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BARD

FINAL REPORT

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**Consequences of Nonequilibrium Pesticide
Fate Processes on Probability of Leaching
from Agricultural Lands**

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CONSEQUENCES OF NON-EQUILIBRIUM PESTICIDE FATE PROCESSES ON PROBABILITY OF LEACHING FROM AGRICULTURAL LANDS

ABSTRACT

Pesticide leaching in heterogeneous field soils is relatively unstudied and is the focus of this project. A wide variety of heterogeneous soils exist, characterized by processes that result from the presence of structural cracks, worm holes, and other preferred pathways within which the majority of transport can occur (called physical non-equilibrium processes), along with the presence of sorption processes that are both equilibrium and kinetic (chemical non-equilibrium processes). Previous studies of pesticide leaching have focused primarily on relatively homogeneous soils, which are less widely distributed in nature, but more studied due to the relative ease with which quantitative theory can be applied to interpret experimental results. The objectives of the proposed project were: first, to gain greater insight into the basic physical and chemical processes that characterize non-equilibrium systems, second, to improve our ability to predict pesticide leaching in heterogeneous field soils, and third, to estimate the consequences of non-equilibrium processes at the field scale by conducting an analysis of the probability of pesticide leaching when non-equilibrium processes prevail. The laboratory, theoretical and modelling aspects of the project were successful; the field aspects less so. We gained greater insight into basic processes in heterogeneous field soils, and we improved and tested tools (simulation models) and the methodology of using such tools for assessing the probability of pesticide leaching as a contribution to broader risk analysis efforts.

CONSEQUENCES OF NONEQUILIBRIUM PESTICIDE FATE PROCESSES ON PROBABILITY OF LEACHING FROM AGRICULTURAL LANDS

Abstract

The main objective of the Israeli part of the research was to study the effect of nonequilibrium adsorption on the transport of pesticides under field conditions. A secondary objective was to determine the effect of organic amendments to the soil on these processes. The work carried out included laboratory column studies to determine the effects of both physical and chemical nonequilibrium on pesticide transport as well as field lysimeter studies.

The vast number of field studies on pesticide transport has shown that most mathematical models used are unable to accurately predict or describe transport. The reason is that these models have assumed instantaneous equilibrium for the sorption process and did not take into account field heterogeneity of both soil chemical and physical properties. More recent models that take into account dynamics and heterogeneity provide better results but still require significant field calibration. This difficulty in predictive capability is further exacerbated by temporal changes in the field moisture content, fluctuations in which affect the sorption and desorption processes.

Laboratory breakthrough curves (BTCs) of selected pesticides were obtained under steady-state, unsaturated conditions using a glass fiber wick to maintain the necessary water tension in the soil column. In all cases (i.e. all soils and flow rates) chloride eluted from the columns at less than 1 pore volume. The explanation for this phenomenon seems to be related to changes in the ratio of the mobile and immobile water contents. BTCs were symmetrical with only minor tailing. BTCs for the pesticides studied exhibited delayed breakthrough (sorption) and tailing indicating that nonequilibrium conditions existed. In a second series of laboratory studies columns were prepared with artificial macropores of different lengths and the effect of these macropores on solute transport was determined. It was observed that short macropores had little or no effect on breakthrough whereas longer ones resulted in a dual inflection BTC.

Two field studies were conducted utilizing mini-lysimeters. In the first study the movement of alachlor, bromacil and atrazine in two soils was studied in the presence and absence of sludge or straw and under different application regimes. The variability observed in pesticide content with depth was such that it masked any treatment effects. A second run was made in the lysimeters with atrazine only, with and without the addition of atrazine degrading microbes. Sludge and composted sludge were also applied to the lysimeters and irrigation was with high quality water and two effluents of different quality. The results showed a clear difference in microbial activity between the soils receiving an organic amendment and those without as well as an effect of irrigation water quality.

Our major conclusion concerning the movement of pesticides in field soils is that inherent spatial variability of field soils is such that a detailed study of the leaching of pesticides on the scale of several centimeters is at best extremely difficult. The presence of organic amendments affects not only pesticide transport but also microbial activity, which can greatly impact pesticide fate.

Achievements

In this study we attempted to enhance our ability to manage pesticide application, not only by increasing our knowledge of basic processes, but also by integrating this knowledge into operational predictive models of pesticide leaching. By combining well-designed laboratory and field experiments with advanced predictive models constructed specifically for the case of heterogeneous soils we hoped to contribute toward the reliable estimation of the probability of pesticide leaching.

One of the main drawbacks on laboratory studies of nonequilibrium processes is that they are generally conducted under saturated conditions and their results are difficult to incorporate into models designed for field scale analysis. We believe that our use of glass fiber wicks to maintain unsaturated conditions in the soil column is one of the first successful attempts at studying this phenomenon under conditions applicable to field studies. It was found that while the basic processes affecting nonequilibrium phenomena in unsaturated soils are the same as in saturated soils, there are subtle differences that may have great import on pesticide transport modeling. These results can eventually (5-10 years, if not sooner) be incorporated into pesticide fate models. This could have been accomplished sooner if not for the untimely passing of the senior US investigator (Dr. J. Waganet).

The benefits that can result from more efficient pesticide application and use are not related to crop yield but to the quality of the environment, specifically groundwater and thus are difficult to put into economic terms.

As mentioned previously, the project began as a joint effort of both teams and was the result of a previous BARD project. The planning was carried out at a joint meeting held in Bet Dagan and during the early stages of the work both sides were in contact, exchanging data and ideas. One of the Israeli participants visited the US partner and took part in planning the fieldwork to be conducted at Cornell. The untimely deaths of two of the investigators (Drs Waganet and Frenkel) and the relocation of the remaining US collaborator resulted in problems making cooperation of the nature originally planned and achieved extremely difficult.

Publication Summary (numbers)

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Refereed (published, in press, accepted)			0	
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Invited review papers			0	
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Books			0	
Master theses			0	
Ph.D. theses			0	
Abstracts			0	
Not refereed (proceedings, reports, etc.)			3	

Patent Summary (numbers)

	Israeli inventor only	US inventor only	Joint IS/US inventors	Total
Submitted	0			
Issued (allowed)	0			
Licensed	0			

Cooperation Summary (numbers)

	From US to Israel	From Israel to US	Together, elsewhere	Total
Visits/Meetings		2		
Sabbaticals		0		
Postdoctorates		0		

- **Cooperation**, briefly explain whether synergistic, complementary or supportive.

The project began as a cooperative effort of both teams and was planned at a joint meeting held in Bet Dagan. During the beginning of the project joint meetings were held and the work plan was coordinated. Due to the untimely deaths of Drs Waganet and Frenkel and the relocation of Dr. Hutson the cooperative nature of the work ceased.

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Ms Laura Chan, student assistant, who maintained her willingness, enthusiasm and tenacity under sometimes trying and difficult circumstances.

The Cornell team also pays tribute to the late Dr Jeff Wagenet, Principal Investigator, whose energy, insight and enthusiasm contributed so much to our BARD projects, and to the development of current concepts of pesticide fate in soils.

CHAPTER 1

INTRODUCTION

This proposal was a continuation of a previous BARD project (US1753-89).

The current project was intended to expand and use the results of the previous project. The prime objective was to examine the consequences of the non-equilibrium transport insofar as it influences our ability to predict leaching hazards in soils of the USA and Israel. This will involve extending the TRANSMIT model to a wider range of conditions than were examined in the previous BARD, and necessitated investigation into the effects of organic matter amendments on pesticide behavior.

DETAILS OF THE PRECEDING BARD PROJECT.

Title: Predicting the effect of kinetic-equilibrium sorption and macropore flow upon pesticide movement in agricultural soil. US 1753-89

Duration: September 1990 -September 1993

<i>Investigators Names</i>	<i>Investigators Institutions</i>
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Objectives of the original project

1) To develop through carefully controlled laboratory experiments, an improved and more realistic representation of pesticide sorption than is presently available for alachlor and atrazine 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 model developed in objective 2 to field data of atrazine and alachlor in both homogeneous and nonhomogeneous soils.

1.1 DESCRIPTION OF THE PROBLEM

There is widespread recognition that the agricultural use of pesticides sometimes results in groundwater and surface water contamination. While there have been numerous studies over the last several years that focus on these issues, there remain unknowns in our understanding of the basic physical, chemical and biological processes that determine site-specific pesticide behavior. One major reason is that over the last decade, the focus has been on the spatial variability of soil properties and processes in relatively *homogeneous* soils. However, a widespread, and until recently under-researched category of soils, the *heterogeneous* soils, also exist and are proving to be quite important to agriculture. Homogeneous and heterogeneous soils can be distinguished in terms of the size of their representative elementary volume (REV), which is defined in terms of the particular soil property being considered (Wagenet, 1985). In this project, where water flow and leaching are primary issues, pore size distribution is a key property. The REV for this project is therefore defined in terms of pore size distribution as the smallest macroscopic unit of soil that expresses all the microscopic variability in pore size distribution present in the soil. A homogeneous soil is generally composed of a relatively narrow range of pore sizes and the REV that characterizes the system is correspondingly small. A heterogeneous soil consists of a larger range of pore sizes, including structural cracks, voids, and macropores, with a commensurately larger REV. A large number of leaching studies have been conducted in homogeneous soils; fewer in heterogeneous soils. The result is a gap in our knowledge that currently prevents us from effectively managing pesticide applications, or from predicting the consequences of such application on non-target components of the environment, such as surface and ground waters.

Studies of leaching of pesticides in heterogeneous soils must focus on the influence of both physical and chemical non-equilibrium processes affecting pesticide mobility. Such processes generally derive from the heterogeneous nature of both the physical structures and pore geometries, and the time-dependent interaction of the adsorbate with the various adsorption sites. The basic processes of water flow, chemical transport and sorption are only partially understood in these systems. New model formulations have been evolved to deal with these more realistic conceptualizations of most soil systems, yet only minimal parameterization of the models has been possible, and no extensive field testing has yet been accomplished. It is proving to be a substantial challenge to simultaneously consider such physical non-equilibrium processes as macropore transport or mobile/immobile water, and at the same time to consider chemical non-equilibrium processes that result from combinations of multiple sorption sites, each possibly described as partly at equilibrium in its chemical behavior, or partly kinetic. Add to this the chemical diffusion of pesticide which redistributes it between mobile and immobile porosity, the swelling and shrinking of organic soils and clay aggregates in response to changes in moisture content and the heterogeneous system becomes conceptually complex and difficult to study.

The above complexity notwithstanding, it is now clear that it is crucial that such systems be well understood, for the leaching of pesticides is probably dominated more by these non-equilibrium processes than by the more classic forms of conceptually simplified transport models that describe homogeneous systems. Whether it be rapid flow along structural anomalies that bypass the soil matrix, or very slow kinetic release of sorbed

pesticide that creates a slow leakage of chemical over a long time at low concentrations, it is important to understand and relate these processes to field behavior of applied pesticides.

One of the crucial consequences of pesticide leaching is its impact upon groundwater quality. Whether the chemical fluxes are relatively large over short times or smaller over long times, there is an impact on the water quality. There has been little attention paid to analysis of this impact as it derives from non-equilibrium processes in heterogeneous porous media. Given previous studies of soil variability in relatively homogeneous systems (reviewed by e.g., Nielsen et al., 1986), and new studies on the influence of non-equilibrium processes in relatively heterogeneous media (discussed below), it should now be possible to take the next step of estimating the combined influences of soil spatial variability and non-equilibrium physical and chemical processes upon the probability of pesticide leaching to groundwater. Probabilistic assessment of pesticide flux to groundwater in the presence of the uncertainties generated by these multiple processes is now well within our computational capabilities (as demonstrated for homogeneous systems by van der Zee and Boesten, 1991), given more understanding of the basic non-equilibrium processes described above. Once accomplished, this analysis will provide regulators, planners and farmers with the opportunity to better evaluate the consequences of non-equilibrium processes on pesticide leaching, and to properly consider the uncertainty of the leaching predictions as risk analysis is conducted.

1.2 OBJECTIVES

The original objectives of this project were defined as:

1. To extend and apply the understanding of physical and chemical non-equilibrium processes for the better management of pesticides through improved capacity to predict pesticide leaching.
2. To establish the credibility of improved predictive tools through the analysis of results obtained from a series of field experiments of pesticide behavior focused on issues of physical aggregation and organic matter content.
3. To estimate the consequences of non-equilibrium processes at the field scale by conducting an analysis of the probability of pesticide leaching when non-equilibrium processes prevail.

Through circumstances largely beyond our control, the field aspects of this project were not successful. The summer of 1995 was the driest on record in Ithaca, and although the mini-lysimeter experiment was laid out and the pesticides applied, there was not a single rain event that produced any leaching. Water was applied by hand, the soils were sampled and analysed, but the results were so inconclusive that they are not reported here. The concept was sound and probably worth repeating, which would have happened under happier circumstances.

Nevertheless, the laboratory and theoretical aspects of the project were illuminating, leading to some new insights into the behavior of pesticides in soils that were amended by

additions of organic matter, and the development and improvement of modeling tools which can be applied to both laboratory and field scenarios.

1.3 BACKGROUND

The rationale and necessity for this project was outlined in the project proposal, but is included here as background information.

There have been many studies over the last two decades that focus on the transport and transformation of pesticides (reviewed by Wagenet and Rao, 1990). In the large majority of the cases presented in the literature, the work has been accomplished on homogeneous soils using basic principles of water flow and chemical transport that evolve from either well-controlled laboratory studies in uniformly packed soil columns, or from field experiments conducted on sites specifically selected to be analogous to the soil column laboratory work. As a result, the current convention for these soils is to describe water movement as the product of a water-content dependent hydraulic conductivity and a gradient in hydraulic potential (Darcy, 1856; Richards, 1931). Chemical transport in these soils has been described as resulting from both the convective macroscopic water flux and the combined processes of hydrodynamic dispersion and chemical diffusion in the aqueous phase (often referred to as the convection-dispersion equation, CDE), coupled mathematically with terms that describe sorption (usually as an equilibrium isotherm), degradation, and volatilization (Nielsen et al. 1986; Wagenet and Rao, 1990). While these studies have led to advances in describing basic flow processes under controlled conditions, they have resulted in only limited success in describing many field cases. This is particularly true in the case of pesticide leaching models, which have only recently been developed and applied to field cases (Wagenet and Rao, 1990).

A major reason for the current lack of agreement between model prediction and field measurement of pesticide leaching is that many field soils are heterogeneous rather than homogeneous. In these latter cases, it is not sufficient to apply models developed for homogeneous cases and then to account for heterogeneity by allowing coefficients to be spatially variable. Heterogeneous systems are often subject to water flow through cracks or macropores that bypass the soil matrix, or to combined equilibrium-kinetic processes of sorption that result from the multiple and different sorption sites that exist in these soils. Neither of these processes of physical non-equilibrium of water flow nor chemical non-equilibrium of pesticide sorption is easily described by the modeling approaches derived from the Richards equation or the CDE.

Studies of non-equilibrium processes have been reported for a number of years, but in lesser numbers than the use of the Richards equation or the CDE. Macropore flow, bypass flow, and mobile/immobile water flow, collectively termed preferential flow by Beven (1991), are examples of the types of physical non-equilibrium conditions studied. In almost all these studies, the models presented have been either analytical solutions or simple numerical solutions limited in their broad applicability (e.g., Addiscott, 1977; Beven and Germann 1981; Davidson, 1985; Nielsen et al. 1986; Steenhuis and Parlange, 1991;). Recent extension of these solutions to field soils (e.g., Steenhuis et al. 1990; Gerke and van Genuchten, 1993; Hutson and Wagenet, 1993) are representative of the first attempts to provide water flow models that consider the heterogeneous soil system under transient field

conditions.

In the case of solute (pesticide) transport, there have been a number of conceptualizations of combined non-equilibrium physical and chemical processes (Oddson et al., 1970; Lapidus and Amundson, 1952; van Genuchten et al. 1974; van Genuchten, 1981; van Genuchten and Wagenet, 1989; Toride et al., 1993). All the above cases have been developed for steady-state, water-saturated conditions. The consideration of a two-domain system, with a proportion of the system relatively mobile and chemically non-reactive, and a proportion relatively non-mobile that consists of chemically reactive surfaces, is the basis of these approaches. These solutions have been successfully applied in a number of laboratory cases (e.g., Garmender et al., 1990, 1991; Lee et al., 1988; Brusseau et al. 1989; Brusseau et al. 1993). Only recently have models based on these concepts been extended to field conditions (Gerke and van Genuchten, 1993; Hutson and Wagenet, 1993), with the former constrained to a dual porosity system and an equilibrium representation of sorption, while the latter considers combined equilibrium-kinetic sorption and subdivides the soil into multiple hydraulic regions, each of which conducts water and pesticide either as a component of the matrix or as a preferred pathway of extremely rapid flow (this model was developed as an objective of the previous BARD project US 1753-89, and is further explained below). Development of models of pesticide leaching that consider such multiple effects are the first steps in increasing our capacity to better predict the probability of pesticide leaching.

There also remain substantial questions regarding the proper representation of non-equilibrium sorption in pesticide leaching models. There are several possible reasons, all of which are potentially present and influential at any one time. The non-hysteretic behavior of the adsorption-desorption isotherm, the influence of wetting-drying cycles at the soil surface on pesticide-organic matter interaction, the timing between pesticide application and the next water application as it affects partitioning between kinetic and equilibrium sorption sites, and the influence of pesticide solubility on its availability to participate in sorption or be transported are all possible processes that need to be better considered as improved pesticide leaching models are developed.

This study was an attempt to enhance our ability to manage pesticides by not only increasing our knowledge of basic process, but also by integrating this new knowledge into operational predictive models of pesticide leaching. The combination of well-designed laboratory and field experiments, and the use of predictive models constructed specifically for the case of heterogeneous field soils, offered the opportunity to make significant contributions to estimating the probability of pesticide leaching. The modeling approach was specifically designed to be flexible in its ability to consider time-varying soil surface conditions of rainfall, irrigation, soil manipulation, pesticide management and the more subtle physical and chemical processes that affect pesticide leaching. Improved capacity to predict pesticide leaching will enable the formulation of risk assessment procedures and regulations for safe pesticide use, where "safe use" in this case refers to pesticide management practices that minimize pesticide leaching beyond the point of application. Without capacity to define safe management practices some pesticides which are of great agricultural importance may have to be banned due to an erroneous presumed risk associated with their use.

CHAPTER TWO

NONEQUILIBRIUM TRANSPORT OF REACTIVE SOLUTES THROUGH LAYERED SOIL PROFILES WITH DEPTH-DEPENDENT ADSORPTION

2.1 INTRODUCTION

Movement of chemical pollutants through heterogeneous soil profiles commonly occurs in the environment. One prominent feature of many heterogeneous soils is the shift in sorption capacity for reactive solutes with depth due to changes in the content of organic matter, the predominant sorbent for organic pollutants in soils (Karickhoff, 1984; Chiou *et al*, 1983; Felsot and Dahm, 1985). In addition, organic materials from sources such as sludge, manure, and crop residues are often applied artificially to soil surfaces to improve soil structure as well as to increase the soil's capacity for retaining reactive chemicals such as pesticides, and hence reduce the potential for groundwater contamination (Shea 1985; Clapp *et al*, 1980). Therefore, understanding chemical transport through heterogeneous soil profiles is essential for more reliable predictions of the fate of pollutants in the environment.

Chemical transport in soil is most commonly described by the advection-dispersion equation (ADE), which is based on the mass-conservation law. Since this equation is most easily solved by assuming a homogeneous medium (van Genuchten and Wierenga, 1986; Biggar and Nielsen, 1967), its application to describe chemical transport in layered and other heterogeneous soil profiles is often accomplished by treating the more complex system as an equivalent single layer (Kreft and Zuber, 1978; Barry and Parker, 1987; Barry *et al*, 1988). Using the method of time moment analysis, Barry and Parker (1987) derived conditions under which the equivalent single layer model would accurately predict effluent concentrations through layered systems.

Analytical approach to the description of transport in multilayered porous media often follows the transfer function approach, as presented by Jury and Roth (1990). Using this approach, Jury and Utermann (1992) developed analytical expressions for the flux and resident concentrations in layered soil for two limiting transport cases, i.e., the zero and perfect travel time correlation between individual layers. In the solutions developed by Moranville *et al*. (1977), Bruch (1970), and Shamir and Harleman (1967), no particular correlation was assumed regarding transport between layers. Rather, each individual layer was treated mathematically as effectively semi-infinite, and the outflow from one layer was taken as the upper boundary condition for the next layer. Most of these analytical solutions, however, are only given in the Laplace domain and would frequently have to be numerically inverted with respect to time or space, and thus may suffer numerical instability for complicated systems (Barry and Parker, 1987).

