.25	100	-2.00	1560	No
	mobile	0.75	10	-2.00	1560	Yes
2-region	immobile	0.50	100	-2.00	2353	No
	mobile	0.50	10	-2.00	2353	Yes
3-region,	immobile	0.25	100	-2.00	1611	No
	mobile	0.73	10	-2.00	1611	Yes
	macropore	0.02	1	-0.03	6.7x10 ⁶	Yes
5-region	Region 1	0.20	10	-5.63	643	Yes
	2	0.20	10	-2.35	909	Yes
	3	0.20	10	-2.06	1180	Yes
	4	0.20	10	-1.82	1520	Yes
	5	0.20	10	-1.50	2220	Yes

* For all soils, mean vertical hydraulic conductivity at -3 kPa was 433 mm d⁻¹.

Table 2. Soil parameters used in simulations using the two-dimensional version of TRANSMIT.

Soil geometry	Region	Relative area	Diameter mm	α kPa	K_s^* mm d ⁻¹	Vertical flow
Linear crack	1-6	0.133	1	-2.00	1176	Yes
	7	0.133	1	-0.03	6.7x10 ⁶	Yes
Cylindrical crack	1	0.020	1	-2.00	1176	Yes
	2	0.061	1	-2.00	1176	Yes
	3	0.102	1	-2.00	1176	Yes
	4	0.143	1	-2.00	1176	Yes
	5	0.184	1	-2.00	1176	Yes
	6	0.224	1	-2.00	1176	Yes
	7	0.265	1	-0.03	6.7x10 ⁶	Yes
Central hole	1	0.020	1	-0.03	6.7x10 ⁶	Yes
	2	0.061	1	-2.00	1176	Yes
	3	0.102	1	-2.00	1176	Yes
	4	0.143	1	-2.00	1176	Yes
	5	0.184	1	-2.00	1176	Yes
	6	0.224	1	-2.00	1176	Yes
	7	0.265	1	-2.00	1176	Yes
Spherical aggregates	1	0.0011	1	-2.00	1176	No
	2	0.0074	1	-2.00	1176	No
	3	0.0200	1	-2.00	1176	No
	4	0.039	1	-2.00	1176	No
	5	0.064	1	-2.00	1176	No
	6	0.096	1	-2.00	1176	No
	7	0.134	1	-2.00	1176	No
	8	0.179	1	-2.00	1176	No
	9	0.229	1	-2.00	1176	No
	10	0.229	1	-2.00	1176	Yes 000

Table 3. Simulations of water and solute flow in soil columns.

Simulation	Soil geometry	Water potential	Flow option	Flux density
		kPa		mm d ⁻¹
Steady-state saturated flow (Fig. 9)				
1	1-region	0	Steady-state	1176
2	2-region, F=0.50	0	Steady-state	1176
3	2-region, F=0.75	0	Steady-state	1176
4	3-region	0	Steady-state	1176
5	5-region	0	Steady-state	1176
Steady-state unsaturated flow (Fig. 10)				
6	1-region	-3	Steady-state	433
7	2-region, F=0.75	-3	Steady-state	433
8	2-region, F=0.75	-3	Steady-state	118
9	5-region	-3	Steady-state	433
Infiltration into initially dry soil (Fig. 11)				
10	3-region	-30000 to -0.2	Transient	1176
11	3-region	-30000 to -0.2	Transient	1761
12	3-region	-30000 to -0.2	Transient	4694
Two-dimensional geometries (Fig. 4)				
13	2-D, linear crack	0	Steady-state	1176
14	Cylindrical crack	0	Steady-state	1176
15	Central hole	0	Steady-state	1176
16	Spherical aggregates	0	Steady-state	1176

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

Fig. 2. Algorithm outlining the procedure for calculating vertical and horizontal fluxes.

Fig. 3. Areas of contact and direction of water flow across a contact plane for a three-region soil, assuming lowest matric potential value in region 2 and highest in region 3. The length of the arrows reflect effective diffusion distances.

Fig. 4. Two-dimensional configurations in TRANSMIT: A) Adjacent columns, e.g. furrow irrigation, B) radial flow, e.g. drip irrigation, C) cross-section through soil with a spherical aggregate. Series 1 shows surface view of geometry in natural soil, series 2 shows equivalent 2-D configurations used in TRANSMIT.

Fig. 5. Water retention curves for the single-, two and three-region soils.

Fig. 6. Vertical hydraulic conductivity relationships for the single-, two-, and three-region soils.

Fig. 7. Water retention in a five-region soil.

Fig. 8. Hydraulic conductivity ($K(\psi)$) for a five-region soil.

Fig. 9. Solute breakthrough curves (saturated, steady-state water flux density, 1174 mm d^{-1}), simulated by TRANSMIT (lines), and calculated by CXTFIT or CXT4 (symbols).

Fig. 10. Simulated solute breakthrough at matric potentials of -3 kPa, simulated by TRANSMIT (lines), and calculated by CXTFIT or CXT4 (symbols).

Fig. 11. Simulated breakthrough of solute from initially unsaturated three-region soil columns, subject to infiltration flux densities of $1x$, $1.5x$, and $4x$ saturated matrix hydraulic conductivity (K_{matrix}). Resident solute distributions after 71 mm (A), 102 mm (B), and 430 mm infiltration, are shown in Fig. 11.

Fig. 12. Distribution of solute in a three-region soil at three times (Fig. 10): Cumulative infiltration was A) 71 mm, B) 102 mm, and C) 430 mm, at an infiltration flux density of 4696 mm d^{-1} ($4 \times K_{\text{matrix}}$).

Fig. 13. Simulated breakthrough of chloride from initially saturated columns having a range of macropore geometries.

CHAPTER THREE

BATCH EQUILIBRIUM STUDIES

INTRODUCTION

A single batch-determined K_d value has been the most popular way of characterizing pesticide sorption in soils, although the many limitations of the method and the data have become more apparent. It is attractive because the procedure is ostensibly simple, and the organic matter partition coefficient (K_{oc}) is perceived as characterizing the sorption potential of a chemical independently of soil type.

Equilibrium sorption

Chiou (1989) summarized evidence for concluding that the sorption of non-ionic molecules is primarily through chemical partition or dissolution into soil organic matter, although Hassett and Banwart (1989) suggests that other, more specific forces may determine sorption.

Wang, et al. (1992) in a detailed study of atrazine sorption by a Laurentian soil from Quebec, showed that sorption increased approximately linearly until the solution concentration reached

about 8 mg d⁻³, when a sorption maximum was reached. Sorption decreased by about 30% as the pH increased from 5 to 8.75. Previous work by Wang et al showed that binding of atrazine by fulvic and humic acids peaked at the pH at which atrazine is protonated, suggesting that organic matter binds primarily the neutral molecule. Binding continues in soil, however, suggesting that some cation exchange is involved.

In solute transport models based on the convection-dispersion equation, interaction between chemical in solution and that sorbed onto the solid phase is characterized by means of an equilibrium sorption isotherm. If the amount sorbed is proportional to concentration, then the isotherm is linear:

$$S = K_d C \quad [3.1]$$

where S is the concentration in the sorbed phase (M M⁻¹), C is concentration in the solution phase (M L⁻³) and K_d is the partition or distribution coefficient. Since pesticide sorption is often proportional to soil organic carbon content, differences between soils can be partly explained by accounting for the fraction of organic carbon,

$$K_d = K_{oc} f_{oc}$$

[3.2]

where K_{oc} is the organic carbon partition coefficient and f_{oc} is the fraction of organic carbon.

If the relationship between C and S is curvilinear, then the Freundlich isotherm is often used,

$$S = K_f C^{n_f}$$

[3.3]

where K_f is the Freundlich constant and n_f is an exponent (which does depend on the concentration units used). Procedures for converting between units are described by Bowman (1982). When S has units of mg kg^{-1} and C has units mg dm^{-3} , then K_f has units of $\text{mg}^{1-n_f} \text{kg}^{-1} (\text{dm}^{-3})^{n_f}$. When n_f is unity then Eq 3.3 reduces to Eq.

3.1.

Throughout this work, we will express concentrations in units of g m^{-3} (or mg dm^{-3}).

A summary of sorption constants for atrazine, alachlor and 2,4-D are presented in Wauchope, et al. (1992), and Montgomery (1993). The 65 atrazine K_{oc} values listed in Montgomery (1993) have a mean of 154, a SD of 79, minimum of 47 and maximum of 394. Six alachlor values range from 73 to 188 $\text{dm}^3 \text{kg}^{-1}$, with a mean of

116. If the values quoted are representative of a wide range of soils, it is interesting to note that the use of a K_{oc} value does not always reduce the variability between soils. As with other soil characteristics it is probably necessary that all analyses be performed using the same methods.

Kinetic sorption

Pignatello (1989) discussed the kinetics of sorption, emphasizing the role of diffusion. The sorptive interaction energies associated with the major sorption mechanisms postulated are low, therefore diffusion is probably the main contributor to slow sorption. This can impact many of our experimental techniques, since extractions may not be complete, equilibrium may only be apparent, and persistence is longer than expected. Diffusion rates can be reduced by sorption, the effective diffusion coefficient is increased by the retardation factor. The diffusion coefficients in the soil organic matter phase are probably much lower than those in aqueous solutions. Diffusion coefficients of organic molecules in synthetic polymers can be many orders of magnitude less than those in water, and mobility can be further reduced by entrapment and dead-end pores.

In most simulation models Eq. 3.1 and Eq. 3.3 are often applied assuming that sorption occurs instantaneously, but

measurements of pesticide sorption indicate that it is a kinetic process. This led to the development of multi-site sorption models, in which some of the sites were subject to slow sorption and desorption and others were 'equilibrium sites'. Usually, just two types of sites are defined, one equilibrium and one kinetic.

For simplicity we assume a linear sorption isotherm for the two sites. Although more complex isotherms may be better descriptors of any individual solute, the additional parameters required would be difficult to obtain in most situations. If a fraction f of sites exhibit local chemical equilibrium and a fraction $1-f$ are subject to kinetically controlled sorption and desorption. For simplicity we assume a linear sorption isotherm for the two sites. Although more complex isotherms may be better descriptors of any individual solute, the additional parameters required would be difficult to obtain for the types of situations to be addressed here. The sorbed concentration is the sum of sorption on the equilibrium (s_1) and kinetic (s_2) sites. Flux density of solute between the kinetic sites (current concentration s_2 $\text{mg} \cdot \text{kg}^{-1}$) and solution phase (concentration c $\text{mg} \cdot \text{dm}^{-3}$) is assumed to depend upon the current level of disequilibrium

$$J_a = \alpha \rho_b ((1-f)k_d c - s_2) \quad [3.4]$$

where J_a is the solute flux density and α is a phase transfer rate coefficient. The value of α is assumed to be the same for all segments, but the fraction of equilibrium sites can vary.

Following van Genuchten and Wagenet (1989) results in a solute transport equation for two-site sorption:

$$\frac{\partial(\theta + f\rho k)c}{\partial t} = \frac{\partial}{\partial z} \left(\theta D \frac{\partial c}{\partial z} - qc \right) - \alpha \rho_b [(1-f)K_{dc} - s_2] - \phi \quad , \quad [3.5]$$

where ϕ is a transformation source/sink term, calculated using a first-order rate constant which applies either to the solution phase only or to both sorbed and solution phase.

Diffusion processes

Another conceptual mechanism explaining the slow approach to equilibrium is diffusion, which in some formulations is mathematically identical to the kinetic sorption described above. Solute can only reach the interior of aggregates through diffusion. Assuming that the chemical sorbs primarily on and in

the organic matter phase then the initial sorption onto the exposed surfaces of the organic matter may be fast, but penetration and diffusion throughout the whole organic matter phase may be slow, especially as it is likely that the diffusion coefficient in this phase is considerably lower than that in solution or in the soil pores. The apparent rate of diffusion will be further slowed by sorption. The major difficulty in applying this concept is the necessity of defining soil geometry and diffusion path lengths. The TRANSMIT model (Chapter 2) can simulate the effects of multiple regions in the soil, each of which has unique hydrological, physical and chemical properties, or can reflect diffusion into aggregates. Examples of the application of these concepts in relation to measured sorption are discussed later.

It is difficult to define exactly which mechanism, or combination of mechanisms (sorption site kinetics, diffusion in inter-aggregate, intra-aggregate or organic matter volumes) controls sorption and desorption. Soil composition and structure, as well as experimental conditions such as degree of crushing, hydration of organic matter, shaking procedure and abrasion, can all play a role. Also, during long measurement periods, degradation can lead to lower solution concentrations which may be interpreted as sorption.

In this work we try to interpret much of our data by including processes such as diffusion, but elucidation of diffusion rates or sorption kinetics *per se* was not one of the objectives of this work. In all soil-related research there is often diverging objectives: on the one hand, detailed studies are required to elucidate processes and mechanisms, and on the other, there is a need to develop techniques for the rapid and simple evaluation of soils, compounds and possible environmental risks.

OBJECTIVES

- 1) Measure atrazine, alachlor and 2,4-D sorption isotherms for the soils used in this work.
- 2) Explore various approaches to representing the Freundlich isotherm and the kinetics of sorption in numerical steady-state and transient leaching models.

PROCEDURE

Soils

Soils were sampled from the sites of the field experiment conducted at the Geneva Vegetable Research Farm and at Caldwell Field, Ithaca (Table 3.1).

Atrazine sorption

C^{14} -labelled atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) was used in the batch studies. This enabled rapid, frequent sampling and reliable analysis at low concentrations. The following general procedure was followed: Volumes of aqueous solutions of $CaSO_4$, ^{14}C labelled atrazine, and unlabelled atrazine, were added to a glass centrifuge tube in amounts to give a total volume of 4 ml, 0.005 M with respect to $CaSO_4$, and a desired atrazine concentration ranging from 50 $\mu g\ dm^{-3}$ to 20 $mg\ dm^{-3}$ having a count rate of about 15000 DPM. Air-dry soil (about 1.6 g) of known water content was added to the solution. The mass of the tubes was recorded after each addition of solution and soil, and after removal of aliquots for analysis, which provided a gravimetric check on the volumetric changes.

The tubes were stoppered, the contents mixed thoroughly on a vortex mixer (20 s), and equilibrated on a reciprocating shaker (?? cycles/minute) for up to 48 hours. At intervals the tubes were centrifuged, and a small aliquot of the supernatant (0.05 to 0.4 ml) was withdrawn from each for counting. The soil in the tube was redispersed on a vortex mixer and the tubes were replaced on the shaker for a further equilibration period. After completion of the adsorption leg of the isotherm (usually 48 hours), all of the supernatant solution was decanted.

To study the effect of drying on desorption, an air-supply tube was inserted into selected centrifuge tubes, and air, at room temperature, was passed across the surface of the soil for a few hours. The remaining tubes, containing entrained solution, were stoppered to prevent evaporation. After weighing the tubes and soil, atrazine-free CaSO_4 solution (about 4 ml) was added to all tubes, and the soil was dispersed, equilibrated and sampled as described for the adsorption leg.

At each sampling time, sorbed chemical was calculated as the difference between that in solution and the total amount added, assuming degradation to be negligible during the period of measurement. Several soil extracts were scanned for the presence of atrazine degradation products, but these were not detected. For each batch study the raw data, the derived input data and the computer program used to perform the calculations were preserved.

Alachlor sorption

Alachlor [2-Chloro-2'-6'-diethyl-N-(methoxymethyl)-acetanilide] sorption isotherms were obtained in a similar way to atrazine, except that immunoassay techniques (Ohmicron Corp.) were used to determine the concentration of alachlor in solution. Samples of the supernatant solution at various times during equilibration were analyzed using Ohmicron Rapid Assay kits.

2,4-D sorption

Sorption of 2,4-D (2,4-dichlorophenoxy acetic acid) was studied using ^{14}C -labelled 2,4-D, following the procedure described above for atrazine. Results were frequently erratic, thought to have been caused by sorption to the walls of glass tubes and vials. The addition of a drop of KOH solution to the CaSO_4 solution before addition of 2,4-D appeared to solve the problem (suggested by U. Mingelgrin, Volcani Center, Israel).

RESULTS AND DISCUSSION

Atrazine, Caldwell field

The batch sorption measurements were not designed to elucidate sorption kinetics; the objective of performing successive analyses with time was to determine whether equilibrium had been reached. Nonetheless, the time required to reach apparent equilibrium shows that sorption is sufficiently slow to negate a local equilibrium assumption.

Results for atrazine are summarized in Table 3.2, grouped according to equilibration time and whether the soil was air-dried before desorption or not. The sorption data indicated that sorption was somewhat non-linear. The Freundlich isotherm (Eq. 3.3) was fitted to the data within each of several broad time

classes. Although the value of the exponent n_f was generally between 0.85 and 0.9, the sorption isotherms were sufficiently curvilinear to lead to apparent K_d values (the ratio S/C) to change by a factor of up to 3 over the range of concentrations likely to be measured in a field or leaching column.

The main conclusions drawn from Table 3.2 were:

- 1) Sorption was much higher in the topsoil than in the subsoil, owing to higher organic carbon levels.
- 2) Equilibration required about 24 hours. A few tubes were equilibrated for 96 hours, and these suggest an increase in sorption but there were few data and these may not be reliable.
- 3) K_d values attained after the adsorption leg were lower than those attained after the desorption leg. This may indicate that equilibrium was not reached on one or both legs, or, less likely, that the isotherm displays hysteresis.
- 4) Air drying appeared to increase the rate of desorption. This could be caused by the pattern of drying which probably led to a mass flux of water and solute to the surface of the soil plug, where precipitation rather than sorption may predominate.

The initial work summarized in Table 3.2 suggested that measured K_d values were sensitive to experimental conditions. Subsequent batch studies were performed using all of the soils simultaneously, so that better comparisons could be made between soils. This was done for all three chemicals. Tables 3.3 (atrazine), 3.4 (alachlor) and 3.5 (2,4-D) summarize these results. Data obtained after 24 h equilibration only was used to calculate the data in these tables. All of the data is stored on diskettes.

The atrazine sorption values listed in Table 3.3 appear to be lower than the values listed in Table 3.2. This could be due to the fact the only one sampling was made, whereas in many of the results in Table 3.2, several samples, each involving centrifugation and redispersal, were taken, so mixing was better. The desorption data for atrazine again suggests that the air-dried soils released atrazine faster than those that remained wet.

Nonetheless, these data show the same trends as those obtained earlier. The differences between the adsorption and desorption legs are even more pronounced. This could be caused by the fact that in this batch study only one sampling was done, at 24 hours, whereas the samples in Table 2.2 were subjected to

centrifugation and resuspension more frequently. It may be that much of the sorption occurred during the fast vortex mixing rather than during the extended reciprocal shaking. If so, it is further evidence that sorption in these soils is a slow process, and that this does need to be reflected in any field simulation models.

Implications of choice of isotherm

In most of the methods we will use to characterize sorption, a linear isotherm is used. However, it does appear as though the curvilinear Freundlich isotherm is often applicable. Table 3.6 shows a Mathcad document set up to predict chemical partitioning arising from assumptions regarding sorption. The procedure allows the shapes of these isotherms to be examined, where a specific sample is located, knowing either an initial solution or total chemical concentration, and the implications that this will have on partitioning and apparent retardation in flowing systems. The consequences of changing soil properties such as water content and sorption parameters can be assessed easily and visually. The examples assumed a constant Freundlich parameter K ($=1 \text{ dm}^3 \text{ kg}^{-1}$), but the exponent K_f was set to 1 (a linear isotherm), 0.8 (the lower bound of the values we measured), and 0.6 (a more extreme case). The Mathcad graphs, which are produced as part of the document in Table 3.6 show the shape of

the isotherm, the fraction of chemical in each phase at different solution concentrations and the retardation factor at different solution concentrations. Curvilinear sorption isotherms result in rising retardation factors as concentration increases, which is likely to have an impact on the shape of the breakthrough curves, suppressing the leading concentrations and producing a tail. These effects will be examined in the following chapter.

Reflecting sorption kinetics in solute transport models

There are several possible reasons for slow sorption and desorption. It is not possible at this stage to identify any one mechanism as predominant. From a practical point of view the fact remains that slow sorption is real and has to be incorporated into solute transport models. Which approach to modelling do we take? The choices arising out of this work are, considering the little we know about kinetics and the possibilities in the models used, are either two-site sorption or first-order transfer in the TRANSMIT model.

Two-site sorption

In LEACHP, as in many other pesticide fate models, sorption of a pesticide was assumed to be directly proportional to its concentration in solution. Local equilibrium was assumed at all times. In the revised version, sorption kinetics and non-linear

isotherms are included as options.

An example of the effects of two-site sorption on the rate of equilibration is presented in Table 3.7, which is a Mathcad* document which can be used to examine the effects of other parameters on the temporal sorption pattern. The input parameters were typical of the values applicable to the batch studies conducted during this project. The problem with using the two-site approach is that it cannot explain accelerated breakthrough of non-sorbing chemicals, and it is unlikely that the phase transfer coefficients will be applicable over a wide range of water contents and soil structure.

Rates of adsorption and desorption are identical if a single phase transfer coefficient is used. In order to reflect differences in rates of adsorption and desorption, different phase transfer coefficients can be used for each sorption leg. However, this approach will not reflect the often-observed decrease of the rate of desorption with increasing time since application.

Sorption in the presence of aggregates

Aggregates in soil can influence sorption and desorption

kinetics in several ways. First, diffusion path lengths are increased, thus it will take longer for solute molecules to come into contact with all sorption sites. Second, diffusion coefficients may be less within the aggregate volume than in the interaggregate volume. Third, the mechanism for movement of solute into an aggregate may be different to that for removal. Slower apparent diffusion coefficients within the aggregates are caused by sorption and perhaps also by increased tortuosity, dead-end pores and stagnant areas. Some of these effects can be demonstrated using the AGGR model (Chapter 1).

Of greater interest is the simulation of different mechanisms of transport into and out of aggregates. Field soils are often dry at the surface when chemicals are applied. If the chemical is applied in solution, or if irrigation is added soon after application, then solute is transported into the interior of the aggregates by both convection and diffusion. Further increments of water may bypass the chemical since molecular diffusion is the only mechanism whereby solute can transfer from the aggregate volume to the mobile interaggregate volume. Subsequent drying is usually slow, with much water lost in the vapor phase. The result of this is that solutes may enter the interior of aggregates more rapidly than they leave. Both processes (convection and diffusion) operate in field soils,

whereas diffusion is the only transport mechanism in steady state column studies.

As an example, we have simulated breakthrough of a pulse of solute (chloride and atrazine) from columns of initially dry and initially wet soil (consisting largely of 1 mm aggregates), subject to leaching at a water flux density of 500 mm/day. All of the chloride was leached within one day (Fig. 3.1), but some of the sorbing chemical remained in the aggregates after 18 days. This simulation demonstrates the large effect that sorption has on transport in aggregated soils, and, in this case, the smaller effect of initial water content of the aggregates. Differences between breakthrough from initially dry and initially wet columns increase as the aggregate diameter increases. This effect is likely to be more important in well-structured field soils than in columns of small aggregates.

DISCUSSION AND CONCLUSIONS

Sorption of pesticides by soils is a kinetic process; the rate is strongly influenced by the sample treatment. These batch sorption studies were not designed to give information regarding kinetics, but it is clear that sorption K_d values could easily range over a factor of five or more, given the effects of non-

linear sorption, shaking procedure, desorption or sorption and drying.

In this work we were more concerned with the representation of the sorption process, with a view to extrapolating it to column and field studies, rather than with the basic chemical and physical reasons for the behavior. If any measure of sorption is to be used successfully on a screening basis, then it needs to be simple to conduct and errors within a range to be expected from a routine laboratory should not impact subsequent evaluations of chemical or soil.

The two-site approach

This approach, when combined with the CDE, leads to enhanced breakthrough, tailing, explains the difference between sorbing and no-sorbing chemicals, but cannot account for physical non-equilibrium (diffusion into aggregates) if that is an important mechanism.

The multi-region/two-dimensional approach

The TRANSMIT model can be used to describe both physical and chemical non-equilibrium. There opportunity is present of basing model parameters on measurable soil composition. It accounts for diffusion into less accessible soil volumes and can simulate

sorption under transient flow conditions.

Despite much effort over the years, no firm conclusions have been reached regarding the mechanisms involved in pesticide sorption in soils, thus unambiguous, quantitative methods of predicting sorption or sorption kinetics are not available.

For modelling at larger scales it is impossible to incorporate process detail at a level which describes, for example, diffusion in a detailed fashion. Representation of kinetic processes should be the objective.