In addition to analytical approaches, solute transport through layered soils can also be described using numerical simulations. An early attempt at such an approach was reported by Selim *et al*. (1977), who simulated solute transport through a range of layer-stratification scenarios with both equilibrium and kinetic adsorption ADE. Recently, Hutson and Wagenet (1996) have extended this effort into the widely used simulation model LEACHM by

Chapter 2

incorporating the two-site nonequilibrium transport parameters (van Genuchten, 1989) into individual layers. One advantage of using numerical over analytical approaches is that non-ideal sorption behaviors (sorption nonlinearity and nonsingularity) can be evaluated.

Although calculations based on the above methods can be used to predict transport through layered soils it would be valuable to obtain experimental results for reactive solutes under well defined conditions designed to test theoretical assumptions and predictions. In this study, we followed the transfer function approach to analyze the travel time probability density function (pdf) of the reactive solute atrazine through soil columns amended with organic material (OM). Our purposes were (i) to characterize transport parameters of atrazine, in terms of a two-site nonequilibrium ADE, through heterogeneous soil profiles amended with two OM's; (ii) to test whether a transfer function model, with parameters based on experiments performed independently on two individual layers, can represent transport through a two layered system; and (iii) to test whether the retentive and nonequilibrium behavior of atrazine would be affected by the distribution of the heterogeneous sorbents in the soil.

2.2 THEORY

The flux-averaged concentration $C_f(z, t)$ of a chemical exiting from a transport volume under steady-state water flow can be viewed as its travel time pdf when the solute is introduced in an infinitely small time interval. Based on the principle of linear superposition, the transfer function model of $C_f(z, t)$ subject to an arbitrary inlet concentration $C_f(0, t)$ can thus be written as a time convolution integral (Jury et al, 1986):

$$C_f(z, t) = \int_0^t C_f(0, t') F_f(z, t - t') dt' \quad (2.1)$$

where z is the distance; t , the time; t' the dummy time variable; $C_f(0, t)$, the inlet concentration of the solute as a function of time; $F_f(z, t)$, the travel time pdf of the solute injected as an infinitely narrow pulse. Parametric representations of $F_f(z, t)$ can be formed based on mechanistic process models. For transport of reactive solutes such as atrazine in our column displacement experiments, $F_f(z, t)$ can be described by a two-site nonequilibrium model. This nonequilibrium transport model, in essence, is a conventional ADE coupled with a term describing rate-limited adsorption (van Genuchten and Wagenet, 1989; Parker and van Genuchten, 1984):

$$\left(1 + \frac{f\rho K_d}{\theta}\right) \frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S_2}{\partial t} = D \frac{\partial^2 C}{\partial z^2} + v \frac{\partial C}{\partial z} \quad (2.2)$$

$$\frac{\partial S_2}{\partial t} = \alpha[(1 - f)K_d C - S_2] \quad (2.3)$$

where ρ is the soil bulk density; θ , the volumetric water content; v , the pore water velocity; K_d , the distribution coefficient of the solute; D , the diffusion-dispersion coefficient; S_2 , the solute concentration on kinetic sorption sites; f , the fraction of equilibrium sorption sites; and α , the first-order kinetic rate constant. $F_f(z,t)$ can be expressed in dimensionless form (Toride et al, 1995):

$$F_f(Z, T) = \Gamma(Z, T) \exp\left(-\frac{\omega T}{\beta R}\right) + \frac{\omega}{R} \int_0^T \sqrt{\frac{\tau}{\beta(1-\beta)(T-\tau)}} \Gamma(Z, \tau) H(\tau, T) d\tau \quad (2.4)$$

where T is the dimensionless time equal to vt/L ; Z , the dimensionless distance equal to z/L ; τ , the dummy variable, and P , R , β and ω are dimensionless parameters defined by

$$\begin{aligned} P &= \frac{vL}{D} & R &= 1 + \frac{\rho K_d}{\theta} \\ \beta &= \frac{\theta + fp K_d}{\theta + \rho K_d} & \omega &= \frac{\alpha(1-\beta)RL}{v} \end{aligned} \quad (2.5)$$

and

$$\Gamma(Z, \tau) = \frac{Z}{\tau} \sqrt{\frac{\beta RP}{4\pi\tau}} \exp\left[-\frac{P(\beta RZ - \tau)^2}{4\beta R\tau}\right] \quad (2.6)$$

and

$$H(\tau, T) = \exp\left[-\frac{\omega\tau}{\beta R} - \frac{\omega(T-\tau)}{(1-\beta)R}\right] I_1\left[\frac{2\omega}{R} \sqrt{\frac{(T-\tau)\tau}{\beta(1-\beta)}}\right] \quad (2.7)$$

where L is the column length and I_1 is the modified Bessel function of order one.

The travel time pdf of solute transport through a two layered soil system can be approximated by taking the outflow of the reactive solute through the first transport volume to be the inlet boundary condition for the second transport volume and assuming that there are no interactions with respect to solute transport at the interface of the two layers (Barry and Parker,

1987). Therefore, the travel time pdf for solute in the second layer can be written as:

$$C_f(Z, T) = C_f(L_1 + L_2, T) = \int_0^T C_f(L_1, t) F_f(L_2, T - t) dt$$

$$= \int_0^T C_f(L_1, P_1, R_1, \beta_1, \omega_1, \tau) F_f(L_2, P_2, R_2, \beta_2, \omega_2, T - \tau) d\tau \quad (2.8)$$

where L_1 is the thickness of the first layer; L_2 is the thickness of the second layer; and P_i , R_i , β_i , and ω_i are the corresponding transport parameters for the first and second layers, respectively. Since we have applied a single step pulse to the inlet end of the first organic layer in our miscible displacement experiments, the $C_f(L_1, T)$ can thus be represented by the analytical solution of the two-site nonequilibrium ADE subject to the upper boundary condition:

$$C_o \quad 0 < T \leq T_o$$

$$C_f(0, T) = \begin{cases} C_o & 0 < T \leq T_o \\ 0 & T > T_o \end{cases} \quad (2.9)$$

$$0 \quad T > T_o$$

This solution is given by (Parker and van Genuchten, 1984):

$$C_f(L_1, T) = \begin{cases} C_o A(Z, T) & 0 < T \leq T_o \\ C_o A(Z, T) - C_o A(Z, T - T_o) & T > T_o \end{cases} \quad (2.10)$$

where

$$A(Z, T) = \int_0^T \Gamma J(a, b) d\tau \quad (2.11)$$

where Γ was given in Eq 2.6, and

$$J(a, b) = 1 - \exp(-b) \int_0^a \exp(-\lambda) I_0[2\sqrt{b\lambda}] d\lambda \quad (2.12)$$

where

$$a = \frac{\omega\tau}{\beta R} \quad (2.13)$$

and

$$b = \frac{\omega(T - \tau)}{(1 - \beta)R} \quad (2.14)$$

and I_0 is the zero-order modified Bessel function. The parametric representation of $F_f(L_2, T)$ is the solution of the two-site nonequilibrium ADE for the second layer subject to a Dirac delta input function. The expression of this solution was given in Eq 2.4, where Z is now replaced by L_2 . Eq 8 states that the concentration at $L_1 + L_2$ to the finite pulse input at $L=0$ can be described by the convolution of Eq 2.4 and Eq 2.10.

2.3 MATERIALS AND METHODS

2.3.1 Materials

All the experiments were conducted with a Niagara silt loam (fine-silty, mixed, mesic Aeric Ochraqualf) which was collected from Caldwell Field Farm at Cornell University, Ithaca, New York. The soil samples were taken from a depth of 0-15 cm and consisted of 1.77% organic carbon (OC), 18.3% clay and 71.0% silt. The two organic materials, sludge and manure, contained 45.24% and 35.40% OC, respectively. The soil, manure and sludge were air dried and passed through a 2-mm sieve prior to use.

The pulse solution for the miscible displacement experiments contained 5 $\mu\text{g/mL}$ atrazine in 0.005 M CaSO_4 and 0.025 M CaCl_2 . The pesticide solutions used in the batch experiments had an initial concentration of 1, 5, 10, 15 and 20 $\mu\text{g/mL}$, and were all prepared in 0.005 M CaSO_4 .

2.3.2 Batch Sorption Experiments

Batch adsorption studies with unamended and OM-amended soils were conducted to determine the distribution coefficient (K_d) of atrazine. The ratios of OM to soil used were equal to those in the soil columns of the miscible displacement experiments. Five g of soil and 15 mL of pesticide solution at different concentrations were added to a 25-mL scintillation vial sealed with a Teflon-lined screw cap. The soil-water mixture was shaken on a reciprocating shaker for 24 hrs. The suspension was allowed to stand for 2 hrs before the supernatant was filtered through a disposable 0.45- μ m nylon filter. The filtrate was then directly injected into a High Pressure Liquid Chromatography column (HPLC) for pesticide determination. All treatments were prepared in triplicates, including blanks (pesticide solution only) and controls (soil and pesticide-free solution). The sorbed concentration was calculated as the difference between the initial concentration and the concentration at equilibrium.

2.3.3 Miscible Displacement Experiments

The experimental conditions for the miscible displacement study are given in Table 2.1. Three groups of soil columns were studied. In one group, termed "layered columns", the OM was amended only to the first 3 cm of the soil column. In another group, the OM was incorporated into the entire soil column, and the soil was macroscopically homogeneous in the vertical direction (uniform columns). The third group of columns contained only the first layer of the layered columns (short columns).

The miscible displacement experiments were carried out under steady-state, saturated upward flow conditions. The amendment rate for both OM_s was 9.8 g/column, equivalent to a surface application of 50 Mg/ha. At this rate, the OM content was 15.3% (dry soil basis) for the first OM-amended layer, and 2.9% (dry soil basis) for the columns homogenized with an OM amendment. For each experiment, the soil was mixed with the selected OM at the desired rate, and was uniformly packed at incremental depths into a glass column (5 cm in diameter to a length which was adjustable using an adaptor at one end). The column was then saturated at a very slow flow rate (0.3 cm/hr) with an isocratic LC pump (Perkin Elmer Model 250). For OM-amended columns, about 10 pore volumes of 0.005 M CaSO_4 were first applied to leach out excessive amounts of soluble salts and organic matter contained in the amendment. After saturation and steady-state flow were established, a pulse of about 1 pore volume of aqueous atrazine and Cl^- solution was applied. The chemicals were then subsequently displaced by tracer-free 0.005 M CaSO_4 . Two flow velocities, referred to as fast (pore water velocity $\sim$ 5 cm/hr) and slow (pore water velocity $\sim$ 1 cm/hr) flow were studied. The effluent samples from the column were collected in glass tubes using an automatic fraction collector. Samples were either analyzed immediately or stored at 4 °C until analysis.

2.3.4 Chemical Analyses

The analysis of effluent samples for pesticide was performed by HPLC and for Cl^- with a Haake-Buchler Digital Chloridometer. The HPLC system was equipped with a Perkin Elmer LC Pump Series 410, a LC-95 UV/Visible Spectrophotometer Detector ($\lambda=220$ nm), a Hewlett Packard ODS Hypersil column (5 mm packing and 125 x 4 mm) and a Rheodyne Model 7125

Syringe Injector with a 100 μL sample loop. The flow rate of the HPLC mobile phase, made of 60% methanol and 40% water, was set at 1 mL/min. The retention time for atrazine under these conditions was 4.8 min. The effluent samples from soil columns were directly injected into the machine. The detection limit of this method was $\sim 5 \mu\text{g/L}$.

2.3.5 Evaluation of Transport Parameters

The unknown parameters for atrazine transport through the soil columns include the distribution coefficient (K_d), the dispersion coefficient (D), the fraction of equilibrium adsorption sites (f), and the first-order rate constant (α). For each material used in packing columns, the value of K_d was determined independently by batch experiments. For D , the breakthrough curve (BTC) of the nonreactive tracer Cl^- was fitted to the solution of the equilibrium ADE (van Genuchten and Alves, 1982) with R fixed to unity ($K_d=0$). The value of D was adjusted iteratively until the minimum sum of squared residuals between the solution and measured data was reached. After K_d and D were determined, the flux concentration of atrazine for each of the uniform and short columns was fitted to the solution of the nonequilibrium ADE (Eq 2.10) to estimate f and α by optimizing the dimensionless parameters β and ω . The numerical procedure for the curve fitting was based on the Levenberg-Marquardt method and the optimization program used was CXTFIT 2.0 (Toride et al, 1995).

The BTCs for the layered columns were analyzed in three ways. First, mean travel times were calculated using measured data. Second, parameters determined on columns which consisted of material matching the material in the layers were used for direct prediction. The outflow from the first layer, calculated using the parameters determined on a short column, was taken as the input function for the second layer. The predicted BTC output from the second layer was then obtained using the parameters determined on the unamended column. A subroutine was added to the CXTFIT 2.0 to specify the input function from the first layer to the second layer. Finally, once the transport parameters for the individual layers were confirmed by this direct prediction, the parameters obtained by fitting the outflow flux concentration of atrazine from a layered column were compared to those obtained from a uniform column to evaluate the relationship between pesticide movement and the distribution of OM in the soil.

2.4 RESULTS AND DISCUSSION

2.4.1. Distribution coefficient

Amendment with OM increased atrazine adsorption in the soil. The measured K_d was $0.93 \text{ cm}^3/\text{g}$ for the unamended soil, was 1.37 and $2.15 \text{ cm}^3/\text{g}$ for the soil amended with manure and sludge, respectively, at the rate of the uniform columns, and was 3.56 and $6.79 \text{ cm}^3/\text{g}$ for the soil amended with manure and sludge in the first OM layer. The adsorption isotherms were highly linear with linear correlation coefficients ranging from 0.972 to 0.997, all significant at $P=0.01$. When these K_d values were normalized by OC% of the soil mixes, the resulting K_{oc} ranged from 51.27 to 89.77, which agrees well with the reported values in the literature (Montgomery, 1993).

We conducted additional batch experiments to test if a linear relationship exists between

K_d and the application rate of OM. The results are plotted in Figure 2.1. The highest OM/Soil ratio (0.152 g/g) in this figure corresponds to that of the OM-amended layer in the layered columns. The correlation coefficient obtained was 0.967 and 0.992 for sludge and manure, respectively, and both were significant at $P=0.01$. The excellent linear correlation between these two variables suggests that a weighted retardation factor of a layered column, calculated using the length of individual layers as a weighting factor, might be a good estimation of the retardation factor of a uniform column which contains the same amount of OM, but homogenized with the soil.

2.4.2 Mean Travel Time

The measured BTCs of atrazine through unamended and OM-amended columns are shown in Figure 2.2. Compared to the unamended columns, the travel time of atrazine appears to have increased in all the columns with OM, as manifested by the suppressed and/or delayed peak, and the pronounced tail of the BTCs. A quantitative evaluation of atrazine travel time in these columns can be achieved through time moment analyses (Aris, 1958; Valocchi, 1985; Parker and Valocchi, 1986) of the flux concentration measured at a fixed depth, $C(t)$. By definition, the i th order time moment of a finite quantity of solute traveling through a porous medium is (Aris, 1958; Valocchi, 1985):

$$M_i = \int_0^{\infty} t^i C(t) dt \quad (2.15)$$

The mean travel time of atrazine normalized with respect to the total mass applied to the column in the miscible experiments can be calculated by:

$$\mu_1' = \frac{M_1}{M_0} - \frac{1}{2} T_0 \quad (2.16)$$

where M_0 , the zero-order time moment, equals the total mass applied as a pulse, and T_0 is the length of the pulse. The term $T_0/2$ is to correct for a non-Dirac input function (Brusseau *et al*, 1990).

The moment analysis for atrazine transport in the miscible experiments was performed on the measured flux concentrations using the trapezoidal rule (Jury *et al*, 1991). It should be noted that the mean travel time obtained through this numerical integration most likely underestimates the true mean to the extent that mass eluted at concentrations below the method detection limit ($C/C_0=0.001$) or mass remaining in the column at the end of the experiment was neglected. Deviation of this mean from the true mean would depend on the degree of nonequilibrium, becoming larger as BTC tailing increases.

The results of time moment analyses are presented in Table 2.2. The travel time of atrazine is expressed as the number of pore volumes, instead of the absolute time, so that the effects of variability in the flow velocity and the length of packed soil among different columns are minimized. For the purpose of comparison, the travel time of Cl^- is also reported. Inspection

of Table 2.2 reveals that under similar flow conditions (fast or slow flow), the mean travel time of atrazine was ordered as sludge > manure > unamended soil, corresponding to the order of K_d measured in batch experiments. The mean travel time of nonsorbing tracer Cl^- , however, was not affected or only negligibly affected by amendment with the OM. This kind of relationship between transport and K_d has been well documented for many organic chemicals (Chiou, 1989; Rao and Jessup, 1983; Jury et al, 1987; O'Connor *et al*, 1980). In fact, theoretically the first normalized absolute moment of a chemical BTC (i.e., the mean travel time) is dependent solely on the retardation factor R (i.e., on K_d) (Valocchi, 1985). These approximated mean travel times probably represent a conservative estimation on the effects of organic amendments, since atrazine BTCs yielded from OM-amended columns tended to have longer tails than those of unamended columns (Figure 2.2).

While mean travel times of atrazine were all increased in the OM-amended columns, the degree of retardation varied with the pattern in which the OM was distributed. Table 2.2 shows that transport of atrazine through the layered columns was retarded to a higher degree than that through the uniform columns, even though both the layered and the uniform columns contained the same amount of OM (9.8 g/column). Apparently the distribution of OM within the columns affects the transport of atrazine.

2.4.3 Direct Prediction by Transfer Function

To evaluate this finding, we used the transfer function approach to test if the BTC from a layered column could be directly predicted, given the transport parameters known for the two individual layers. For this purpose, we conducted additional miscible displacement experiments using columns that contained only the first OM-amended layers of the layered columns (short columns). Using K_d values from the batch experiments, the atrazine flux concentrations from the short columns were fitted to eq 2.10 using CXTFIT 2.0. The fitted values of f and α , along with the batch-determined K_d values, are shown (in bold) in Table 2.3. The outflow from each OM-amended layer, calculated using the transport parameters fitted to the short column experiments, was taken as the input to the second unamended layer to directly predict the BTC from a layered column. The measured and predicted BTCs are plotted in Figure 2.3, where the travel time in the x-axis for the layered column was scaled using the pore volume of the second layer.

Overall, the transfer function approach was remarkably successful in predicting the transport of atrazine through the two-layer system for all the columns examined, given that the input to the transfer function calculations is based on batch and column experiments which are independent of the layered column experiments. Barry and Parker (1987) applied a similar approach, i.e., the convolution approximation, to calculate the BTC of Cl^- through a two-layered column where the presence of mobile-immobile water was evident. They showed that the convolution approximation accurately predicted Cl^- transport through the column. The agreement between the predicted and measured BTCs confirms that there was little interference in solute transport from the interface of the two layers, and that the higher retardation of atrazine observed in the layered columns was, in fact, due to the difference in distribution of the OM. That is, the longer mean travel times observed for layered columns than for uniform columns are either totally or primarily due to the difference in OM distribution, not to some effect which is not included in the direct prediction process (e.g., to some effect of the interface itself).

2.4.4 Non-equilibrium Transport Parameters

The estimated transport parameters for the uniform columns (α and f fitted, K_d from batch) and for the layered columns (K_d , α and f fitted) are also listed in Table 2.3. The fitted curves for these columns are compared to the measured data in Figure 2.4. The two-site nonequilibrium model describes atrazine BTCs well, with the coefficient of determination for all columns ≥ 0.959 . Amendment with OM changed the nonequilibrium transport behavior of atrazine. In general, a decreased f was obtained in OM-amended columns under both leaching velocities, implying that the majority of the sorption sites contributed by the OM were rate-limited sites. Except for the layered columns, the f values were obtained using distribution coefficients which were independently determined using batch experiments. The batch adsorption procedure we used for estimating K_d employed 24 hrs as the equilibration period for all soil treatments, chosen, in part, to minimize the effect of atrazine degradation on the results. This period may be inadequate to permit the sorption to fully reach equilibrium, and therefore may underestimate the real distribution coefficient (Pignatello and Xing, 1996). This would be particularly true for soils amended with OM if many of the sorption sites associated with the OM are nonequilibrium sites. Since using a larger K_d would lower the f estimated by curve fitting to a given BTC, a larger difference in f values would be expected between the unamended soil and soils amended with the OM if a longer equilibration time were allowed for the batch sorption experiments.

Table 2.3 also reveals that f is related to K_d or, more precisely, OC%. Amendment with sludge, which increased K_d more than did manure, resulted in a lower f . We observed a similar trend for alachlor elution data in concurrent experiments with sterilized columns (data not shown). Such a relationship is consistent with the observation that the majority of OM sorption sites were nonequilibrium sites, as discussed previously. However, in the study reported by Brusseau (1992) who conducted transport experiments on four hydrophobic organic compounds in three aquifer materials, the f values were not found to vary with OC% in a similar fashion. The nonequilibrium transport of these low-polarity compounds may have been dominated by physical processes, i.e., mass diffusion between mobile and immobile water regions (Brusseau *et al*, 1991).

As noted by other researchers (Gaber *et al*, 1995; Gerner *et al*, 1991; Brusseau *et al*, 1991), the rate constant (α) was dependent on flow velocity, being higher for fast flow than slow flow in all columns (Table 2.3). These results indicate that the rate-limited adsorption may have been caused by retarded mass transfer to intraparticle or intrasorbent adsorption sites (Hamaker *et al*, 1966; Rao *et al*, 1982; Brusseau, 1991), rather than by a slow adsorption reaction. The enhanced physical mixing of the solute at the fast flow, as suggested by a higher dispersion coefficient (Table 2.1), probably facilitated mass transfer to the interior sorption sites of the sorbents, and thus resulted in a higher α .

The values of the fitted overall K_d for layered columns are, except for the manure-amended column leached at fast flow, greater than both the weighted K_d calculated from the R values of the two individual layers, and the K_d determined independently by batch experiments

(uniform columns section of Table 2.3). For manure amended columns subjected to the fast flow, the BTCs are virtually identical for the two distributions (Figure 2.4). However, when the flow rate was reduced, we found again a greater retardation in the layered column. Experiments with these two columns were repeated, and the same results were observed.

Overall, we found, when compared to the uniform column, the layered column either had a higher overall K_d or a higher f , or both, indicating an enhanced accessibility to the sorption sites of the organic amendments. Although transport of atrazine via nonequilibrium process was determined by the combined effects of all transport parameters, this conclusion is supported by the longer travel times of atrazine observed for the layered columns, in contrast to those of the nonsorbing Cl^- , which were essentially the same for both types of columns (Table 2.2).

2.4.5 Effects of Layer Ordering

In studying chemical transport in heterogeneous soil profiles, Selim *et al* (1977) conducted experiments on transport of 2,4-D through a two-layered soil column, and found that the effluent concentration was not affected by the order of layers. Similar observations have also been reported by Panigatti for fluometuron (cited in Selim *et al*, 1977). We checked the effect of layer ordering on atrazine transport using a layered, sludge-amended column. After completion of the first leaching, a second pulse was applied to the same column from the other end. No discernible difference between the two BTCs was observed (data not shown). These results demonstrate that it is the concentration of OM in the soil, not the placement of OM, that affects the transport. The enhanced accessibility to the adsorption sites of the OM in the layered columns probably resulted from less shielding on OM sorbents by soil minerals due to an increased OM concentration in the soil. A similar interaction between OM and clay has been described by Koskinen and Harper (1990).

Table 2.1 Miscible Displacement Experimental Conditions

Miscible Displacement Experimental Conditions							
flow regime	amendment treatment	length (cm)	density (g/cm ³)	pore vol (cm ³)	soil water content (cm ³ /cm ³)	pore velocity (cm/h)	dispersion coeff (cm ² /h)
fast	sludge manure	14.0	1.25	Uniform Column 153.9	0.560	5.093	1.038
		14.5	1.21		0.550	4.876	0.753
	unamended	14.0	1.25		0.528	5.050	1.853
		14.5	1.21		0.543	1.042	0.156
slow	sludge manure	14.5	1.21	156.0	0.548	0.944	0.272
	unamended	14.0	1.25	145.4	0.529	1.011	0.267
fast	sludge manure	14.5	1.21	Layered Column ^a 151.8	0.533	4.869	1.183
		14.0	1.25		0.528	4.931	1.068
	sludge manure	14.5	1.21		0.533	0.949	0.198
		14.5	1.21		0.528	0.961	0.201
fast	sludge manure	3.5	1.07	Short Column (First OM Layer) 43.0	0.626	4.978	1.561
		3.5	1.07		0.627	4.977	1.225
	sludge manure	3.5	1.07		0.626	0.971	0.221
		3.5	1.07		0.627	0.978	0.314

^a Values are overall for the entire column.

Table 2.2 Estimated Mean Travel Time (in Pore Volumes) for Atrazine and Chloride

Estimated Mean Travel Time (in Pore Volumes) for Atrazine and Cl ⁻					
flow regime	amendment treatment	uniform column		layered column	
		atrazine	Cl ⁻	atrazine	Cl ⁻
fast	sludge	4.894	1.000	5.613	1.001
	manure	3.897	0.984	4.122	0.977
	unamended	3.405	0.986		
slow	sludge	5.490	1.002	6.166	0.966
	manure	4.771	0.979	5.038	0.964
	unamended	3.673	1.004		

Table 2.3 Estimated Non-equilibrium Transport Parameters of Atrazine

Estimated Nonequilibrium Transport Parameters of Atrazine ^a					
flow regime	amendment treatment	K_d^b (cm ³ /g)	α (h ⁻¹)	f	r^2
fast	sludge	2.15	0.13 (0.12-0.14)	0.54 (0.49-0.58)	0.959
		1.37	0.39 (0.37-0.42)	0.62 (0.60-0.64)	0.978
	unamended	0.93	0.17 (0.16-0.19)	0.67 (0.64-0.71)	0.993
		2.15	0.04 (0.04-0.04)	0.61 (0.59-0.63)	0.990
slow	manure	1.37	0.07 (0.07-0.08)	0.63 (0.54-0.72)	0.980
	unamended	0.93	0.06 (0.05-0.07)	0.73 (0.70-0.77)	0.974
Layered Column					
fast	sludge	1.97 2.20 (2.20-2.20)	0.29 (0.28-0.29)	0.50 (0.48-0.53)	0.991
slow	manure	1.28 1.21 (1.19-1.22)	0.54 (0.53-0.55)	0.64 (0.59-0.69)	0.985
	sludge	1.97 2.36 (2.34-2.38)	0.10 (0.09-0.11)	0.52 (0.46-0.57)	0.988
	manure	1.37 1.80 (1.78-1.82)	0.05 (0.05-0.06)	0.66 (0.61-0.70)	0.986
Short Column (OM Layer)					
fast	sludge	6.79	0.20 (0.20-0.21)	0.51 (0.46-0.56)	0.989
slow	manure	3.58	0.16 (0.15-0.17)	0.54 (0.48-0.60)	0.991
	sludge	6.79	0.11 (0.10-0.12)	0.44 (0.33-0.56)	0.987
	manure	3.58	0.11 (0.11-0.12)	0.60 (0.55-0.65)	0.990

^a Values in parentheses indicate 95% confidence limits in the fitting process. Values in bold are used in the "direct prediction by transfer function" calculations. ^b The K_d values for the uniform columns and the short columns are from batch sorption experiments. For the layered columns, the first K_d value is a length-weighted K_d calculated from the retardation factors of individual layers. The second K_d value (and all the α and f values) are fitted from the flux concentrations.

Figure 2.1. Distribution coefficient measured at various OM/soil ratios.

Figure 2.2. Breakthrough curves of atrazine measured in the miscible displacement experiments.

Figure 2.3. Measured atrazine breakthrough curves from layered soil columns in comparison to those directly predicted by transfer function using parameters determined for individual layers. The input flux concentration for the second, unamended, layer is the fitted outflow from the first, OM-amended, layer.

Travel Time (Pore Volume)

Figure 2.4. Comparison of atrazine breakthrough curves through layered and uniform OM-amended soil columns. The optimized parameter values for the fitted BTCs are reported in Table 2.3. The fitted overall K_d was used for layered columns.

CHAPTER 3

EFFECTS OF NONEQUILIBRIUM TRANSPORT ON ALACHLOR DEGRADATION

3.1 INTRODUCTION

Contamination of ground water by pesticides and other chemicals migrating through the soil and vadose zone poses a potential hazard to human health. In an effort to minimize this risk, various models have been developed to predict pesticide fate in the environment (e.g., Wagenet and Hutson, 1989; Carsel *et al*, 1984; Jury *et al*, 1983), and they all consist of process parameters characterizing transport and degradation. The degradation coefficients used in modeling have been mostly derived from incubation experiments, in which degradation is assessed independent of transport process. However, the validity of using degradation rate parameters obtained from such static soil-water experiments to describe the behavior of pesticides in field conditions where degradation and transport occur simultaneously remains to be investigated.

Coupled-process study of degradation and transport has started to receive increased attention (see review by Rao *et al*, 1993). In this approach, degradation and transport are evaluated simultaneously in one experiment (Pivetz *et al*, 1996; Angley *et al*, 1992; Gamerdinger *et al*, 1990; Zhong *et al*, 1986). Experimental evidence has shown that transport can have a profound effect on degradation. Pivetz *et al* (1996) reported that PNP was degraded more rapidly through the path of preferential flow, probably due to improved microbial activities in these flow regions as a result of increased oxygen supply. Angley *et al* (1992) reported that degradation rate of a variety of alkylbenzenes was flow velocity-dependent, and differed by at least one order of magnitude from batch biodegradation experiments. They attributed this discrepancy to the difference in the degree of mixing and aeration conditions in the experimental systems. We also notice that the degradation rate constant measured by Comfort *et al* (1992) from a leaching column was about double those measured for batch incubation experiments.

In view of the apparent role of degradation in the fate of pesticides, it is essential that an accurate estimator on degradation rate be used in the assessment models. This requires the development of a reliable methodology that evaluates degradation under transport conditions. Our purposes were therefore to test the reliability and feasibility of miscible displacement experiments as a means to derive degradation coefficients necessary for predicting environmental fate of pesticides by models, and to compare, in particular, the degradation coefficients obtained from batch incubation and miscible displacement experiments.

3.2 MATERIALS AND METHODS

3.2.1 Soil and Organic Materials

The soil used in this study was a Niagara silt loam (fine-silty, mixed, mesic Aeric Ochraqualf) collected from Caldwell Field Farm at Cornell University, Ithaca, New York. The soil samples were taken from a depth of 0-15 cm and consisted of 1.77% organic carbon, 18.3% clay and 71.0% silt. The three organic materials (OMs) used were sludge, manure and alfalfa, containing 45.2%, 35.4% and 42.5% organic carbon, respectively. The soil, manure and sludge were air dried and passed through a 2-mm sieve prior to use. Fresh alfalfa was cut into

approximately 1-cm pieces before being added to the soil.

3.2.2 Pesticide

The herbicide alachlor was selected for this study because it is one of the most widely used agrochemicals and has a relatively short persistence in soils. A stock alachlor solution of $4000 \mu\text{g mL}^{-1}$ was made by dissolving analytical grade formula (labeled purity 96%) in methanol. The solution was stored in glass wrapped with aluminum foil under 4°C .

3.2.3 Batch Sorption Experiments

The distribution coefficient (K_d) of alachlor in unamended or OM amended soils was examined in triplicate. The soil was mixed with each OM at a ratio of 0.0029 (OM/soil), equivalent to an OM application rate of 9.82 g/column used in the column displacement experiments. This rate was selected based on an OM application rate of 50 Mg ha^{-1} in agricultural fields. Alachlor solution, with a concentration of 1, 5, 10, 20 or $40 \mu\text{g mL}^{-1}$, was prepared in 0.005M CaSO_4 . For each soil treatment, approximately 5 g of soil and 15 mL of the pesticide solution were added into a 25-mL scintillation vial sealed with a Teflon-lined screw cap. The vial was shaken on a reciprocating shaker for 24 hours at room temperature ($\sim 23^{\circ}\text{C}$). The supernatant was then filtered through a disposable $0.45\text{-}\mu\text{m}$ nylon filter. The filtrate was directly injected into a High Pressure Liquid Chromatography (HPLC) column for alachlor analysis. The sorbed concentration was calculated based on the difference between the initial concentration and the concentration measured at equilibrium.

3.2.4 Batch Incubation Experiments

Duplicate incubation experiments were performed in 250-mL Pyrex beakers. The same OM rate as in the batch sorption experiments was used. The soil was mixed at the desired rate with each OM that was previously leached to remove excessive soluble salts and organic matter. A 200 g (dry weight) of soil or soil-OM mixture was then placed into each beaker. The soil sample was conditioned for two weeks prior to pesticide addition by adding an appropriate amount of distilled water, determined by weighing, to bring the water content to the field capacity (33%, dry soil basis). An aliquot (20 g) of the soil was then fortified with 0.5 mL of alachlor stock solution in methanol to yield an application rate of $10 \mu\text{g g}^{-1}$ (dry weight). After allowing methanol to evaporate for 24 hours, the aliquot was carefully mixed with the entire soil sample. The beaker was then covered with a glass lid and incubated under room temperature ($23 \pm 2^{\circ}\text{C}$) in the dark for 82 days. The weight of each beaker was checked on a weekly basis, and distilled water was added as needed to compensate for the loss of water. The first sampling was taken at day 0, immediately following homogenization with the fortified aliquot. Subsequent sampling was taken at day 2, 4, 8, 16, 27, 44, 58 and 82.

At each sampling event, about 20 g of soil sample was removed from the flask into a 60-mL HDPE (high density polyethylene) bottle. The soil was extracted twice by shaking with two 30 mL aliquots of methanol on a reciprocating shaker for 30 min. The two extracts were combined by careful pipetting after being clarified by settling for over 12-16 hours, and vaporated under vacuum to less than 5 mL. The extract was brought to a final volume of 5 mL by the addition of distilled water before being injected to a HPLC column for alachlor analysis. The mass recovery yielded with this extraction procedure was 83 to 97%, and varied slightly with soil treatments. The absolute extraction efficiency, however, was not crucial to our results since all

subsequent pesticide concentrations were expressed as a percentage of the initial concentration on day 0 for each soil treatment. For the soil amended with sludge, alachlor analysis was performed by RaPID Immunoassay following the procedure provided by Ohmicron (Newtown, PA). The mass recovery of this method was found to be $94 \pm 11\%$ with a detection limit of $< 25 \mu\text{g/kg}$.

3.2.5 Miscible Displacement Experiments

The miscible displacement experiments were carried out at room temperature ($23 \pm 1^\circ\text{C}$) under steady-state saturated flow conditions in glass columns measuring 5 cm in internal diameter and 14.5 cm in length. Exact length of packed soil varied slightly among columns. For each experiment, the soil was mixed with the selected OM at 9.82 g/column as indicated previously, and was uniformly packed at incremental depths into the column. The column was then saturated by an up-flow procedure at a flow rate of 0.3 cm h^{-1} with an isocratic LC pump (Perkin Elmer Model 250). After saturation was attained, the flow velocity was adjusted to a steady state at the desired rate. For columns which were amended with sludge or manure, about 10 pore volumes of 0.005 M CaSO_4 were allowed to pass through the column to leach out soluble salts and organic matter contained in the amendment. A pulse of about one pore volume of aqueous alachlor, at a concentration of $20 \mu\text{g mL}^{-1}$, and Cl^- solution was then applied. The chemicals were subsequently displaced by tracer-free 0.005 M CaSO_4 . The effluent samples from the column were collected in glass tubes using an automatic fraction collector. Samples were either analyzed immediately or stored at 4°C until analysis. The experimental conditions for column displacement experiments are summarized in Table 3.1.

Upon completion of leaching, soil was extruded from each column by applying air from one end and sectioned into four samples. The non-eluted alachlor in the soil was extracted and analyzed using the same procedure as that described for samples of incubation experiments.

3.2.6 Analytical Procedures

The analysis of effluent samples for alachlor was performed by HPLC and for Cl^- by a Haake-Buchler Digital Chloridometer. The HPLC system was equipped with a Perkin Elmer LC Pump Series 410, a LC-95 UV/Visible Spectrophotometer Detector ($\lambda=220 \text{ nm}$), a Hewlett Packard ODS Hypersil column (5 mm packing and $125 \times 4 \text{ mm}$) and a Rheodyne Model 7125 Syringe Injector with a $100 \mu\text{l}$ sample loop. The flow rate of the mobile phase, comprised of 60% methanol and 40% water, was set at 1 mL min^{-1} . The retention time for alachlor under these conditions was about 11.5 min. The detection limit of this method was $0.02 \mu\text{g mL}^{-1}$.

3.2.7 Calculation of Degradation Coefficient under Transport Conditions

Assuming that the degradation of alachlor obeys first order kinetics, the mass loss of alachlor for a closed system (e.g., a batch incubator or a soil column with no flow) can be written as:

$$-dm = \mu m dt \quad [3.1]$$

where dm is the mass degraded during time interval dt ; μ , the degradation coefficient; and m , the mass subject to degradation. By integrating Eq. 3.1, we obtain an exponential decay equation as a function of time:

$$M_d = M_i - M_i e^{-\mu T} \quad [3.2]$$

where M_d is the mass degraded after time T and M_i is the initial mass in the column at time zero. Eq. 3.4 is not directly applicable to columns in our miscible displacement experiments, because alachlor was dynamically removed from the system by transport, and the leached mass was no longer available for degradation. To account for the dynamic loss of alachlor by leaching, it is necessary to characterize the mean travel time of the eluted alachlor in the column. This was accomplished by numerical integration on the measured BTC using the following equation:

$$t = \frac{\sum_{i=1}^{N-1} \left[\frac{1}{2} (t_i + t_{i+1}) \right] \left\{ \frac{1}{2} [f(t_i) + f(t_{i+1})] v \right\} \Delta t_i}{\sum_{i=1}^{N-1} \frac{1}{2} [f(t_i) + f(t_{i+1})] v \Delta t_i} - t' \quad [3.3]$$

where t is the estimated mean travel time of alachlor; $f(t_i)$ is the measured concentration of alachlor in the effluent fraction at time t_i ; N is the total number of effluent fractions; v is the velocity of water flow; Δt_i is the time interval between fraction i and $i+1$ ($t_{i+1} - t_i$); and t' is the time equal to $\frac{1}{2}$ pulse length and is to correct for a non-Dirac input function. The denominator in Eq. 3.5 is the total mass leached in the effluent, and is represented by the area under the BTC. Thus, M_d in Eq. 3.4 for a column subject to leaching can be written as:

$$M_d = M_i (e^{-\mu t'} - e^{-\mu T}) - M_l (e^{-\mu T} - e^{-\mu t'}) \quad [3.4]$$

where T is the duration of the column displacement experiment. The second term on the right-hand side serves as a correction factor for the mass loss which would be accounted in a closed system.

The mass balance equation for the column at the end of the experiment is expressed as:

$$M_i - M_r = M_d + M_l \quad [3.5]$$

where M_r is the non-eluted residue mass in column, and M_l is pesticide leached. Combining Eq. 3.6 and 3.7 yields:

$$M_i - M_r = M_i e^{-\mu t'} - M_i e^{-\mu T} - M_l e^{-\mu T} + M_l e^{-\mu t'} + M_l \quad [3.6]$$

Eq. 3.6 is a non-linear equation containing a single unknown, i.e., the degradation coefficient μ . To obtain μ , this equation was solved using a Newton-Raphson algorithm. Rearranging Eq. 3.6 yields a function $f(\mu)$:

$$f(\mu) = M_i e^{-\mu t'} - M_i e^{-\mu T} - M_l e^{-\mu T} - M_l e^{-\mu t} + M_l - M_i + M_r \quad [3.7]$$

An iteration procedure is executed as follows:

$$\mu^{(n+1)} - \mu^n = \delta^{(n+1)} = -\frac{f(\mu^n)}{f'(\mu^n)} \quad [3.8]$$

where μ^n denotes the value of μ at the n th iteration, $f'(\mu^n)$ is the derivative of $f(\mu^n)$. The iteration is terminated when δ/μ^n is less than a predetermined value (0.1%). Normally, the algorithm converges within 4 iterations. Eq. 3.6 indicates that μ is not only dependent on the mass balance, but also is affected by the shape of a BTC.