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TABLE 3.1 Properties of the soils used in this study.

1) Classification:

Caldwell Field: (Niagra silt loam (fine, mixed, mesic Aeric Ochraqualf)

Geneva: Cazenovia silt loam (fine loamy, mixed, mesic Oxyaquic Glossudalf)

2) Physical and chemical properties

Horizon	Organic matter	pH	CEC	Silt	Clay
		(CaCl ₂)	(NH ₄ Cl)		
	%		cmol/kg	%	%
Niagra A	6.0	5.7	14.9	71	18
Niagra B	3.9	5.1	12.3	72	24
Cazenovia A	4.4	5.4	11.4	37	15
Cazenovia B	3.4	6.0	12.9	32	31

TABLE 3.2. Freundlich parameters for atrazine sorption by
Caldwell Field soil.

Elapsed Time (hr)	Horizon	Freundlich parameters ($S=KC^n$)						At a water content of 0.25 kg/kg			
		K	sd(lnK)	n	sd(n)	R2	No. of samples	apparent Kd	values at C	(mg/l) =	
								1.0	0.1	0.01	0.001
ADSORPTION											
1	Top	1.22	.020	.913	.010	.998	15	1.220	1.491	1.821	2.225
3	Top	1.40	.027	.878	.011	.991	51	1.395	1.848	2.447	3.241
18-24	Top	3.00	.027	.876	.010	.993	51	2.998	3.989	5.307	7.061
42-46	Top	2.46	.017	.824	.007	.997	31	2.460	3.689	5.532	8.296
94	Top	3.07	.013	.838	.005	.999	3	3.065	4.451	6.463	9.384
1	Sub	.28	.058	.917	.030	.985	15	0.281	.340	.412	.498
3	Sub	.38	.068	.950	.029	.956	51	0.383	.430	.482	.541
18-24	Sub	.45	.049	.897	.021	.956	87	0.448	.567	.719	.912
42-46	Sub	.53	.025	.822	.012	.993	31	0.525	.790	1.191	1.794
94	Sub	.88	.033	.956	.017	.999	3	0.879	.973	1.076	1.191
DESORPTION											
Dried											
0	Top	Yes	4.18	.069	.845	.025	.991	11	4.179	5.971	8.532
2	Top	Yes	3.39	.043	.861	.016	.998	7	3.387	4.665	6.424
4	Top	Yes	4.62	.054	.916	.019	.987	29	4.618	5.604	6.799
18-24	Top	Yes	4.26	.056	.900	.019	.984	33	4.263	5.367	6.757
42-48	Top	Yes	3.29	.026	.846	.010	.998	14	3.287	4.686	6.681
0	Top	No	5.93	.094	.831	.030	.987	11	5.930	8.751	12.914
2	Top	No	5.10	.043	.866	.014	.998	7	5.104	6.949	9.460
4	Top	No	5.87	.072	.877	.023	.982	28	5.871	7.793	10.344
18-24	Top	No	4.95	.061	.889	.020	.984	32	4.953	6.395	8.258
42-48	Top	No	3.93	.028	.863	.011	.998	15	3.927	5.384	7.381
0	Sub	Yes	1.02	.087	.879	.037	.983	11	1.049	1.386	1.832
2	Sub	Yes	0.75	.061	.836	.026	.994	7	0.753	1.098	1.602
4	Sub	Yes	0.96	.096	.907	.037	.959	26	0.957	1.185	1.469
18-24	Sub	Yes	1.02	.109	.968	.041	.946	33	1.024	1.103	1.187
42-48	Sub	Yes	0.99	.129	.840	.057	.944	14	0.989	1.430	2.066
0	Sub	No	1.52	.163	.818	.060	.948	11	1.516	2.305	3.505
2	Sub	No	1.15	.079	.855	.030	.992	7	1.149	1.605	2.241
4	Sub	No	1.60	.102	.895	.036	.959	27	1.602	2.040	2.597
18-24	Sub	No	1.13	.091	.899	.031	.963	33	1.132	1.428	1.802
42-48	Sub	No	1.42	.176	.869	.078	.912	13	1.415	1.913	2.586

TABLE 3.3 Adsorption of atrazine after 24 hour equilibration, for four soils at a single concentration, showing the effect of drying on subsequent desorption.

Soil	Mean conc. after 24 h mg/dm ³	K _d value		SD	Reps	Pathway/ treatment
		Mean	Median			
		dm ³ kg ⁻¹				
Caldwell topsoil	0.38	1.79	1.85	0.34	6	Adsorption
	0.11	10.80	11.00	0.62	3	Desorption
	0.15	8.09	8.19	0.54	3	Drying/desorp
Caldwell subsoil	0.50	0.62	0.54	0.20	6	Adsorption
	0.15	5.26	5.02	0.59	3	Desorption
	0.19	4.52	4.54	0.68	3	Drying/desorp
Geneva topsoil	0.39	1.49	1.64	0.47	6	Adsorption
	0.13	6.80	6.40	0.79	3	Desorption
	0.19	5.48	5.03	1.52	3	Drying/desorp
Geneva subsoil	0.45	1.04	1.09	0.13	6	Adsorption
	0.14	6.82	6.68	0.90	3	Desorption
	0.20	4.73	4.76	0.64	3	Drying/desorp

TABLE 3.4. Adsorption of alachlor after 24 hour equilibration, for four soils, three concentrations and six replicates.

Soil	Mean conc after 24 hr.	K _d value		SD
		Mean	Median	
	mg dm ⁻³	dm ³ kg ⁻¹		
Caldwell topsoil	4.85	2.88	2.90	0.49
	0.39	4.04	3.99	0.57
	0.041	5.39	3.75	4.50
Caldwell subsoil	8.23	0.83	0.79	0.62
	0.75	0.96	1.04	0.51
	0.064	2.88	1.50	3.28
Geneva topsoil	5.70	2.01	2.08	0.78
	0.50	2.62	2.57	0.47
	0.043	4.70	4.46	1.81
Geneva subsoil	8.28	0.73	0.61	0.47
	0.62	1.47	1.46	0.49
	0.051	3.08	2.72	1.58

TABLE 3.5 Adsorption of 2,4-D after 24 hour equilibration, for four soils, three concentrations and six replicates.

Soil	Mean conc after 24 hr.	K _d value		SD
		Mean	Median	
	mg dm ⁻³	dm ³ kg ⁻¹		
Caldwell topsoil	5.5	1.39	1.44	0.15
	0.19	2.05	2.13	0.30
Caldwell subsoil	6.8	0.65	0.61	0.23
	0.27	0.70	0.60	0.27
Geneva topsoil	5.2	1.56	1.58	0.24
	0.16	2.72	2.23	1.14
Geneva subsoil	7.1	0.59	0.50	0.23
	0.25	0.90	0.85	0.19

TABLE 3.6 A Mathcad document for calculating equilibrium sorption isotherms, and partitioning between sorbed and solution phases.

Fractional water content (θ)	$\theta := .35$	Bulk density of soil (ρ , kg/dm ³)	$\rho := 1.35$
Kd value (K, L/kg)	$k := 1.0$	Freundlich exponent	$k_f := .6$
Total chemical in soil (T, mg/dm ³)	$T := 10$	Solute concentration at start (c, mg/l)	$c := 0.00$

Usually, 1) the starting concentration, or 2) the total amount of chemical is known, therefore one of these should be defined, the other set to zero.

The greater of 1) the total amount of chemical, calculated from the solution concentration, and, 2) the specified total, will be used in the calculation.

$$\text{Let Option}_1 := T \text{ and } \text{Option}_2 := \theta \cdot c + \rho \cdot k \cdot c^{k_f}$$

The total amount of chemical is the maximum of the two possible totals:

$$\text{Amount} := \begin{pmatrix} \text{Option}_1 \\ \text{Option}_2 \end{pmatrix} \quad \text{Total} := \max(\text{Amount})$$

In this particular example, $\text{Total} = 10$

Solving for concentration, with a convergence criterion (TOL):

$$\text{TOL} := \frac{\text{Total}}{100000}$$

$$\text{Estimate: } c := 1 \quad \text{Equil_conc} := \text{root}[(\text{Total} - \theta \cdot c) - \rho \cdot k \cdot c^{k_f}, c]$$

$$\begin{aligned} \text{Solution: } \text{Equil_conc} &= 11.699 & \text{Sorbed: } \text{Equil_sorb} &= k \cdot \text{Equil_conc}^{k_f} \\ & & \text{Equil_sorb} &= 4.374 \end{aligned}$$

Sorption isotherm: For concentrations $\text{Conc} := 0.1, 0.2 \dots 2 \cdot \text{Equil_conc}$ calculate the following:

$$\begin{aligned} \text{New_conc}(\text{Conc}) &:= \text{Conc} & \text{New_total}(\text{Conc}) &:= \text{Conc} \cdot \theta + \rho \cdot k \cdot \text{Conc}^{k_f} \\ \text{New_sorbed}(\text{Conc}) &:= k \cdot \text{Conc}^{k_f} & \text{Soln_frac}(\text{Conc}) &:= \frac{\text{Conc} \cdot \theta}{\text{New_total}(\text{Conc})} \\ \text{Sorb_frac}(\text{Conc}) &:= \rho \cdot k \cdot \frac{\text{Conc}^{k_f}}{\text{New_total}(\text{Conc})} & \text{Fraction} &:= 0..1 \end{aligned}$$

$$\text{Retardation_factor}(\text{Conc}) := 1 + \frac{\rho \cdot k \cdot \text{New_conc}(\text{Conc})^{k_f - 1}}{\theta}$$

$$\text{R_test_case} := 1 + \rho \cdot k \cdot \frac{\text{Equil_conc}^{k_f - 1}}{\theta}$$

Results

Soil
 $\theta = 0.35$
 $\rho = 1.35$

Chemical
 $k = 1$
 $k_f = 1$

Test case
Equil_conc = 5.882
Total = 10

Results

Soil
 $\theta = 0.35$
 $\rho = 1.35$

Chemical
 $k = 1$
 $k_f = 0.8$

Test case
Equil_conc = 8.07
Total = 10

Results

Soil
 $\theta = 0.35$
 $\rho = 1.35$

Chemical
 $k = 1$
 $k_f = 0.6$

Test case
Equil_conc = 11.699
Total = 10

TABLE 3.7. A Mathcad document displaying the rate of transfer between sorbed and solution phases, assuming a two-site sorption mechanism...

ta required:

Fraction of equilibrium sites (f)	f := .1	Fractional water content (θ)	$\theta := .86$
		Bulk density of soil (ρ , kg/dm ³)	$\rho := 0.344$
Phase transfer coefficient (α , d ⁻¹)	$\alpha := .693$	Kd value (Kd, L/kg)	kd := 3.0

Usually, i) the total amount of chemical, OR, ii) the starting concentration plus the amount sorbed on the kinetic sites, is known, therefore one of these should be defined, the other set to zero.

Total chemical in soil (T, mg/dm ³)	T := 10	Solute concentration at start (c, mg/l)	c := 0
		Sorbed on kinetic site (s2, mg/kg)	s2 := 00

If the amount of chemical in solution, plus that sorbed on the kinetic sites is greater than the specified total, then this will determine the amount of chemical per volume of soil.

$$\text{Let Total1} := T \quad \text{and} \quad \text{Total2} := \theta \cdot c + f \cdot \rho \cdot \text{kd} \cdot c + \rho \cdot s2$$

The total amount of chemical is the maximum of the two possible totals:

$$\text{Amount} := \begin{pmatrix} \text{Total1} \\ \text{Total2} \end{pmatrix} \quad \text{Total} := \max(\text{Amount})$$

In this particular example, Total = 10

Define here the time steps and time period for the calculation, for example time = 0..1 means starting at time zero and incrementing in steps of 0.01 to 1 day.

$$\text{time} := 0..1..4$$

Calculation of equilibration

For each of these times, new sorbed and solution concentrations will be calculated, using the equations described in the LEACHM manual.

$$a := \frac{(f - 1) \cdot \text{kd} \cdot \rho}{\theta + f \cdot \text{kd} \cdot \rho} - 1$$

$$b := \frac{(1 - f) \cdot \text{kd} \cdot \text{Total}}{\theta + f \cdot \text{kd} \cdot \rho}$$

$$\text{The amount of chemical sorbed on the kinetic sites is} \quad s2_new(\text{time}) := \frac{(a \cdot s2 + b) \cdot \exp(\alpha \cdot a \cdot \text{time}) - b}{a}$$

$$\text{and the concentration in solution is thus} \quad c_new(\text{time}) := \frac{\text{Total} - \rho \cdot s2_new(\text{time})}{(\theta + f \cdot \rho \cdot \text{kd})}$$

amount sorbed on the equilibrium sites depends upon the new solution concentration:

$$s1_new(\text{time}) := f \cdot c_new(\text{time}) \cdot \text{kd}$$

Fraction of chemical in each phase

$$s1_frac(time) := \frac{s1_new(time) \cdot \rho}{Total}$$

$$s2_frac(time) := \frac{s2_new(time) \cdot \rho}{Total}$$

$$c_frac(time) := \frac{c_new(time) \cdot \theta}{Total}$$

AGGATR Jan 20, 1988 1:00:28 PM

Breakthrough of atrazine from 210 mm columns.
Water flux: 500 mm/d; solute added in initial 50 mm.

AGGATR Jan 20, 1988 1:00:28 PM

Breakthrough of chloride from 210 mm columns.
Water flux: 500 mm/d; solute added in initial 50 mm.

Fig. 3.1. Simulation of effluent concentration for sorbing and non-sorbing solutes added to columns of aggregated and apedal soil.

CHAPTER FOUR

STEADY-STATE COLUMN STUDIES

The steady state column studies were intended to complement the batch sorption studies, providing information about effective K_d values in dynamic soil-water systems. Using parameter optimization procedures, analytical and numerical solutions to the convection-dispersion equation were fitted to measured breakthrough curves so as to estimate parameter values under dynamic (flowing water) rather than static conditions.

The usual procedure for studying solute breakthrough is to use relatively few soil columns, packed to ensure uniformity, and to analyze the breakthrough data in great detail. If a model having sufficient parameters is optimized, it is almost always possible to obtain good fits between prediction and experiment. This approach has highlighted the problem of non-unique parameter values. In this project we attempted to measure many breakthrough curves using simpler techniques, to examine the variability between columns and elucidate the major features of the breakthrough curves common to all columns of similar soil and chemical. In addition, a number of carefully monitored slow-flux breakthrough curves were used to try to develop a better model for describing sorption in heterogeneous media.

The objectives of this work were:

- 1) To examine the shape of atrazine, alachlor, 2,4-D and chloride breakthrough curves under relatively rapid flow conditions in topsoil and subsoil samples from Geneva and Caldwell soils.
- 2) Develop parameters for the convection dispersion equation through parameter optimization.
- 3) To examine variability between columns.

PROCEDURE

Breakthrough curves

Glass chromatographic columns (214 mm long, 25 mm inside diameter) were filled with air-dry soil. Four soils were used: A and B horizons from Caldwell Field, Ithaca, NY, and the Vegetable Research Farm, Geneva, NY). The columns were clamped vertically and saturated from below using 0.005 M CaSO_4 . Since atrazine was usually measured spectrophotometrically, and colored soluble organic matter could interfere, the columns were leached with the CaSO_4 solution until absorbance measured at 221 nm dropped to a low, apparently constant, level. The pumps used were either a constant flow syringe pump or a programmable HPLC pump (Fig. 1).

A pulse of atrazine (in CaSO_4) was introduced into the column, while maintaining a constant flow rate. Flow rates were

either 0.4 ml min^{-1} or 0.2 ml min^{-1} , corresponding to fluxes of 0.0815 mm^{-1} or $0.0407 \text{ mm min}^{-1}$. The duration of the pulse was 112 or 225 minutes, so that the same quantity of chemical was introduced into the column regardless of the flow rate.

Concentrations in the pulse were usually, but not always, 8 mg dm^{-3} (atrazine and alachlor), $100 \text{ } \mu\text{g dm}^{-3}$ (2,4-D) and $1.34 \text{ mmol dm}^{-1}$ (Cl^{-1}). Outflow from the column was led directly through a flow cell on a UV spectrophotometer (which recorded absorbance at 221 nm, and then to a fraction collector. Chloride analyses were performed on the samples from the fraction collector, using a chloridometer. Immunoassay techniques (Ohmicron Corp.) were used to analyze 2,4-D and some of the alachlor effluent samples.

Data processing

Initial analysis of the data consisted of adjustments to recorded times and volumes to account for time and volume lags between the chemical source and the column, and between the column and the spectrophotometer detector or fraction collector. Drift in the base line was accounted for by assuming that the rate of drift was constant during the duration of measurement. A single computer program (BTC.FOR, Appendix 4.1) was prepared to perform these calculations. The procedure for processing data from each column is preserved in this code. An example of the data from a single column, subject first to a slow and then to a

fast flow rate, is listed in Appendix 4.2. In all cases discussed here, both herbicide and chloride concentrations were adjusted to total to 100% recovery, since degradation was assumed negligible during the short period of measurement. Output from the BTC program consisted of absolute and relative concentrations as a function of both time and water flux (expressed as pore volumes) (Appendix 4.3). Pore volumes were calculated in two ways: from the measured mass of water in the column and from the measured dry bulk density of the column, assuming complete saturation and a particle density of 2.65 kg m^{-3} . These values did not always agree, perhaps because the particle density was less than 2.65 kg m^{-3} . The mean of the two water contents was used for all of the data discussed in this work. In addition, output files (Appendix 4.4) were generated to serve as input data files for the CXTFIT parameter optimization program (Parker and van Genuchten, 1984).

CXTFIT was used to fit the CDE, assuming linear sorption and local equilibrium. CXTFIT was modified to read parameters other than those optimized. For example, CXTFIT can optimize the value of the retardation factor (RF), but the modified version reads and prints all variables that are involved in calculating the RF, namely, the fractional water content (θ), ρ and K_d . On output θ and ρ will be the same as the input values, but K_d will be

changed to correspond to the best-fit RF value. Experimental values for all parameters in the CDE equation are known, except for dispersion coefficient and K_d values, which were fitted.

RESULTS AND DISCUSSION

Measured and fitted breakthrough curves for Cl^- , atrazine, alachlor and 2,4-D are shown graphically in Figs. 4.2 to 4.8. Fitted curves are shown as a function of time, which separates curves from different flow rates, and as a function of pore volume, which highlights the degree of retardation of the breakthrough curves. Note that the x-axis scales vary, but that the y-axis (C/C_0) always ranges from 0 to 1. Although the measured curves are scattered, they do show a certain consistency of pattern.

Chloride breakthrough curves from both A and B horizons of both soils and the herbicide breakthrough curves from both B horizons were more uniform, smoother, and had shapes typical of ideal convection-dispersion behavior. However, herbicide breakthrough curves from A horizon soils were very variable and often departed markedly from ideal CDE behavior.

Measured breakthrough curves were characterized by recording the pore volumes at which the 1st, 5th, 16th, 50th, 84th, 95th

and 99th percentiles appeared, calculated assuming 100% recovery in the measured BTC. Median values for the 16th, 50th and 84th percentile breakthrough pore volumes are plotted in Fig. 4.9. It appears as though atrazine breakthrough from the A horizon soils was retarded to the greatest extent, that alachlor was retarded to a lesser extent, and that chloride breakthrough was slightly enhanced. The single set of 2,4-D breakthrough curves (on Caldwell A horizon soil) suggested retardation similar to that of atrazine, decreasing with increasing water flow velocity. Most of the chloride BTC's showed enhance breakthrough in comparison to that predicted assuming the K_d value to be zero. There was little difference between the 0.4 and 0.2 ml min⁻¹ flow rates.

Parameter fitting for chloride tracer

Initially, the two-site/two-region CDE was fitted to the data, in the form of the CXT4 parameter-optimization program of Parker and van Genuchten (1984). Applying CXT4 to the measured breakthrough curves resulted in a wide range of parameter values, which varied widely between duplicate BTC's for the same soil and chemical. They were difficult to interpret, and were probably non-unique. The simpler single-region CXTFIT model was applied to the chloride breakthrough data to obtain best-fit dispersivity and K_d values for some of the parameters in the CDE. For CXTFIT the only unknown parameters were the retardation factor and the dispersion coefficient. Although the K_d value for Cl⁻ would be

expected to be zero, preferential flow and negative adsorption may lead to apparent K_d values less than unity. The best-fit RF (or apparent K_d) value for Cl^- was used as a reference for evaluating the retardation of atrazine and alachlor.

Parameters other than K_d and bulk density were either measured (water content, bulk density), or imposed (water flux density, pulse length). CXTFIT optimized the retardation factor,

$$RF = 1 + \rho K_d / \theta \quad (4.1)$$

thus any combination of ρ , K_d and θ leading to the same 'whole-soil' RF value will give breakthrough curves of identical shape, providing that the water flux density is the same. Thus if the flowing solution explores only part of the whole soil volume, a reduction in effective θ will increase pore water velocity (v) in the mobile soil volume, and the apparent RF will decrease. Physically, this mechanism explains enhanced breakthrough, but, calculated on a whole soil basis, apparent K_d values may be negative. An example is shown in Table 4.1, showing combinations of θ , q , and K_d which lead to identical breakthrough curves having the same dispersivity values.

Data in Table 4.1 suggest that chloride did not move through the whole soil volume. Fixing all parameters except λ resulted in high λ values (columns a). Lower λ values are obtained if either or all of q , θ or K_d are allowed to float

(columns b, c, d). Clearly, q cannot vary if the pulse length is constant, otherwise the solute mass balance will change. Higher pore water velocities, at the same water flux, can be obtained by reducing the water content (columns c). At the measured water content a good fit is obtained with a negative K_d value (columns d). Both columns c and d indicate that the chloride penetrates only part of the soil volume. This is probably caused by stagnant regions in the column into which solute movement is limited by diffusion. Pore water velocity was inversely related to the proportion of the water volume explored. Physically, a negative K_d value implies negative adsorption, but there is no reason to believe that negative adsorption would decrease as pore water velocity increases. Assuming that the 'mobile' phase corresponds to either 0.38 (fast flow) or 0.45 (slow flow), compared to a total water content of 0.521, implies actual pore water velocities in the mobile region of 0.2144 and 0.090 cm min⁻¹.

Both increased dispersivity or decreased water content will advance the start of breakthrough; the difference between them is that decreasing the water content leads to an increase in peak height, whereas increasing dispersivity leads to broadening and lowering of the peak.

Herbicide breakthrough curves

CXTFIT was applied to the atrazine, alachlor and 2,4-D breakthrough curves, allowing only the RF and dispersion coefficient to be fitted. As with the chloride data, the breakthrough concentrations were adjusted to total 100% recovery. Since the water content and bulk density were fixed for Cl^- , atrazine and alachlor, differences in the RF were reflected as differences in K_d value. Negative K_d values merely indicate enhanced breakthrough, and do not have any other physical significance. Results of fitting CXTFIT to all breakthrough curves for which both Cl^- and a herbicide were measured concurrently are shown in Table 4.2.

Several factors complicate the determination of sorption parameters. First, the batch studies reported in the previous chapter suggest that sorption is best described by a Freundlich isotherm, whereas CXTFIT assumes a linear isotherm. Second, the batch studies indicated that sorption was slow, so sorption in the columns is likely to depend upon the flow rate. Third, any fitted K_d value has to be adjusted to reflect the actual volume of soil accessible to the chemical.

Applying CXTFIT using the measured water contents led to the prediction of K_d values lower than measured in the batch studies. These results indicate that access to all sorption sites was

limited, probably owing to slow diffusion into aggregates or stagnant areas. The batch studies showed that equilibrium sorption required about 24 hours, even with mixing and shaking. Thus local equilibrium should certainly not be expected in a column, with rapid flow, short resident times and no mixing. Retardation of the herbicides relative to that of chloride are shown in Fig. 4.10. These data emphasize the variability found between columns of the same soil, and the much larger differences between soils and chemicals. All breakthrough curve data for which both herbicide and Cl data were available are summarized in Table 4.2.

Simulating the breakthrough curves

The TRANSMIT model (Hutson and Wagenet, 1995) can account for the wide range of breakthrough curves shapes measured, using a multi-region approach. The examples shown for that model were simulation using the experimental conditions used here. There is no means of knowing exactly how the geometry of any particular column should be defined. The value of the TRANSMIT simulations lie in the fact that they demonstrate how easily differently-shaped breakthrough curves can be obtained.