3.3 RESULTS AND DISCUSSION

3.3.1 Distribution Coefficient

Batch sorption experiments were performed to measure partitioning of alachlor between solid and liquid phases at equilibrium or quasi-equilibrium conditions. This method has been used frequently to obtain distribution coefficient of pesticides needed in modeling despite markedly different conditions between batch and transport experiments (e.g., Chen and Wagenet, 1997; Gamedainger *et al*, 1990). A second alternative to estimate K_d is by miscible displacement experiments using the approach of time moment analysis (Valocchi, 1985; Brusseau *et al.*, 1990). However, this latter method might not result in a valid K_d for alachlor sorption under the conditions of our experiments due to the low mass recovery obtained from effluent, presumably by degradation during transport. Different degradation coefficients associated with solution and sorbed phases would alter the shape of the BTC, thereby lead to a K_d which becomes degradation-dependent.

Results of batch experiments are presented in Table 3.2. The adsorption of alachlor was linear over the range of the concentrations used for all soil treatments. The linear correlation coefficients were all significant at $P=0.001$ ($r \geq 0.976$) except for the soil amended with alfalfa for which the correlation coefficient was significant at $P=0.01$ ($r=0.952$). In comparison to the unamended soil ($K_d=1.623$), adsorption of alachlor was increased significantly by amendment with sludge ($K_d=3.78$) and manure ($K_d=2.419$), and was only altered slightly by alfalfa ($K_d=1.847$). Based on these adsorption coefficients, about 35% of the added alachlor was sorbed in the unamended soil, and 56%, 45% and 38% in the soil amended with sludge, manure, and alfalfa, respectively.

3.3.2 Degradation under Incubation Conditions

The results of incubation experiments are shown in Fig. 3.1. All data are plotted as natural logarithm of the percentage of the mass recovered from each soil at day 0 with time. These results reflect degradation of alachlor occurred under aerobic and minimum water flow conditions. The degradation coefficient (μ) was determined by linear regression analysis of the data and was the slope of the line assuming first-order kinetics. The half-life of persistence ($t_{1/2}$) could then be calculated using $t_{1/2}=0.693/\mu$. For all four soil treatments, the linear correlation coefficient was ≥ 0.973 , and was statistically significant at $P=0.001$, indicating that the assumption of first-order kinetics was valid for the conditions of our experiments over the incubation period. Several previous investigations conducted under a broad range of soil and environmental conditions also showed that disappearance of alachlor followed a first order kinetics (Yen *et al.*, 1994; Pothuluri *et al.*, 1990; Walker *et al.*, 1992). Although alachlor degradation in sterilized soils was not investigated in this study, existing data showed that alachlor degradation in soil was mediated by microorganisms (Beestman and Deming, 1974).

Alachlor degradation rate varied widely among soil treatments. Degradation was apparently inhibited by the presence of sludge. The half-life of alachlor was 31.7 days in the sludge-amended soil which was substantially longer than that measured for the unamended soil ($t_{1/2}=24.1$ day). Amendment with alfalfa and manure, however, both increased degradation rate, and resulted in a shorter persistence of the herbicide with a half-life of 14.6 and 21.4 days, respectively. These results are in good agreement with those reported elsewhere for surface soils using incubation experiments (Yen *et al.*, 1994; Pothuluri *et al.*, 1990; Walker *et al.*, 1992).

The inhibitory effects of sludge on pesticide degradation have been observed by Doyle *et al.* (1978) for a number of structurally unrelated pesticides. The specific reaction inhibited was found to be dealkylation. However, the primary degradation reactions of alachlor by microorganisms in soil were identified to be hydrolysis (Chesters *et al.*, 1989). The inhibitory effect observed in our experiments was more likely a result of the enhanced adsorption associated with sludge addition which reduced the concentration of alachlor in the solution phase (Table 3.2). Several studies investigating degradation rates have demonstrated that soil microorganisms degrade chemicals in the solution phase preferentially, and chemicals in the sorbed phase (especially those located at the internal sites of sorbents) are less accessible to microorganisms primarily due to physical obstacles (see review by Scow, 1993). It is possible that the large amount of salts in the sludge might be toxic to microorganisms, and thereby adversely affect microbial activities. This possibility was precluded by the preleaching procedure used to reduce the amount of soluble salts to a minimum prior to amendment.

The enhanced degradation of alachlor by manure and alfalfa might be interpreted in terms of increased microbial activities. Although these OM's also enhanced the adsorption, the increased supply of nutrients associated with these OM's probably stimulated microbial growth and, therefore, the degradation of alachlor. This would be particularly true for the soil amended with alfalfa, because the fresh plant tissue was readily available for microbial use. The ultimate effect of OM amendment on degradation would hence be determined by the net effect of the enhanced adsorption and the stimulated microbial activities.

3.3.3 Effects of Transport on Degradation

The measured alachlor BTCs for all soil columns are presented in Figs. 3.2 and 3.3. Results of soil analysis and estimated degradation coefficients are given in Table 3.3. In accord with the incubation experiments, degradation rate of alachlor was accelerated by amendment

with alfalfa and manure, and was inhibited by sludge. Degradation rate of alachlor, however, was substantially increased in the conditions of column leaching experiments compared to that obtained in incubation flasks for all soil treatments. The $t_{1/2}$ based on the $\square$ estimated by Eq. 3.6 using the measured BTC and soil analysis data was less than 14.7 days, regardless of flow rates and OM treatments, corresponding to a degradation rate constant of at least twice as fast as was measured in the incubation experiments.

Two prime factors can be identified that apparently contributed to the discrepancy of degradation rates observed in the incubation and column displacement experiments: the soil aeration condition and the degree of nonequilibrium sorption. In the column displacement experiments, the soil was leached at saturated, steady-state flow, and was less aerobic in comparison to that in the incubation experiments, where water content of the soil was maintained at field capacity (33%). Based on the existing experimental evidence obtained for a variety of surface and subsurface soils (Pothuluri *et al*, 1990), however, alachlor would degrade more slowly in less aerobic environment, which was opposite to our results. Thus the faster degradation rates observed for the column displacement experiments was most likely attributable to the second factor, i.e., the degree of nonequilibrium sorption during transport.

Nonequilibrium sorption of organic chemicals during transport through soils and other porous media has been reported by many researchers (e.g., Brusseau *et al*, 1991; Gaber *et al*, 1995; Chen and Wagenet, 1997). It is a condition that the chemical partitioning between the liquid phase and solid phase fails to reach equilibrium due to the rapid transport through a soil. van Genuchten and Wagenet (1989) presented a mathematical model describing transport of chemicals under nonequilibrium conditions. This model divides the total sorption sites of a soil into two domains: type-I sites on which sorption is assumed to be at equilibrium with solution phase, and type-II sites on which sorption is time-dependent. Chemical degradation is assumed to follow the first-order kinetics, with respective degradation coefficients for each phase of the chemical in the solution phase, sorbed on type-I sites and sorbed on type-II sites.

The degradation rates obtained in the incubation experiments were felt to represent those under equilibrium conditions with respect to sorption. Although complete equilibrium might not be achieved (Pignatello and Xing, 1996), results of our batch sorption experiments showed that pseudo-equilibrium sorption of alachlor was practically attained in all soil treatments within 24 hours of vigorous shaking. In the leaching columns, the residence time of alachlor was shortened by transport. Thus the reaction time allowed between alachlor and the soil was also shortened compared to the incubation flasks where water flow was essentially zero. Obviously, the reduced reaction time in the columns would limit the sorption to reach equilibrium. The existence of nonequilibrium sorption of alachlor during transport through the columns was evidenced by the asymmetric shape of alachlor BTCs (Figs 3.2 and 3.3), in contrast to the symmetric BTCs of the nonsorbing Cl^- (Fig.3.4). The degree of nonequilibrium sorption, however, could not be assessed reliably by inverse parameter estimation partially due to the uncertainty regarding the respective degradation rates associated with the alachlor in the solution and sorbed phases. The degradation rates measured from column displacement experiments therefore are considered to represent those in nonequilibrium sorption conditions. It is evident, based on the faster degradation rates observed for column displacement experiments (Table 3.3), that nonequilibrium transport favored alachlor degradation.

As reported by Angley *et al* (1992) for alkylbenzenes, we also found that degradation rate of alachlor was flow velocity-dependent. Faster degradation occurred when the flow velocity was increased (Table 3.3). These results demonstrate again that alachlor degradation was positively related to the degree of nonequilibrium which is expected to increase with the flow

rate due to the reduced sorption reaction time.

The difference in the degree of nonequilibrium is reflected by the altered concentrations of alachlor in terms of its partitioning between the solution and sorbed phases. The effect of nonequilibrium sorption on alachlor distribution in these two phases depends on the direction of the sorption reaction. When adsorption dominates (i.e., $\partial c/\partial t < 0$), nonequilibrium sorption limits the adsorption to proceed to the maximum extent, and therefore would result in a higher concentration in the solution phase in comparison to an equilibrium system. However, when desorption dominates (i.e., $\partial c/\partial t > 0$), a lower concentration in the solution phase would result because nonequilibrium limits the rate at which the sorbed chemical moves back into the solution. The ultimate effect of nonequilibrium on degradation rate relies on the relative magnitude of degradation coefficients associated with the solution and sorbed phases. Although we show that nonequilibrium sorption influenced alachlor degradation, which implies different degradation coefficients associated with the solution and sorbed phases, it is difficult to draw any conclusion on these rate constants from our experiments.

3.3.4 Alachlor Residues in Soil

Persistence of pesticide in soil after exhaustive leaching and its significance in the evaluation of pesticide degradation using miscible displacement experiments have been discussed by Gamberdinger *et al* (1990). The quantity of noneluted pesticide can be significant, but varies with pesticide. For example, we found 7.6 to 26.7% of the alachlor applied remained uneluted in the column (Table 3.3). In concurrent experiments with atrazine, however, this amount was less than 5% (data not shown). The quantity of noneluted alachlor seemed to be positively related to its K_d . Under both fast and slow flow conditions, the amount of soil residues was in the consistent order as the K_d measured for each soil in batch sorption experiments (Table 3.3). No apparent trend with flow velocity was detected. Apparently the noneluted pesticide was not leachable or less leachable by water, because a large portion of the pesticide was distributed in the upper soil profile of the column (Fig. 3.5).

The formation of the noneluted pesticide is termed sequestration (Alexander, 1995). These sequestered chemicals are regarded to have diffused to the remote sorption sites within soil particles or soil organic matter, and hence will be less readily biodegradable and leachable as residence time increases. The hazard of such sequestered chemicals will also be decreasing as a result of their increased physical inaccessibility to the biological targets. Although more definite studies need to be performed to assess the ultimate fate and behavior of such sequestered pesticides, there is a potential that these molecules may be released and reactivated in the future when the soil is subject to physical disturbance such as wet-dry cycling and tillage operations.

3.4 CONCLUSIONS

The dependence of pesticide degradation rate on transport process is an important phenomenon that must be considered when evaluating the potential of a pesticide to contaminate ground water. However, to date our understanding of this phenomenon is extremely limited, even in a qualitative way. In this study, we show that degradation rate of alachlor not only varies between static and dynamic soil-water systems, but also is flow-velocity dependent. Degradation rates measured under the leaching conditions were at least twice as fast as were measured in the incubation experiments, indicating that nonequilibrium transport favored alachlor degradation.

We also presented a numerical approach (Eq. 3.6) for the independent determination of

degradation coefficient (μ) under transport conditions. Since in the derivation of μ , we did not introduce any assumption other than a first-order kinetic law, so Eq. 3.6 is applicable to any flow systems, including unsaturated and transit flow, as long as the travel time probability density function or $f(t)$ of the interested chemical can be described (in these cases, $f(t)vdt$ can be expressed in a more general form $f(t)dV$, where dV is the interval of effluent volume). However, the μ calculated by Eq. 3.6, in essence, is an average μ over the time period examined, hence it will be time-scale dependent if the real degradation kinetics does not follow first order precisely.

Table 3.1 Miscible displacement experimental conditions

Flow regime	Amendment treatment	Length cm	Density g cm ⁻³	Pore volume cm ³	Soil water content cm ³ cm ⁻³	Pore velocity cm h ⁻¹	Dispersion coefficient cm ² h ⁻¹
Fast	Unamended	14	1.25	145.2	0.528	5.05	1.853
	Sludge	14	1.25	153.9	0.560	5.093	1.038
	Manure	14.5	1.21	156.5	0.550	4.876	0.753
	Alfalfa	14.5	1.21	161.4	0.571	5.034	0.814
Slow	Unamended	14	1.25	145.4	0.529	1.011	0.267
	Sludge	14.5	1.21	154.5	0.543	1.042	0.156
	Manure	14.5	1.21	156.0	0.548	0.944	0.272
	Alfalfa	14.5	1.21	156.7	0.551	1.067	0.172

Table 3.2 Batch sorption results

Amendment treatment	K_d	r
	$\text{mL}^3 \text{g}^{-1}$	
Unamended	1.632	0.991
Sludge	3.78	0.988
Manure	2.419	0.976
Alfalfa	1.847	0.952

Table 3.3 Degradation coefficient calculated from miscible displacement experiments using Eq. 3.6.

Flow regime	Amendment treatment	Mass Recovery		μ_{bic}	μ_{real}	$t_{1/2}$
		Effluent	Soil			
		———— % ————				
Fast	Unamended	83.4	9.4	0.0129	0.0042	6.88
	Sludge	76.7	26.7	0.0110	NM†	NM
	Manure	66.3	16.5	0.0205	0.0076	3.80
	Alfalfa	79.9	11.2	0.0151	0.0052	5.54
Slow	Unamended	68.8	7.6	0.0047	0.0028	10.31
	Sludge	49.9	22.1	0.0049	0.0019	14.73
	Manure	43.8	16.1	0.0065	0.0033	8.75
	Alfalfa	59.3	8.3	0.0064	0.0042	6.88

† NM=degradation not measurable (mass recovery >100%).

Figure 3.1 Persistence of alachlor in soils amended with organic material under incubation conditions.

Figure 3.2. Measured and fitted flux concentrations of alachlor at fast flow velocity. The fitted breakthrough curves were calculated using μ_{bfc} determined by effluent mass balance using Eq. 3.6, assuming the same degradation rates for both solution and sorbed phases.

Figure 3.3. Measured and fitted flux concentrations of alachlor at slow flow velocity. The fitted breakthrough curves were calculated using μ_{bte} determined by effluent mass balance using Eq. 3.6, assuming the same degradation rates for both solution and sorbed phases.

Figure 3.4. Distribution of alachlor residues remaining in soil after leaching.

CHAPTER FOUR

NUMERICAL SIMULATION OF PESTICIDE TRANSPORT IN SOILS WITH ORGANIC AMENDMENTS

4.1 INTRODUCTION

Chapters 2 and 3 described the movement of pesticides in columns which had been amended with organic matter from various sources. The main conclusions in these chapters were:

- In order to fit the CDE it was necessary to use non-equilibrium transport
- There were differences in behavior depending upon whether or not the amendment was confined to one part of the column or spread through the whole column
- It was not possible to predict breakthrough by assuming that all of the organic matter was confined to one region.

Analytical solutions were developed for the special cases of layered columns. In order to extend and apply non-equilibrium concepts to field situations, numerical models are necessary. LEACHM (Hutson and Wagenet (1992) is a suite of models which describe water and solute transport in the unsaturated zone. Different chemical suites are described in each version; pesticides are included in LEACHP, nutrients in LEACHN and salinity in LEACHC. In this chapter we describe the modifications that were made to the LEACHP model in order to be able to simulate numerically the breakthrough curves corresponding to those obtained through the analytical solutions in Chapters 2 and 3. It is essential that we verify the numerical solutions for saturated, steady state water flow before applying them to transient unsaturated flow situations.

4.2 ADAPTATION OF LEACHP TO NON-EQUILIBRIUM TRANSPORT

While LEACHP has supposedly been able to simulate non-equilibrium transport, it became apparent during the course of this work that there were some errors in the code and that the LEACHM simulations did not always match results from analytical solutions. Closer examination showed that previous verification studies, by chance, used transport parameters that happened to give ideal simulations of solute breakthrough. At the time, not having had any reason to do comparisons with a wider range of measured data, we were satisfied with the simulations. However, comparison of LEACHM simulations using a wider range of parameters with the improved analytical solutions contained in CXTFIT2, (Toride *et al*, 1995) indicated that while the peak concentrations appeared at approximately the correct time (i.e. the displacement of the peak owing to kinetic sorption processes was approximately correct), the width of the breakthrough curves were incorrect. These errors suggested that dispersion was not being

simulated correctly.

Numerical dispersion in LEACHM has always been present owing to the procedure used to simulate solute transport. Initially, in order to maintain mass balance and to describe boundary conditions precisely, it was decided to use upstream weighting, as described here.

The general form of the CDE used in LEACHM is:

$$\frac{\partial c_L}{\partial t}(\theta + \rho K_d + \varepsilon K_H^*) = \frac{\partial}{\partial z} \left[\theta D(\theta, q) \frac{\partial c_L}{\partial z} - qc_L \right] \pm \varphi \quad (4.1)$$

where all concentrations c are solution concentrations, and φ indicates source and/or sink terms.

The nodal concentrations included in the second term on the right hand side of Eq .4.1 depended upon the direction of water flux (Figure 4.1). In general the accumulation or loss of solute in segment i owing to convection was written:

$$\begin{aligned} \frac{\partial}{\partial z} (qc)_i^{j+1/2} = & \beta_1 q_{i-1/2} (c_{i-1}^j + c_{i-1}^{j+1}) / \Delta z_3 \\ & - \beta_2 q_{i+1/2} (c_i^j + c_i^{j+1}) / \Delta z_3 \\ & - \beta_3 q_{i+1/2} (c_{i+1}^j + c_{i+1}^{j+1}) / \Delta z_3 \\ & + \beta_4 q_{i-1/2} (c_i^j + c_i^{j+1}) / \Delta z_3 \end{aligned} \quad (4.2)$$

where

$$\beta_1 = 1 \text{ and } \beta_4 = 0 \text{ when } q_{i-1/2} > 0$$

$$\beta_1 = 0 \text{ and } \beta_4 = 1 \text{ when } q_{i-1/2} < 0$$

$$\beta_2 = 1 \text{ and } \beta_3 = 0 \text{ when } q_{i+1/2} > 0$$

$$\beta_2 = 0 \text{ and } \beta_3 = 1 \text{ when } q_{i+1/2} < 0$$

so that the finite difference form of the CDE equation was written as:

$$\begin{aligned}
& (\theta_i^{j+1} c_i^{j+1} - \theta_i^j c_i^j) / \Delta t + K_H^* (\epsilon_i^{j+1} c_i^{j+1} - \epsilon_i^j c_i^j) / \Delta t \\
& + \rho K_d \frac{(c_i^{j+1} - c_i^j)}{\Delta t} = \frac{D_{i-1/2}^{j+1/2}}{\Delta z_1 \Delta z_3} (c_{i-1}^{j+1} + c_{i-1}^j - c_i^{j+1} - c_i^j) \\
& - \frac{D_{i+1/2}^{j+1/2}}{\Delta z_2 \Delta z_3} (c_i^{j+1} + c_i^j - c_{i+1}^{j+1} - c_{i+1}^j) + \beta_1 q_{i-1/2} (c_{i-1}^j + c_{i-1}^{j+1}) / \Delta z_3 \\
& - \beta_2 q_{i+1/2} (c_i^j + c_i^{j+1}) / \Delta z_3 - \beta_3 q_{i+1/2} (c_{i+1}^j + c_{i+1}^{j+1}) / \Delta z_3 \\
& + \beta_4 q_{i-1/2} (c_i^j + c_i^{j+1}) / \Delta z_3 + \phi_i^j
\end{aligned} \tag{4.3}$$

4.2.1 Numerical dispersion corrections in LEACHM

The finite difference solution of Eq. 4.3 may cause considerable smearing of the concentration profile owing to numerical dispersion. Numerical dispersion corrections were described by van Genuchten and Wierenga (1974) for explicit schemes and by Bresler (1973) for implicit differencing schemes. Both used higher order terms in the finite differencing. If the second order terms are assumed to represent numerical dispersion then it is assumed that the third and higher order terms are negligibly small, or that they are minimized by choosing an appropriate time and space grid. In a model such as LEACHM there are constraints on the choice of time step length (Δt) and depth node spacing (Δz), thus the introduction of some numerical dispersion is unavoidable.

Bresler's (1973) approach was followed in version 1 of LEACHM, but experience and careful comparison between simulated and analytical solutions of Eq. 4.1 for steady-state conditions led to the adoption of an empirical but apparently effective numerical dispersion correction. An estimate of numerical dispersion was obtained by simulating, without any correction, solute movement in a soil column having uniform water content and flux density. These simulated solute distributions were compared to those generated using an analytical solution to Eq. 4.1 (Jury *et al*, 1983). This enabled the magnitude of numerical dispersion in LEACHM to be estimated. For the range of Δt values (<1 day) and Δz values (<100 mm) commonly used in LEACHM it was found that the numerical dispersion error was approximately equivalent to a dispersivity (λ) increase of $0.16\Delta z/\theta$. Values of Δt and q had no discernible influence, apart from the fact that D_m is calculated using q . Identification of the relationship between λ and D_m as a function of Δz allows D_m to be corrected in LEACHM to minimize the impact of numerical dispersion. Thus the minimum effective dispersivity is $1.6/\theta$ mm for a 10 mm node spacing and $16/\theta$ mm for a 100 mm spacing. If a dispersivity less than the minimum is specified in the data file then a value of $0.16\Delta z/\theta$ is used.

Later versions of the model used an improved, but still empirical numerical dispersion correction. Comparisons of solute breakthrough curves with CXTFIT (Parker and van Genuchten, 1984) showed that without any correction, LEACHM was in error by a dispersivity equivalent to about $0.5\Delta z$ (where Δz is the segment thickness) when the specified dispersivity was 0, and had no error when the specified dispersivity was $2\Delta z$. Between these values a regression equation was derived which adjusted the specified dispersivity so that the breakthrough curves match those predicted by CXTFIT. This equation was:

$$\lambda_{\text{used}} = -0.84 + 1.264\lambda_{\text{desired}} - 0.6458\Delta z. \quad (R^2=99.8\%) \quad (4.4)$$

where λ_{used} is the dispersivity used in the simulations and λ_{desired} is the dispersivity specified in the input data.

In the latest version, developed specifically in response to the problems experienced in simulating non-equilibrium chemical transport, the solute transport routine was re-examined and it was decided to use a central-difference Crank-Nicolson approach, rather than the upstream weighting procedure, as this procedure is, within limits, free of numerical dispersion. Upstream weighting was maintained at the boundary nodes, but all other nodes used the central differencing approach. In this case, Eq. 4.2 becomes

$$\frac{\partial}{\partial z} (qc)_i^{j+1/2} = \frac{q_{i-1/2}(c_{i-1}^j + c_{i-1}^{j+1} + c_i^j + c_i^{j+1}) - q_{i+1/2}(c_{i+1}^j + c_{i+1}^{j+1} + c_i^j + c_i^{j-1})}{4\Delta z} \quad (4.5)$$

For the boundary layers Eq. 4.2 was maintained, assuming no dispersion or diffusion across the boundary layers.

4.2.2 Sorption kinetics

A two-site sorption option is included in LEACHM. Following van Genuchten and Wagenet (1990) a fraction $1-f$ of sites display local chemical equilibrium and a fraction f are subject to kinetically controlled sorption and desorption. For simplicity a linear sorption isotherm applies to all 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. The sorbed concentration is the sum of sorption on the kinetic (s_1) and equilibrium (s_2) sites. Flux density of solute between the kinetic sites (current concentration s_2 in mg kg^{-1}) and solution phase (concentration c in mg dm^{-3}) is assumed to depend upon the current level of disequilibrium

$$J_a = \alpha p_b((1-f)K_d c - s_2) \quad (4.6)$$

where J_a is the solute flux density, α is a phase transfer rate coefficient. The value of α is

assumed to be the same for all columns, but the fraction of equilibrium sites can vary. The solution technique was similar to that described in Hutson and Wagenet (1992), but was combined with the revised convective transport procedure.

4.3 COMPARISON BETWEEN ANALYTICAL AND NUMERICAL SOLUTIONS

4.3.1 Procedure

A range of combinations of K_d , α and dispersivity values were used in analytical and numerical simulations to verify the numerical procedures in LEACHP. These values are not specifically related to any of the breakthrough curves measured during the course of this project, although column dimensions and flow rates were similar to the laboratory column studies (Table 4.1). Breakthrough curves were simulated using CXTFIT2 (analytical solution) and LEACHP (numerical solution).

4.3.2 Results

Breakthrough curves corresponding to the parameters listed in Table 4.1 are shown in Figure 4.2 (for equilibrium sorption) and Figure 4.3 (for kinetic sorption). These results suggest that analytical and numerical solutions are in excellent agreement when the dispersivity values lie between $0.5\Delta z$ and $2\Delta z$. The shape of simulated breakthrough curves were similar to the analytical for both equilibrium and kinetic sorption.

4.4 SIMULATION OF BREAKTHROUGH FROM UNIFORM COLUMNS

The column experiments described in Chapter 2 and 3 were simulated in order to ensure that the numerical and analytical solutions for the range of column and soil properties were in reasonable agreement.

4.4.1 Procedure

The parameter optimization package CXTFIT2 was used to obtain best-fit values for dispersivity, fraction of equilibrium sites and the phase transfer coefficients. This procedure was described in Chapter 2. A summary of the results, including details of column lengths, amendments, best-fit transport parameters and corresponding input data for LEACHM are listed in Table 4.2 for both uniform and layered columns.

Using the best-fit transport parameters, LEACHP was used to simulate each of the uniform-column breakthrough curves. The shapes of these curves were compared with those generated using CXTFIT2, which represent the closest match between measured and fitted curves. These comparisons enable direct comparison between analytical and numerical solutions for the range of transport parameters encountered in this project.

4.4.2 Results

Numerical (LEACHP) and analytical (CXTFIT2) breakthrough curves are shown in Figures 4.4. These results show that agreement between the two methods is good, which means that extending the application of LEACHP simulations to scenarios which have no analytical solutions is based on a verified code in terms of assumptions, processes and numerical solutions. It does not necessarily mean that either the analytical solutions or the LEACHM simulations are applicable to specific laboratory or field situations.

4.5 SIMULATION OF BREAKTHROUGH FROM LAYERED COLUMNS

4.5.1 Procedure

LEACHP was modified so that depth-dependent sorption parameters could be used in the simulations. In the past, single K_{oc} and phase transfer values were specified for each chemical species, and the only way in which sorption could be varied through the profile was by varying the organic carbon content of the soil, which in turn led to varying K_d values. To properly simulate layered soils, each layer was defined in terms of unique K_{oc} values and phase transfer kinetics. This involved adding an additional data table to the LEACHP input file.

LEACHP was used to simulate atrazine breakthrough from each layered column. The layered columns consisted of a 35 mm section of amended (sludge or manure) soil overlying a 105 mm column of unamended soil. The simulations were therefore performed using parameters derived from the uniform column breakthrough experiments. Parameter fitting (CXTFIT2) was used to estimate the overall or lumped transport parameters.

4.5.2 Results

Numerical (LEACHP) and analytical (CXTFIT2) breakthrough curves are shown in Figure 4.5. In most instances, CXTFIT2 could fit the two-site CDE to the breakthrough curves (Chapter 2) fairly well, so these curves were used to indicate the shape of the measured curves. In all cases the LEACHP simulations showed earlier breakthrough than was measured. Length-weighted K_d values were lower than those derived from the breakthrough curves (Chapter 2), with the exception of the manure-amended column under fast flow.

4.6 FACTORS WHICH INFLUENCE BREAKTHROUGH SIMULATIONS FROM LAYERED COLUMNS.

4.6.1 Effect of direction of flow or layer ordering.

Simulations were conducted of layered columns (LASLOWMA) in which the order of the layers was reversed. In the first case, flow was from top to bottom, then from bottom to top, and finally, a column with the amendments distributed as multiple thin layers was simulated. Results demonstrate that any combination of layers, provided that they are similar in total, lead to the

same breakthrough curve. In other words, the direction of flow and the order of layers have no effect. This finding agrees with experimental observations both in this project and by others (Selim *et al*, 1977).

4.6.2 Calculation of overall properties of mixed soil

The overall properties of the column were calculated by Guo *et al* (1997) using length-weighted retardation factors. However, the procedure could probably be improved by taking the properties of each individual soil component into account.

A spreadsheet procedure was developed to calculate soil parameters in unamended, and amended soil, both layered and mixed. Densities and K_d values for soil organic matter, soil minerals and organic amendment are defined. If the bulk density and composition of the soil is known then the overall K_d values can be calculated. The example (Table 4.3) shows the spreadsheet for a sludge-amended layered column. Shaded blocks contain input data, and the calculated K_d values for each layer, and the column mean bulk density, porosity and particle density are bold-faced.

This procedure can be used to calculate the effective K_{oc} values for each soil component. Since the unamended soil K_d value is known (0.93 L/kg) the K_{oc} for soil organic matter is adjusted (with no amendment) until the K_d value is 0.93 L/kg. This corresponded to a K_{oc} of 53 L/kg. Then, 9.8 g amendment is entered, together with its f_{oc} (0.452 for sludge, 0.354 for manure). The K_{oc} -amendment is adjusted until the overall K_d value equals the measured batch K_d value. This procedure was performed for both sludge and manure on short (3.5 cm) and long (14 cm) columns (Table 4.4). The final step is to calculate the overall K_d value for layered columns by setting the length of layer 2 to 10.64 cm, with no amendment. The calculated overall K_d value represents the value expected from a mixture of the two layers.

The K_{oc} value for sorption of atrazine to manure (about 50 L/kg) is about the same as that for soil humus. The K_{oc} value for sludge is 97 L/kg, which is why breakthrough curves from sludge-amended soils are retarded to a greater degree.

4.6.3. The effect of number of layers and degree of mixing of amendment on solute breakthrough.

In this example we simulated the breakthrough of chemical from layered and mixed column. A hypothetical example is used because all column properties need to stay constant with the exception of the K_d values.

1. For layered columns, breakthrough curves were identical, regardless of the order of the layers (or direction of flow). Thus for a two-layer column, breakthrough curves were identical for both amended soil overlying unamended soil, and unamended over amended. This was true for both equilibrium and kinetic sorption.

2. Breakthrough curves do differ slightly depending on the way in which the organic amendment

is distributed, that is, whether it is layered in thick or thin segments, or distributed evenly through the soil column. Three simulations were conducted to predict breakthrough from a non-sorbing soil (no organic matter) to which a sorbing amendment was added. The amendment was added to i) the upper half of the column, ii) to alternate segments (25 amended, 25 unamended) and iii) mixed uniformly through the column. Simulations suggest that the only effect of layering or mixing is to change the apparent dispersivity (Figure 4.6). CXTFIT was used to obtain apparent dispersivity values, assuming that K_d value, water content, water flux density and pulse length were identical for all three columns, and that dispersivity was the only parameter that was unknown (Figure 4.7, Table 4.5).

These simulations suggest that for all practical purposes, the method of incorporation has little influence on simulated breakthrough curves, provided that the mixing method does not alter access of the chemical to the sorbing amendment. For example, if equilibrium sorption is assumed, the assumption holds no matter how the amendment is distributed. Similarly, the same kinetic parameters were applied to non-equilibrium sorption in order to obtain the results shown in Figure 4.6, which again suggests that amendment distribution affects only dispersivity.

Similar simulations were performed using data derived from the laboratory columns; despite uncertainties regarding dispersivity and bulk density in treated and untreated parts of the column, the results also suggested that the degree to which the amendment is incorporated or mixed influences only the apparent dispersivity.

The measured curves suggest that concentrating the amendment in part of the column leads to higher sorption and hence retardation. This behaviour is not predicted by LEACHP, which cannot predict changes in access to sorption sites. To predict this behaviour we need a greater understanding of the geometry of the soil mineral and organic components in relation to convective and diffusive solute transport pathways.

4.7 DISCUSSION

Models based upon the convection-dispersion equation are commonly applied to field scenarios, despite the fact that there are a number of field conditions that may cause the behaviour of solutes under natural conditions to depart from the ideal. These conditions are associated with preferential flow, more complex non-equilibrium processes than are reflected in a two-site model, and inhomogeneous soil structure that leads to restricted or slow access to parts of the soil. Nonetheless, we use simpler CDE-based transport models because in many instances flow rates in soil are far slower than sorption or diffusion, and the CDE describes observed solute transport quite well. Transport parameters are often obtained by parameter optimization using chemical breakthrough data obtained from controlled laboratory column studies.

In the case of pesticides, which sorb strongly to organic matter, a major uncertainty in applying CDE-based models (such as LEACHP) to field soils is the effect of soil organic matter distribution on pesticide transport. Is it important to know the exact distribution of organic

matter near the surface, where it varies rapidly with depth, or is it sufficient to merely know the total amount? Results from these simulations suggest that, as far as CDE modelling is concerned, the distribution of organic matter is less important than the total quantity, provided that degradation is not related to depth in the profile. So if an amendment is added to the soil, the model would suggest that it is not vitally important to know the depth of incorporation, or the degree to which the amendment is layered, as long as accessibility of sorption sites does not change. This also implies when breakthrough curves from columns of alternative amendment distributions are compared, differences can be ascribed to access to sorption sites. This is especially true if there are differences in apparent K_d values, rather than small differences in dispersivity.

From this and other work, it is clear that we need to be able to describe the structure and geometry of soils and amendments. All of the techniques we currently use depend upon a fitting procedure for parameter evaluation, raising the problem of non-unique solutions and doubtful applicability to transient, unsaturated flow conditions, and other soil and chemical combinations. To start with, more work is required in characterizing soil organic matter and soil structure. This needs to be done in a way that enables rapid classification of soils, organic matter and amendments, and the classification needs to be related to solute transport. It is revealing that every soil scientist knows the range of densities of the mineral components of soils, but few have any idea as to the density of organic matter, whether or not it shrinks or swells, its distribution on a micro-scale, and the ease with which inorganic and organic molecules penetrate or traverse the organic regions of soil. This knowledge, generalized across a spectrum of soil-vegetation-climate combinations, will enable a far deeper understanding of the processes and kinetics of pesticide transport in soil.

TABLE 4.1 TRANSPORT PARAMETERS USED FOR COMPARING ANALYTICAL AND NUMERICAL SOLUTIONS TO THE CDE.

All columns: Column length 35 mm, Water flux density 660 mm d⁻¹
Pulse length 42.37 mm, Bulk density 1.15 kg dm⁻³
Organic C 1%.

Equilibrium /kinetic	Segment thickness	Fraction of equilibrium sites	Phase transfer coefficient	Koc value	Dispersivity
	mm		day ⁻¹	L kg ⁻¹	mm
E1	1.75	1	-	690	0.4375
K1	1.75	0.51	4.8	679	0.4375
E2	1.75	1	-	690	0.875
K2	1.75	0.51	4.8	679	0.875
E3	1.75	1	-	690	1.75
K3	1.75	0.51	4.8	679	1.75
E4	1.75	1	-	690	3.5
K4	1.75	0.51	4.8	679	3.5
E5	1.75	1	-	690	7
K5	1.75	0.51	4.8	679	7
E6	0.875	1	-	690	0.4375
K6	0.875	0.51	4.8	679	0.4375
E7	0.875	1	-	690	0.875
K7	0.875	0.51	4.8	679	0.875
E8	0.875	1	-	690	1.75
K8	0.875	0.51	4.8	679	1.75
E9	0.875	1	-	690	3.5
K9	0.875	0.51	4.8	679	3.5
E10	0.875	1	-	690	7
K10	0.875	0.51	4.8	679	7

TABLE 4.2. COLUMN AND TRANSPORT PARAMETERS FOR SIMULATIONS
CORRESPONDING TO MEASURED COLUMN DATA.

LEACHP filename	Uniform or layered column	Water flow	Amendment	Column length	Bulk density	Porosity	Pore volume	Water content	Calculated particle density	Pulse length
				mm	kg dm ⁻³		mm		kg dm ⁻³	days
Lofastsl	Uniform	Fast	Sludge	140	1.25	0.528	78.4	0.56	2.841	0.1145
Lofastma	Uniform	Fast	Manure	140	1.21	0.543	77.0	0.55	2.689	0.1196
Lofastun	Uniform	Fast	Unamended	140	1.25	0.528	73.9	0.528	2.648	0.1155
Loslowsl	Uniform	Slow	Sludge	140	1.21	0.543	76.0	0.543	2.648	0.5598
Loslowma	Uniform	Slow	Manure	140	1.21	0.543	76.7	0.548	2.677	0.6179
Loslowun	Uniform	Slow	Unamended	140	1.25	0.528	74.1	0.529	2.654	0.5770
Shfastsl	Uniform	Fast	Sludge	35	1.07	0.626	21.9	0.626	2.861	0.0293
Shfastma	Uniform	Fast	Manure	35	1.07	0.627	21.9	0.627	2.869	0.0293
Shslowsl	Uniform	Slow	Sludge	35	1.07	0.626	21.9	0.626	2.861	0.1502
Shslowma	Uniform	Slow	Manure	35	1.07	0.627	21.9	0.627	2.869	0.1491
Lafastsl	Layered	Fast	Sludge	140	1.21	0.543	74.6	0.533	2.591	0.1198
Lafastma	Layered	Fast	Manure	140	1.25	0.528	73.9	0.528	2.648	0.1183
Laslowsl	Layered	Slow	Sludge	140	1.21	0.543	74.6	0.533	2.591	0.6147
Laslowma	Layered	Slow	Manure	140	1.21	0.543	73.9	0.528	2.564	0.607

LEACHP filename	Uniform or layered column	Amendment	Surface flux	Pore water density	Dispersion coefficient	Dispersivity	K _d	Phase transfer coeff.	Phase transfer coeff.	Equilib. sites fraction
			mm/day	cm hr ⁻¹	cm hr ⁻¹	mm	L kg ⁻¹	hr ⁻¹	d ⁻¹	
Lofastsl	Uniform	Sludge	684.5	5.093	1.038	2.038	2.15	0.13	3.12	0.54
Lofastma	Uniform	Manure	643.6	4.876	0.753	1.544	1.37	0.39	9.36	0.62
Lofastun	Uniform	Unamended	639.9	5.05	1.853	3.669	0.93	0.17	4.08	0.67
Loslowsl	Uniform	Sludge	135.8	1.042	0.156	1.497	2.15	0.04	0.96	0.61
Loslowma	Uniform	Manure	124.2	0.944	0.272	2.881	1.37	0.07	1.68	0.63
Loslowun	Uniform	Unamended	128.4	1.011	0.267	2.641	0.93	0.06	1.44	0.73
Shfastsl	Uniform	Sludge	747.9	4.978	1.561	3.136	6.79	0.2	4.80	0.51
Shfastma	Uniform	Manure	748.9	4.977	1.225	2.461	3.58	0.16	3.84	0.54
Shslowsl	Uniform	Sludge	145.9	0.971	0.221	2.276	6.79	0.11	2.64	0.44
Shslowma	Uniform	Manure	147.2	0.978	0.314	3.211	3.58	0.11	2.64	0.60
Lafastsl	Layered	Sludge	622.8	4.869	1.183	2.430	n/a	0.29	6.96	0.50
Lafastma	Layered	Manure	624.9	4.931	1.068	2.166	n/a	0.54	12.96	0.64
Laslowsl	Layered	Sludge	121.4	0.949	0.198	2.086	n/a	0.1	2.40	0.52
Laslowma	Layered	Manure	121.8	0.961	0.201	2.092	n/a	0.05	1.20	0.66

TABLE 4.3 Calculation of Kd values in a multi-component soil.

Assumption: Known volume of soil, two layers. Each layer consists of mineral particles, humus and a variable quantity of a third organic matter phase.

	Short		Long	
	Layer 1	Layer 2	Layer 1	Layer 2
1). Volume of soil				
Length (layer 1)	3.36			
Length (layer 2):	10.84			
Diameter:	5.00			
Total volume is:	274.89			
Volume (layer 1)	65.97			
Volume (layer 2)	208.92			
Overall values for mixture of two materials:				
Kd	2.179 L/kg			
BD	1.221 kg/dm ³			
Porosity	0.545			
Particle d	2.682 kg/dm ³			
K values				
Unamended soil Foc	0.0177	0.0177	0.0177	0.0177
Humus density	2.650	2.650	2.650	2.650
Mass humus	1.829	7.858	7.858	7.858
Mass humus C	1.076	4.622	4.622	4.622
Vol humus	0.406	1.744	1.744	1.744
Organic amendment				
Organic C fraction	0.452	0.452	0.452	0.452
Amendment density	2.650	2.650	2.650	2.650
Vol amendment	3.698	0.000	0.000	0.000
Soil mineral density	2.650	2.650	2.650	2.650
Vol mineral	22.534	96.801	96.801	96.801
Mass mineral	59.716	256.523	256.523	256.523
Total vol solids	26.638	98.545	98.545	98.545
Total mass	71.345	264.380	264.380	264.380
BD check	1.081	1.265	1.265	1.265
Porosity	0.596	0.528	0.528	0.528
Overall Kd	6.822 L/kg	0.927 L/kg	0.927 L/kg	0.927 L/kg
Overall OM added	15.923 %	0.000 %	0.000 %	0.000 %

TABLE 4.4. Derived atrazine K_{oc} values for humus, manure and sludge.