Fig. 4.11 shows breakthrough curves predicted using several different assumptions regarding parameter values using the single region CDE-based LEACHM model (Hutson and Wagenet, 1993). These

simulated breakthrough curves (Fig. 4.11) show how easily very differently shaped breakthrough curves can be obtained using data extracted from the batch study measurements.

The two-dimensional form of the TRANSMIT model (Chapter 2) was used to simulate breakthrough from soil columns having properties similar to those used in this work. The advantage of this model over the AGGR model is that it can be applied to transient and unsaturated conditions as well as to steady-state column flow. The disadvantages are that only a single aggregate size is reflected and that currently the geometry of the aggregate does not correspond exactly to spherical or cubic shapes.

AGGR, the steady-state flow version of the DSB model (Scow and Hutson, 1992), can also simulate curves having a range similar to those measured. The shape of the breakthrough curves (Chapter 1) depend on the distribution of aggregate sizes, and assumptions regarding sorption and diffusion in the aggregates.

CONCLUSIONS

It is possible to measure breakthrough curves on a carefully packed soil column, and subsequently fit one of a number of models, and by parameter optimization, obtain parameter values

which enable breakthrough curves to be fitted quite accurately. However, these parameter values will probably not apply to replicate columns of the same soil, unless great care has been taken to pack the column in an identical manner. Doing this is of doubtful value, as the column, packed or undisturbed, is unlikely to be representative of a natural soil. Another shortcoming of column studies is that the flow regime is usually saturated and steady-state. This means that there are no matric potential differences between adjacent volume elements within the column which can be responsible for convective flow of solute from one region to another. Thus the entry of solute into more stagnant or 'immobile' areas is restricted in comparison to what is likely in the field when water infiltrates into an unsaturated soil.

REFERENCES

Hutson, J.L. and R.J. Wagenet. 1995. A multi-region model describing water flow and solute transport in heterogeneous soils. (in press, Soil Sci. Soc. Am. J.)

Parker, J.C. and M. Th. van Genuchten. 1984. Determining transport parameters from laboratory and field tracer experiments. Bull. 84-3, VA Agric. Exp. Stn., Blacksburg, VA. 96 pp.

Table 4.1. CDE parameter values obtained using CXTFIT.

(Boldface indicates a fixed value, the others were fitted.)

	Fast flow				Slow flow			
	a	b	c	d	a	b	c	d
θ	0.5209	0.5209	0.3801	0.5209	0.5209	0.5209	0.4500	0.5209
q	0.0815	0.1123	0.0815	0.0815	0.0407	0.0471	0.0407	0.0407
λ	192	111	112	111	64	47	47	47
K_d	0	0	0	-0.112	0	0	0	-0.056
R^2	0.726	.998	.998	.998	0.864	.982	.982	.982

Table 4.2. Parameter optimization data for all complete breakthrough curve sets.

Column	Code*	θ	ρ kg/dm ³	v cm/min	λ cm	Kd	RF	R2	Column	Code	λ cm	Kd	RF	R2	RFherb/RFCl of herb
3201	1	0.580	1.18	0.082	11.17	1.37	3.78	0.96	3301	4	2.55	-0.19	0.62	0.98	6.10
3202	1	0.580	1.18	0.041	3.37	0.29	1.58	0.99	3302	4	4.32	-0.12	0.76	1.00	2.09
3601	1	0.551	1.22	0.082	1.91	0.36	1.79	0.93	3701	4	3.55	-0.09	0.80	0.98	2.25
3603	1	0.551	1.22	0.041	2.9	0.35	1.76	0.79	3701	4	3.55	-0.09	0.80	0.98	2.21
3801	1	0.517	1.23	0.082	0.75	1.55	4.69	0.95	3901	4	0.11	-0.02	0.94	0.98	4.97
3803	1	0.547	1.23	0.041	0.81	1.00	3.25	0.89	3901	4	0.11	-0.02	0.94	0.98	3.44
3602	2	0.551	1.22	0.082	1.19	0.43	1.94	0.93	3702	4	3.39	-0.07	0.85	0.99	2.27
3604	2	0.551	1.22	0.041	2.63	0.37	1.81	0.69	3702	4	3.39	-0.07	0.85	0.99	2.12
3802	2	0.542	1.23	0.082	0.36	1.78	5.05	0.91	3902	4	1.09	-0.00	0.99	1.00	5.10
3804	2	0.547	1.23	0.041	1.06	1.11	3.49	0.70	3902	4	1.09	-0.00	0.99	1.00	3.53
6401	2	0.487	1.17	0.082	0.23	0.04	1.09	0.97	6501	4	0.28	0.05	1.11	0.96	0.96
6402	2	0.487	1.17	0.041	0.76	0.06	1.14	0.97	6502	4	0.92	0.06	1.15	0.95	0.99
6601	2	0.579	1.15	0.082	1.86	0.12	1.25	0.92	6701	4	1.78	0.20	1.39	0.85	0.90
6801	2	0.490	1.13	0.082	6.33	0.15	1.35	0.97	6901	4	1.32	-0.09	0.82	0.99	1.64
6802	2	0.533	1.13	0.041	1.29	0.03	1.07	1.00	6902	4	1.25	-0.05	0.90	1.00	1.19
4002	3	0.563	1.21	0.041	7.62	1.36	3.91	0.93	4102	4	1.9	-0.04	0.91	1.00	4.31
4003	3	0.563	1.21	0.020	4.52	1.09	3.33	0.93	4103	4	1.46	-0.06	0.87	1.00	3.84
2401	5	0.563	1.31	0.082	3.95	-0.03	0.94	1.00	2501	8	1.73	-0.12	0.72	0.99	1.31
2402	5	0.563	1.31	0.041	2.36	0.11	1.25	1.00	2502	8	1.57	-0.06	0.86	0.99	1.46
2601	5	0.666	1.20	0.082	2.18	-0.13	0.76	1.00	2701	8	2.75	-0.22	0.61	0.98	1.25
2602	5	0.666	1.20	0.041	3.29	-0.13	0.77	0.99	2702	8	3.29	-0.17	0.69	0.97	1.12
2801	5	0.556	1.26	0.082	7.72	-0.10	0.78	1.00	2901	8	9.34	-0.13	0.70	1.00	1.12
2802	5	0.556	1.26	0.041	5.59	0.07	1.15	1.00	2902	8	4.08	-0.07	0.84	0.98	1.37
3001	5	0.537	1.32	0.041	2.71	-0.09	0.78	1.00	3101	8	4.53	0.08	1.20	0.92	0.65
3002	5	0.537	1.32	0.082	9.22	-0.01	0.97	0.99	3102	8	0.73	-0.18	0.56	0.59	1.72
3003	5	0.537	1.32	0.082	5.39	-0.05	0.87	1.00	3103	8	12.63	-0.10	0.76	0.96	1.15
5801	6	0.498	1.20	0.082	11.57	0.33	1.80	0.97	5901	8	24.75	0.54	2.30	0.92	0.78
6001	6	0.465	1.28	0.082	9.92	0.28	1.78	0.95	6101	8	4.72	0.08	1.22	0.98	1.46
6201	6	0.567	1.28	0.062	0.87	-0.09	0.79	0.99	6301	8	1.06	-0.09	0.80	0.98	0.99
6202	6	0.567	1.28	0.041	2.1	-0.06	0.87	1.00	6302	8	1.14	-0.14	0.68	0.98	1.28
5401	9	0.485	1.41	0.082	2.63	0.90	3.62	0.99	5501	12	1.58	0.04	1.12	0.99	3.23
5402	9	0.476	1.41	0.041	0.55	0.92	3.72	0.68	5502	12	1.05	0.03	1.10	0.96	3.28
5601	9	0.594	1.27	0.082	1.32	1.49	4.18	0.95	5701	12	1.98	0.01	1.02	0.93	4.07
5602	9	0.462	1.27	0.041	3.75	1.77	5.84	0.86	5702	12	0.93	-0.09	0.80	0.95	7.32
4801	13	0.452	1.26	0.082	8.03	0.48	2.35	0.96	4901	16	3.5	-0.03	0.92	0.99	2.54
4802	13	0.452	1.26	0.041	5.27	0.36	2.01	0.99	4902	16	3.06	-0.05	0.86	0.99	2.33
5001	13	0.497	1.27	0.082	3.13	0.29	1.74	1.00	5101	16	0.91	-0.06	0.84	1.00	2.08
5002	13	0.497	1.27	0.041	1.73	0.42	2.08	0.99	5102	16	1.3	0.02	1.06	0.99	1.96
5202	13	0.586	1.38	0.041	3.48	0.24	1.55	1.00	5302	16	1.92	-0.09	0.78	0.99	1.98
7401	13	0.478	1.38	0.082	1.45	-0.03	0.92	0.99	7501	16	1.67	-0.03	0.91	1.00	1.00
7402	13	0.478	1.38	0.041	2.26	-0.00	0.99	1.00	7502	16	1.88	-0.02	0.94	1.00	1.05
7001	14	0.569	1.27	0.082	1.54	-0.16	0.64	1.00	7101	16	3.01	-0.14	0.70	0.99	0.92
7002	14	0.569	1.27	0.041	4.35	0.06	1.13	0.93	7102	16	2.05	-0.09	0.81	0.99	1.39
7201	14	0.475	1.17	0.082	1.47	-0.06	0.85	1.00	7301	16	1.89	-0.07	0.82	1.00	1.04
7202	14	0.475	1.17	0.041	1.44	-0.06	0.85	1.00	7302	16	1.33	-0.07	0.82	1.00	1.05

*Code	Location	Horizon	Chemical
1	Caldwell	A	Atrazine
2	Caldwell	A	Alachlor
3	Caldwell	A	2,4-D
4	Caldwell	A	Chloride
5	Caldwell	B	Atrazine
6	Caldwell	B	Alachlor
8	Caldwell	B	Chloride
9	Geneva	A	Atrazine
10	Geneva	A	Alachlor
12	Geneva	A	Chloride
13	Geneva	B	Atrazine
14	Geneva	B	Alachlor
16	Geneva	B	Chloride

Fig. 4.1. Schematic of apparatus used to measure breakthrough of solutes.

RTS Dec 14, 1994 9:22:27 PM

Atrazine breakthrough curves, measured.
Caldwell A horizon.

RTS Dec 14, 1994 9:22:27 PM

Atrazine breakthrough curves, measured.
Caldwell B horizon.

RTS Dec 14, 1994 9:22:27 PM

Atrazine breakthrough curves, fitted.
Caldwell A horizon.

RTS Dec 14, 1994 9:22:27 PM

Atrazine breakthrough curves, fitted.
Caldwell B horizon.

RTS Dec 14, 1994 9:22:27 PM

Atrazine breakthrough curves, fitted.
Caldwell A horizon.

RTS Dec 14, 1994 9:22:27 PM

Atrazine breakthrough curves, fitted.
Caldwell B horizon.

Fig. 4.2. Breakthrough curves for atrazine, measured on soil from Caldwell Field.

MSARL Dns 15, 1994 07:02:00 AM

Alachlor breakthrough curves, measured.
Caldwell A horizon.

MSARL Dns 15, 1994 07:02:00 AM

Alachlor breakthrough curves, measured.
Caldwell B horizon.

PVS Dns 15, 1994 07:02:00 AM

Alachlor breakthrough curves, fitted.
Caldwell A horizon.

PVS Dns 15, 1994 10:02:00 AM

Alachlor breakthrough curves, fitted.
Caldwell B horizon.

PVS Dns 15, 1994 07:02:00 AM

Alachlor breakthrough curves, fitted.
Caldwell A horizon.

PVS Dns 15, 1994 07:02:00 AM

Alachlor breakthrough curves, fitted.
Caldwell B horizon.

Fig. 4.3. Breakthrough curves for alachlor, measured on soil from Caldwell Field.

Sun Dec 15, 1996 11:07:09 AM

Chloride breakthrough curves, measured.
Caldwell A horizon.

Sun Dec 15, 1996 11:07:09 AM

Chloride breakthrough curves, measured.
Caldwell B horizon.

Sun Dec 15, 1996 11:07:09 AM

Chloride breakthrough curves, fitted.
Caldwell A horizon. Chloride breakthrough curves, fitted.
Caldwell B horizon.

Sun Dec 15, 1996 11:07:09 AM

Chloride breakthrough curves, fitted.
Caldwell A horizon.

Sun Dec 15, 1996 11:07:09 AM

Chloride breakthrough curves, fitted.
Caldwell B horizon.

Fig. 4.4. Breakthrough curves for chloride, measured on soil from Caldwell Field.

PVT3.Dat, 15, 1994, 1:00:01 PM

Atrazine breakthrough curves, measured.
Geneva A horizon.

PVT3.Dat, 15, 1994, 1:00:01 PM

Atrazine breakthrough curves, measured.
Geneva B horizon.

PVT3.Dat, 15, 1994, 1:00:01 PM

Atrazine breakthrough curves, fitted.
Geneva A horizon.

PVT3.Dat, 15, 1994, 1:00:01 PM

Atrazine breakthrough curves, fitted.
Geneva B horizon.

PVT3.Dat, 15, 1994, 1:00:01 PM

Atrazine breakthrough curves, fitted.
Geneva A horizon.

PVT3.Dat, 15, 1994, 1:00:01 PM

Atrazine breakthrough curves, fitted.
Geneva B horizon.

Fig. 4.5. Breakthrough curves for atrazine, measured on soil from Geneva Research Farm.

Plot 6 Dec 15, 1984 12:00:01 PM

Alachlor breakthrough curves, measured.
Geneva A horizon.

Plot 6 Dec 15, 1984 12:00:02 PM

Alachlor breakthrough curves, measured.
Geneva B horizon.

Plot 6 Dec 15, 1984 12:00:03 PM

Alachlor breakthrough curves, fitted.
Geneva A horizon.

Plot 6 Dec 15, 1984 12:00:04 PM

Alachlor breakthrough curves, fitted.
Geneva B horizon.

Plot 6 Dec 15, 1984 12:00:05 PM

Alachlor breakthrough curves, fitted.
Geneva A horizon.

Plot 6 Dec 15, 1984 12:00:06 PM

Alachlor breakthrough curves, fitted.
Geneva B horizon.

Fig. 4.6. Breakthrough curves for alachlor, measured on soil from Geneva Research Farm.

MSBATE.Dat, 15, 1994, 2:08:04 PM

Chloride breakthrough curves, measured.
Geneva A horizon.

MSBATE.Dat, 15, 1994, 2:08:04 PM

Chloride breakthrough curves, measured.
Geneva B horizon.

MSBATE.Dat, 15, 1994, 2:08:04 PM

Chloride breakthrough curves, fitted.
Geneva A horizon.

MSBATE.Dat, 15, 1994, 2:08:04 PM

Chloride breakthrough curves, fitted.
Geneva B horizon.

MSBATE.Dat, 15, 1994, 2:08:04 PM

Chloride breakthrough curves, fitted.
Geneva A horizon.

MSBATE.Dat, 15, 1994, 2:08:04 PM

Chloride breakthrough curves, fitted.
Geneva B horizon.

Fig. 4.7. Breakthrough curves for chloride, measured on soil from Geneva Research Farm.

FILE: 4-1100 1:00:00 PM

2,4-D breakthrough curves, measured.
Caldwell A horizon.

FILE: 4-1100 1:00:00 PM

2,4-D breakthrough curves, fitted.
Caldwell A horizon.

FILE: 4-1100 1:00:00 PM

2,4-D breakthrough curves, fitted.
Caldwell A horizon.

Fig. 4.8. Breakthrough curves for 2,4-D, measured on soil from Caldwell Field.

Fig. 4.9. Median values for the 16th, 50th and 84th percentile breakthrough pore volumes.

Mobility of atrazine, alachlor and
2,4-D, relative to chloride.

CODES:

HERBICIDE	SOILS			
	Caldwell A	Field B	Geneva A	Geneva B
Atrazine	1	5	9	13
Alachlor	2	6	10	14
2,4-D	3	-	-	-

Fig. 4.10. Retardation of herbicides relative to that of chloride.

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Fig. 4.11. Breakthrough curves, simulated using LEACHP, using typical estimates for sorption parameters from Chapter 2.

Appendix 4.1. Program used to process the breakthrough data.

```

REAL ODSOIL,CUMPV1(150,10),CUMPV2(150,10),TIME1(150,10)
#,TIME2(150,10),FLUXDEN(10),RECOVERY(10)
REAL PUMPRATE(10),PULSETIME(10),CONC(150,10),VOLDDET(10)
REAL PULSEVOL(10),CUMCHEN(150,10),CONCIN(10),TIME(150,10)
REAL TOTCHEN(10)
-----
REAL P(7),p1(7),Dpv(7),dtime(7),cconc(7)
real meanc,meanco,meano,measmax
integer no(7)
-----
C-----
INTEGER IDTYPE(10),OBS(10),OBSHRT(10),ADJUST(10),IFILE(10)
CHARACTER*90 TITLE
character*90 chemicals
Character*6 CODE(10)
character*10 ccode
character file0*8,file1*12,file2*12
P1=3.14159
C File names
WRITE(*,9901)
9901 FORMAT(' ENTER INPUT DATA FILE NAME')
READ(*,9901)FILE0
8001 FORMAT(A5)
OPEN(10,FILE=FILE0,STATUS='OLD')
WRITE(*,('A')) ' Starting to read data'
C Remove or replace this section to suit desired file specification.
C Data - unit 10 Output - unit 11 For CXTFIT input - unit 12
C Additional output (not used) - units 13....
C
OPEN(9,FILE=TITLE,STATUS='UNKNOWN')
WRITE(9,9000)FILE0,'.OUT'
C
WRITE(9,9000)FILE0,'.CMT'
8000 FORMAT(A8,A4)
8003 FORMAT(A8,A2)
REWIND 9
C-----
8002 FORMAT(A12)
8000 FORMAT(A10)
READ(9,8002)FILE1
READ(9,8002)FILE2
OPEN(11,FILE=FILE1,STATUS='UNKNOWN')
WRITE(11,('A')) FILE1
C
OPEN(12,FILE=FILE2,STATUS='UNKNOWN')
WRITE(12,('A')) FILE2
C-----
READ(10,('IX'))
READ(10,('A90'))TITLE
READ(10,('COL'))COL
READ(10,('COLSOIL'))COLSOIL
READ(10,('COLSOILWAT'))COLSOILWAT
READ(10,('COLLENGTH'))COLLENGTH
READ(10,('COLDIAM'))COLDIAM
READ(10,('CAPWAT'))CAPWAT
READ(10,('VOLSOURCE'))VOLSOURCE
READ(10,('PWATER'))PWATER
READ(10,('NCHEN'))NCHEN
READ(10,('CODE(J),J=1,NCHEN'))CODE(J),J=1,NCHEN
READ(10,('A90'))chemicals
READ(10,('PUMPRATE(J),J=1,NCHEN'))PUMPRATE(J),J=1,NCHEN
READ(10,('PULSETIME(J),J=1,NCHEN'))PULSETIME(J),J=1,NCHEN
READ(10,('VOLDDET(J),J=1,NCHEN'))VOLDDET(J),J=1,NCHEN
READ(10,('IDTYPE(J),J=1,NCHEN'))IDTYPE(J),J=1,NCHEN
READ(10,('ADJUST(J),J=1,NCHEN'))ADJUST(J),J=1,NCHEN
READ(10,('IFILE(J),J=1,NCHEN'))IFILE(J),J=1,NCHEN
C Column, water and soil details
COLAREA=PI*COLDIAM*COLDIAM/4.
COLVOL=PI*COLLENGTH*COLDIAM*COLDIAM/4.
SOILMASS=COLVOL*COLSOIL
ODSOIL=SOILMASS*100./(100.+PWATER)
WATER=COLSOILWAT-ODSOIL*COL
BD=ODSOIL/COLVOL
C Pore volume and theta can be calculated from porosity or from
C measured fractional water content
PoreVOL1=COLVOL*(1.-BD/2.65)
PoreVOL2=WATER
THETA1=PoreVOL1/COLVOL
THETA2=WATER/COLVOL
DO 100 J=1,NCHEN
PULSEVOL(J)=PULSETIME(J)*PUMPRATE(J)
TOTCHEN(J)=PULSEVOL(J)*CONCIN(J)
FLUXDEN(J)=PUMPRATE(J)/COLAREA
100 CONTINUE
C-----
C Start of processing of breakthrough curves
READ(10,('NOBS'))NOBS
READ(10,('IX'))
DO 108 J=1,NCHEN
obsno(J)=0
108 OBS(J)=9999
C-----
C Read data
DO 110 I=1,NOBS
C Each column has slightly different adjustments for baseline drift
C and/or zero setting. Assume baseline drift linear over duration
C of experiment.
C-----
C Read for BTC24425
if(file0.eq.'btc24425')then
READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
write(*,('TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2),
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
conc(I,1)=conc(I,1)+239.*time(I,1)/1162.
conc(I,2)=conc(I,2)+63.*+95.*time(I,2)/1140.
endif
C-----
C Read for BTC26427
if(file0.eq.'btc26427')then
READ(10,*)TIME(I,1),DUM,dum,TIME(I,2),DUM,CONC(I,2)
#,dum,dum,dum,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4),CONC(I,1)
conc(I,2)=conc(I,2)+1020.*time(I,2)/1100.+76.
write(*,('TIME(I,1),DUM,dum,TIME(I,2),DUM,CONC(I,2)
C Read for BTC28429
if(file0.eq.'btc28429')then
READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
endif
C-----
C Read for BTC30431
if(file0.eq.'btc30431')then
READ(10,*)TIME(I,1),CONC(I,1),dum,TIME(I,2),DUM,CONC(I,2)
#,TIME(I,3),DUM,CONC(I,3),TIME(I,4),CONC(I,4),TIME(I,5)
#,CONC(I,5),TIME(I,6),CONC(I,6)
cc 48.441 is revised conversion from height to concentration
conc(I,1)=(conc(I,1)+5.)*48.441
write(*,('TIME(I,1),conc(I,1)
C-----run without this adjustment-----
ccc conc(I,2)=conc(I,2)-244.*time(I,2)/730.
endif
C-----
C Read for BTC32433
if(file0.eq.'btc32433')then
READ(10,*)TIME(I,1),DUM,conc(I,1),TIME(I,2),DUM,CONC(I,2)
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
conc(I,1)=conc(I,1)+784.*time(I,1)/1348.
C-----
conc(I,2)=conc(I,2)+11.202
write(*,('TIME(I,1),DUM,conc(I,1),TIME(I,2),DUM,CONC(I,2)
C
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
endif
C-----
C Read for BTC34435
if(file0.eq.'btc34435')then
READ(10,*)TIME(I,1),ht1,conc(I,1),TIME(I,2),ht2,CONC(I,2)
time(I,1)=time(I,1)-92.
write(*,('TIME(I,1),DUM,conc(I,1),TIME(I,2),DUM,CONC(I,2)
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
conc(I,1)=(ht1+5.*time(I,1)/(1152.-92.1))* .0096*14279.3+26.44
conc(I,2)=(ht2+4.*time(I,2)/1332.1)*.011*14279.3+26.44
endif
C-----
C Read for BTC36437 and BTC38439
if(file0.eq.'btc36437'.or.file0.eq.'btc38439')then
READ(10,*)TIME(I,1),conc(I,1),TIME(I,2),CONC(I,2)
#,TIME(I,3),conc(I,3),TIME(I,4),CONC(I,4)
#,TIME(I,5),conc(I,5),TIME(I,6),CONC(I,6)
C Subtract half time for one tube and run as though on chart.
time(I,1)=time(I,1)-5.
time(I,2)=time(I,2)-5.
time(I,3)=time(I,3)-5.
time(I,4)=time(I,4)-12.5
time(I,5)=time(I,5)-12.5
time(I,6)=time(I,6)-12.5
endif
C-----
C Read for BTC40441
if(file0.eq.'btc40441')then
READ(10,*)TIME(I,1),conc(I,1),TIME(I,2),CONC(I,2)
#,TIME(I,3),conc(I,3),TIME(I,4),CONC(I,4)
#,TIME(I,5),conc(I,5)
C Subtract half time for one tube and run as though on chart.
time(I,1)=time(I,1)-5.
time(I,2)=time(I,2)-12.5
time(I,3)=time(I,3)-12.5
time(I,4)=time(I,4)-22.5
time(I,5)=time(I,5)-22.5
endif
C-----
C Read for BTC48449
if(file0.eq.'btc48449')then
READ(10,*)TIME(I,1),DUM,CONC(I,1),DUM,CONC(I,2)
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
conc(I,1)=conc(I,1)+time(I,1)*(324.-)/1372.
time(I,2)=time(I,1)
endif
C-----
C Read for BTC50451
if(file0.eq.'btc50451')then
READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
IF(TIME(I,1).GT.0.)conc(I,1)=conc(I,1)+140.*time(I,1)/1044.
endif
C-----
C Read for BTC52453
if(file0.eq.'btc52453')then
READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
IF(TIME(I,1).GT.0.)conc(I,1)=conc(I,1)-15.7
IF(TIME(I,2).GT.0.)conc(I,2)=conc(I,2)-76.03
endif
C-----
C Read for BTC54455
if(file0.eq.'btc54455')then
READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
conc(I,1)=conc(I,1)+500.*time(I,1)*(218.-500.)/1336.
C-----reduced observations to 133-----
ccc conc(I,2)=conc(I,2)-25.*time(I,2)*(25.-1024.)/3380.
endif
C-----
C Read for BTC56457
if(file0.eq.'btc56457')then
READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
#,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
conc(I,1)=conc(I,1)+1444.
conc(I,2)=conc(I,2)+1586.
endif
C-----
C Read for BTC58459
if(file0.eq.'btc58459')then
READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),CONC(I,2)

```

```

      conc(i,1)=conc(i,1)+2463.*time(i,1)/1020.
    endif
C -----
C Read for BTC60461
  IF (file0.eq.'btc60461') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),CONC(I,2)
    conc(i,1)=conc(i,1)-146.
  endif
C -----
C Read for BTC62463
  IF (file0.eq.'btc62463') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)-219.+time(i,1)*(219.+292.)/1300.
    conc(i,2)=conc(i,2)+75.+time(i,2)*(112.-75.)/1300.
  endif
C -----
C Read for BTC64465
  IF (file0.eq.'btc64465') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)+407.+time(i,1)*(2035.-407.)/1200.
    conc(i,2)=conc(i,2)+287.
  endif
C -----
C Read for BTC66467
  IF (file0.eq.'btc66467') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),CONC(I,2)
    conc(i,1)=conc(i,1)+575.+(1438.-575.)*time(i,1)/1100.
  endif
C -----
C Read for BTC68469
  IF (file0.eq.'btc68469') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)-149.+time(i,1)*(149.+894.)/600.
    conc(i,2)=conc(i,2)+time(i,2)*74./1400.
  endif
C -----
C Read for BTC70471
  IF (file0.eq.'btc70471') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)+time(i,1)*(1191.)/500.
    conc(i,2)=conc(i,2)+238.+time(i,2)*1428./600.
  endif
C -----
C Read for BTC72473
  IF (file0.eq.'btc72473') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)+time(i,1)*755./1200.
    conc(i,2)=conc(i,2)+time(i,2)*128./1100.
  endif
C -----
  IF (file0.eq.'btc74475') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)+time(i,1)*1181./1300.
    conc(i,2)=conc(i,2)-time(i,2)*217./1300.
  endif
C -----
  DO 102 J=1,NCHEM
    IF (TIME(I,J).LT.-0.0001) OBS(J)=MIN0(I-1,OBS(J))
    CUMCHEM(I,J)=0.
  102 CONTINUE
C -----
  DO 117 J=1,NCHEM
    OBS(J)=MIN0(NOBS,OBS(J))
  117 CONTINUE
C -----
C Adjust times for period of flow from source to top of column
  DO 125 J=1,NCHEM
    DO 120 I=1,OBS(J)
      write(*,*)I,J,TIME1(I,J),VOLSOURCE,PUMPRATE(J)
      TIME1(I,J)=TIME(I,J)-VOLSOURCE/PUMPRATE(J)
    C Adjust detection time by total tubing residence time
      TIME2(I,J)=TIME(I,J)-VOLSOURCE/PUMPRATE(J)-VOLDIST(J)/PUMPRATE(J)
    C Adjust detection time by half the fraction collector residence time
      IF (IDETTYPE(J).EQ.2.AND.I.GT.1) THEN
        TIME2(I,J)=TIME2(I,J)-(TIME(I,J)-TIME(I-1,J))/2.
      ENDIF
      IF (TIME2(I,J).GE.0.) OBSNET(J)=OBSNET(J)+1
    120 CONTINUE
  125 CONTINUE
C -----
C Cumulative mass of chemical (conc * vol)
  DO 135 J=1,NCHEM
    ifgcum1=0
    ifgcum2=0
    DO 130 I=1,OBS(J)
      IF (time2(I,J).GT.0.) then
        IF (IDETTYPE(J).EQ.1) THEN
          IF (ifgcum1.eq.0) CUMCHEM(I,J)=CONC(I,J)*TIME2(I,J)*PUMPRATE(J)/2.
          IF (ifgcum1.GT.0) CUMCHEM(I,J)=CUMCHEM(I-1,J)+(CONC(I,J)
            #+CONC(I-1,J))*(TIME2(I,J)-TIME2(I-1,J))*PUMPRATE(J)/2.
          ifgcum1=1
        ENDIF
        IF (IDETTYPE(J).EQ.2) THEN
          IF (ifgcum2.eq.0) CUMCHEM(I,J)=CONC(I,J)*TIME1(I,J)*PUMPRATE(J)
          IF (ifgcum2.GT.0) CUMCHEM(I,J)=CUMCHEM(I-1,J)+CONC(I,J)
            #*(TIME1(I,J)-TIME1(I-1,J))*PUMPRATE(J)
          ifgcum2=1
        ENDIF
      ENDIF
    130 CONTINUE
  135 CONTINUE
C -----
C Adjust for 100% recovery if desired by adjusting solution concs.
    conc(i,1)=conc(i,1)+2463.*time(i,1)/1020.
    endif
  C -----
  C Read for BTC60461
  IF (file0.eq.'btc60461') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),CONC(I,2)
    conc(i,1)=conc(i,1)-146.
  endif
  C -----
  C Read for BTC62463
  IF (file0.eq.'btc62463') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)-219.+time(i,1)*(219.+292.)/1300.
    conc(i,2)=conc(i,2)+75.+time(i,2)*(112.-75.)/1300.
  endif
  C -----
  C Read for BTC64465
  IF (file0.eq.'btc64465') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)+407.+time(i,1)*(2035.-407.)/1200.
    conc(i,2)=conc(i,2)+287.
  endif
  C -----
  C Read for BTC66467
  IF (file0.eq.'btc66467') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),CONC(I,2)
    conc(i,1)=conc(i,1)+575.+(1438.-575.)*time(i,1)/1100.
  endif
  C -----
  C Read for BTC68469
  IF (file0.eq.'btc68469') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)-149.+time(i,1)*(149.+894.)/600.
    conc(i,2)=conc(i,2)+time(i,2)*74./1400.
  endif
  C -----
  C Read for BTC70471
  IF (file0.eq.'btc70471') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)+time(i,1)*(1191.)/500.
    conc(i,2)=conc(i,2)+238.+time(i,2)*1428./600.
  endif
  C -----
  C Read for BTC72473
  IF (file0.eq.'btc72473') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)+time(i,1)*755./1200.
    conc(i,2)=conc(i,2)+time(i,2)*128./1100.
  endif
  C -----
  IF (file0.eq.'btc74475') then
    READ(10,*)TIME(I,1),DUM,CONC(I,1),TIME(I,2),DUM,CONC(I,2)
    #,TIME(I,3),CONC(I,3),TIME(I,4),CONC(I,4)
    conc(i,1)=conc(i,1)+time(i,1)*1181./1300.
    conc(i,2)=conc(i,2)-time(i,2)*217./1300.
  endif
  C -----
  DO 102 J=1,NCHEM
    IF (TIME(I,J).LT.-0.0001) OBS(J)=MIN0(I-1,OBS(J))
    CUMCHEM(I,J)=0.
  102 CONTINUE
  C -----
  DO 117 J=1,NCHEM
    OBS(J)=MIN0(NOBS,OBS(J))
  117 CONTINUE
  C -----
  C Adjust times for period of flow from source to top of column
  DO 125 J=1,NCHEM
    DO 120 I=1,OBS(J)
      write(*,*)I,J,TIME1(I,J),VOLSOURCE,PUMPRATE(J)
      TIME1(I,J)=TIME(I,J)-VOLSOURCE/PUMPRATE(J)
    C Adjust detection time by total tubing residence time
      TIME2(I,J)=TIME(I,J)-VOLSOURCE/PUMPRATE(J)-VOLDIST(J)/PUMPRATE(J)
    C Adjust detection time by half the fraction collector residence time
      IF (IDETTYPE(J).EQ.2.AND.I.GT.1) THEN
        TIME2(I,J)=TIME2(I,J)-(TIME(I,J)-TIME(I-1,J))/2.
      ENDIF
      IF (TIME2(I,J).GE.0.) OBSNET(J)=OBSNET(J)+1
    120 CONTINUE
  125 CONTINUE
  C -----
  C Cumulative mass of chemical (conc * vol)
  DO 135 J=1,NCHEM
    ifgcum1=0
    ifgcum2=0
    DO 130 I=1,OBS(J)
      IF (time2(I,J).GT.0.) then
        IF (IDETTYPE(J).EQ.1) THEN
          IF (ifgcum1.eq.0) CUMCHEM(I,J)=CONC(I,J)*TIME2(I,J)*PUMPRATE(J)/2.
          IF (ifgcum1.GT.0) CUMCHEM(I,J)=CUMCHEM(I-1,J)+(CONC(I,J)
            #+CONC(I-1,J))*(TIME2(I,J)-TIME2(I-1,J))*PUMPRATE(J)/2.
          ifgcum1=1
        ENDIF
        IF (IDETTYPE(J).EQ.2) THEN
          IF (ifgcum2.eq.0) CUMCHEM(I,J)=CONC(I,J)*TIME1(I,J)*PUMPRATE(J)
          IF (ifgcum2.GT.0) CUMCHEM(I,J)=CUMCHEM(I-1,J)+CONC(I,J)
            #*(TIME1(I,J)-TIME1(I-1,J))*PUMPRATE(J)
          ifgcum2=1
        ENDIF
      ENDIF
    130 CONTINUE
  135 CONTINUE
  C -----
  C Pore volumes
  CUMPV1(I,J)=TIME2(I,J)*PUMPRATE(J)/POREVOL1
  CUMPV2(I,J)=TIME2(I,J)*PUMPRATE(J)/POREVOL2
  C Use this if average porevol is desired
  CUMPV(I,J)=(CUMPV1(I,J)+CUMPV2(I,J))/2.
  thatal=(thatal+thata2)/2.
  endif
  130 CONTINUE
  135 CONTINUE
  C -----
  C Adjust for 100% recovery if desired by adjusting solution concs.
    DO 132 J=1,NCHEM
      WRITE(*,*)J,OBS(J),recovery(j),CUMCHEM(OBS(J),J),TOTCHEM(J)
      recovery(j)=CUMCHEM(OBS(J),J)/TOTCHEM(J)
      IF (ADJUST(J).EQ.1) THEN
        DO 133 I=1,OBS(J)
          CONC(I,J)=CONC(I,J)*TOTCHEM(J)/CUMCHEM(OBS(J),J)
          CUMCHEM(I,J)=TOTCHEM(J)*CUMCHEM(I,J)/CUMCHEM(OBS(J),J)
        133 CONTINUE
      ENDIF
    132 CONTINUE
  C -----
  C Output
  DO 300 J=1,NCHEM
    WRITE(11,*)A90,'TITLE'
    WRITE(11,*) Code: ',CODE(J)
    WRITE(11,*) Actual recovery: ',recovery(j)
    WRITE(11,*) Time Conc PVL PV2 C/Co Recovery'
    DO 400 I=1,OBS(J)
      WRITE(11,91)TIME2(I,J),CONC(I,J),CUMPV1(I,J),CUMPV2(I,J)
      #,CONC(I,J)/CONCIN(J),CUMCHEM(I,J)/TOTCHEM(J)
    400 CONTINUE
  C -----
  C Calculate breakthrough curve statistics
  P(1)=.01
  P(2)=.05
  P(3)=.16
  P(4)=.50
  P(5)=.84
  P(6)=.95
  P(7)=.99
  meanco=0.
  cumppvo=0.
  timeo=0.
  cumleao=0.
  JJ=1
  nn=0
  DO 450 I=1,OBS(J)
    nn=nn+1
    cumleao=CUMCHEM(I,J)/TOTCHEM(J)
    IF (conc(I,J).GT.meanco) then
      meanco=conc(I,J)
      pvmmax=CUMPV1(I,J)
      cmax=conc(I,J)
      tmax=TIME2(I,J)
      massmax=CUMCHEM(I,J)/TOTCHEM(J)
    endif
    IF (JJ.LE.7) THEN
      JJ=JJ
    20 CONTINUE
  C -----
  DO 20 J1=JJ,7
    IF (cumleao.GE.P(J1)) THEN
      slope=(cumleao-cumleao)/(time2(I,J)-timeo)
      dtime(J1)=time2(I,J)-(cumleao-p(J1))/slope
      slope=(cumleao-cumleao)/(CUMPV1(I,J)-CUMPVo)
      dpv(J1)=CUMPV1(I,J)-(cumleao-p(J1))/slope
      Cconc(J1)=conc(I,J)
      no(J1)=nn
      JJ=J1+1
    ENDIF
  20 CONTINUE
  C -----
  ENDIF
  timeo=amax1(0.,time2(I,J))
  cumleao=CUMCHEM(I,J)/TOTCHEM(J)
  cumppvo=CUMPV1(I,J)
  meanco1=conc(I,J)
  450 continue
  C -----
  write(11,4652)
  4652 format(/, Breakthrough curve ',/)
  write(*,*)title
  write(11,*)title
  C -----
  write(11,*)CODE(J),J3=1,NCHEM
  write(11,*)chemicals
  write(11,*)
  # Code Rate Percentile Time Pore vol Conc Obs no',
  # Recovery PVL PV2'
  write(*,*)
  # Code Rate Percentile Time Pore vol Conc Obs no',
  # Recovery PVL PV2'
  DO 51 J1=1,7
    WRITE(*,99)code(j),pvmrate(j),p(j1),dtime(j1),dpv(j1),cconc(j1)
    #,no(j1),recovery(j),porevol1,porevol2
    WRITE(11,99)code(j),pvmrate(j),p(j1),dtime(j1),dpv(j1),cconc(j1)
    #,no(j1),recovery(j),porevol1,porevol2
  99 format(a6,f5.1,f7.2,f9.3,f10.3,f10.4,i8,f9.2,2f8.1)
  51 continue
  write(11,*)('/')
  300 CONTINUE
  91 format(f8.2,e10.3,2f6.2,2f9.4)
  C -----
  End of stats
  DO 1000 J=1,NCHEM
    IF (IFILE(J).EQ.1) THEN
      IF (J.EQ.1) OPEN(12,FILE=CODE(1),STATUS='UNKNOWN')
      IF (J.EQ.2) OPEN(12,FILE=CODE(2),STATUS='UNKNOWN')
      IF (J.EQ.3) OPEN(12,FILE=CODE(3),STATUS='UNKNOWN')
      IF (J.EQ.4) OPEN(12,FILE=CODE(4),STATUS='UNKNOWN')
      IF (J.EQ.5) OPEN(12,FILE=CODE(5),STATUS='UNKNOWN')
      IF (J.EQ.6) OPEN(12,FILE=CODE(6),STATUS='UNKNOWN')
      IF (J.EQ.7) OPEN(12,FILE=CODE(7),STATUS='UNKNOWN')
    C Output for cxtfit
    WRITE(12,*)CODE(J)
    write(12,*) 2 MODE: 1 - resident; 2 - effluent fluxes'
    write(12,*) 0 NREDU: 0 - input conc. not reduced'
    write(12,*) 40 MIT: Max.no. of iterations(0 - simulate'
    write(12,*) (i6,a28,a13)'OBSnet(J), NOB: No. of '
  1000 CONTINUE

```

```

$, 'observations, less than 90'
write(12,*)' 0 NSKIP: 0 Problem executed.'
$, '1 data read only'
write(12,*)' 0 NPRNT: 1 (prints input c(x,t), 0 not)'
write(12,*(f10.4,a22))'THETA1,' Theta
write(12,*(f10.3,a22))' BD,' Bulk density'
write(12,*)' 0.0 Uniform initial conc. in ',
$, 'column'
write(12,*(e10.4,10x,a22))'CONCIN(J),'Concentration in pulse'
write(12,*)' ESTIMATE Fit? Y(1)/N(0) BMIN BMAX'
write(12,*(f8.4,a22,a23))'FLUXDEN(J),' 0 0.0'
$, ' 9999.0 Flux density'
write(12,*)' 0.1 1 0.0 9999.0',
$, ' Dispersivity'
write(12,*)' 0.1 1 -1.0 9999.0',
$, ' Kd '
write(12,*(f8.3,a22,a23))'PULSETIME(J),' 0 0.0'
$, ' 9999.0 Pulse length'
write(12,*)' 0.0 0 0.0 9999.0',
$, ' 1st order k'
write(12,*)' 0.0 0 0.0 9999.0',
$, ' Zero order k'

C
write(12,*)' Obs. no. Distance Time PV '
$, 'Concentration'
ii=0
do 1100 i=1,obs(j)
if(time2(i,j).ge.0.)then
ii=ii+1
write(12,*(i7,f12.2,f13.3,e15.4))'ii,collelength,time2(i,j)
$,cumpv1(i,j),conc(i,j)
endif
1100 continue
ELSEIF(1)FILE(J).EQ.2)THEN
C Output for cxt4
rewind 9
ilength=len_trim(code(j))
ccode=code(j)
WRITE(9,*)',ccode:(ilength),'2s'
rewind 9
READ(9,*(a8))code(j)
IF(J.EQ.1)OPEN(13,FILE=CODE(1),STATUS='UNKNOWN')
IF(J.EQ.2)OPEN(13,FILE=CODE(2),STATUS='UNKNOWN')
IF(J.EQ.3)OPEN(13,FILE=CODE(3),STATUS='UNKNOWN')
IF(J.EQ.4)OPEN(13,FILE=CODE(4),STATUS='UNKNOWN')
IF(J.EQ.5)OPEN(13,FILE=CODE(5),STATUS='UNKNOWN')
IF(J.EQ.6)OPEN(13,FILE=CODE(6),STATUS='UNKNOWN')
IF(J.EQ.7)OPEN(13,FILE=CODE(7),STATUS='UNKNOWN')
WRITE(13,*)CODE(J)
write(13,*)' 4 MODE: 3 - resident; 4 - effluent fluxes'
write(13,*)' 0 NREDU: 0 - input conc. not reduced'
write(13,*)' 40 MIT: Max.no. of iterations(0 - simulate'
write(13,*(i6,a28,a13))'OBSnet(J),' NOB: No. of '
$, 'observations, less than 50'
write(13,*)' 0 NSKIP: 0 Problem executed.'
$, '1 data read only'
write(13,*)' 0 NPRNT: 1 (prints input c(x,t), 0 not)'
write(13,*(f10.2,a22))'COLLENGTH,' Column length'
write(13,*(f10.4,a22))'THETA1,' Theta
write(13,*(f10.3,a22))' BD,' Bulk density'
write(13,*)' 0.0 Uniform initial conc. in ',
$, 'column'
write(13,*(e10.4,10x,a22))'CONCIN(J),'Concentration in pulse'
write(13,*)' 0 NLIQ'
write(13,*)' ESTIMATE Fit? Y(1)/N(0) BMIN BMAX'
write(13,*(f8.4,a22,a23))'FLUXDEN(J),' 0 0.0'
$, ' 9999.0 Flux density'
write(13,*)' 0.1 1 0.0 9999.0',
$, ' Dispersivity'
write(13,*)' 0.1 1 -1.0 9999.0',
$, ' Kd '
write(13,*(f8.3,a22,a23))'PULSETIME(J),' 0 0.0'
$, ' 9999.0 Pulse length'
write(13,*)' 0.0 1 1.0 1.0',
$, ' Fraction '
write(13,*)' 0.1 1 0.0 9999.0',
$, ' Phase transfer coefficient'
write(13,*)' 0.0 0 0.0 9999.0',
$, ' PSI '

C
write(13,*)' Obs. no. Distance Time '
$, 'Concentration'
ii=0
do 1200 i=1,obs(j)
if(time2(i,j).ge.0.)then
ii=ii+1
write(13,*(i7,f12.2,f13.3,e15.4))'ii,collelength,time2(i,j)
$,conc(i,j)
endif
1200 continue
ENDIF
1000 continue
end

```

Appendix 4.2. Sample input data file for BTC.FOR. (All breakthrough data are stored in this format.

```

btc28&29          BREAKTHROUGH CURVE DATA FILE      Caldwell subsoil
Experiment:  btc 28 (2 x Atrazine) and btc 29 (2 x chloride)  3/23/92 Caldwell subsoil
260.00           Mass of empty column (g)
394.70           Mass of packed column (g)
450.955          Mass of saturated column (g)
21.4             Length of column (cm)
2.5             Diameter of column (cm)
.1              Mass of water in end caps (g)
10              Volume between chemical source and column (ml)
1.6             Air-dry soil water content (% by mass)
4              No of curves (chemicals x runs)
'28#1' '28#2'   '29#1' '29#2'   Code
Atrazine Atrazine Chloride Chloride Chemicals
0.40      0.20      0.40      .20      Pumprate (ml/minute)
112        225        112        225      Pulse time (minutes)
8000       8000       1.34       1.34     Chemical concentration (ppb;me/l)
2.32       2.32       4.85       4.85     Volume between column and detector (ml)
1           1           2           2       1: Chart read; 2: fraction collector
1           1           1           1       Adjust for 100% recovery: 0 (no), 1(yes)
1           1           1           1       Output: 1 - CXTFIT; 2 - CXT4
                    55
                    Maximum number of observations
time1      ht(mm)1      ppb1      time2      Ht2      ppb2      time3      mEq3      time4      mEq4
0           0           0           24          0           0           10          6.1           10          0
4           0           0           44          0           0           20          2.9           20          0
24          1           47.3186      64          0           0           30          0.3           30          0
44          2           94.6372      84          0           0           40          2.1           55          0
64          16.5        780.7569      104         0           0           50          10.           80          0
84          42          1987.381      124         1           43.3754      60          24.6          105         0
104         63          2981.072      144         4           173.5016     70          58.3          130         0
124         79.5        3761.829      164         9           390.3786     80          104.5         155         0
144         91.5        4329.652      184         16          694.0064     90          164.5         180         2.2
164         96          4542.586      204         24          1041.01      100         223.2         205         24.2
184         88          4164.037      224         33          1431.388     110         264.7         230         34
204         71          3359.621      244         42          1821.767     120         297.3         255         54.8
224         55          2602.523      264         50          2168.77      130         333.5         280         63.2
244         43          2034.7        284         59          2559.149     140         350.8         305         87.8
264         34.5        1632.492      304         67.5        2927.84      150         378.3         330         85.9
284         27          1277.602      324         73          3166.404     160         399.6         355         92.6
304         21.518      1018.202      344         78          3383.281     170         403.5         380         111.5
324         18          851.7348      364         81          3513.407     180         369.7         405         97.8
344         15          709.779       384         81          3513.407     190         339.9         430         98
364         12          567.8232      404         79          3426.657     200         295.8         455         83.7
384         9.5         449.5267      424         75.5        3274.843     210         254.9         480         70.3
404         7          331.2302      444         71          3079.653     220         223.2         505         65.9
424         6          283.9116      464         66          2862.776     230         177.2         530         55.4
-1          -1          -1            484         61.5        2667.587     240         155.1         555         41.3
-1          -1          -1            504         57.5        2494.086     250         133.2         580         34.2
-1          -1          -1            524         53          2298.896     260         113.1         605         25.5
-1          -1          -1            544         49          2125.395     270         101.5         630         31.9
-1          -1          -1            564         45          1951.893     280         105.1         655         14.7
-1          -1          -1            584         41.5        1800.079     290         76.2          680         20.1
-1          -1          -1            604         39          1691.641     300         71.9          705         10.6
-1          -1          -1            624         35          1518.139     310         71.5          730         12.8
-1          -1          -1            644         33          1431.388     320         59.3          755         4.2
-1          -1          -1            664         30          1301.262     330         56.5          780         10
-1          -1          -1            684         28          1214.511     340         46.7          805         13.3
-1          -1          -1            704         25          1084.385     350         48.4          830         8.8
-1          -1          -1            724         23.5        1019.322     360         42.4          855         10
-1          -1          -1            744         22          954.2588     370         39.4          880         5.3
-1          -1          -1            764         20          867.508      380         39.9          905         8.9
-1          -1          -1            784         19          824.1326     390         26.6          930         6.8
-1          -1          -1            804         17          737.3818     400         30.3          955         0.1
-1          -1          -1            824         15          650.631      410         26.7          1005        0
-1          -1          -1            844         14          607.2556     420         22            1030        5.7
-1          -1          -1            864         13          563.8802     430         15.3          1055        2.4
-1          -1          -1            884         12          520.5048     440         23.6          1080        7
-1          -1          -1            904         11          477.1294     450         14            1105        9.1
-1          -1          -1            924         10          433.754      460         20.3          1130        3.8
-1          -1          -1            944         9           390.3786     470         19            1155        0
-1          -1          -1            964         8           347.0032     480         18.7          1180        6.3
-1          -1          -1            984         8           347.0032     490         16.6          1205        2.9
-1          -1          -1           1004         7           303.6278     500         9.9           1230        1.3
-1          -1          -1           1024         6.5        281.9401     510         7.6           1255        4.3
-1          -1          -1           1044         6           260.2524     520         7.7           1280        1