	Short column (3.36 cm)	Long column (14 cm)	Overall K_d in layered column
	K_{oc} L/kg	K_{oc} L/kg	K_d L/kg
Humus	53	53	n/a
Manure	57	47	1.44
Sludge	97	98	2.18

TABLE 4.5 Effect of layering and mixing of amendment on apparent dispersivity values, using CXTFIT. (Dispersivity specified in input data was 2.8 mm throughout.)

Incorporation of amendment	Kd values		Fitted dispersivity value
	Amended	Unamended	
Amended (70 mm) over unamended (70 mm).	1.5	0	3.82
Amended (2.8 mm) over unamended (2.8 mm), repeated 25 times.	1.5	0	3.06
Mixed uniformly.	0.75	n/a	2.76

Figure 4.1 The influence of water flux direction on the nodal concentrations that determine concentration changes at node i.

Chemical breakthrough; 5 dispersivity values; equilibrium sorption
Analytical and numerical solutions (at two node spacings).

Figure 4.2. Breakthrough curves for equilibrium sorption and five dispersivity values, obtained using CXTFIT2 (Toride et al, 1995), and simulated with LEACHP using 20 (●) or 40 (+) node spacings.

Chemical breakthrough; 5 dispersivity values; kinetic sorption
Analytical and numerical solutions (at two node spacings).

Figure 4.3. Breakthrough curves for kinetic sorption and five dispersivity values, obtained using CXTFIT2 (Toride et al, 1995), and simulated with LEACHP using 20 (•) or 40 (+) node spacings.

Figure 4.4. A comparison of simulated and analytical (CXTFIT2) breakthrough curves for uniform columns. Short columns are on the left-hand side of the graphs, long ones are on the right-hand side. Manure is designated by $\bullet$, sludge by $+$, and unamended columns by $\circ$.

Figure 4.5 Simulated and best-fit (CXTFIT2) atrazine breakthrough curves from layered columns (upper layer amended with organic material).

Figure 4.6. The simulated effect of layering and complete mixing of amended and unamended soil on atrazine breakthrough curves. The two groups of curves show simulations for kinetic and equilibrium sorption.

Figure 4.7. The effect of layering and mixing on atrazine breakthrough where amendment is thoroughly mixed (a), incorporated as 25 layers (b), and as two layers. One amended and the other unamended (c). Simulations denoted by lines and best-fit (CXTFIT) values as symbols

CHAPTER 5

SOLUTE TRANSPORT IN MULTIPLE POROSITY MEDIA: USE OF A VARIABLE FIRST- ORDER MASS TRANSFER COEFFICIENT

5.1 LITERATURE REVIEW

The environmental fate and subsequent impact upon groundwater of chemicals applied to soil has been increasingly studied during the past few decades. Traditionally, solute transport through porous media has been modeled with a one-dimensional form of the mechanistic and deterministic convection-dispersion equation (CDE) (Nielsen *et al*, 1986; van Genuchten and Wagenet, 1989). The CDE presumes that solute movement is a result of the combined processes of convection and diffusion (Wagenet, 1990). Diffusion is the result of a concentration gradient and convective transport is associated with the bulk movement of water through porous media. When terms for sorption, degradation and volatilization are incorporated into the CDE, it has been shown to describe well the results from miscible displacement experiments for weakly or non-sorbing solutes in a relatively homogeneous porous media (Nielsen *et al*, 1986; Wagenet and Rao, 1990). However, for heterogeneous media (Rao *et al*, 1980a,b; Yimin and Ghodrati, 1995) or for chemicals and porous media that exhibit non-ideal sorption characteristics (Rubin, 1983; Gaber *et al*, 1992; Ma and Selim, 1996; Pignatello and Xing, 1996) the CDE in its classical form has been shown to be an insufficient model for describing transport experiments.

Often these insufficiencies (i.e. early breakthrough, prolonged tailing, multiple peak concentrations) have been attributed to different yet interconnected chemical and physical processes which interact uniquely in each porous medium. Our current knowledge of these processes in heterogeneous soils is insufficient to precisely describe the flow dynamics. As a result, several relatively simple mathematical expressions have been proposed as a way of representing these processes in chemical fate and transport models that describe non-equilibrium conditions.

Non-equilibrium models assume the soil matrix consists of independent fractions exhibiting different mass transfer mechanisms (physical and/or chemical) with respect to each other (van Genuchten and Wierenga, 1976; Rao *et al*, 1980a,b; Nkedi-Kizza *et al*, 1984; Brusseau *et al*, 1989; Chen and Wagenet, 1995). Some of these conceptualized processes and their representation in fate and transport models are discussed below, beginning with the processes affecting non-equilibrium transport due to non-ideal chemical (sorption) interactions, followed by a discussion of transport-related (physical) non-equilibrium.

5.2 CHEMICAL NON-EQUILIBRIUM

The steady-state, conventional one-dimensional CDE with sorption is characterized by a nearly symmetric breakthrough-curve (BTC) and is given by (Wagenet and Rao, 1990)

$$\frac{\partial c}{\partial t} + \frac{\rho \partial s}{\theta \partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (5.1)$$

where c is the macroscopic-average liquid concentration (M/L^3), t is time (T), v is the average pore water velocity (the Darcy flux of water divided by the average macroscopic volumetric water content, L/T), x is the space coordinate (L), D is the effective dispersion coefficient (L^2/T), ρ is the bulk density of the soil (M/L^3), θ is the macroscopic volumetric water content (L^3/L^3), and s is the sorbed concentration (M/M).

The effective dispersion coefficient has been approximated by a linear relationship between the molecular diffusion coefficient and a term accounting for mechanical dispersion (Wagenet, 1983; Nielsen *et al*, 1986) and is given by

$$D = D_{m,e} + \lambda |v| \quad (5.2)$$

where $D_{m,e}$ is the effective molecular diffusion coefficient corrected for tortuosity and porosity (L^2/T) and λ is the dispersivity of the porous media (L) (Wagenet, 1983). Tortuosity was conceived as a function of the ratio of the direct linear and effective path lengths (Olsen and Kemper, 1968). Dispersivity is a measure of mechanical dispersion (mixing) generated by a distribution of pore sizes, causing the flux of water through one pore to be slightly different than its neighbors (Bear, 1988). Useful approximate relationships and ranges of values for determining $D_{m,e}$ and λ can be found in the literature (Millington and Quirk, 1960; Wagenet, 1983). Recent studies indicate that the dispersion coefficient is not a constant that can be applied to the entire transport volume, but in fact is dependent upon solute travel distance and is highly affected by inhomogeneities (Jaynes *et al*, 1988; Porro *et al*, 1993; Zhang, 1995).

The sorption component of Eq. 5.1 has been simplified by assuming a linear, reversible and instantaneous reaction between the solution and sorbed phases. For this condition, s can be given by (Nielsen *et al*, 1986)

$$s = kc \quad (5.3)$$

in which k is the linear partitioning coefficient for solute between the liquid and solid phases (V/M). Substituting Eq. 5.3 into Eq. 5.1 and simplifying, we obtain the CDE with the local equilibrium assumption (LEA)

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (5.4)$$

in which R is the retardation coefficient and is given by

$$R = 1 + \frac{\rho k}{6} \quad (5.5)$$

This relationship is referred to as the LEA (Elrick *et al.*, 1966; van Genuchten *et al.*, 1974; Nielsen *et al.*, 1986) because it carries with it the simplifying concept that the solute reacts instantaneously and reversibly with the soil matrix. This model has been fairly successful for experimental results obtained from batch studies (Dao and Lavy, 1978; Huang *et al.*, 1984; Kookana *et al.*, 1992). However, increasing evidence suggests that the LEA assumption may not always be valid (Pignatello, 1989), as it has been unsuccessful in describing the simultaneous tailing and retardation observed in many miscible displacement experiments (Davidson *et al.*, 1968; van Genuchten *et al.*, 1974; Gaber *et al.*, 1992).

Numerous criteria have been proposed to determine whether the LEA is appropriate for a particular experiment (Valocchi, 1985; Brusseau *et al.*, 1989; Bahr, 1990; Gaber *et al.*, 1992). Typically these criteria depend upon the interaction of transport parameters such as pore-water velocity, dispersion coefficient, partitioning coefficient, sorption rate (for a non-equilibrium process, which is discussed later), and boundary conditions. The extent of parameter interactions is a measure of the Damkohler number which represents the ratio of a characteristic transport time to a characteristic reaction time (Gaber *et al.*, 1992).

The shortcomings of the LEA are clear when the simultaneous interactions of physical diffusion and rate-limited sorption are considered, a phenomenon known as non-equilibrium sorption (Pignatello and Xing, 1996). Physical diffusion limitations were linked to the diffusion of the chemical through natural organic matter matrices and diffusion through intra-particle nanopores. Pignatello and Xing (1996) also suggested numerous conditions conducive to rate-limited sorption, such as distributed rate constants, kinetic hysteresis and concentration dependence of sorption rates. Simplified conceptual representations of these processes have been used in conjunction with the CDE to better describe experimental data (van Genuchten *et al.*, 1974; Selim *et al.*, 1976; Brusseau *et al.*, 1989; Chen and Wagenet, 1995).

If one considers the reaction between the sorptive matrix and the chemical in solution to be a rate-limited process rather than instantaneous, then the time rate of change of the chemical in the sorbed phase can be most simply represented as a first-order (FO) relationship by (van Genuchten *et al.*, 1974; Nielsen *et al.*, 1986)

$$\frac{\partial s}{\partial t} = \alpha(kc - s) \quad (5.6)$$

in which α is a FO rate coefficient ($1/T$) and kc is the amount sorbed at equilibrium. This FO rate expression has improved the predictive capacity of the CDE but the results usually were not transferable to different experimental conditions. In particular, Eq. 5.6 may not adequately describe experiments with large pore-water velocities or systems containing large aggregates (van Genuchten *et al.*, 1974; Pignatello *et al.*, 1993).

Other modeling approaches have been proposed to better describe transport experiments, including

a practical model which categorizes the sorption sites into two fractions (van Genuchten *et al*, 1974; Selim *et al*, 1976; Nkeddi-Kizza *et al*, 1984). One of the fractions exhibits instantaneous sorption and is always in equilibrium with the solution phase, while the other fraction is characterized by a FO rate-limited reaction. This type of model has been fairly successful in predicting the results of miscible displacement experiments (Gamerding *et al*, 1991; Pignatello *et al*, 1993; Gaber *et al*, 1992). Under high flow conditions the two-site model produced a good fit to experimental effluent BTC's (Rao *et al*, 1979; Gamerding *et al*, 1990, 1991). However, model parameters (rate coefficients and relative fractions of each of the sites) can be dependent upon the experimental conditions (Gamerding *et al*, 1991; Brusseau, 1992) and are not necessarily transferable between experiments.

Recent modifications to the two-site (or multi-site) approach involve the incorporation of non-linear reversible kinetics, hysteresis, FO degradation terms, multiple site sorption, and continuously distributed sorption site models (Brusseau *et al*, 1989; van Genuchten and Wagenet, 1989; Chen and Wagenet, 1995; Ma and Selim, 1996). These models have shown improved success in describing experimental BTC's, with reviews of the mechanisms of chemical non-equilibrium and conceptualized methods for dealing with them given by Pignatello and Xing (1996) and Ma and Selim (1996).

5.3 PHYSICAL NON-EQUILIBRIUM

In the previous section it was mentioned that for *weakly or non-interacting* solutes in a *homogeneous* porous medium the CDE was a reasonable predictive tool. A relatively less studied soil system, and a probably more widespread one is a *heterogeneous* system that may exhibit macroscopically discontinuous flow domains. For instance, in soils that have apparent non-matrix type flows (i.e. anomalies such as wormholes, structural cracks, aggregated media, or other types of 'preferential flow' (Wagenet and Germann, 1989) it is questionable whether the conventional CDE will be a successful predictive tool (Wagenet, 1990). Such structural anomalies can, under certain conditions, produce rapid bypass-flow (or short-circuiting) of water through the soil (Booltink and Bouma, 1991; Radulovich *et al*, 1992; Bootink *et al*, 1993; Flury *et al*, 1994) and hence the underlying groundwater quality may be significantly affected by any transported chemicals (Wagenet, 1990). The potential for this phenomenon has been realized by many researchers (Steenhuis *et al*, 1990a,b; Czapar *et al*, 1992; Flury *et al*, 1994; Ahuja *et al*, 1995; Heathman *et al*, 1995; Yimin and Ghodrati, 1995; Flury, 1996). In order to study solute transport under these conditions with the CDE, it is necessary to represent many simultaneous flow regimes in conceptualizing a non-homogenous flowing system. Such adaptations give rise to the physical non-equilibrium (PNE) models (Lafolie, 1993; Heathman *et al*, 1995).

The concept of PNE has been recognized by soil scientists for the past few decades. Traditionally, it has been associated with the heterogeneous flow fields (hydraulic regions) that are encountered in natural porous media (Skopp and Warrick 1974; van Genuchten and Wierenga, 1976; Grisak and Pickens, 1980; Rao *et al*, 1980a, 1980b; van Genuchten *et al*, 1984; Brusseau and Rao, 1990; Chen and Wagenet, 1992a, 1992b; Gerke and van Genuchten, 1993; Haggerty and Gorelick, 1995) with much of the attention being given to the mechanisms of mass transfer of solutes between different flow regions.

Coats and Smith (1964) were some of the earlier contributors to the development of PNE theory. They proposed a two-region model in which the soil water was divided into two overlapping continua

(regions): mobile and immobile. Chemical transport in such soils is thought to consist of longitudinal (in the mean flow direction) and lateral diffusive transport between the mobile and immobile domains (Li *et al*, 1994). The longitudinal transport occurs in the mobile region due to convection and dispersion, while the lateral diffusive transport takes place between the mobile and immobile regions. Subsequent to Coats and Smith, others (Skopp and Warrick, 1974; van Genuchten and Wierenga, 1976) have added terms for sorbate/sorbent reactions. Haggerty and Gorelick (1995) recently summarized forms of the governing convective and diffusive mass transfer equations for this and other types of models. For the FO, two-region model with sorption, these equations are given by Haggerty and Gorelick (1995)

$$A \frac{\partial c_m}{\partial t} + B \frac{\partial c_{im}}{\partial t} = D \frac{\partial^2 c_m}{\partial x^2} - Q \frac{\partial c_m}{\partial x} \quad (5.7)$$

$$B \frac{\partial c_{im}}{\partial t} = \omega(\lambda c_m - c_{im}) \quad (5.8)$$

where A (dimensionless) is the parameter that relates concentration within the mobile zone to concentration within a unit volume of the porous medium, B (dimensionless) is the parameter that relates concentration within the immobile zone to concentration within a unit volume of the porous medium, D (L^2/T) is the effective dispersion coefficient in the mobile zone (same as Eq. 5.2), Q is Darcian water flux (L/T), ω is a FO mass transfer coefficient ($1/T$), λ is a distribution coefficient relating c_{im} (the immobile water concentration (M/L^3)) and c_m (the mobile water concentration (M/L^3)) at equilibrium. These coefficients are defined such that they are consistent with the two-region model of van Genuchten and Wierenga (1976). The FO mass transfer coefficient (ω) is a constant, lumped parameter that conceptually represents the geometry and diffusive properties of the porous media and solute. Hence, the mass transfer between regions is controlled by the macroscopic concentration gradient between domains.

The mobile/immobile transport model is conceptually consistent with respect to the observed characteristics of some of the reported column breakthrough experiments. Early solute breakthrough followed by prolonged tailing (Anderson, 1979; Li and Ghodrati, 1994) can be related to the phenomena of two quasi-separated (overlapping) flow regimes. The pore-water velocity is a function of the effective mobile water content, where the mobile water content is usually some fraction of the total macroscopic volumetric water content. The pore water velocity for a mobile/immobile matrix ($v_m = Q/\theta_m$, θ_m is the mobile water content (Gerke and van Genuchten, 1993)) is greater than that for a homogeneous matrix ($(v = Q/\theta) i.e. \theta_m \leq \theta$), which results in early breakthrough of the chemical. Also, the non-symmetric BTC's can be associated with the diffusive exchange between regions. The extent of tailing and the shape of the initial breakthrough front are affected by the assumptions regarding the overall form of the inter-region mass transfer mechanisms.

Experimentally, the FO two-region model described in Eq. 5.7 and Eq. 5.8 (Skopp and Warrick, 1974; van Genuchten and Wierenga, 1976) has shown success in predicting the preferential flow and tailing of BTC's (van Genuchten and Wierenga, 1977; Rao *et al*, 1979; Li and Ghodrati, 1994; Li *et al*, 1994). However, the two-region model has come under some scrutiny because it lacks a practical and physically measurable parameter vector (i.e. A and B in Eq. 5.7 and ω in Eq. 5.8) (Rao *et al*, 1980a; Ma and Selim, 1996). Typically, these parameters are obtained through curve fitting the data to the proposed

theoretical model (Parker and van Genuchten, 1984). The difficulty of *a priori* obtaining transport parameters complicates the process of model validation. To verify a conceptual model it is necessary to be able to measure or estimate parameters independent from the data of the BTC (Rao *et al*, 1980a,b; Brusseau *et al*, 1989). Thus, it would be beneficial to be able to relate the physical properties of the system to the FO mass transfer coefficient in Eq. 5.8 and the relative distribution coefficients in Eq. 5.7.

Some studies have attempted to relate the FO transfer coefficients to a Fickian diffusion model in which diffusion through ideal and assumed geometries are considered (Rao *et al*, 1980a, 1980b; Rao *et al*, 1982; van Genuchten, 1985; Gerke and van Genuchten, 1993). The mobile phase, in such aggregated systems, consists of the larger pores between aggregates and the conceptualized immobile phase is composed of smaller pores within the aggregate (Li *et al*, 1994) that are isolated from the mobile phase. For systems of aggregates, Rao *et al* (1980a, 1980b) reasoned that the FO phase transfer coefficient (ω in Eq. 5.8) could be related to the solute residence time in the soil and thus was affected by pore-water velocity. However, van Genuchten (1985) showed that scaled with the lateral diffusion time (i.e. $\omega \propto D_T / a^2$ where D_T is the effective transverse diffusion coefficient and a is the length scale of the aggregate). For the mobile/immobile concept the relationship of van Genuchten (1985) seems more satisfactory (Li *et al*, 1994).

Other two-region transport models that incorporate an exact model for Fickian diffusion into uniform assumed geometries have also been proposed. Models for solute transport through a media of uniformly spherical aggregates (Rasmuson and Neretnieks, 1980) and for solute transport through a single continuous macropore embedded within an otherwise uniform matrix (van Genuchten *et al*, 1984) have been presented. In the spherical model the immobile region was the aggregates, whereas for the cylindrical model the matrix was the immobile region. Such models may be adequate to describe mass transfer at the laboratory scale (Rao *et al*, 1980a, 1980b; van Genuchten *et al*, 1984; Ball and Roberts, 1991) but may not be adequate to predict concentration histories in a heterogeneous medium (Ball and Roberts, 1991; Haggerty and Gorelick, 1995).

Natural porous media may contain a wide range of particle sizes (sand, silt, clay and organic colloids) as well as a variety of aggregate shapes (e.g. cylinders and spheres). A model based upon a single uniformly sized aggregate (e.g. spheres) may not successfully model solute transport in natural porous media (Ball and Roberts, 1991; Haggerty and Gorelick, 1995). Hence, a more plausible model would account for the effects caused by a distribution of aggregate sizes. Lafolie (1993) found that the influence of a distribution of aggregates depended upon the velocity, and consequently on the proportion of aggregates in situations of local equilibrium or physical non-equilibrium. Lafolie also looked at the possibilities of using a mean radius to characterize the effects of the entire distribution. It was concluded that the usefulness of a mean radius depended strongly on the contrast between the mobile phase residence time and the distribution of characteristic diffusion times and that in most cases a mean radius cannot be used in place of the distribution. Therefore, there is a need for a model that allows the possibility of a soil composed of a variety of aggregate sizes.