```

Appendix 4.3: Sample output from BTC.FOR, showing processed breakthrough data.

btc28&29.OUT

Experiment: btc 28 (2 x Atrazine) and btc 29 (2 x chloride) 3/23/92 Caldwell subsoil

Code: 28#1

Actual recovery : 8.393539E-01

Time	Conc	PV1	PV2	C/Co	Recovery
-30.80	.000E+00	.00	.00	.0000	.0000
-26.80	.000E+00	.00	.00	.0000	.0000
-6.80	.564E+02	.00	.00	.0070	.0000
13.20	.113E+03	.09	.09	.0141	.0008
33.20	.930E+03	.23	.23	.1163	.0125
53.20	.237E+04	.38	.36	.2960	.0493
73.20	.355E+04	.52	.50	.4440	.1153
93.20	.448E+04	.66	.64	.5602	.2050
113.20	.516E+04	.80	.78	.6448	.3126
133.20	.541E+04	.94	.91	.6765	.4306
153.20	.496E+04	1.08	1.05	.6201	.5463
173.20	.400E+04	1.22	1.19	.5003	.6464
193.20	.310E+04	1.36	1.32	.3876	.7257
213.20	.242E+04	1.51	1.46	.3030	.7873
233.20	.194E+04	1.65	1.60	.2431	.8361
253.20	.152E+04	1.79	1.73	.1903	.8748
273.20	.121E+04	1.93	1.87	.1516	.9053
293.20	.101E+04	2.07	2.01	.1268	.9302
313.20	.846E+03	2.21	2.15	.1057	.9509
333.20	.677E+03	2.35	2.28	.0846	.9679
353.20	.536E+03	2.49	2.42	.0669	.9814
373.20	.395E+03	2.64	2.56	.0493	.9918
393.20	.338E+03	2.78	2.69	.0423	1.0000

Breakthrough curve

Experiment: btc 28 (2 x Atrazine) and btc 29 (2 x chloride) 3/23/92 Caldwell subsoil

Code	Rate	Percentile	Time	Pore vol	Conc	Obs no	Recovery	PV1	PV2
28#1	.4	.01	28.955	.204	930.1880	5	.84	55.0	58.4
28#1	.4	.05	53.419	.377	3551.6270	7	.84	55.0	58.4
28#1	.4	.16	83.162	.587	4481.8150	8	.84	55.0	58.4
28#1	.4	.50	145.195	1.025	4961.0030	11	.84	55.0	58.4
28#1	.4	.84	235.229	1.661	1522.1260	16	.84	55.0	58.4
28#1	.4	.95	312.310	2.205	845.6254	19	.84	55.0	58.4
28#1	.4	.99	369.693	2.611	394.6252	22	.84	55.0	58.4

Experiment: btc 28 (2 x Atrazine) and btc 29 (2 x chloride) 3/23/92 Caldwell subsoil
Code: 28#2

Actual recovery : 7.913600E-01

Time	Conc	PV1	PV2	C/Co	Recovery
-37.60	.000E+00	.00	.00	.0000	.0000
-17.60	.000E+00	.00	.00	.0000	.0000
2.40	.000E+00	.01	.01	.0000	.0000
22.40	.000E+00	.08	.08	.0000	.0000
42.40	.000E+00	.15	.15	.0000	.0000
62.40	.548E+02	.22	.21	.0069	.0003
82.40	.219E+03	.29	.28	.0274	.0018
102.40	.493E+03	.36	.35	.0617	.0058
122.40	.877E+03	.43	.42	.1096	.0134
142.40	.132E+04	.50	.49	.1644	.0256
162.40	.181E+04	.57	.56	.2261	.0429
182.40	.230E+04	.64	.62	.2878	.0658
202.40	.274E+04	.71	.69	.3426	.0938
222.40	.323E+04	.79	.76	.4042	.1270
242.40	.370E+04	.86	.83	.4625	.1655
262.40	.400E+04	.93	.90	.5002	.2083
282.40	.428E+04	1.00	.97	.5344	.2543
302.40	.444E+04	1.07	1.04	.5550	.3027
322.40	.444E+04	1.14	1.10	.5550	.3520

342.40	.433E+04	1.21	1.17	.5413	.4007
362.40	.414E+04	1.28	1.24	.5173	.4478
382.40	.389E+04	1.35	1.31	.4864	.4924
402.40	.362E+04	1.42	1.38	.4522	.5341
422.40	.337E+04	1.49	1.45	.4214	.5729
442.40	.315E+04	1.56	1.52	.3940	.6092
462.40	.290E+04	1.63	1.58	.3631	.6428
482.40	.269E+04	1.70	1.65	.3357	.6739
502.40	.247E+04	1.77	1.72	.3083	.7025
522.40	.227E+04	1.84	1.79	.2843	.7288
542.40	.214E+04	1.92	1.86	.2672	.7533
562.40	.192E+04	1.99	1.93	.2398	.7759
582.40	.181E+04	2.06	2.00	.2261	.7966
602.40	.164E+04	2.13	2.06	.2055	.8158
622.40	.153E+04	2.20	2.13	.1918	.8334
642.40	.137E+04	2.27	2.20	.1713	.8496
662.40	.129E+04	2.34	2.27	.1610	.8643
682.40	.121E+04	2.41	2.34	.1507	.8782
702.40	.110E+04	2.48	2.41	.1370	.8910
722.40	.104E+04	2.55	2.47	.1302	.9029
742.40	.932E+03	2.62	2.54	.1165	.9138
762.40	.822E+03	2.69	2.61	.1028	.9236
782.40	.767E+03	2.76	2.68	.0959	.9324
802.40	.713E+03	2.83	2.75	.0891	.9406
822.40	.658E+03	2.90	2.82	.0822	.9482
842.40	.603E+03	2.97	2.89	.0754	.9552
862.40	.548E+03	3.04	2.95	.0685	.9616
882.40	.493E+03	3.12	3.02	.0617	.9674
902.40	.438E+03	3.19	3.09	.0548	.9726
922.40	.438E+03	3.26	3.16	.0548	.9775
942.40	.384E+03	3.33	3.23	.0480	.9820
962.40	.356E+03	3.40	3.30	.0445	.9861
982.40	.329E+03	3.47	3.37	.0411	.9900
1002.40	.329E+03	3.54	3.43	.0411	.9936
1022.40	.274E+03	3.61	3.50	.0343	.9970
1042.40	.274E+03	3.68	3.57	.0343	1.0000

Breakthrough curve

Experiment: btc 28 (2 x Atrazine) and btc 29 (2 x chloride) 3/23/92 Caldwell subsoil

Code	Rate	Percentile	Time	Pore vol	Conc	Obs no	Recovery	PV1	PV2
28#2	.2	.01	113.472	.401	876.9794	9	.79	55.0	58.4
28#2	.2	.05	168.587	.595	2302.0710	12	.79	55.0	58.4
28#2	.2	.16	239.545	.846	3699.7580	15	.79	55.0	58.4
28#2	.2	.50	386.050	1.363	3617.5390	23	.79	55.0	58.4
28#2	.2	.84	630.536	2.226	1370.2800	35	.79	55.0	58.4
28#2	.2	.95	827.443	2.921	602.9233	45	.79	55.0	58.4
28#2	.2	.99	982.666	3.469	328.8673	53	.79	55.0	58.4

Experiment: btc 28 (2 x Atrazine) and btc 29 (2 x chloride) 3/23/92 Caldwell subsoil
Code: 29#1

Actual recovery : 409.628300						
Time	Conc	PV1	PV2	C/Co	Recovery	
-27.13	.149E-01	.00	.00	.0111	.0000	
-22.13	.708E-02	.00	.00	.0053	.0000	
-12.12	.732E-03	.00	.00	.0005	.0000	
-2.12	.513E-02	.00	.00	.0038	.0000	
7.88	.244E-01	.06	.05	.0182	.0041	
17.88	.601E-01	.13	.12	.0448	.0081	
27.88	.142E+00	.20	.19	.1062	.0176	
37.88	.255E+00	.27	.26	.1904	.0345	
47.88	.402E+00	.34	.33	.2997	.0613	
57.88	.545E+00	.41	.40	.4066	.0976	
67.88	.646E+00	.48	.47	.4822	.1407	
77.88	.726E+00	.55	.53	.5416	.1890	
87.88	.814E+00	.62	.60	.6076	.2433	
97.88	.856E+00	.69	.67	.6391	.3003	
107.88	.924E+00	.76	.74	.6892	.3619	
117.88	.976E+00	.83	.81	.7280	.4269	
127.88	.985E+00	.90	.88	.7351	.4925	

137.88	.903E+00	.97	.94	.6735	.5526
147.88	.830E+00	1.04	1.01	.6192	.6079
157.88	.722E+00	1.11	1.08	.5389	.6561
167.88	.622E+00	1.19	1.15	.4644	.6975
177.88	.545E+00	1.26	1.22	.4066	.7338
187.88	.433E+00	1.33	1.29	.3228	.7626
197.88	.379E+00	1.40	1.36	.2826	.7879
207.88	.325E+00	1.47	1.42	.2427	.8095
217.88	.276E+00	1.54	1.49	.2060	.8279
227.88	.248E+00	1.61	1.56	.1849	.8444
237.88	.257E+00	1.68	1.63	.1915	.8615
247.88	.186E+00	1.75	1.70	.1388	.8739
257.88	.176E+00	1.82	1.77	.1310	.8856
267.88	.175E+00	1.89	1.84	.1303	.8973
277.88	.145E+00	1.96	1.90	.1080	.9069
287.88	.138E+00	2.03	1.97	.1029	.9161
297.88	.114E+00	2.10	2.04	.0851	.9237
307.88	.118E+00	2.17	2.11	.0882	.9316
317.88	.104E+00	2.24	2.18	.0772	.9385
327.88	.962E-01	2.32	2.25	.0718	.9449
337.88	.974E-01	2.39	2.32	.0727	.9514
347.88	.649E-01	2.46	2.38	.0485	.9557
357.88	.740E-01	2.53	2.45	.0552	.9606
367.88	.652E-01	2.60	2.52	.0486	.9650
377.88	.537E-01	2.67	2.59	.0401	.9685
387.88	.374E-01	2.74	2.66	.0279	.9710
397.88	.576E-01	2.81	2.73	.0430	.9749
407.88	.342E-01	2.88	2.79	.0255	.9771
417.88	.496E-01	2.95	2.86	.0370	.9804
427.88	.464E-01	3.02	2.93	.0346	.9835
437.88	.457E-01	3.09	3.00	.0341	.9866
447.88	.405E-01	3.16	3.07	.0302	.9893
457.88	.242E-01	3.23	3.14	.0180	.9909
467.88	.186E-01	3.30	3.21	.0138	.9921
477.88	.188E-01	3.37	3.27	.0140	.9934
487.88	.464E-01	3.45	3.34	.0346	.9965
497.88	.320E-01	3.52	3.41	.0239	.9986
507.88	.210E-01	3.59	3.48	.0157	1.0000

Breakthrough curve

Experiment: btc 28 (2 x Atrazine) and btc 29 (2 x chloride) 3/23/92 Caldwell subsoil

Code	Rate	Percentile	Time	Pore vol	Conc	Obs no	Recovery	PV1	PV2
29#1	.4	.01	19.912	.141	.1423	7	409.63	55.0	58.4
29#1	.4	.05	43.649	.308	.4016	9	409.63	55.0	58.4
29#1	.4	.16	71.872	.508	.7258	12	409.63	55.0	58.4
29#1	.4	.50	129.121	.912	.9025	18	409.63	55.0	58.4
29#1	.4	.84	225.182	1.590	.2478	27	409.63	55.0	58.4
29#1	.4	.95	335.774	2.371	.0974	38	409.63	55.0	58.4
29#1	.4	.99	452.343	3.194	.0242	50	409.63	55.0	58.4

Experiment: btc 28 (2 x Atrazine) and btc 29 (2 x chloride) 3/23/92 Caldwell subsoil
Code: 29#2

Actual recovery : 111.061400

Time	Conc	PV1	PV2	C/Co	Recovery
-64.25	.000E+00	.00	.00	.0000	.0000
-59.25	.000E+00	.00	.00	.0000	.0000
-49.25	.000E+00	.00	.00	.0000	.0000
-31.75	.000E+00	.00	.00	.0000	.0000
-6.75	.000E+00	.00	.00	.0000	.0000
18.25	.000E+00	.06	.06	.0000	.0000
43.25	.000E+00	.15	.15	.0000	.0000
68.25	.000E+00	.24	.23	.0000	.0000
93.25	.198E-01	.33	.32	.0148	.0016
118.25	.224E+00	.42	.41	.1673	.0202
143.25	.306E+00	.51	.49	.2285	.0456
168.25	.493E+00	.59	.58	.3682	.0865
193.25	.569E+00	.68	.66	.4247	.1337
218.25	.791E+00	.77	.75	.5900	.1993
243.25	.773E+00	.86	.83	.5772	.2634

268.25	.834E+00	.95	.92	.6222	.3325
293.25	.100E+01	1.04	1.00	.7492	.4158
318.25	.881E+00	1.12	1.09	.6572	.4888
343.25	.882E+00	1.21	1.18	.6585	.5620
368.25	.754E+00	1.30	1.26	.5624	.6245
393.25	.633E+00	1.39	1.35	.4724	.6769
418.25	.593E+00	1.48	1.43	.4428	.7261
443.25	.499E+00	1.56	1.52	.3723	.7675
468.25	.372E+00	1.65	1.60	.2775	.7983
493.25	.308E+00	1.74	1.69	.2298	.8239
518.25	.230E+00	1.83	1.78	.1713	.8429
543.25	.287E+00	1.92	1.86	.2143	.8667
568.25	.132E+00	2.01	1.95	.0988	.8777
593.25	.181E+00	2.09	2.03	.1351	.8927
618.25	.954E-01	2.18	2.12	.0712	.9006
643.25	.115E+00	2.27	2.20	.0860	.9102
668.25	.378E-01	2.36	2.29	.0282	.9133
693.25	.900E-01	2.45	2.38	.0672	.9208
718.25	.120E+00	2.54	2.46	.0894	.9307
743.25	.792E-01	2.62	2.55	.0591	.9373
768.25	.900E-01	2.71	2.63	.0672	.9448
793.25	.477E-01	2.80	2.72	.0356	.9487
818.25	.801E-01	2.89	2.80	.0598	.9554
843.25	.612E-01	2.98	2.89	.0457	.9604
868.25	.900E-03	3.07	2.97	.0007	.9605
905.75	.000E+00	3.20	3.10	.0000	.9605
943.25	.513E-01	3.33	3.23	.0383	.9648
968.25	.216E-01	3.42	3.32	.0161	.9666
993.25	.630E-01	3.51	3.40	.0470	.9718
1018.25	.819E-01	3.60	3.49	.0611	.9786
1043.25	.342E-01	3.68	3.57	.0255	.9814
1068.25	.000E+00	3.77	3.66	.0000	.9814
1093.25	.567E-01	3.86	3.75	.0423	.9861
1118.25	.261E-01	3.95	3.83	.0195	.9883
1143.25	.117E-01	4.04	3.92	.0087	.9892
1168.25	.387E-01	4.12	4.00	.0289	.9925
1193.25	.900E-02	4.21	4.09	.0067	.9932
1218.25	.819E-01	4.30	4.17	.0611	1.0000
1243.25	.000E+00	4.39	4.26	.0000	1.0000
1268.25	.000E+00	4.48	4.35	.0000	1.0000

Breakthrough curve

Experiment: btc 28 (2 x Atrazine) and btc 29 (2 x chloride) 3/23/92 Caldwell
subsoil

Code	Rate	Percentile	Time	Pore vol	Conc	Obs no	Recovery	PV1	PV2
29#2	.2	.01	104.489	.369	.2242	10	111.06	55.0	58.4
29#2	.2	.05	145.928	.515	.4934	12	111.06	55.0	58.4
29#2	.2	.16	203.274	.718	.7906	14	111.06	55.0	58.4
29#2	.2	.50	322.077	1.137	.8824	19	111.06	55.0	58.4
29#2	.2	.84	514.422	1.816	.2296	26	111.06	55.0	58.4
29#2	.2	.95	798.109	2.818	.0801	38	111.06	55.0	58.4
29#2	.2	.99	1149.099	4.057	.0387	51	111.06	55.0	58.4

Appendix 4.4. File generated by BTC.FOR, serving as input data to CXTFIT.FOR.

```

28#1
2  MODE: 1 - resident; 2 - effluent fluxes
0  NREDU: 0 - input conc. not reduced
40 MIT: Max.no. of iterations(0 - simulate
20      NOB: No. of observations,
0  NSKIP: 0 Problem executed, 1 data read only
0  NPRNT: 1 (prints input c(x,t), 0 not)
.5557      Theta
1.262      Bulk density
0.0        Uniform initial conc. in column
.8000E+04   Concentration in pulse
ESTIMATE Fit? Y(1);N(0) BMIN BMAX
.0815      0      0.0 9999.0 Flux density
0.1        1      0.0 9999.0 Dispersivity
0.1        1      -1.0 9999.0 Kd
112.000    0      0.0 9999.0 Pulse length
0.0        0      0.0 9999.0 1st order k
0.0        0      0.0 9999.0 Zero order k

Obs. no.   Distance   Time   PV   Concentration
1          21.40     13.200 .093 .1128E+03
2          21.40     33.200 .234 .9302E+03
3          21.40     53.200 .376 .2368E+04
4          21.40     73.200 .517 .3552E+04
5          21.40     93.200 .658 .4482E+04
6          21.40    113.200 .799 .5158E+04
7          21.40    133.200 .941 .5412E+04
8          21.40    153.200 1.082 .4961E+04
9          21.40    173.200 1.223 .4003E+04
10         21.40    193.200 1.364 .3101E+04
11         21.40    213.200 1.505 .2424E+04
12         21.40    233.200 1.647 .1945E+04
13         21.40    253.200 1.788 .1522E+04
14         21.40    273.200 1.929 .1213E+04
15         21.40    293.200 2.070 .1015E+04
16         21.40    313.200 2.212 .8456E+03
17         21.40    333.200 2.353 .6765E+03
18         21.40    353.200 2.494 .5356E+03
19         21.40    373.200 2.635 .3946E+03
20         21.40    393.200 2.776 .3383E+03

29#1
2  MODE: 1 - resident; 2 - effluent fluxes
0  NREDU: 0 - input conc. not reduced
40 MIT: Max.no. of iterations(0 - simulate
51      NOB: No. of observations,
0  NSKIP: 0 Problem executed, 1 data read only
0  NPRNT: 1 (prints input c(x,t), 0 not)
.5557      Theta
1.262      Bulk density
0.0        Uniform initial conc. in column
.1400E+01   Concentration in pulse
ESTIMATE Fit? Y(1);N(0) BMIN BMAX
.0815      0      0.0 9999.0 Flux density
0.1        1      0.0 9999.0 Dispersivity
0.1        1      -1.0 9999.0 Kd
112.000    0      0.0 9999.0 Pulse length

Obs. no.   Distance   Time   PV   Concentration
31         21.40     413.200 2.917 .2713E+04
32         21.40     433.200 3.058 .2213E+04
33         21.40     453.200 3.200 .1813E+04
34         21.40     473.200 3.341 .1513E+04
35         21.40     493.200 3.483 .1213E+04
36         21.40     513.200 3.625 .9302E+03
37         21.40     533.200 3.766 .7368E+03
38         21.40     553.200 3.908 .5356E+03
39         21.40     573.200 4.050 .3946E+03
40         21.40     593.200 4.192 .2924E+03
41         21.40     613.200 4.334 .2124E+03
42         21.40     633.200 4.476 .1522E+03
43         21.40     653.200 4.618 .1015E+03
44         21.40     673.200 4.760 .7368E+03
45         21.40     693.200 4.902 .5356E+03
46         21.40     713.200 5.044 .3946E+03
47         21.40     733.200 5.186 .2924E+03
48         21.40     753.200 5.328 .2124E+03
49         21.40     773.200 5.470 .1522E+03
50         21.40     793.200 5.612 .1015E+03
51         21.40     813.200 5.754 .7368E+03

```

CHAPTER FIVE

THE FIELD LEACHING EXPERIMENTS

INTRODUCTION

The field leaching experiments were intended to complement the laboratory studies, and provide pesticide leaching data which could be used to verify the simulation models. The soils used in the laboratory batch and column experiments were sampled from the field sites.

Relevant previous work done at the Caldwell Field site included that by Knighton and Wagenet(1987), who studied the water regime and NO_3^- and Br^- distributions in three 120m x 10 m plots, of which one was left fallow and the other two planted to rape (*Brassica napus* L.) and oats (*Sativa avena* L.). Neutron access tubes were installed at 3 m intervals along the length of each cropped plot. In the fallow plot, tensiometers were installed at depths of 300 and 450 mm. Field-measured water retention was spatially variable, although the characteristic curve at each site was well-defined. At any matric potential between 0 and -80 kPa, the range of water content (volume fraction) was about 0.08. Nitrate and Br concentrations showed spatial variability, but the spatial distribution patterns were

similar for both anions in all plots, suggesting that variability was due to local changes in hydraulic properties. The variance of the surface (0 to 300 mm) concentrations was greater than for the 300 to 600 mm or 600 to 900 mm depths. McVoy (1994) intensively instrumented a 30 by 30 m area in Caldwell Field with recording tensiometers in an attempt to identify preferential leaching events. Unlike the spatially uniform nature of drying, the response of the tensiometers during and immediately after rainfall suggested that infiltration is more variable between sites, events and depths. However, the matric potential of the soil water at the end of infiltration was uniformly about -3 kPa; the time required to fully respond to infiltration ranged from minutes to days. McVoy ascribed these differences to differences in antecedent water content, amount and intensity of rainfall, soil structure and preferential flow. We do not know whether or not the large spatial and temporal variability in infiltration fluxes translates into equally large variations in solute fluxes. His work also provided much information regarding water retention and conductivity parameters which we used in our work.

Ogden et al (1992) used undisturbed monoliths (300 x 300 x 300 mm) from this site to examine small-scale variability of drainage water fluxes. Distributions of fluxes over a grid of 50 x 50 mm cells was log-normal. Geometric scaling alone, when

applied to multiple executions of the LEACHM model, was inadequate to describe the variability in drainage. Generalized scaling, in which porosity was not assumed constant, adequately described drainage in 3 out of 4 cases.

Previous work at this site suggests that spatial and temporal variability of water flux could play an important role in determining solute transport patterns. The TRANSMIT model (Hutson and Wagenet, 1995) described earlier was formulated to account for spatial differences in water fluxes.

The field experiment was conducted to examine the distribution of atrazine and alachlor following application in early summer. The modelling results will be described and discussed in the following chapter.

PROCEDURE

Sites

Field sites were chosen at Caldwell Field, located on the Cornell Agricultural Experiment Station in Ithaca, NY, and at the Vegetable Research Farm in Geneva, N.Y. These sites are referred to as Caldwell Field and Geneva. Plot dimensions and sampling sites are illustrated in Fig. 5.1.

Soils

The soil at Caldwell Field is classified as Niagra silt loam (fine -silty, mixed, mesic, Aeric Ochraqualfs). That at Geneva is classified as Cazenovia, a fine-loamy, mixed, mesic Oxyaquic Glossudalf.

Other properties of the soils are listed in Table 3.1

Chemical applications

Chemicals were applied by spraying a concentrated solution onto the surface of the plots. The intended rates of application and time of application are listed in Table 5.1. At Caldwell Field all plots were treated with all chemicals on the same day. At Geneva all the plots received atrazine on the first application date, half receiving Cl and half receiving Br as a tracer. Alachlor was applied to those plots which received Br, the remainder received alachlor and Cl on the second application date.

Table 5.1. Time and amount of chemical applications at Caldwell and Geneva (BARD plots).

Site	Date	Day no.	Alachlor <-----mg/m ²	Atrazine ₂	Br	Cl	Applied to plots sampled at sites
Caldwell	071992	201	300	118	-	100	1-8
Geneva	072892	210	300	118	-	100	1-4, 9
Geneva	072892	210	-	118	100	-	5-8
Geneva	082192	234	300	-	-	100	5-8

Rainfall

Originally it was planned to irrigate some of the plots after application of the chemical in order to accentuate downward leaching. However, the exceptionally wet summer of 1992 (a total of 190 mm during July) made this both impossible and unnecessary. Rainfall in relation to application and sampling dates is summarized in Fig. 5.2.

Sampling

Plots were sampled four to five times after application of the chemical, with the exception of the plot that received the delayed alachlor application, which was sampled only twice. Soil samples were taken using an auger, washed in water and rinsed in deionized water between cores. Samples were stored at -4C before analysis. The position of each sampling site was recorded, so that at the next sampling time, samples could be taken in approximately the same area. It was hoped that this would lead to a reduction in spatial variability.

Table 5.2 Sampling dates and codes.

Caldwell Field			Geneva		
Date	Day number	Sampling series	Date	Day number	Sampling series
06/30/92	201	Background	06/30/92	201	Background
07/28/92	210	A	08/05/92	218	B
08/17/92	230	C	08/19/92	232	E
09/08/92	252	F	09/13/92	257	G
10/20/92	294	H	11/03/92	308	I

Analytical procedure

Samples were thawed, mixed and about 10 g sampled. A further 10 g sample was oven-dried to determine water content. The field-moist sample was extracted with 30 ml of 3:1 methanol/water. Tubes were shaken at 200 rpm for 30 minutes, allowed to stand overnight and shaken again for 30 minutes. After settling, about 5 ml was removed for analysis and centrifuged for 15 minute. The extract was analyzed using Ohmicron immunoassay kits.

Analytical data were recorded in spreadsheet files for calculation, summation and checking.

RESULTS AND DISCUSSION

The field observations are summarized in Fig. 5.3 (Caldwell Field) and Fig. 5.4 (Geneva). These figures show the depth distribution of water, atrazine and alachlor at each sampling site and sampling time.

Concentrations of chemical varied widely, both spatially and temporally (examples: Fig. 5.5, 5.6, 5.7). Because the recovery of chemical varied widely between sampling sites, and it appeared as though high concentrations may be associated with particular sampling sites, the distribution of atrazine and alachlor through the profile was calculated separately for each sampling site. Depths of the 1st, 5th, 16th, 50th, 84th and 95th percentiles were calculated assuming concentration was uniform throughout each sampling depth interval. Graphs showing these depths for each sampling site are shown in Fig. 5.8 (Caldwell Field) and Fig. 5.9 (Geneva). Similar calculations for Cl and Br would be meaningless because much of the chloride and Br was probably leached below the monitored depth. Elapse of time after application leads to lower concentrations, downward movement of the center of mass and a greater distribution of chemical. Some of the apparent increase in chemical distribution is caused by the increase in variability relative to the decreasing resident

concentrations, some is undoubtedly due to reduced sorption in the B horizons of both soils. The Cl and Cl+Br tracers become more uniformly distributed through the soil (Fig. 5.7, for Geneva) than do the herbicides, which tend to be concentrated at shallower depths. Replotting center of mass against time (Fig. 5.10) demonstrates both the progression and variability of leaching.

When evaluating field leaching, the effects of degradation should not be ignored. If degradation rates are higher towards the soil surface, then, without any leaching, depth to the center of mass will increase by virtue of the unequal degradation rates. Fig. 5.11 shows the amount of atrazine and alachlor recovered at each of the sampling sites at Caldwell Field. Recovery at the first sampling time tended to be low, perhaps owing to the fact that much of the chemical was concentrated in a very shallow layer at the soil surface, and was perhaps not well sampled. The second, third and final sampling showed decreasing recovery with time, consistent with continuing degradation. Interestingly, the highest concentrations of both atrazine and alachlor were found in soils from the same sites. These data suggest that variability in the amount of chemical solution initially applied was responsible for the different amounts recovered. Soil hydrological or sorption properties could also explain these

data, but the samples were drawn from an area of about 1 m² and the likelihood of soil differences being responsible for consistently higher concentrations throughout the profile as small.

Variability in concentrations and recovery make it extremely difficult to reach any conclusions about the occurrence of macropore flow. Occasional occurrences of high herbicide concentrations at depth may indicate rapid downward movement or may merely be analytical or sampling error or contamination. The likelihood of significant preferential flow, based on various modelling assumptions will be examined in the following chapter.

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McVoy, C.W. 1994. Measurement of temporal and spatial variability of soil-water in a grass meadow. Unpub. Ph.D dissertation, Cornell University, Ithaca, NY.

Ogden, C.B., R.J. Wagenet, H.M van Es and J.L. Hutson. 1992. Quantification and modeling of macropore drainage. *Geoderma* 55:17-35.

Fig. 5.1. Plot dimensions and sampling sites at Caldwell Field and Geneva.

Chemical applications and sampling at Geneva
in relation to rainfall.

release Jan. 4, 1996 10:25:39 AM

Chemical applications and sampling at Caldwell Field
in relation to rainfall.

Fig. 5.2. Rainfall in relation to dates of chemical application and soil sampling. Chemical application dates are marked as a and b; sampling dates are marked as c, d, e, and f.

[GRAPHS ON FOLLOWING PAGES]

Fig. 5.3 Distribution of water, atrazine, and alachlor on each of four sampling dates at Caldwell Field.
Day 210 (*), day 230 (□), day 252 (+---), and day 294 (x...).

Caldwell - BARD site 1

Caldwell - BARD site 2

Caldwell - BARD site 3

Caldwell - BARD site 4

Caldwell - BARD site 5

Caldwell - BARD site 6

Caldwell - BARD site 7

Caldwell - BARD site 8

Caldwell - BARD site 1

Caldwell - BARD site 2

Caldwell - BARD site 3

Caldwell - BARD site 4

Caldwell - BARD site 5

Caldwell - BARD site 6

Caldwell - BARD site 7

Caldwell - BARD site 8

Caldwell - BARD site 1

Caldwell - BARD site 2

Caldwell - BARD site 3

Caldwell - BARD site 4

Caldwell - BARD site 5

Caldwell - BARD site 6

Caldwell - BARD site 7

Caldwell - BARD site 8

[GRAPHS ON FOLLOWING PAGES]

Fig. 5.4 Distribution of water, atrazine and alachlor on each of four sampling dates at Geneva:
Day 218 (*), day 232 (□), day 257 (+---),
and day 308 (x...).

Geneva - BARD site 1

Geneva - BARD site 2

Geneva - BARD site 3

Geneva - BARD site 4

Geneva - BARD site 5

Geneva - BARD site 6

Geneva - BARD site 7

Geneva - BARD site 8

Geneva - BARD site 1

Geneva - BARD site 2

Geneva - BARD site 3

Geneva - BARD site 4

Geneva - BARD site 5

Geneva - BARD site 6

Geneva - BARD site 7

Geneva - BARD site 8

Geneva - BARD site 1

Geneva - BARD site 2

Geneva - BARD site 3

Geneva - BARD site 4

Geneva - BARD site 5

Geneva - BARD site 6

Geneva - BARD site 7

Geneva - BARD site 8

Concentration of atrazine
Caldwell Field, BAR, Day 210

Concentration of atrazine
Caldwell Field, BAR, Day 230

Concentration of atrazine
Caldwell Field, BAR, Day 252

Concentration of atrazine
Caldwell Field, BAR, Day 294

Fig. 5.5. Atrazine concentrations measured at Caldwell Field.

Concentration of alachlor
Caldwell Field, BARD, Day 210

Concentration of alachlor
Caldwell Field, BARD, Day 230

Concentration of alachlor
Caldwell Field, BARD, Day 252

Concentration of alachlor
Caldwell Field, BARD, Day 294

Fig. 5.6. Alachlor concentrations measured at Caldwell Field.

Fig. 5.7. Cl + Br concentrations measured at Caldwell Field and Geneva. At Geneva, a second Cl application was made on day 234.

Fig. 5.8a. Depth to the 16th (*), 50th (), 84th (+) and 95th (x) percentiles of atrazine mass at Caldwell Field.

Fig. 5.8b. Depth to the 16th (*), 50th (□), 84th (+) and 95th (x) percentiles of alachlor mass at Caldwell Field.

Distribution of atrazine
Geneva, BARD, Day 218

Distribution of atrazine
Geneva, BARD, Day 257

Distribution of atrazine
Geneva, BARD, Day 232

Distribution of atrazine
Geneva, BARD, Day 308

Fig. 5.9a. Depth to the 16th (*), 50th (□), 84th (+) and 95th (x) percentiles of atrazine mass at Geneva.

Fig. 5.9b. Depth to the 16th (*), 50th (□), 84th (+) and 95th (x) percentiles of alachlor mass at Geneva.

Fig. 5.10. Depth to center of mass for each sampling site at each sampling date.

Fig. 5.11. Recovery of atrazine and alachlor at each sampling site, Caldwell Field.

CHAPTER SIX

A PRAGMATIC FIELD-SCALE APPROACH
FOR MODELING PESTICIDES

The modelling approach described here was developed in response to a variety of needs. In particular, the need for a model which executes rapidly was required for long-term simulations, and a simple representation of preferential flow following the conceptual model of Addiscott (1977), enabled the LEACHM model to be applied to structured soils without requiring additional soils data. Much of the material presented here has been published (Hutson and Wagenet, 1993). The conceptual basis of the model is described here since it was one of the approaches used to simulate the field leaching experiments, described in the following chapter.

The scale at which pesticide environmental fate assessments are conducted is increasing. The availability of digitized data bases of such natural resources as soil, topography and land use, along with more detailed and readily useable information on cropping patterns, climate and chemical use, have combined to make simulation modeling and geographic information systems (GIS) the tools of choice in many contemporary studies of pesticide fate. At the same time that these tools have gained wide

acceptance, large-scale field sampling programs related to pesticide fate have, due to the cost of such programs, become difficult to conduct. They are simply too expensive on a site-by-site basis. This has led further to the adoption of computational methods as a substitute for direct observation.

The proper application of these technologies often require a skilled computer specialist, as well as appropriate soil scientists, hydrologists, crop scientists or others knowledgeable in natural processes. Yet, even with these individuals working as a team, there are at least two major questions left unanswered in most studies. First is the issue of the choice of the model to use, and second is the reliability of the computer output with respect to representing real-life conditions. A proper answer for the former depends upon the purpose of the simulation, with several existing models now providing options that vary in terms of computing time, representation of basic process, model flexibility, and input data demands. The latter question includes issues of field sampling and confidence limits on both measurements and computer predictions.

An important example is the estimation of pesticide leaching. It has been appreciated for at least two decades (Nielsen et al, 1973) that movement of water and solutes in soil is spatially variable. A number of models have been developed to

describe leaching (reviewed by e.g. Nielsen et al.), and some have been developed to specifically treat pesticides (PRZM, Carsel et al. 1985; LEACHP, Wagenet and Hutson, 1989; Leistra et al., 1980; CALF, Nicholls et al. 1982). These models are sometimes used by industry and regulatory agencies (PRZM by EPA and pesticide registrants) or by scientists engaged in research studies (LEACHP, CALF, others). Yet, in most use of models there is little attention given to the level of representation of basic process that is required for environmental fate assessments. This is an important issue, particularly when the models may be used to provide management guidance, for the more simplified is the representation of leaching, the less is the demand for input data characterizing field soil-water properties. With the advent of large scale assessments using GIS and soil survey data bases to estimate leaching, it is important to accelerate the development of simplified, yet acceptably accurate pesticide leaching models that minimize input data requirements, in the process minimizing further soil characterization and field-measurement beyond the information contained in existing data bases.

MODELING APPROACH

LEACHP, the pesticide version of LEACHM (Wagenet and Hutson 1989), and CALF (Nicholls et al 1982) were used as beginning

points in this study. CALF includes simplified descriptions of water and chemical movement, adopted from the work of Addiscott (1977). By contrast, LEACHP uses the same approach as the LEACHM models in general (Wagenet and Hutson, 1989), in which the Richards equation is used to describe water flow and the convection-dispersion equation (CDE) is used for solute transport. The numerical solution of these equations is time-consuming owing to the short time steps that are necessary. The concepts embodied in CALF were used to prepare new water and solute transport routines for LEACHM. The new model is called LEACHA to distinguish it from LEACHP.

Conceptual approach

Addiscott (1977) described a capacity model (Addiscott and Wagenet, 1985) for fallow soils in which the soil water is divided into mobile and immobile phases. After rainfall, percolation of water and dissolved solute is allowed in the mobile phase only. Rules for the subsequent slow approach to equilibration between mobile and immobile phases within a depth, or model segment, and between adjacent segments, vary among the various versions of Addiscott's model. In CALF, Nicholls, et al. (1982) used a simplified version of Addiscott's model to simulate pesticide fate. All evapotranspiration is removed from the top segment, equilibration between adjacent segments is driven by differences in water content rather than water potential, and

mobile and immobile phases within segments are assumed to reach equilibrium each day.

The pertinent differences between CALF, LEACHP and LEACHA are illustrated in Table 6.1. LEACHA requires definition of water contents for field capacity (W_f), wilting point (W_{wp}), the division between mobile and immobile water (W_d), and an evaporation or 'air-dry' limit (W_a). These water contents are calculated from the water retention curves using matric potentials which can be defined in the model. LEACHP and LEACHA calculate transpiration sink terms for each segment in the same way: weighting water withdrawal according to root distribution, water potentials and hydraulic conductivity. In CALF and LEACHA, evaporation is extracted from the upper 50 mm of soil until the evaporation limit is reached, whereas in LEACHP the evaporative flux is the surface boundary flux determined with the numerical solution of the Richards equation and the potential evaporation. These differences, together with differences in the water redistribution process, mean that the water mass balance terms generated by LEACHA and LEACHP will differ slightly. LEACHA and LEACHP are similar in other respects, except that LEACHA uses only daily time steps. This makes the sequence of calculations in the modified transport routine:

- i) subtract the evaporation and transpiration from each

- segment;
- ii) subtract degradation from the pesticide pool in each segment;
 - iii) partition chemical between sorbed, solution and precipitated phases, assuming complete equilibrium between mobile and immobile phases;
 - iv) if there is rain, perform the leaching process;
 - v) redistribute water and solute vertically, according to water potential and concentration differences;
 - vi) repeat chemical partitioning as in (iii) above;
 - vii) perform mass balance checks, print data if required.

Calculation of leaching in LEACHA

On days during which there is rain or irrigation, both the applied water and dissolved solute is added to the surface segment. There is no upper limit to this temporary water content. If W_I , C_I , W_M and C_M represent the water content (mm) and solution concentration (mg/l) of the immobile and mobile phases before the addition of rain or irrigation, and W_p and C_p are the depth (mm) and concentration (mg/l) of applied or percolating water, then after addition:

$$W_I' = W_I + \min(W_d - W_I, W_p) \quad (1)$$

$$W_p' = W_p - \min(W_d - W_I, W_p) \quad (2)$$

$$C_I' = [C_p(W_I' - W_I) + C_I W_I] / W_I' \quad (3)$$

$$W_M' = W_M + W_p' \quad (4)$$

$$C_M' = [C_P(W_M' - W_M) + C_M W_M] / W_M' \quad (5)$$

where the prime indicates updated values. The range of possible W and C values are $W_I \geq W_a$; $W_M \geq 0$ when $W_I = W_d$; $W_M = 0$ when $W_I < W_d$; C_I and $C_M \geq 0$.

If $(W_M' + W_I)$ exceeds W_{fc} then $(W_M' - W_{fc})$ mm water, having a concentration C_M' mg/l, moves to the next segment. $W_M' - W_{fc}$ becomes the new W_P , C_M' the new C_P , and equations (1) to (5) are repeated. This procedure is repeated down the profile until either $(W_I' + W_M') < W_{fc}$, or the lowest segment is encountered, at which point drainage is incremented by $(W_M' - W_{fc})$ mm water and chemical leached is incremented by $C_M'(W_M' - W_{fc})$ mg m⁻².

If $(W_M' + W_I)$ does not exceed W_{fc} , and also for days on which there is no rainfall, each segment i is brought towards equilibration with the segment $i+1$ beneath, starting at the top of the profile. This is done by i) calculating the amount of water required to move upwards or downwards so that $\psi_i - \Delta Z = \psi_{i+1}$, and ii) allowing half of this water to move, together with its dissolved solute.

If W_E is the amount of water (mm) moving between segments, then for the segment losing water:

$$W_M' = \max(0, W_M - W_E) \quad (6)$$

$$W_e' = W_e - \max(0, W_M - W_e) \quad (7)$$

$$W_I' = W_I - W_e' \quad (8)$$

The amount of pesticide dissolved in W_e mm water (M_e , mg m⁻²) is

$$M_e = C_M(W_M - W_M') + C_I(W_I - W_I'), \quad (9)$$

and the concentration (mg l⁻¹) of the transferred pesticide is

$$C_e = M_e/W_e. \quad (10)$$

M_e mg pesticide is removed from the total pool of solute in the segment, but solution concentrations do not change at this stage.

For the segment gaining water:

$$W_I' = \max(W_d, W_I + W_e) \quad (11)$$

$$W_e' = W_e - W_I' - W_I \quad (12)$$

$$W_M' = W_M + W_e' \quad (13)$$

$$C_I' = [C_e(W_I' - W_I) + C_I W_I]/W_I' \quad (14)$$

$$C_M' = [C_e(W_M' - W_M) + C_M W_M]/W_M' \quad (15)$$

The updated values of C and W for segment $i+1$ are then used to adjust segments $i+1$ and $i+2$.

Calculation of pesticide partitioning in LEACHA

After all segments have been adjusted, the chemical is repartitioned between solution, sorbed and precipitated phases, assuming complete equilibrium between mobile and immobile phases. The total chemical in each segment per square meter (T_c) is calculated as

$$T_c = C_I W_I + C_I W_I + S \rho \Delta Z + P \quad (16)$$

where S is sorbed chemical (mg kg^{-1}), ρ is bulk density (kg dm^{-3}), P is precipitated chemical (mg m^{-2}) and ΔZ is segment thickness (mm).

Total water content in each segment (W_{tot}) is

$$W_{\text{tot}} = W_M + W_I. \quad (17)$$

Solution concentration cannot exceed the solubility (C_{sat}) of the chemical. Assuming a linear sorption isotherm,

$$S = K_d C \quad (18)$$

where K_d is the partition coefficient ($\text{dm}_3 \text{ kg}^{-1}$), and the solution concentration C , in both mobile and immobile phases is

$$C = \max[C_{\text{sat}}, \text{TOTAL} / (\Delta Z \rho K_d + W_{\text{tot}})], \quad (19)$$

the sorbed concentration is

$$S = K_d C, \quad (20)$$

and the precipitate, if any, is

$$P = \text{TOTAL} - CW - \Delta Z \rho S. \quad (21)$$

The intelligent use of the three modelling approaches described in this report (the multi-region TRANSMIT model, the single region LEACHP model with chemical non-equilibrium, and the two-region, capacity-based LEACHA model) requires an appreciation of the assumptions inherent in the models and the extent to which they may influence the predictions. This is particularly important for prospective simulations of scenarios for which few measured input data are available. The assumptions and rules

implicit in the CALF and LEACHA models are conceptually simple, but their implications are not easily comprehended. For example, segment thickness in LEACHA and CALF has little influence on the prediction of net downward water flux, and has a relatively small influence on leaching, but it will influence daily redistribution in much the same way as numerical dispersion influences the outcome of a CDE-based model. On the other hand, for LEACHP a dispersivity value has to be estimated, preferential flow is not included and local chemical equilibrium is assumed. The validity of the LEACHP code, and the values of parameters such as dispersivity, can be established for well-defined conditions for which analytical solutions are available, making this modelling approach attractive from a theoretical point of view. But there is no basis for assuming that the same principles, and only those principles, are applicable at the field-scale, particularly in structured soils. The computationally-simpler approach followed in LEACHA contains a framework which is easily adapted to describing many of the field-scale spatial heterogeneities, such as preferred pathways and macroporosity, which render the CDE-equation inappropriate for field application.

There is no clear answer to the question of which is the best modeling approach. The choice depends on the purpose of the exercise, particularly upon the degree of resolution to which an estimation is required. This choice, once made, determines the

degree of theoretical rigor and the amount of data required. The latter must then be considered in terms of the amount of data available. For field-scale simulations, where several different transport mechanisms may apply, data are limited, and variability and uncertainty high, the need for long-term and multiple simulations make less sophisticated, more pragmatic approaches such as CALF and LEACHA attractive alternative to a CDE-based model.

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TABLE 6.1. Comparison of the CALF, LEACHA and LEACHM models

	CALF	LEACHA	LEACHM
Classification	<---- Functional ---->		Mechanistic
Solution method	<---- Tipping-bucket ---->		Finite difference
Water flow model	<---- Capacity ----> mobile/immobile		Richards equation (mobile only)
Redistribution	Water content gradient	Water potential gradient	Richards equation
Solute transport	<---- Convection ----> mobile/immobile		Convection- dispersion
Evaporation	<---- Extracted from ----> upper 50 mm		Surface flux boundary condition
Transpiration	Not included	<---- Root distribution and Darcy's law ---->	
Pesticide sorption	Linear (K_d increases with time)	<---- Linear sorption (K_d constant) ---->	

CHAPTER SEVEN

SIMULATIONS OF THE FIELD LEACHING EXPERIMENTS

In the previous chapters several models were described which could possibly aid in the prediction of pesticide fate in soils. They are all extensions of the LEACHM model (Wagenet and Hutson, 1987), incorporating the options of capacity-based mobile-immobile flow option, Freundlich sorption, two-site kinetic sorption, and multi-region/two-dimensional concepts. These extensions enable the departures from 'ideal' behavior observed during the batch and column studies to be reflected.

Classic convection-dispersion behavior, with linear sorption and local equilibrium, cannot explain the slow approach to equilibrium observed during the batch equilibrium studies, nor the enhanced breakthrough of both chloride and pesticide in columns subject to the faster flow rates (about 1100 mm/day) imposed during the steady-state column experiments.

The extensions to the LEACHP model and the new multi-region TRANSMIT model developed during the course of this project enable many of the departures from ideal behavior to be simulated. Unfortunately, there are many possible mechanisms involved in

non-equilibrium solute transport. In natural soils, different mechanisms probably determine flow patterns and behavior at different times. Ideally, a model is required which can reflect as many of these processes, as realistically as possible, over a wide range of soils, chemicals, water regimes and boundary conditions. A limitation of many of the conceptual models constructed to explain solute breakthrough under steady-state conditions, is that they cannot be applied to unsaturated, transient flow which dominates field transport. A model such as TRANSMIT can reflect several transport mechanisms, ranging from classical single-region CDE to multi-region flow, with some regions accessible only by diffusion. Intermediate in this spectrum are the two-region, mobile/immobile models. TRANSMIT can be configured as a two-region model; under steady-state flow it matches breakthrough curves predicted by analytical solution to the two-region CDE. TRANSMIT is a very flexible model for situations in which boundary conditions and/or soil properties are likely to vary across adjacent soil domains. Limitations to its use are parameter estimation and execution time.

The major features of the models used to simulate the field leaching experiments are summarized in Table 7.1.

Table 7.1. Major features of the models used in this work.

Model	Model type	Water flow	Domains	Sorption	Solute transport
LEACHA	Capacity	Tipping bucket	Two	Linear	Mobile-immobile
LEACHP	Mechanistic	Richards	One	Linear	CDE
LEACHK	Mechanistic	Richards	One	2-site, kinetic	CDE
TRANSMIT	Mechanistic	Richards	Five	Linear	CDE

The first three models listed are options within the LEACHP model, designated here as LEACHA, LEACHP, and LEACHK for convenience; they are not separate models. All else except the transport process or sorption mechanism are identical. TRANSMIT (Chapter 2) is an independent model, although developed from LEACHP, it differs significantly in concept and structure.

PROCEDURE

Simulations of atrazine, alachlor, chloride and bromide distributions were performed using:

- 1) LEACHA, with the threshold between mobile and immobile water set at -200 kPa,
- 2) LEACHP, using linear sorption and local equilibrium,
- 3) LEACHK, linear sorption, all sorption kinetic, with the phase transfer coefficient set at 0.693 d^{-1} .
- 4) the TRANSMIT model, using five regions; hydraulic properties

were determined by a lognormal distributed of geometric scaling factors.