In chromatographic systems, variability in the particle size has long been known to affect solute transport (Purnell, 1962 and Dougharty, 1972 cited in Haggerty and Gorelick, 1995). Villermeaux (1990) noted that certain distributions of FO mass transfer coefficients and diffusion from certain distributions of spheres could yield similar BTC's (supported by Haggerty and Gorelick, 1995). Rappoldt (1990)

presented a model that estimated the diffusion characteristics of solute into aggregates by means of a function closely related to the surface area to volume ratio (S/V). For diffusion models, differently shaped aggregates may be approximated by a uniform aggregate shape provided that the uniform aggregates are chosen to give the same S/V ratios (Rao *et al*, 1982; Rappoldt, 1990). The accuracy of this approximation is dependent upon the shape contrast between the actual and uniform aggregates. For most geometrical shapes, there is a shape-independence of diffusion processes (van Genuchten, 1985; van Genuchten and Dalton, 1986; Rappoldt, 1990) so that the error from the approximation may be unimportant.

The applicability of the mobile/immobile concept to most structured porous systems (stratified and/or structured) has been questioned (Li *et al*, 1994). For soils that may exhibit macroscopic discontinuities such as cracks, wormholes, roots, and macrofauna (Wagenet and Germann, 1989) the physical basis of the model may be unclear (Li *et al*, 1994). To assess accurately the transport characteristics of this medium, it may be necessary to include more than one flow region, each having its own hydraulic properties and mass transfer mechanisms (Grisak and Pickens, 1980; Steenhuis *et al*, 1990a, 1990b; Chen and Wagenet, 1992a, 1992b; Gerke and van Genuchten, 1993; Li *et al*, 1994; Hutson and Wagenet, 1995; Gwo *et al*, 1996). For soils with macropores the matrix may not be immobile. Omoti and Wild (1979) performed tracer experiments and revealed rapid transport through pores too small to be considered macropores. There is also evidence that contaminants move through small pores continuously in addition to discrete/rapid pulses through large pores (Jardine *et al*, 1990; Wilson *et al*, 1993).

An increase in the number of regions considered should permit a model to improve on simulations of transport experiments. However, such an increase in the number of regions (stagnant or not) introduces new variables. In the best case, it would be possible to measure or estimate these variables from the physical and chemical properties of the system (Rao, 1980a, 1980b; Brusseau, 1989). Li *et al* (1994) reasoned that for low flow velocity ranges the FO transfer coefficient (ω) was proportional to the pore water velocity ($\omega = V^2/D$, V = pore water velocity, D = longitudinal effective dispersion coefficient) which agreed with the findings of Rao *et al* (1980a, 1980b). For high pore water velocities Li *et al* (1994) concluded that ω was proportional to the transverse diffusion coefficient ($\omega = D_T/a^2$, D_T = transverse diffusion coefficient, a = length scale), which was also found by others (van Genuchten, 1985; van Genuchten and Dalton, 1986). For transient conditions it may be possible to group different hydraulic regions into pore sizes (Wilson *et al*, 1992; Gwo *et al*, 1996) to determine model parameters. Gerke and van Genuchten (1993) presented a FO dual porosity model in which the water and chemical transfer relationships had a shape factor for approximating an assumed geometrical system. However, the shape factor was time and concentration independent. This could lead to significant deviations from the exact theoretical model depending upon the concentration dependence of the shape factor (van Genuchten, 1985). Van Genuchten (1985) suggested that using such an approximation might be within the allowable limits of large-scale studies.

The objectives of this study are first to expand upon the shape factor approach to modeling water and chemical flow through structured soils (van Genuchten, 1985; van Genuchten and Dalton, 1986; Gerke and van Genuchten, 1993). Using the shape characteristics of diffusion into aggregates of known geometry it is possible to regress simple equations to approximate exact analytical diffusion models. Second, the regressed equations can then be used to obtain simple shape factors that are concentration

dependent. Third, these shape factors can then be incorporated into a multi-region water flow and solute transport model. This model will then represent a structured medium consisting of non-uniformly shaped aggregates (e.g. spheres and hollow cylinders).

5.4 THEORY

The multi-region water flow and solute transport model (TRANSMIT) of Hutson and Wagenet (1995) was modified to better approximate the geometric properties of structured media (plates, spheres, cylinders). For the purposes of this study only steady-state water flow was considered.

TRANSMIT is a multi-region model that assumes the existence of multiple interacting regions. Each region is defined by distinct physical and chemical properties. For example, it is possible to describe a mobile/immobile type of system, or even a system in which there exists a distribution of flow fields (i.e. a system of intertwined matrix and preferential flow regions). In TRANSMIT vertical solute flux for each region and horizontal diffusive exchange between regions occurs in an alternating fashion. Given a particular time-step TRANSMIT simulates vertical solute transport for each region j to k (if vertical transport is considered in region j) followed by a horizontal equilibration between all regions over the same time-step. Vertical solute flux is governed by the CDE and for each region j is given by

$$\frac{\partial c_j}{\partial t}(\theta_j + \rho_j K_j) = \frac{\partial}{\partial z} \left[\theta_j D(\theta_j, q_j) \frac{\partial c_j}{\partial z} - q_j c_j \right], \quad (5.9)$$

where for each region j , c is aqueous solute concentration (M/L^3), θ is the local volumetric water content (L^3/L^3), ρ is the soil bulk density (M/L^3), K is the linear sorption partitioning coefficient (L^3/M), q is solute flux density (L/T), $D(\theta, q)$ is the effective dispersion coefficient and is the sum of molecular diffusion and hydrodynamic dispersion (L^2/T). Equation 5.9 was solved numerically using the finite difference scheme of Hutson and Wagenet (1992). The molecular diffusion coefficient (D_c) in soil is estimated by adjusting the aqueous diffusion coefficient (D_o) for the effects of water content and tortuosity (Jury, *et al*, 1983); Hutson and Wagenet, 1995) and is given by

$$D_c = D_o \frac{\theta^{3.33}}{\theta_s^2}, \quad (5.10)$$

and θ_s is the porosity of the matrix. The hydrodynamic dispersion coefficient is assumed to be linearly related to pore-water velocity and is determined by

$$D_m = \lambda \frac{q}{\theta}, \quad (5.11)$$

where λ is the dispersivity (L). For further details about Eqs. 5.9, 5.10 and 5.11 see Hutson and Wagenet (1995).

After vertical solute transport for each region is complete, horizontal diffusive exchange is

simulated for the same time-step. Because the horizontal transfer routines are significantly different from those of TRANSMIT it is necessary to develop the concepts and equations more rigorously.

5.5 HORIZONTAL DIFFUSIVE EQUILIBRATION

The approach is similar to that of van Genuchten (1985) and Gerke and van Genuchten (1993). Those authors used a shape factor to adjust a FO mass transfer coefficient such that the coefficient could be used to approximate exact geometric shapes. The analytical solutions for diffusion into known geometric aggregates are based upon Fickian diffusion and the general equations of Haggerty and Gorelick (1995):

$$\frac{\partial c_r}{\partial t} = \frac{D_a}{r^{\nu-1}} \frac{\partial}{\partial r} \left[r^{\nu-1} \frac{\partial c_r}{\partial r} \right], \quad (5.12)$$

where D_a is the apparent diffusion coefficient (L^2/T), r is the radius (L) and ν is the dimensionality of the aggregate (for $\nu = 1$, the geometry is layered; $\nu = 2$, the geometry is cylindrical; $\nu = 3$, the geometry is spherical). When working with average macroscopic properties it may be more appropriate to work with average aggregate concentrations. Those are given by

$$c' = \frac{\nu}{a^\nu} \int_0^a r^{\nu-1} c_r dr, \quad (5.13)$$

where c' is the average concentration and a is the length scale of the aggregate (for spheres/cylinders, a equals the radius, for sheets/layers, a equals the half-width of the layers). The boundary conditions for Eq. 5.12 can be taken as

$$\frac{\partial c_r}{\partial t} = 0 \quad \text{when } r = 0 \quad (5.14)$$

$$c_r = c_a \quad \text{when } r = a, \quad (5.15)$$

where c_a is the concentration at the boundary. Analytical solutions for this set of equations are available for various initial conditions and no flow (Carslaw and Jaeger, 1959; Crank, 1975). We will consider two such diffusion models: 1) diffusion into a sphere and 2) diffusion within a hollow cylinder containing a continuous axial pore.

5.5.1 Sphere - defining a shape factor

For a uniform initial concentration of c_0 and constant surface boundary condition of c_i the analytical solution for diffusion of a non-interacting solute into a sphere was given by Crank (1975) as

$$\frac{c - c_0}{c_1 - c_0} = C = 1 + \frac{2a}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{a} \exp \frac{-D_a n^2 \pi^2 t}{a^2}, \quad (5.16)$$

where C is relative concentration (dimensionless). We can define the dimensionless time for diffusion into a sphere by

$$T_s = \frac{D_a t}{a^2} \quad (5.17)$$

Upon substituting Eq. 5.17 into 5.16 and using 5.13 we obtain the analytical solution for the average concentration of a sphere as a function of dimensionless time (van Genuchten, 1985)

$$c_s' = \begin{cases} 6\sqrt{\frac{T_s}{\pi}} - 3T_s + 12\sqrt{T_s} \sum_{n=1}^{\infty} \text{ierfc} \frac{n}{\sqrt{T_s}}, & T_s \leq 0.1 \\ 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp[-n^2 \pi^2 T_s]}{n^2}, & T_s > 0.1, \end{cases} \quad (5.18)$$

where c_s' is the relative concentration (i.e. c_s/c_b , the ratio of sphere and diffusing source concentrations).

A generic FO diffusion model can be defined by assuming that the driving force for mass transfer is governed by the macroscopic average concentration gradient between independent domains (i.e. for example, between mobile and immobile regions) and can be given by

$$\frac{\partial c_i'}{\partial t} = \alpha(C_1 - c_i'), \quad (5.19)$$

in which α is a FO rate coefficient ($1/T$), c_i' (e.g. the immobile phase) is the average relative concentration of the diffusing domain (similar to Eq. 5.18) and C_1 is the constant concentration source (i.e. the mobile region). We wish to define an α which effectively makes the FO model approximate diffusion into a sphere. If we assume a constant concentration solute source in the mobile region (i.e. $C_1 = 1$) we can integrate Eq. 5.19 to obtain the average concentration of the immobile phase as a function of time for the FO diffusion model

$$c_i' = 1 - \exp[-\alpha t] \quad (5.20)$$

Equation 5.20 needs to be cast into dimensionless form so the properties of the two different models (eg. sphere and FO) can be compared and evaluated. We begin by defining a FO dimensionless time by the following relationship

$$T_i = \alpha t \quad (5.21)$$

Upon substituting Eq. 5.21 into 5.20 we obtain an equation analogous to Eq. 5.18 for the FO diffusion model

$$c' = 1 - \exp[-T_l] \quad (5.22)$$

The plots of Eqs. 5.18 and 5.22 have approximately the same shapes and are displaced from each other along the dimensionless time axis (Fig. 5.1). The shape similarity of those curves has led to models that incorporate some of the diffusion and geometric characteristics of a medium into the FO transfer coefficient (Rao *et al*, 1980a, 1980b; van Genuchten, 1985; van Genuchten and Dalton, 1986).

A shape factor can be used to convert an aggregate of given shape and size into a FO model (van Genuchten, 1985). Let the shape factor (F) be defined by

$$F = \left[\left(\frac{T_s}{T_l} \right)^{1/2} \right]_{c'} \quad (5.23)$$

where T_s , and T_l , are dimensionless times for diffusion into a sphere and the FO model, respectively, each of which are evaluated at relative immobile region concentration c' (c_s' and c_l') (van Genuchten, 1985). Here the relative concentrations (c_s' and c_l') are determined by a procedure that considers the current concentrations of the independent regions (mobile and immobile) for each system (spherical and FO). For example, the relative concentrations are determined by the region having the lowest concentration, i.e. for a sphere, if the sphere concentration is less than the surrounding mobile region, then c_s' is determined by the ratio of sphere to mobile phase concentrations. However, for reasons described later, if the sphere concentration is greater than that of the surrounding mobile fluid then the relative concentration (c_s') is calculated as the relative concentration difference between regions. For the time being let us assume that we can obtain a c_s' that can be used whether there is diffusion into or out of any particular region (spheres and FO) of interest. A description of the procedure will be presented later. Now, using this shape factor (Eq. 5.23) a FO mass transfer coefficient (α) can be derived that will approximate diffusion into/out of a sphere. The FO coefficient takes the following form (van Genuchten, 1985; van Genuchten and Dalton, 1986; Gerke and van Genuchten, 1993)

$$\alpha = \frac{D_0}{F^2 a^2}, \quad (5.24)$$

where a is the characteristic length of the aggregate (i.e. radius of the sphere, cylinder, or half-width of a rectangular solid or plane sheet) and D_0 is the effective molecular diffusion coefficient for the aggregate. The proper and rigorous way to evaluate Eq. 5.23 would be to invert 5.18 and 5.22 to obtain T as a function of c' (c_s' and c_l') and subsequently substitute those directly into Eq. 5.23. However, the inversion of Eq. 5.18 is cumbersome (van Genuchten, 1985). Another approach preferred by many is to assume an average constant value for c' (i.e. $c' = 0.5$) and read from plots (Fig. 5.1) the corresponding value for T (van Genuchten, 1985) and substitute those values into Eq. 5.23. The overall accuracy of this approximation is

a function of the concentration dependence of the shape factor. For certain geometries this may not be a bad approximation, but for others it could generate significant deviations from the exact analytical models (van Genuchten, 1985; van Genuchten and Dalton, 1986). Thus, an alternative and simple procedure for calculating an approximate concentration dependent shape factor is needed.

An ideal approach would be to obtain a simple equation relating concentration to dimensionless time. To approach this problem, consider the derivative of Eq. 5.18, which is given by

$$\frac{\partial c'}{\partial T_s} = \frac{3}{\sqrt{T_s}\pi} - 3 + \frac{6}{\sqrt{T_s}} \sum_{n=1}^{\infty} \text{ierfc} \frac{n}{\sqrt{T_s}} + 12\sqrt{T_s} \sum_{n=1}^{\infty} \frac{i}{\sqrt{\pi}} \exp\left[\frac{-n^2}{T_s}\right] \frac{n}{T_s^{3/2}}, \quad T_s \leq 0.$$

$$= \frac{-6}{\pi^2} \sum_{n=1}^{\infty} \frac{-n^2\pi^2}{n^2} \exp[-n^2\pi^2 T_s] \quad (5.25)$$

The plot of Eq. 5.25 is a slowly decaying function of dimensionless time (Fig. 5.2). As the concentration gradient diminishes (i.e. the relative concentration number approaches unity) the derivative approaches zero. If we now plot Eq. 5.25 versus the concentration (Eq. 5.18), each of which is calculated at the same dimensionless time, we obtain a relationship that gives the derivative as a function of concentration (Fig. 5.3):

$$\frac{\partial c'_s}{\partial T_s} = F(c'_s) \quad (5.26)$$

This derivative behaves in a similar way to the function

$$\frac{\partial c'_s}{\partial T_s} = A_1 + A_2 c'_s + \frac{A_3}{c'_s}, \quad (5.27)$$

where A_i are fitting constants (Table 5.1). The plot of Eq. 5.27 is also included in Fig. 5.3 and it should be recognized that this gives a very good approximation to the exact diffusion model. Equation 5.27 can be integrated to obtain T_s as a function of c'_s . The definite integral of Eq. 5.27 is given by

$$T_s^* = B_1 \text{Log}[(B_2 + c_s'^*)^2 (B_3 + c_s'^*)^{B_4}] - B_1 \text{Log}[(B_2)^2 (B_3)^{B_4}] \quad (5.28)$$

where the only variable is c'_s , and all B_i are obtained through curve-fitting Eq. 5.27 to the plot in Fig. 5.3 and recombining constants (Table 5.2). The integration was accomplished for T_s from zero to T_s^* and c'_s from zero to $c_s'^*$, where T_s^* and $c_s'^*$ are the current dimensionless time and concentration, respectively. To obtain the coefficients (A_i and B_i) Eq. 5.27 was fitted to the exact diffusion problem (Fig. 5.3) using a non-linear least-squares regression software package (Statgraphics Plus, Vers 6.0, 1992). The fitted

coefficients (B_i) (Table 5.1) and the comparison of the approximate model (Eq. 5.28) with the exact analytical model (Eq. 5.18; Fig. 5.4) show excellent agreement. Now, to complete the process Eq. 5.22 was inverted to obtain T_l as a function of c_l' :

$$T_l^* = \text{Log} \left[\frac{1}{1 - c_l'^*} \right] \quad (5.29)$$

in which the integration has been carried out for T_l from zero to T_l^* and c_l' from zero to $c_l'^*$; where T_l^* and $c_l'^*$ are the current dimensionless times and concentrations, respectively. Substituting Eqs. 5.28 and 5.29 into 5.23 gives the shape factor as a function of c' (c_s' and c_l'). This can then be used in Eq. 5.19 to obtain a concentration dependent FO mass transfer coefficient that approximates diffusion into a sphere:

$$F^2 = \left[B_1 \text{Log}[(B_2 + c_s'^*)^2 (B_3 + c_s'^*)^{B_1}] - B_1 \text{Log}[(B_2)^2 (B_3)^{B_1}] \right] / \text{Log}[1 / (1 - c_s'^*)] \quad (5.30)$$

It is noteworthy that Eqs. 5.28-5.29 have been developed for diffusion of a solute into a region from an outside source: for the sphere it was for diffusion into the sphere from a constant outside source; for the FO model it was diffusion into the immobile region from the constant concentration mobile region. It is necessary to justify the use of such an approach for diffusion in the reverse direction (i.e. from the sphere to an outside sink). Fortunately, the equations behave symmetrically. For example, in the case of a sphere with an initial concentration of unity and with a constant outside concentration equal to zero, then a plot of sphere concentration with time will obey the following property

$$c_{s,out}' = 1 - c_s' \quad (5.31)$$

where $c_{s,out}'$ is the sphere concentration with time (relative to the initial value of 1 unit) when the solute is diffusing out and c_s' is the concentration as given by Eq. 5.18 and the relevant boundary conditions (Fig. 5.5). The curves are mirror images across a horizontal line drawn through 0.5 on the vertical concentration axis. If one plots together on the same figure the absolute values of the derivatives of Eqs. 5.31 and 5.18 a similar result is obtained (Fig. 5.6). However, in this case the line of symmetry is drawn through 0.5 of the horizontal concentration axis. This tells us that the magnitude of the derivatives are equal for the same gradients in relative concentration independent of whether solute fluxes are into or out of a region. The result of this is that the form of Eq. 5.27 can also be used for a situation in which solute diffuses out of a sphere and into a surrounding medium. The only difference is the right-hand side (RHS) of Eq. 5.27 should be multiplied by a negative; the c_s' must be replaced by $(1 - c_s')$ and c_s' is now calculated as the difference in concentration between the sphere and outside source. For the case of a sphere with an initial concentration of unity and a zero concentration boundary condition then the difference would be one, and so on for other scenarios. The resulting equation can then be integrated to give the dimensionless time for diffusion out of a sphere as a function of the concentration in the sphere,

$$T_s^* = B_1' \text{Log}[(B_2' + c_s'^*)^2 (B_3' + c_s'^*)^{B_1'}] - B_1' \text{Log}[(B_2' + 1)^2 (B_3' + 1)^{B_1'}],$$

where the coefficients (B_i') are listed in Table 5.3. The above equation can be used to determine a shape

factor for the situations in which solute fluxes are out of a sphere. These relationships (i.e. diffusion into and out of a region are symmetric relationships) are often assumed in the literature (van Genuchten, 1985; van Genuchten and Dalton, 1986; Jarvis, 1994; Gerke and van Genuchten, 1993). The FO model obeys the same relationships that the relative concentration used should always be less than or equal to unity.

It is now possible to define a multi-region model with a distribution of spherical aggregate sizes. The shape factor coefficients (A and B_i) are constant between aggregates and the only thing that changes is the effective radius of a given aggregate size group (Eq. 5.24). The spheres are considered to be the immobile flow domains and are surrounded by a mobile matrix. The spheres all exchange material with the mobile phase simultaneously and direct sphere-to-sphere exchange is not allowed. In the following section a numerical model for solute transport through a structured media consisting of spherical aggregates is developed.