Sample data files are listed in Appendix 7.2 (LEACHP) and 7.3 (TRANSMIT). Atrazine was applied on different dates to each half of the plots, thus there were five chemical/application date combinations for each location (Table 5-1). TRANSMIT can simulate only one chemical at a time, so multiple runs are necessary for more than one chemical. The following simulated data were recorded: mass balance and profile data for the field sampling days, daily chemical fluxes passing depths of 100 mm, 300 mm and 600 mm, and daily chemical concentrations (mg dm^{-3}) at each 25 mm depth node. The latter data were used to calculate daily depths and concentrations for the 1st, 5th, 16th, 50th, 84th, 95th and 99th percentiles of the vertical chemical distribution in the profile. All simulations were started on January 1 (Day 1) to establish a realistic soil water profile by the time of chemical application (Day 200). Simulations continued to the final sampling date (Day 320).

RESULTS AND DISCUSSION

All chemical applications were followed by rainfall shortly after application (Fig. 5.1). The largest rainfall event (20 mm) followed the second application of alachlor at Caldwell Field. The longest dry period after application followed the second application of alachlor at Geneva. Fig. 7.1 shows application and sampling dates in relation to simulated cumulative soil water fluxes at the surface, and at depths of 100 mm, 300 mm, and 600 mm. Downward fluxes are defined as positive and upward fluxes as negative. Simulated soil water fluxes suggest that downward water fluxes are greatly reduced at 300 mm, owing to evapotranspiration, so it is likely that chemical will leach below 300 mm as rapidly as it does from the surface.

Using the mean and standard deviation of the center of mass (Chapter 5) of the herbicide distribution in the profile as an index of depth of the chemical, measured and simulated depths were compared. Detail for the first 20 days of atrazine leaching at Caldwell Field is shown in Fig. 7.2. Differences between the models were established during the first few days after application. LEACHA and LEACHK predicted slightly deeper leaching because a greater proportion of the applied chemical remains in solution and is available for transport. There was

little difference between the TRANSMIT and LEACHP models. Unlike the steady-state column leaching simulations (Chapter 4), water flux through the regions were controlled largely by rainfall flux and did not differ across regions to nearly the same extent. If rainfall fluxes were to increase, then overflow from less permeable to more permeable regions would be accentuated, leading to preferential transport. LEACHA predicted some initial rapid leaching; after that the atrazine moved into the immobile region where it was usually bypassed by infiltrating water. Fig. 7.3 shows predicted leaching data for atrazine and alachlor at both Caldwell Field and Geneva for the period of the experiment. The CDE-based models all predicted similar 50th percentile depths; the Addiscott mobile/immobile flow model (LEACHA) generally predicted shallower depths, but occasionally predicted deeper depths. LEACHA is particularly sensitive to water content at the time of sampling and to the occurrence of rain soon after application. This is further illustrated in Figs. 7.4 and 7.5, which show simulated cumulative chemical fluxes at a depth of 100 mm. LEACHA usually shows a single pronounced downward flux event, after which fluxes are small. This behavior is determined to a large extent by the way in which LEACHA is constructed. The procedure followed in LEACHA during each daily time step is i) apply chemical if necessary, all of which goes into solution (limited by solubility), ii) subtract sink terms, iii) add rain

if necessary, and transport solute in mobile phase, iv) re-equilibrate across sorbed, solution, mobile and immobile phases. Once the rapid transport in the mobile phase is complete, subsequent leaching is slow.

The CDE-based models, on the other hand, assume that all of the soil water is available for movement, so chemical is not bypassed by infiltrating water. Kinetic sorption and desorption seldom had much effect on leaching, since there was time between leaching events for equilibrium between sorbed and solution phases to be reached. Considering the shallow depths involved, and the 25 mm node spacing used in the models, the difference between the CDE model simulations and the measured centers of mass are similar. In only one case (alachlor applied on day 226, Caldwell Field) did the Addiscott model predict deeper leaching than the CDE model, and in this case the measured depth to the center of mass at the end of the experiment was deeper than those simulated. Atrazine applied at Geneva also leached deeper than predicted, but in this case the Addiscott routine did not predict such a large initial leaching flux.

A single execution of each of the models was demonstrated here. These models have a large number of input variables which can influence the outcome of the simulations. The most important

of these are assumptions regarding evapotranspiration and chemical degradation. Decreasing evapotranspiration will increase downward water fluxes and hence leaching. Changing the pattern of degradation not only changes the amount of chemical in the profile but can alter its distribution. Thus an increasing depth to the center of mass with time can be caused solely by more rapid degradation of chemical nearer the soil surface, without any leaching involved.

Variability in the field data make it extremely difficult to reach conclusions about the occurrence of macropore flow. Occasional occurrences of high herbicide concentrations at depth may indicate rapid downward movement or may merely be analytical or sampling error or contamination.

Predicted temporal changes in herbicide and Cl^- concentrations are shown in Fig. 7.6 (LEACHP), 7.7 (LEACHA) and 7.8 (TRANSMIT) for atrazine and chloride at Caldwell Field. These graphs predict the concentration of atrazine to be reduced by degradation to very low levels at the end of the experiment. This corresponds approximately to measured values. Assumptions about degradation kinetics and the variation of degradation rate constants through the profile will have a large effect on the distribution of chemical. Simulations of chloride concentration

distributions showed it to be spread throughout the profile, again matching observed distributions, at least qualitatively. The TRANSMIT simulations showed slightly less leaching of Cl than the LEACHP simulations and are not discussed separately.

Given the large number of parameters in these models, there is little point in attempting to optimize a few in order to get a closer match between measured and observed chemical distributions. From our measurements and simulations, including many simulations not shown here, we know that the most important factors are first, the estimation of infiltration and evapotranspiration, which determine the downward flux of water, and second, description of sorption and leaching during the first few days following application.

CONCLUSIONS

Given the uncertainties regarding degradation rates at different depths, and the large spatial variability found in the field measurements, all of the models performed reasonably well. Of all the models tested, only the TRANSMIT model has the capability of reflecting chemical behavior in batch, column and field. LEACHA cannot be applied to column or batch studies since daily time steps are used and complete equilibration is assumed

at the end of each day, so it cannot simulate the approach to equilibration over shorter periods. LEACHP, based on a single-region CDE, using linear sorption and local equilibrium, does not reflect any non-equilibrium processes. Incorporating two-site kinetic sorption does enable a slow approach to equilibrium in batch studies and enhanced breakthrough of herbicides in column flow to be simulated, but it cannot explain enhanced Cl breakthrough or preferential flow caused by physical non-equilibrium. Incorporating a Freundlich isotherm does enable tailing in breakthrough curves to be simulated, but the isotherms measured in this work (Chapter 3) were not sufficiently non-linear to explain the tailing often observed. The TRANSMIT model, using some simple and justifiable assumptions about regions of differing hydraulic properties, can reflect all of these observations, at least qualitatively.

These simulations suggest that preferential flow at the two sites studied was not important, since the chemical always had the opportunity to sorb before it could be transported down the profile. If preferential flow depends on the occurrence of rain very soon after chemical is applied, then temporal differences in rainfall distribution in relation to time of chemical application could be very important. This topic is explored further in Chapter 8, where multiple executions of LEACHA are performed to

assess the likely impact of rainfall variability on preferential flow.

Cumulative rain and soil water flux at four depths
Caldwell Field, Richards' equation.

FLUXESM May 28, 1994 20:14 PM

Cumulative rain and soil water flux at four depths
Geneva, Richards' equation.

Fig. 7.1. Cumulative rain, and simulated net soil water flux at each of four depths in the profile: (—) rain; (— —) surface; (---) 100 mm; (-·-) 300 mm; (····) 600 mm.

atc50abb Dec. 21, 1994 10:33:50 PM

Center of mass of atrazine,
Caldwell Field, days 200 to 220.

Fig. 7.2 Leaching of atrazine during the first 20 days following application at Caldwell Field.

Fig. 7.3. Depth to center of herbicide mass, simulated using several models (—) LEACHA; (---) LEACHP, F, K. Measured values are means and standard deviations.

ALACHLOR.Dat, 20, 1994, 1:23:45 PM

ATRAZINE.Dat, 20, 1994, 1:23:45 PM

ALACHLOR.Dat, 20, 1994, 1:23:45 PM

ATRAZINE.Dat, 20, 1994, 1:23:45 PM

Fig. 7.4. Cumulative herbicide fluxes, simulated for a depth of 100 mm using LEACHP (—), LEACHK (---) and LEACHA (.....). Application dates (a,b); sampling dates (c,d,e,f).

CLIRCALA May 23, 1994 2:55:54 PM

CLIRCALA May 23, 1994 2:57:01 PM

CABROBPA May 23, 1994 2:58:17 PM

CABROBPA May 23, 1994 2:58:21 PM

Fig. 7.5. Cumulative Cl⁻ and Br⁻ fluxes, simulated for depths of 100 mm and 300 mm using LEACHP and LEACHA. First application: 100 mm (—), 300 mm (— —); second application: 100 mm (- - - -), 300 mm (· · · · ·). Application dates (a,b); sampling dates (c,d,e,f).

CATRORP Dec. 22, 1994 1:27:27 PM

Atrazine, Caldwell Field.
Simulated by LEACHP.

Chloride and bromide, Caldwell Field.
Simulated by LEACHP.

Fig. 7.6. Temporal changes in concentration of atrazine (mg/dm³) and Cl (relative concentration), predicted by LEACHP for atrazine and chloride at Caldwell Field.

CATRGPRDs Dec. 22, 1994 3:15:01 PM

Atrazine, Caldwell Field.
Simulated by LEACHA.

Chloride and bromide, Caldwell Field.
Applied day 201. Simulated by LEACHA.

Fig. 7.7. Temporal changes in concentration of atrazine (mg/dm³) and Cl (relative concentration), predicted by LEACHA for atrazine and chloride at Caldwell Field.

Atrazine, Caldwell Field.
Simulated by TRANSMIT.

Chloride and bromide, Caldwell Field.
Applied day 201. Simulated by TRANSMIT.

Fig. 7.8. Temporal changes in concentration of atrazine (mg/dm³) and Cl (relative concentration), predicted by TRANSMIT for atrazine and chloride at Caldwell Field.

Appendix 7.1. Input data file for LEACHP (Caldwell Field).

caldwelp < DOS Filename, 8 characters with no extension. Used in batch runs--(started as LEACHP<filename).

LEACHP PESTICIDE DATA FILE.

All numeric data are in positions 1 to 78, comments may extend to position 120.

Unless defined as 'not read' a value must be present for each item, although it may not be used.

Free format with blank delimiters. Preserve division and heading records. No. of depth segments may be changed.

1 <Date format (1: month/day/year; 2: day/month/year). Dates must be 6 digits, 2 each for day, mo, yr.
 010192 <Starting date. No date in the input data should precede this date.
 320 <Ending date or day number. The starting date is day 1. (A value <010101 is treated as a day number).
 0.05 <Largest time interval within a day (0.1 day or less).
 0.010 <Maximum water flux per time step. (Dimensionless: flux (mm)/segment thickness (mm)).
 1 <Number of repetitions of rainfall, crop and chemical application data.
 600 <Profile depth (mm), preferably a multiple of the segment thickness.
 25 <Segment thickness (mm). (The number of segments should be between about 8 and 30).
 2 <Lower boundary condition: 1:fixed depth water table; 2:free drainage; 3:zero flux 4:lysimeter.
 1300 <If the lower boundary is 1 or 5: initial water table depth (mm).

2 <Number of output files: 1: OUT only; 2: OUT + SUM; 3: OUT + SUM + BTC

2 <Number of output files: 1: OUT only; 2: OUT + SUM; 3: OUT + SUM + BTC

--- For the *.OUT file :

1 <Units for depth data: 1: ug/kg, 2: mg/m2 per segment. (Not used in LEACHW)
 1 <Node print frequency (print data for every node (1), alternate nodes (2)).
 3 <Print options: 1, 2 or 3. To select one of the following 3 options.
 1 <Option 1: Time steps/print (these are not of equal length)
 5.00 <Option 2: Print at fixed time intervals (days between prints)
 7 <Option 3: No. of prints (the times for which are specified below)
 3 <Tables printed: 1: mass balance; 2: + depth data; 3: + crop data

--- For the *.SUM file :

1.00 <Summary print interval (d)
 100 <Surface to [depth 1?] mm (Three depth segments for the
 300 <Depth 1 to [depth 2?] mm summary file. Zero defaults to nodes
 600 <Depth 2 to [depth 3?] mm closest to thirds of the profile)

--- For the *.BTC (breakthrough) file :

1.0 <Incremental depth of drainage water per output (mm)

-- List here the times at which the *.OUT file is desired for print option 3.

-- The number of records must match the 'No. of prints' under option 3 above.

Date or Day no.	Time of day (to nearest tenth)	(At least one must be specified even if print option is not 3)
--------------------	-----------------------------------	---

063092	.5	(These dates can be past the last day)
072892	.5	
081092	.5	
081792	.5	
090892	.5	
102092	.5	
480	.5	

8	19.	70.	0.9	5	.000	-10.	.00	20.
9	19.	74.	0.9	5	.000	-10.	.00	20.
9	19.	74.	0.9	5	.000	-10.	.00	20.
10	25.	74.	0.9	5	.000	-10.	.00	20.
10	25.	74.	0.9	5	.000	-10.	.00	20.
11	25.	74.	0.9	5	.000	-10.	.00	20.
11	25.	74.	0.9	5	.000	-10.	.00	20.
12	25.	74.	0.9	5	.000	-10.	.00	20.
12	25.	74.	0.9	5	.000	-10.	.00	20.

2 < Use listed water contents (1) or potentials (2) as starting values.
Particle density: Clay Silt and sand Organic matter (kg/dm3) (to calculate porosity)
2.65 2.65 1.10

For a uniform profile: Any non-zero value here will override those in
the table below (only if retentivity model is 0).

0.0 <Soil bulk density (kg/dm3)
-0.00 <'Air-entry value' (AEV) (kPa) (a in eq 2.1 to 2.4).
0.00 <Exponent (BCAM) in Campbell's water retention equation (b in eq. 2.1 to 2.4).
0000 -0.0 <Conductivity (mm/day) and corresponding matric potential (kPa) (for potential-based version of eq.
2.5).
0.0 <Pore interaction parameter (P) in Campbell's conductivity equation (eq.2.5 in manual).
0 <Dispersivity (mm) (eq. 3.12). (Read, but not used in LEACHW)

Soil | Soil retentivity | Bulk | Match K(h) curve at: | Dispersivity
segment | parameters | density | K | Matric | using | (not read
no. | AEV BCAM | kg/dm3 | mm/d | pot'l | P | in LEACHW)
| kPa | | | | kPa | | mm

1 | -1.00 | 3.00 | 1.54 | 1 | -20. | 1.0 | 100.
1 | -1.00 | 3.00 | 1.54 | 1 | -20. | 1.0 | 100.
2 | -1.00 | 3.50 | 1.54 | 1 | -20. | 1.0 | 100.
2 | -1.00 | 3.50 | 1.54 | 1 | -20. | 1.0 | 100.
3 | -1.00 | 4.00 | 1.54 | 1 | -20. | 1.0 | 100.
3 | -1.00 | 4.00 | 1.54 | 1 | -20. | 1.0 | 100.
4 | -1.00 | 4.50 | 1.54 | 1 | -20. | 1.0 | 100.
4 | -1.00 | 4.50 | 1.54 | 1 | -20. | 1.0 | 100.
5 | -1.50 | 5.00 | 1.54 | 1 | -20. | 1.0 | 100.
5 | -1.50 | 5.00 | 1.54 | 1 | -20. | 1.0 | 100.
6 | -2.00 | 5.50 | 1.50 | 1 | -20. | 1.0 | 100.
6 | -2.00 | 5.50 | 1.50 | 1 | -20. | 1.0 | 100.
7 | -2.40 | 6.00 | 1.50 | 1 | -20. | 1.0 | 100.
7 | -2.40 | 6.00 | 1.50 | 1 | -20. | 1.0 | 100.
8 | -2.70 | 6.40 | 1.50 | 1 | -20. | 1.0 | 100.
8 | -2.70 | 6.40 | 1.50 | 1 | -20. | 1.0 | 100.
9 | -2.90 | 6.70 | 1.58 | 1 | -20. | 1.0 | 100.
9 | -2.90 | 6.70 | 1.58 | 1 | -20. | 1.0 | 100.
10 | -3.00 | 7.00 | 1.58 | 1 | -20. | 1.0 | 100.
10 | -3.00 | 7.00 | 1.58 | 1 | -20. | 1.0 | 100.
11 | -3.00 | 7.00 | 1.58 | 1 | -20. | 1.0 | 100.
11 | -3.00 | 7.00 | 1.58 | 1 | -20. | 1.0 | 100.
12 | -3.00 | 7.00 | 1.58 | 1 | -20. | 1.0 | 100.
12 | -3.00 | 7.00 | 1.58 | 1 | -20. | 1.0 | 100.

CROP DATA

Data for at least one crop must be specified, even if no crop desired.
For fallow soil, set flag below to 0, or germination past the simulation end date.

1 <Plants present: 1 yes, 0 no. This flag overrides all other crop data.
1 <No. of crops (>0), even if bypassed. Dates can be past last day of simulation.
1 <Growth: 1:No(use root data specified above, crop cover below); 2:Yes.
-1500 <Wilting point (soil) kPa.
-3000 <Min.root water pot'l(kPa).
1.1 <Maximum ratio of actual to potential transpiration (dry surface).
1.05 <Root resistance (weights water uptake by depth). (>1, No weighting: 1.0). See Eq. 2-16.

Crop no	Germination Date	Emergence Date	Maturity Date	Harvest Date	Rel. root depth	Crop cover fraction	Pan factor	Annual N uptake kg/ha	(read in LEACHN only)
1	060192	060292	061092	061092	103192	.20	0.5	1.0	1.00

INITIAL PROFILE CHEMICAL DATA

5 < Number of chemical species. At least one must be specified.

Soil layer	Chem1	Chem2	Chem3	Chem4
	---mg/kg dry soil---			
1	0.0	0.0	0.0	000.0 0
1	0.0	0.0	0.0	000.0 0
2	0.0	0.0	0.0	000.0 0
2	0.0	0.0	0.0	000.0 0
3	0.0	0.0	0.0	000.0 0
3	0.0	0.0	0.0	000.0 0
4	0.0	0.0	0.0	000.0 0
4	0.0	0.0	0.0	000.0 0
5	0.0	0.0	0.0	000.0 0
5	0.0	0.0	0.0	000.0 0
6	0.0	0.0	0.0	000.0 0
6	0.0	0.0	0.0	000.0 0
7	0.0	0.0	0.0	000.0 0
7	0.0	0.0	0.0	000.0 0
8	0.0	0.0	0.0	000.0 0
8	0.0	0.0	0.0	000.0 0
9	0.0	0.0	0.0	000.0 0
9	0.0	0.0	0.0	000.0 0
10	0.0	0.0	0.0	000.0 0
10	0.0	0.0	0.0	000.0 0
11	0.0	0.0	0.0	000.0 0
11	0.0	0.0	0.0	000.0 0
12	0.0	0.0	0.0	000.0 0
12	0.0	0.0	0.0	000.0 0

Concentration (mg/l) below profile, used with lower boundaries 1 or 5

0.0 0.0 0.0 0.0 0.0

500 < Depth (mm) of water in mixing cell (boundaries 1 and 5 only). Enter 0 for no mixing cell.

CHEMICAL PROPERTIES

Chem No.	Name	Solubility mg/dm3	Vapour Density mg/dm3	Link	Plant Uptake 1(yes),0(no)
1	Alachlor1	.2420E+03	.3400E-03	0	0
2	Atrazine	.3300E+02	.3540E-05	0	0
3	Chloride	.1000E+06	.0000E-00	0	0
4	Bromide	.1000E+06	.0000E-00	0	0
5	Alachlor2	.2420E+03	.3400E-03	0	0

Chem No.	Linear(1) or Freundlich(2)	Linear isotherm Koc 1/kg	2-site model f alpha	Freundlich isotherm Kfoc Exponent (unit dependent!)	(See Table 3.1, p. 3-24 in manual)
1	1	170.0	1.0	.000	000.0 0.00
2	1	100.0	1.0	.000	000.0 0.00
3	1	000.0	1.0	.000	000.0 0.00
4	1	000.0	1.0	.000	000.0 0.00
5	1	170.0	1.0	.000	000.0 0.00

Diffusion coefficients: (see pages 3-5 to 3-7 in manual)

120 <Molecular diffusion coefficient in water (mm2/day)
0.001 <Adjustment in Bresler's equation (a in equation 3.10 (ver.3)
10 <Adjustment in Bresler's equation (b in equation 3.10)
120 <Molecular diffusion coefficient in air (mm2/day)
.1400E+06 <Air diff. coeff. enhancement to account for atmospheric pressure fluctuations.

* The values of L1,L2--->Ln ('Link' in the Chemical Properties above)

* determine which species form a transformation chain.

* Setting Ln = 0 breaks the pathway, Ln = 1 restores it.

*

* Transformation pathways----->

* | RATE 1 | RATE 2 | RATE 3 | RATE 4
* SE1---/L1/--->SE2---/L2/--->SE3---/L3/--->SE4---/L4/--->...

* | RATE 5 | RATE 6 | RATE 7 | RATE 8 | Degradation pathways
* | | | | |
* v v v v v
* PRODUCT PRODUCT PRODUCT PRODUCT

*

TRANSFORMATION AND DEGRADATION RATE CONSTANTS

1 <Rate constants apply to bulk soil (1), or solution phase only (0)
Temperature and water content effects (transformation rate constants only):

0 <Include temperature subroutine and adjustments? yes(1), no(0)
 3 <Q10: factor by which rate constant changes per 10 C increase
 20 <Base temperature: at which rate constants below apply
 35 <Optimum temperature: Q10 relationship applies from 0 C to here
 50 <Maximum temperature: Rate constants decrease from optimum to here
 .08 <High end of optimum water content range: air-filled porosity
 -300 <Lower end of optimum water content: matric potential kPa
 -1500 <Minimum matric potential for transformations kPa
 0.6 <Relative transformation rate at saturation

 TRANSFORMATION RATE CONSTANTS (may be adjusted as specified above)

Layer no	Alachlor1	Atrazine	Chloride	Bromide	Alachlor2
	<----- day ^ -1 ----->				
1	0.0462E-00	0.1155E-01	0.0000E-00	0.0000E-00	0.0462E-00
1	0.0450E-00	0.1120E-01	0.0000E-00	0.0000E-00	0.0450E-00
2	0.0440E-00	0.1093E-01	0.0000E-00	0.0000E-00	0.0440E-00
2	0.0430E-00	0.1064E-01	0.0000E-00	0.0000E-00	0.0430E-00
3	0.0420E-00	0.1035E-01	0.0000E-00	0.0000E-00	0.0420E-00
3	0.0400E-00	0.1006E-01	0.0000E-00	0.0000E-00	0.0400E-00
4	0.0393E-00	0.0978E-01	0.0000E-00	0.0000E-00	0.0393E-00
4	0.0381E-00	0.0950E-01	0.0000E-00	0.0000E-00	0.0381E-00
5	0.0370E-00	0.0922E-01	0.0000E-00	0.0000E-00	0.0370E-00
5	0.0358E-00	0.0890E-01	0.0000E-00	0.0000E-00	0.0358E-00
6	0.0347E-00	0.0860E-01	0.0000E-00	0.0000E-00	0.0347E-00
6	0.0335E-00	0.0830E-01	0.0000E-00	0.0000E-00	0.0335E-00
7	0.0323E-00	0.0810E-01	0.0000E-00	0.0000E-00	0.0323E-00
7	0.0311E-00	0.0780E-01	0.0000E-00	0.0000E-00	0.0311E-00
8	0.0300E-00	0.0750E-01	0.0000E-00	0.0000E-00	0.0300E-00
8	0.0289E-00	0.0720E-01	0.0000E-00	0.0000E-00	0.0289E-00
9	0.0277E-00	0.0690E-01	0.0000E-00	0.0000E-00	0.0277E-00
9	0.0265E-00	0.0660E-01	0.0000E-00	0.0000E-00	0.0265E-00
10	0.0254E-00	0.0630E-01	0.0000E-00	0.0000E-00	0.0254E-00
10	0.0242E-00	0.0600E-01	0.0000E-00	0.0000E-00	0.0242E-00
11	0.0231E-00	0.0580E-01	0.0000E-00	0.0000E-00	0.0231E-00
11	0.0219E-00	0.0550E-01	0.0000E-00	0.0000E-00	0.0219E-00
12	0.0208E-00	0.0520E-01	0.0000E-00	0.0000E-00	0.0208E-00
12	0.0196E-00	0.0490E-01	0.0000E-00	0.0000E-00	0.0196E-00

 DEGRADATION RATE CONSTANTS (not influenced by water or temperature)

Layer no	Chemical 1	Chemical 2	Chemical 3	Chemical 4	Chemical 5
	<----- day ^ -1 ----->				
1	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
1	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
2	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
2	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
3	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
3	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
4	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
4	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
5	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
5	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
6	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
6	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
7	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
7	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
8	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
8	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
9	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
9	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
10	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
10	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
11	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
11	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
12	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00
12	0.0000E-00	0.0000E-01	0.0000E-01	0.0000E-01	00.0000E-00

CHEMICAL APPLICATIONS

2 < Number of broadcast applications. (At least 1. Can be past last date.)

Start of date (or day no.)	Incorporation (segments, 0 is surface)	Alachlor1	Atrazine	Chloride	Bromide	Alachlor2
		mg/sq.m (1mg/sq.m = .01kg/ha)				
071992	0	300	118	100	0	0
081392	0	0	0	0	100	300

RAIN/IRRIGATION AND WATER COMPOSITION

Choosing the steady-state flow option will prevent calls to the water flow subroutine, fix fluxes and concentrations

at those specified below and maintain theta constant with time. Interrupted steady-state can be specified by appropriate times and amounts. For the steady-state flow option, use a uniform soil column.

 1 < Water flow: Richards (1), modified Addiscott (2), steady-state (3).
 -5 < For Addiscott : matric potential at field capacity (kPa).
 -200 < : division between mobile and immobile water (kPa).
 0.4 < For steady-state: Water content in uniform column (theta)
 209 < Number of water applications. Some or all can be past last day.

Start time	Amount	Surface flux	Dissolved in water (can be 0)				
Date or	Time of	mm	density	Chem1	Chem2	Chem3	Chem4.....
Day no.	day		mm/d	mg/l			
3	.3	3.3	16.5	00.00	00.00	00.00	00.00
5	.3	10.9	20.0	00.00	00.00	00.00	00.00
9	.3	.3	1.3	00.00	00.00	00.00	00.00
10	.3	1.3	6.3	00.00	00.00	00.00	00.00
13	.3	2.3	11.4	00.00	00.00	00.00	00.00
14	.3	5.1	20.0	00.00	00.00	00.00	00.00
15	.3	7.4	14.7	00.00	00.00	00.00	00.00
23	.3	2.9	5.8	00.00	00.00	00.00	00.00
24	.3	14.1	20.0	00.00	00.00	00.00	00.00
29	.3	1.8	8.9	00.00	00.00	00.00	00.00
38	.3	2.4	4.8	00.00	00.00	00.00	00.00
40	.3	.5	1.0	00.00	00.00	00.00	00.00
47	.3	11.0	20.0	00.00	00.00	00.00	00.00
48	.3	1.3	2.5	00.00	00.00	00.00	00.00
49	.3	2.8	14.2	00.00	00.00	00.00	00.00
50	.3	.5	2.5	00.00	00.00	00.00	00.00
51	.3	.3	1.3	00.00	00.00	00.00	00.00
52	.3	2.0	10.2	00.00	00.00	00.00	00.00
54	.3	3.0	15.2	00.00	00.00	00.00	00.00
56	.3	4.3	8.7	00.00	00.00	00.00	00.00
57	.3	3.3	16.5	00.00	00.00	00.00	00.00
58	.3	.8	3.8	00.00	00.00	00.00	00.00
60	.3	6.1	12.2	00.00	00.00	00.00	00.00
62	.3	1.0	5.1	00.00	00.00	00.00	00.00
67	.3	.5	2.5	00.00	00.00	00.00	00.00
68	.3	2.0	10.2	00.00	00.00	00.00	00.00
69	.3	1.0	5.1	00.00	00.00	00.00	00.00
71	.3	18.0	20.0	00.00	00.00	00.00	00.00
78	.3	6.0	11.9	00.00	00.00	00.00	00.00
81	.3	4.4	8.8	00.00	00.00	00.00	00.00
85	.3	4.5	9.0	00.00	00.00	00.00	00.00
86	.3	4.5	20.0	00.00	00.00	00.00	00.00
87	.3	38.9	38.9	00.00	00.00	00.00	00.00
88	.3	.5	1.0	00.00	00.00	00.00	00.00
90	.3	6.8	20.0	00.00	00.00	00.00	00.00
93	.3	3.6	17.8	00.00	00.00	00.00	00.00
99	.3	1.3	6.3	00.00	00.00	00.00	00.00
102	.3	3.8	19.1	00.00	00.00	00.00	00.00
103	.3	9.9	20.0	00.00	00.00	00.00	00.00
108	.3	13.0	20.0	00.00	00.00	00.00	00.00
109	.3	2.3	11.4	00.00	00.00	00.00	00.00
110	.3	9.4	20.0	00.00	00.00	00.00	00.00
111	.3	7.6	20.0	00.00	00.00	00.00	00.00
113	.3	1.3	6.3	00.00	00.00	00.00	00.00
115	.3	1.3	6.3	00.00	00.00	00.00	00.00
116	.3	10.9	20.0	00.00	00.00	00.00	00.00
117	.3	8.1	20.0	00.00	00.00	00.00	00.00
122	.3	2.3	11.4	00.00	00.00	00.00	00.00
123	.3	2.3	11.4	00.00	00.00	00.00	00.00
124	.3	13.0	20.0	00.00	00.00	00.00	00.00
125	.3	2.3	11.4	00.00	00.00	00.00	00.00
127	.3	3.8	19.1	00.00	00.00	00.00	00.00
130	.3	2.8	14.0	00.00	00.00	00.00	00.00
135	.3	4.8	20.0	00.00	00.00	00.00	00.00
137	.3	3.6	17.8	00.00	00.00	00.00	00.00
138	.3	.3	1.3	00.00	00.00	00.00	00.00
139	.3	5.1	20.0	00.00	00.00	00.00	00.00
140	.3	.5	2.5	00.00	00.00	00.00	00.00
145	.3	1.5	7.6	00.00	00.00	00.00	00.00
146	.3	3.8	19.1	00.00	00.00	00.00	00.00
148	.3	4.3	20.0	00.00	00.00	00.00	00.00

149	.3	4.1	20.0	00.00	00.00	00.00	00.00	00.00
152	.3	25.1	25.1	00.00	00.00	00.00	00.00	00.00
153	.3	31.5	31.5	00.00	00.00	00.00	00.00	00.00
154	.3	6.9	20.0	00.00	00.00	00.00	00.00	00.00
157	.3	.5	2.5	00.00	00.00	00.00	00.00	00.00
158	.3	3.8	19.1	00.00	00.00	00.00	00.00	00.00
159	.3	1.0	5.1	00.00	00.00	00.00	00.00	00.00
172	.3	18.5	20.0	00.00	00.00	00.00	00.00	00.00
173	.3	1.8	8.9	00.00	00.00	00.00	00.00	00.00
174	.3	1.0	5.1	00.00	00.00	00.00	00.00	00.00
176	.3	4.1	20.0	00.00	00.00	00.00	00.00	00.00
179	.3	1.0	5.1	00.00	00.00	00.00	00.00	00.00
180	.3	3.3	16.5	00.00	00.00	00.00	00.00	00.00
186	.3	8.1	20.0	00.00	00.00	00.00	00.00	00.00
197	.3	1.8	8.9	00.00	00.00	00.00	00.00	00.00
198	.3	4.1	20.0	00.00	00.00	00.00	00.00	00.00
191	.3	14.5	20.0	00.00	00.00	00.00	00.00	00.00
193	.3	2.3	11.4	00.00	00.00	00.00	00.00	00.00
195	.3	12.4	20.0	00.00	00.00	00.00	00.00	00.00
196	.3	3.0	15.2	00.00	00.00	00.00	00.00	00.00
197	.3	13.0	20.0	00.00	00.00	00.00	00.00	00.00
198	.3	11.9	20.0	00.00	00.00	00.00	00.00	00.00
200	.3	23.1	23.1	00.00	00.00	00.00	00.00	00.00
201	.3	7.1	20.0	00.00	00.00	00.00	00.00	00.00
202	.3	5.6	20.0	00.00	00.00	00.00	00.00	00.00
203	.3	3.3	16.5	00.00	00.00	00.00	00.00	00.00
205	.3	15.7	20.0	00.00	00.00	00.00	00.00	00.00
206	.3	11.9	20.0	00.00	00.00	00.00	00.00	00.00
207	.3	.3	1.3	00.00	00.00	00.00	00.00	00.00
209	.3	15.2	20.0	00.00	00.00	00.00	00.00	00.00
212	.3	4.1	20.0	00.00	00.00	00.00	00.00	00.00
213	.3	33.0	33.0	00.00	00.00	00.00	00.00	00.00
214	.3	3.0	15.2	00.00	00.00	00.00	00.00	00.00
218	.3	3.0	15.2	00.00	00.00	00.00	00.00	00.00
222	.3	3.3	16.5	00.00	00.00	00.00	00.00	00.00
224	.3	5.1	20.0	00.00	00.00	00.00	00.00	00.00
227	.3	29.7	29.7	00.00	00.00	00.00	00.00	00.00
229	.3	3.8	19.1	00.00	00.00	00.00	00.00	00.00
231	.3	4.1	20.0	00.00	00.00	00.00	00.00	00.00
232	.3	.8	3.8	00.00	00.00	00.00	00.00	00.00
235	.3	.3	1.3	00.00	00.00	00.00	00.00	00.00
241	.3	.8	3.8	00.00	00.00	00.00	00.00	00.00
242	.3	46.2	46.2	00.00	00.00	00.00	00.00	00.00
243	.3	.5	2.5	00.00	00.00	00.00	00.00	00.00
247	.3	3.0	15.2	00.00	00.00	00.00	00.00	00.00
248	.3	13.0	20.0	00.00	00.00	00.00	00.00	00.00
253	.3	16.8	20.0	00.00	00.00	00.00	00.00	00.00
254	.3	.3	1.3	00.00	00.00	00.00	00.00	00.00
255	.3	28.7	28.7	00.00	00.00	00.00	00.00	00.00
263	.3	14.2	20.0	00.00	00.00	00.00	00.00	00.00
266	.3	4.3	20.0	00.00	00.00	00.00	00.00	00.00
267	.3	14.2	20.0	00.00	00.00	00.00	00.00	00.00
270	.3	22.6	22.6	00.00	00.00	00.00	00.00	00.00
271	.3	6.1	20.0	00.00	00.00	00.00	00.00	00.00
272	.3	5.6	20.0	00.00	00.00	00.00	00.00	00.00
275	.3	1.3	6.3	00.00	00.00	00.00	00.00	00.00
283	.3	.5	2.5	00.00	00.00	00.00	00.00	00.00
284	.3	1.5	7.6	00.00	00.00	00.00	00.00	00.00
285	.3	1.8	8.9	00.00	00.00	00.00	00.00	00.00
286	.3	2.3	11.4	00.00	00.00	00.00	00.00	00.00
289	.3	2.0	10.2	00.00	00.00	00.00	00.00	00.00
290	.3	13.7	20.0	00.00	00.00	00.00	00.00	00.00
291	.3	1.5	7.6	00.00	00.00	00.00	00.00	00.00
293	.3	6.6	20.0	00.00	00.00	00.00	00.00	00.00
294	.3	.5	2.5	00.00	00.00	00.00	00.00	00.00
295	.3	1.3	6.3	00.00	00.00	00.00	00.00	00.00
296	.3	1.8	8.9	00.00	00.00	00.00	00.00	00.00
298	.3	5.3	20.0	00.00	00.00	00.00	00.00	00.00
299	.3	12.4	20.0	00.00	00.00	00.00	00.00	00.00
301	.3	4.1	20.0	00.00	00.00	00.00	00.00	00.00
304	.3	3.3	16.5	00.00	00.00	00.00	00.00	00.00
306	.3	.3	1.3	00.00	00.00	00.00	00.00	00.00
307	.3	4.8	20.0	00.00	00.00	00.00	00.00	00.00
308	.3	15.7	20.0	00.00	00.00	00.00	00.00	00.00
310	.3	1.8	8.9	00.00	00.00	00.00	00.00	00.00
311	.3	6.4	12.7	00.00	00.00	00.00	00.00	00.00
312	.3	3.8	19.0	00.00	00.00	00.00	00.00	00.00
316	.3	1.8	8.9	00.00	00.00	00.00	00.00	00.00
317	.3	3.8	19.1	00.00	00.00	00.00	00.00	00.00
318	.3	6.9	20.0	00.00	00.00	00.00	00.00	00.00

319	.3	.5	2.5	00.00	00.00	00.00	00.00	00.00
323	.3	1.8	3.6	00.00	00.00	00.00	00.00	00.00
324	.3	2.0	4.1	00.00	00.00	00.00	00.00	00.00
325	.3	2.0	10.2	00.00	00.00	00.00	00.00	00.00
327	.3	.5	2.5	00.00	00.00	00.00	00.00	00.00
328	.3	21.1	21.1	00.00	00.00	00.00	00.00	00.00
329	.3	6.6	20.0	00.00	00.00	00.00	00.00	00.00
330	.3	8.1	20.0	00.00	00.00	00.00	00.00	00.00
335	.3	.8	3.8	00.00	00.00	00.00	00.00	00.00
342	.3	.3	.5	00.00	00.00	00.00	00.00	00.00
343	.3	1.0	2.0	00.00	00.00	00.00	00.00	00.00
346	.3	6.6	13.2	00.00	00.00	00.00	00.00	00.00
347	.3	7.4	14.7	00.00	00.00	00.00	00.00	00.00
350	.3	1.6	3.1	00.00	00.00	00.00	00.00	00.00
351	.3	1.6	3.1	00.00	00.00	00.00	00.00	00.00
352	.3	4.7	9.3	00.00	00.00	00.00	00.00	00.00
353	.3	15.5	20.0	00.00	00.00	00.00	00.00	00.00
355	.3	4.9	20.0	00.00	00.00	00.00	00.00	00.00
364	.3	.8	3.8	00.00	00.00	00.00	00.00	00.00
365	.3	5.1	20.0	00.00	00.00	00.00	00.00	00.00
366	.3	18.0	20.0	00.00	00.00	00.00	00.00	00.00
370	.3	3.0	15.2	00.00	00.00	00.00	00.00	00.00
371	.3	2.5	12.7	00.00	00.00	00.00	00.00	00.00
375	.3	.8	3.8	00.00	00.00	00.00	00.00	00.00
379	.3	11.3	20.0	00.00	00.00	00.00	00.00	00.00
380	.3	4.6	9.1	00.00	00.00	00.00	00.00	00.00
388	.3	2.5	12.7	00.00	00.00	00.00	00.00	00.00
389	.3	1.0	5.1	00.00	00.00	00.00	00.00	00.00
396	.3	.3	1.3	00.00	00.00	00.00	00.00	00.00
398	.3	1.0	2.0	00.00	00.00	00.00	00.00	00.00
401	.3	1.0	2.0	00.00	00.00	00.00	00.00	00.00
403	.3	3.0	15.2	00.00	00.00	00.00	00.00	00.00
420	.3	7.5	15.0	00.00	00.00	00.00	00.00	00.00
428	.3	2.2	4.3	00.00	00.00	00.00	00.00	00.00
429	.3	2.2	4.3	00.00	00.00	00.00	00.00	00.00
430	.3	.6	1.3	00.00	00.00	00.00	00.00	00.00
431	.3	8.5	17.0	00.00	00.00	00.00	00.00	00.00
433	.3	4.5	8.9	00.00	00.00	00.00	00.00	00.00
434	.3	.9	1.8	00.00	00.00	00.00	00.00	00.00
442	.3	4.3	8.5	00.00	00.00	00.00	00.00	00.00
448	.3	2.3	4.6	00.00	00.00	00.00	00.00	00.00
449	.3	14.7	20.0	00.00	00.00	00.00	00.00	00.00
450	.3	4.6	9.2	00.00	00.00	00.00	00.00	00.00
451	.3	4.6	9.2	00.00	00.00	00.00	00.00	00.00
452	.3	4.6	9.2	00.00	00.00	00.00	00.00	00.00
453	.3	6.9	13.8	00.00	00.00	00.00	00.00	00.00
454	.3	3.6	7.1	00.00	00.00	00.00	00.00	00.00
455	.3	9.9	19.8	00.00	00.00	00.00	00.00	00.00
456	.3	11.5	20.0	00.00	00.00	00.00	00.00	00.00
457	.3	11.7	20.0	00.00	00.00	00.00	00.00	00.00
458	.3	10.4	20.0	00.00	00.00	00.00	00.00	00.00
459	.3	7.1	14.2	00.00	00.00	00.00	00.00	00.00
460	.3	2.3	11.5	00.00	00.00	00.00	00.00	00.00
466	.3	3.3	16.5	00.00	00.00	00.00	00.00	00.00
467	.3	54.1	54.1	00.00	00.00	00.00	00.00	00.00
469	.3	1.5	3.1	00.00	00.00	00.00	00.00	00.00
470	.3	3.3	16.5	00.00	00.00	00.00	00.00	00.00
471	.3	.3	1.3	00.00	00.00	00.00	00.00	00.00
472	.3	13.0	20.0	00.00	00.00	00.00	00.00	00.00
473	.3	43.2	43.2	00.00	00.00	00.00	00.00	00.00
474	.3	7.6	20.0	00.00	00.00	00.00	00.00	00.00
477	.3	18.3	20.0	00.00	00.00	00.00	00.00	00.00
478	.3	3.6	7.1	00.00	00.00	00.00	00.00	00.00
479	.3	.0	.1	00.00	00.00	00.00	00.00	00.00
480	.3	26.4	26.4	00.00	00.00	00.00	00.00	00.00
481	.3	2.0	10.2	00.00	00.00	00.00	00.00	00.00
482	.3	16.0	20.0	00.00	00.00	00.00	00.00	00.00
483	.3	1.5	7.6	00.00	00.00	00.00	00.00	00.00

POTENTIAL ET (WEEKLY TOTALS, mm), DEPTH TO WATER TABLE (mm)
 MEAN WEEKLY TEMPERATURES AND MEAN WEEKLY AMPLITUDE (degrees C)

Week no.	ET	Water table	Mean temp	Amplitude	pan	lin+pan
1	2.7	0.	-6	4.5	.0	2.7
2	2.7	0.	.0	3.0	.0	2.7
3	.0	0.	-10.2	5.5	.0	.0
4	.8	0.	-4.7	3.5	.0	.8
5	.0	0.	-3.8	3.4	.0	.0

6	.0	0.	-7.6	6.0	.0	.0
7	.0	0.	-4.0	5.2	.0	.0
8	3.2	0.	1.2	3.0	.0	3.2
9	.3	0.	-2.3	4.6	.0	.3
10	7.3	0.	3.9	4.2	.0	7.3
11	.0	0.	-6.7	4.9	.0	.0
12	.0	0.	-6.0	6.0	.0	.0
13	3.8	0.	.8	3.8	.0	3.8
14	4.8	0.	1.2	4.1	.0	4.8
15	10.5	0.	5.2	6.5	.0	10.5
16	11.0	0.	6.4	4.7	.0	11.0
17	16.0	0.	10.3	5.0	.0	16.0
18	17.7	0.	10.0	6.9	.0	17.7
19	18.3	0.	11.1	6.2	26.3	21.9
20	23.7	0.	15.2	6.0	27.7	27.7
21	26.1	0.	13.6	9.2	36.8	36.8
22	16.4	0.	11.2	4.6	26.4	26.4
23	29.2	0.	18.8	6.2	27.4	27.4
24	29.1	0.	16.7	8.5	49.8	49.8
25	22.9	0.	15.5	4.8	28.4	28.4
26	27.5	0.	16.6	7.4	34.0	34.0
27	27.7	0.	17.5	6.5	41.7	41.7
28	29.4	0.	19.7	5.3	28.7	28.7
29	31.2	0.	20.6	5.6	30.5	30.5
30	23.9	0.	17.6	3.7	14.5	14.5
31	28.6	0.	18.7	5.8	34.5	34.5
32	27.9	0.	18.5	5.5	27.9	27.9
33	22.8	0.	16.3	4.2	16.5	16.5
34	29.0	0.	17.9	6.9	31.2	31.2
35	31.0	0.	19.9	6.0	27.4	27.4
36	25.8	0.	17.3	5.5	22.9	22.9
37	25.9	0.	15.8	6.9	26.9	26.9
38	27.8	0.	17.9	6.0	26.2	26.2
39	19.8	0.	11.6	6.9	20.8	20.8
40	14.9	0.	7.9	6.6	19.0	19.0
41	18.4	0.	10.8	6.8	14.0	14.0
42	13.0	0.	7.3	5.2	11.2	11.2
43	8.7	0.	4.4	5.0	15.5	15.5
44	8.1	0.	3.8	4.5	11.7	10.7
45	5.9	0.	2.3	4.6	.0	5.9
46	6.4	0.	3.2	4.3	.0	6.4
47	6.3	0.	2.9	4.3	.0	6.3
48	6.5	0.	4.7	2.0	.0	5.9
49	1.3	0.	-1.5	3.3	.0	1.3
50	.0	0.	-4.3	4.8	.0	.0
51	.6	0.	.5	3.0	.0	.6
52	.0	0.	-5.4	4.2	.0	.0
53	6.9	0.	1.1	4.7	.0	6.9
54	2.4	0.	-2.9	3.6	.0	2.4
55	.0	0.	-4.0	3.6	.0	.0
56	3.0	0.	-2.2	4.7	.0	3.0
57	.0	0.	-7.2	5.1	.0	.0
58	.0	0.	-9.3	7.2	.0	.0
59	.0	0.	-5.0	4.6	.0	.0
60	.0	0.	-8.9	6.5	.0	.0
61	.0	0.	-10.7	7.4	.0	.0
62	.0	0.	-1.1	4.2	.0	.0
63	.0	0.	-7.8	4.4	.0	.0
64	.0	0.	-5.5	6.8	.0	.0
65	.0	0.	3.1	5.0	.0	.0
66	1.8	0.	2.9	4.3	.0	1.8
67	11.8	0.	6.3	5.7	.0	11.8
68	14.3	0.	8.3	5.6	.0	14.3
69	12.7	0.	7.9	5.6	.0	12.7

Appendix 7.2. Differentiation between regions in TRANSMIT
(Caldwell Field and Geneva). Extracted from
TRANSMIT input data file.

SPATIAL SCALING AND WEIGHTING COEFFICIENTS.
(Items marked * will be adjusted to total 1 in the model)

5 [No. of soil columns: 1 or greater (cannot be 2 for 2-D)]
2 [2-dim (1), macropore (2), sensitivity (3)]

```

1      [Overflow at the surface: 0 (no) ,1 (yes)]
0      [Lateral equilibration during infiltration: yes(1), no(0)]
1 1 1 1 1      (Vertical flow: yes (1); no (0))
.24 .46 .71 1.09 2.06      (Geometric scaling factor for hydraulic properties)
      1 1 1 1 1      (Bulk density adjustment)
      1 1 1 1 1      (Relative Area *) (1 3 5 7...., 7 5 3 1... or 1 1 1
1000 1000 1000 1000 1000      (Depth of scaling, mm)
      1 1 1 1 1      (Relative Irrigation weighting *) To get equal
dept

```

File 1 Pg 1 Ln 53 Pos 1

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1 1      (Vertical flow: yes (1); no (0))
71 1.09 2.06      (Geometric scaling factor for hydraulic properties)
1 1 1      (Bulk density adjustment)
1 1 1      (Relative Area *) (1 3 5 7...., 7 5 3 1... or 1 1 1
1000 1000 1000      (Depth of scaling, mm)
1 1 1      (Relative Irrigation weighting *) To get equal dept
1 1 1      (Chemical application weighting *) equal to relativ
1 1 1      (Partition coefficient adjustment)
0 50 50      (Diffusion diameter mm, equal for 2-D)
00 10000 10000 10000      (Surface seal limit mm/day, not used in steady-
1 1 1      (Rate constant adjustment)
10 10 10      (Distance for root:soil gradient, mm. Default is 10
1 1 1      (Fraction of equil. sites (for two-site sorption)
1 1 1      (Phase transfer coefficient day**-1)
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