5.5.2 Spheres - numerical model development

Initially, we consider general relationships for the structured porous media in a way similar to Gerke and van Genuchten (1993). We define the total porosity (ϵ), mobile porosity (ϵ_f), porosity of immobile region i (ϵ_{mi}) and total immobile porosity (ϵ_m) of the bulk soil volume by

$$\epsilon = \frac{V_p}{V_t} \quad \epsilon_f = \frac{V_{pf}}{V_t} \quad \epsilon_{mi} = \frac{V_{pmi}}{V_{mi}} \quad \epsilon_m = \sum_{i=1}^n \frac{V_{pmi}}{V_{tm}} \quad (5.32a,b,c,d)$$

where V_p is the total void volume, V_t is the bulk volume, V_{pf} is the pore volume the mobile region, V_{tf} is the volume of the mobile region, V_{pmi} is the pore volume of the immobile region i , V_{mi} the volume of the immobile region i and V_{tm} is the total immobile volume. The total number of immobile regions considered is n . The total pore volume can be calculated as

$$V_p = V_{pf} + \sum_{i=1}^n V_{pmi}, \quad (5.33)$$

and the total bulk volume is computed by

$$V_t = V_{tf} + V_{tm} \quad (5.34)$$

The total macroscopic porosity can be calculated by

$$\epsilon = \epsilon_f \frac{V_{tf}}{V_t} + \sum_{i=1}^n \epsilon_{mi} \frac{V_{mi}}{V_t} \quad (5.35)$$

and the volumetric water contents of the mobile, immobile region i and the bulk media are

$$\theta_f = \frac{V_{wf}}{V_{tf}}, \quad \theta_{mi} = \frac{V_{wmi}}{V_{tmi}}, \quad \theta = \frac{\theta_f \frac{V_{tf}}{V_t} + \sum_{i=1}^n \theta_{mi} \frac{V_{tmi}}{V_t}}{V_{tf} + \sum_{i=1}^n V_{tmi}} \quad (5.36a,b,c)$$

where the subscript w is for water.

The governing equations for simultaneous mass exchange between the mobile and immobile regions parallel those given by Gerke and van Genuchten (1993) with slight modification. The change in concentration of the mobile region is a function of the simultaneous changes in concentration of the immobile regions and is given by

$$\frac{\Delta(\theta_f R_f c_f)}{\Delta t} = \sum_{i=1}^n -\frac{\Gamma_{smi}}{V_{tf}/V_t}, \quad (5.37)$$

and the change in concentration of immobile region i due to diffusive exchange with the mobile region is given by

$$\frac{\Delta \theta_{m,i} R_{m,i} c_{m,i}}{\Delta t} = \frac{\Gamma_{smi}}{V_{tmi}/V_t}, \quad (5.38)$$

where c_f and $c_{m,i}$ are the mobile and immobile phase solute concentrations (M/L^3), R_f and $R_{m,i}$ are the mobile and immobile (for region i) retardation coefficients (Eqs. (5.40a,b) below) and Γ 's are the diffusive exchange terms. The diffusive exchange terms contain the previously introduced shape factor (F) and are given by Eq. 5.39.

$$\Gamma_{smi} = \frac{D_a}{a^2 F_{fi}^2} \theta_{mi} \frac{V_{tmi}}{V_t} (c_f - c_{mi}), \quad (5.39)$$

$$R_f = 1 + \frac{\rho_f K_f}{\theta_f} \quad R_{mi} = 1 + \frac{\rho_{mi} K_{mi}}{\theta_{mi}} \quad (5.40a,b,c)$$

where all variables are defined as previously.

If we substitute Eqs. 5.39 and 5.40 into 5.38 we obtain the desired matrix of equations necessary to solve the problem. Consider a system composed of n -immobile regions and a single mobile region. Using Eq. 5.40 in 5.38 and 5.39 we obtain

$$\frac{\Delta(\theta_f R_f c_f)}{\Delta t} = \sum_{i=1}^n -\frac{V_t D_{fi} \theta_{mi} V_{tmi}}{V_{tf} a_i^2 F_{fi}^2 V_t} (c_f - c_{mi}), \quad \text{and} \quad (5.41)$$

$$\frac{\Delta(\theta_{mi} R_{mi} c_{mi})}{\Delta t} = \frac{V_i}{V_{mi}} \frac{D_{fi} \theta_{mi} V_{mi}}{a_i^2 F_{fi}^2 V_i} (c_f - c_{mi}), \quad (5.42)$$

where Eq. 5.41 is the mass balance equation for the mobile region and Eq. 5.42 the mass balance equation for the immobile region, and F_{fi} is the shape factor for the coupled regions f and i (f and i are the mobile and immobile subscripts, respectively). The mobile region diffusive transfer is summed over all possible immobile regions, whereas the immobile region only has a term accounting for diffusive exchange with the single mobile region. These equations were numerically solved using a central-difference Crank-Nicholson scheme.

Before deriving the finite difference equations, Eqs. 5.41 and 5.42 are simplified to the following forms

$$\frac{\Delta c_f}{\Delta t} = \sum_{i=1}^n \frac{-1}{V_f} \frac{D_{fi} \theta_{mi} V_{mi}}{a_i^2 F_{fi}^2 \theta_f R_f} (c_f - c_{mi}), \quad \text{and} \quad (5.43)$$

$$\frac{\Delta c}{\Delta t} = \frac{D_{fi}}{a_i^2 F_{fi}^2 R_{mi}} (c_f - c_{mi}), \quad (5.44)$$

from which we can formulate the difference equations. Let us define all of the concentrations on the right-hand side (RHS) of Eqs. 5.43 and 5.44 to be average concentrations over a discrete time-step (Δt).

$$c_f = \frac{c_f^{k+1} + c_f^k}{2}, \quad \text{and} \quad c_{mi} = \frac{c_{mi}^{k+1} + c_{mi}^k}{2}, \quad (5.45a,b)$$

where $k+1$ and k represent values for the new and past time-steps.

We also introduce the harmonic mean of the shape factor (F), which can be given by

$$\frac{1}{F_{fi}^{2'}} = \frac{1}{2} \left(\frac{1}{F_{fi}^{2^{k+1}}} + \frac{1}{F_{fi}^{2^k}} \right), \quad (5.46)$$

where the $k+1$ superscript refers to a calculated shape factor that uses new predicted concentrations, and the k superscript denotes a shape factor calculated from the previous time-step concentrations (see Eqs. 5.23, 5.28 and 5.29).

If we make the left-hand side (LHS) of Eqs. 5.43 and 5.44 discrete and make the proper substitutions with Eqs. 5.45a,b and 5.46 then we obtain the difference form of the equations

$$\frac{c_f^{k+1} - c_f^k}{\Delta t} = \sum_{i=1}^n \frac{-1}{V_{if}} \frac{D_{fi} \theta_{mi} V_{imi}}{a_i^2 F_{fi}^{2'} \theta_f R_f} \left(\frac{c_f^{k+1} + c_f^k - c_{mi}^{k+1} - c_{mi}^k}{2} \right), \quad \text{and} \quad (5.47)$$

$$\frac{c_{mi}^{k+1} - c_{mi}^k}{\Delta t} = \frac{D_{fi}}{a_i^2 F_{fi}^{2'} R_{mi}} \left(\frac{c_f^{k+1} + c_f^k - c_{mi}^{k+1} - c_{mi}^k}{2} \right) \quad (5.48)$$

Collecting all of the unknown $(k+1)$ concentrations and their coefficients on the LHS and all of the known (k) concentrations and their coefficients on the RHS we obtain the following system of equations

$$c_f^{k+1} \left(\frac{1}{\Delta t} + \sum_{i=1}^n \frac{D_{fi} \theta_{mi} V_{imi}}{a_i^2 F_{fi}^{2'} 2 V_{if} \theta_f R_f} \right) - \sum_{i=1}^n \frac{c_{mi}^{k+1} D_{fi} \theta_{mi} V_{imi}}{a_i^2 F_{fi}^{2'} V_{if} \theta_f R_f 2} =$$

$$c_f^k \left(\frac{1}{\Delta t} - \sum_{i=1}^n \frac{D_{fi} \theta_{mi} V_{imi}}{a_i^2 F_{fi}^{2'} 2 V_{if} \theta_f R_f} \right) + \sum_{i=1}^n \frac{c_{mi}^k D_{fi} \theta_{mi} V_{imi}}{a_i^2 F_{fi}^{2'} V_{if} \theta_f R_f 2}, \quad \text{and} \quad (5.49)$$

$$c_{mi}^{k+1} \left(\frac{1}{\Delta t} + \frac{D_{fi}}{a_i^2 F_{fi}^{2'} R_{mi} 2} \right) - c_f^{k+1} \left(\frac{D_{fi}}{a_i^2 F_{fi}^{2'} R_{mi} 2} \right) =$$

$$c_{mi}^k \left(\frac{1}{\Delta t} - \frac{D_{fi}}{a_i^2 F_{fi}^{2'} R_{mi} 2} \right) + c_f^k \left(\frac{D_{fi}}{a_i^2 F_{fi}^{2'} R_{mi} 2} \right) \quad (5.50)$$

where Eq. 5.50 is written for the n immobile regions (spheres). The above forms an $n+1$ by $n+1$ matrix that can be solved for the $n+1$ unknowns. The so-formed matrix is of the following form

$$\begin{bmatrix} X_{1,1} & X_{1,2} & \cdots & X_{1,n+1} \\ X_{2,1} & X_{2,2} & 0 & 0 \\ \vdots & 0 & \ddots & 0 \\ X_{n+1,1} & 0 & 0 & X_{n+1,n+1} \end{bmatrix} \begin{bmatrix} c_f^{k+1} \\ c_{m1}^{k+1} \\ \vdots \\ c_{mn}^{k+1} \end{bmatrix} = \begin{bmatrix} Y_1 \\ Y_2 \\ \vdots \\ Y_{n+1} \end{bmatrix}, \quad (5.51)$$

where all X 's and Y 's are known coefficients on the LHS and RHS of Eqs. 5.47 and 5.48, respectively.

The above matrix (Eq. 5.51) is solvable in principle, but there is a non-unique solution because we used estimated new concentrations (c_a^{k+1}) to calculate the harmonic mean of the shape factor ($F_{f,i}^{2'}$). This is overcome by using an efficient iterating scheme. The procedure is straight forward, and operationally follows these steps:

- i) for the first iteration the new concentrations are estimated by setting them all equal to the current region concentration,
- ii) over the given time-step, the model runs and calculates the new concentrations from Eq. 5.51,
- iii) a convergence test is applied to see if the new concentrations match the concentrations used to determine the previous shape factor parameter,
- iv) if the concentrations in step iii are different, then the two concentrations are averaged and the result is used to determine a better shape factor estimate; if the concentrations are the same, then convergence is achieved and the program leaves the horizontal equilibration routine,
- v) step iv continues until convergence is achieved, this usually occurs within ten iterations except when the concentrations between interacting regions are similar then convergence is usually achieved in less than three iterations.

The above equations and iterating scheme for horizontal diffusive exchange were evaluated using a symbolic mathematics software package (MathcadPlus, Vers. 6.0, 1995) prior to programming the routines in Fortran. This was done to ensure that the equations would mass balance and to evaluate how well the iterating scheme would perform under extreme concentration gradients and with several regions operative simultaneously (up to 6 regions were simulated; a single mobile region with five spherical immobile regions). It was found that mass balance was always achieved and, as mentioned previously, the iterating scheme was found to be satisfactory.

Other, more efficient iterating schemes could easily be incorporated into the model, but for the present study the procedure outlined here was acceptable.

5.5.3 Solid cylinder with axial pore - defining a shape factor

The analytical solution for solute diffusion into a cylinder with a continuous axial pore and no flow was given by Carslaw and Jaeger (1959) as

$$c = \frac{-ak_3 \left(k_1' - bk_2' \ln\left(\frac{r}{b}\right) \right) + bk_3' \left(k_1 + ak_2 \ln\left(\frac{r}{a}\right) \right)}{ak_2k_1' + bk_1k_2' + abk_2k_2' \ln\left(\frac{b}{a}\right)} - \pi \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)}{G1(\alpha_n)} Z \quad (5.52)$$

$$Z = \frac{(k_1'\alpha_n J1(b\alpha_n) - k_2'J0(b\alpha_n))G2(\alpha_n)(k_3k_1'\alpha_n J1(b\alpha_n) - k_2'J0(b\alpha_n)) - k_3'(k_1\alpha_n J1(a\alpha_n) + k_2J0(a\alpha_n))}{(k_1'\alpha_n J1(b\alpha_n) - k_2'J0(b\alpha_n))G2(\alpha_n)(k_3k_1'\alpha_n J1(b\alpha_n) - k_2'J0(b\alpha_n)) - k_3'(k_1\alpha_n J1(a\alpha_n) + k_2J0(a\alpha_n))} \quad (5.53)$$

where c is the concentration in the solid cylinder as a function of radius and time (M/L^3), a is pore radius and b is the radius of the solid cylinder (L), r is radius (L), k 's are constants determined from the boundary

conditions, D is the effective molecular diffusion coefficient of the solid cylinder (L^2/T), J_0 and J_1 are zero and first order bessel functions of the first kind, Y_0 and Y_1 are zero and first order bessel functions of the second kind, the α_n 's are the n roots of the equation

$$\begin{aligned} & (k_1 \alpha J_1(a\alpha) + k_2 J_0(a\alpha)) (k_1' \alpha Y_1(b\alpha) - k_2' Y_0(b\alpha)) - \\ & (k_1 \alpha Y_1(a\alpha) + k_2 Y_0(a\alpha)) (k_1' \alpha J_1(b\alpha) - k_2' J_0(b\alpha)) = 0 \end{aligned} \quad (5.54)$$

Functions $G1$ and $G2$ are given by

$$\begin{aligned} G1(\alpha_n) = & \left(k_1'^2 a_n^2 + k_2^2 \right) (k_1 a_n J_1(a a_n) + k_2 J_0(a a_n))^2 - \\ & \left(k_1^2 a_n^2 + k_2'^2 \right) (k_1' a_n J_1(b a_n) - k_2' J_0(b a_n))^2 \end{aligned} \quad (5.55)$$

and

$$\begin{aligned} G2(\alpha_n) = & J_0(r a_n) (k_1 a_n Y_1(a a_n) + k_2 Y_0(a a_n)) - \\ & Y_0(r a_n) (k_1 a_n J_1(a a_n) + k_2 J_0(a a_n)) \end{aligned} \quad (5.56)$$

The above equations (5.52-5.56) can be augmented with the following general boundary conditions,

$$k_1 \frac{\partial c}{\partial r} - k_2 c = k_3 \quad \text{for } r = a, \quad (5.57)$$

$$k_1' \frac{\partial c}{\partial r} - k_2' c = k_3' \quad \text{for } r = b. \quad (5.58)$$

As in the case of the sphere we want to define a characteristic shape for diffusion of solute into a cylinder. Therefore, we choose boundary conditions similar to the spherical case, such that

$$\begin{aligned} c &= 1 \quad \text{for } r = a \\ \frac{\partial c}{\partial r} &= 0 \quad \text{for } r = b \end{aligned} \quad (5.59a,b)$$

Using the above boundary conditions we can determine the coefficients appearing in Eqs. 5.57-5.58. They are given by

$$k_1 = 0 \quad k_2 = -1 \quad k_3 = 1 \quad k_1' = 1 \quad k_2' = 0 \quad k_3' = 0 \quad (5.60a,b,c,d,e,f)$$

A notable simplification of Eqs. 5.52-5.56 arises when we make the appropriate substitutions with

the above coefficients. Finally, for a hollow cylinder with a constant concentration boundary condition at a , zero-flux boundary condition at b and a zero initial solute concentration, the analogs to Eqs. 5.52-5.56 are given by two equations of the form

$$c = 1 - \pi \sum_{n=1}^{\infty} \exp[-D\alpha_n^2 t] J_1(b\alpha_n)^2 \frac{Y_0(r\alpha_n)J_0(a\alpha_n) - J_0(r\alpha_n)Y_0(a\alpha_n)}{J_0(a\alpha_n)^2 - J_1(b\alpha_n)^2}, \quad (5.61)$$

$$Y_0(a\alpha)J_1(b\alpha) - J_0(a\alpha)Y_1(b\alpha) = 0 \quad (5.62)$$

As before, the α_n 's are the roots of Eq. 6.62 and the functions $G1$ and $G2$ have been removed by using the boundary condition coefficients (Eqs. 6.60 a-f). For Eqs. 6.61-6.62 to be consistent with the spherical model development section it is necessary to cast them into dimensionless time. To do this we define the following relationships

$$T_c = \frac{Dt}{(b-a)^2} \quad \text{and} \quad \beta_n^2 = (b-a)^2 \alpha_n^2, \quad (5.63a,b)$$

where T_c is dimensionless time and β_n is a new root parameter used to maintain the fundamental form of Eqs. 5.61-5.62. Substituting Eqs. 5.63 a,b into Eq. 5.61-5.62 we obtain the following

$$c = 1 - \pi \sum_{n=1}^{\infty} \frac{\exp[-\beta_n^2 T_c] J_1\left(b \frac{\beta_n}{b-a}\right)^2}{J_0\left(a \frac{\beta_n}{b-a}\right)^2 - J_1\left(b \frac{\beta_n}{b-a}\right)^2} Z', \quad (5.64)$$

$$Z' = Y_0\left(r \frac{\beta_n}{b-a}\right) J_0\left(a \frac{\beta_n}{b-a}\right) - J_0\left(r \frac{\beta_n}{b-a}\right) Y_0\left(a \frac{\beta_n}{b-a}\right), \quad (5.65)$$

$$Y_0\left(a \frac{\beta}{b-a}\right) J_1\left(b \frac{\beta}{b-a}\right) - J_0\left(a \frac{\beta}{b-a}\right) Y_1\left(b \frac{\beta}{b-a}\right) = 0. \quad (5.66)$$

In summary, the above equations are concentration (c) in the cylinder as a function of dimensionless time (T_c) and radius (r) (Eq. 5.64-5.65) and $\frac{\beta_n}{b-a}$ are the roots of Eq. 5.66.

As in the spherical case, we wish to work with the average concentration in the cylinder. This is given by Eq. 5.13 with $v=2$, the denominator (a^v) replaced by $b^2 - a^2$ (where a is the pore radius and b is the radius of the cylinder), the lower and upper limits of integration equal to a and b , respectively, and c given by Eq. 5.64-5.65. To obtain data for the average cylinder concentration as a function of time (T_c)

the integration was carried out using Mathematica (Vers. 2.0, 1991). The derivative of the average concentration was also evaluated as a function of time using the same software. Unfortunately, in the cylindrical system the plots of average concentration and their derivatives are not unique. In addition, they have a geometric dependence on the choice of a and b . For example, Fig. 5.7 is a plot of average concentration as a function of dimensionless time for a series of a and b values viz. $b/a=5$, $b/a=15$ and $b/a=30$. The FO model is also plotted in Fig. 5.7. The shapes of the concentration profiles for the FO and cylindrical models are similar. As in the spherical case we can also plot time rate of change of concentration versus concentration profiles for the present case. These are shown in Fig. 5.8 for the same series of radius ratios used to generate Fig. 5.7. The shapes of these plots are similar to that of the sphere, thus we expect Eqs. 5.27-5.28 to be reasonable approximations to the diffusion properties for the hollow cylinder. The coefficients obtained from fitting Eqs. 5.27-5.28 to a series of radius ratios (ξ) are tabulated in Tables 5.1-5.3. The coefficients from the ξ 's (Tables 5.2-5.3) were then fitted to a series of regression equations so that coefficients for different ξ 's could be interpolated from those tabulated. This was an efficient method for obtaining the coefficients because there is a significant effort involved in obtaining the data in Figs. 5.1-5.3. For instance, for Eq. 5.64-5.65 and its derivative to be stable and without large oscillations at the boundary it was necessary to seek the first 50 roots of Eq. 5.66, a significant task compared to using regression equations to obtain approximate values. The plots of these coefficients and their fitted equations are shown in Figs. 5.9-5.10. To illustrate the close approximation of fitting Eq. 5.27 to the analytical model of the hollow cylinder, we have included plots of the average concentration of the cylinder and its derivative (Eq. 5.64-5.65) as well as the fitted equation (Eq. 5.27) for a series of ξ 's (Fig. 5.11). These fitted relationships are shown to represent fairly well the characteristics for diffusion in a hollow cylinder. The goodness of fit decreases with an increase of ξ . For an ξ equal to 30 the error from the approximation is a maximum of ten percent over the range of concentrations considered. Thus, the same approach used to determine a shape factor for diffusion into a sphere could be used to approximate the characteristics of a hollow cylinder.

The analytical solutions for the hollow cylinders behave symmetrically which agrees with the spherical case. This enables us to use the same shape factor for diffusion into and out of a hollow cylinder. The relative concentration used in Eqs. 5.28-5.29 is chosen such that it is always less than or equal to unity. For example, if the concentration surrounding the pore (c_{matrix}) is less than that of the pore (c_{pore}) then the relative concentration to be used is c_{matrix} / c_{pore} . Also, as in the sphere, if the concentration in the solid portion of the cylinder is greater than that of the pore, then the actual relative concentration used is the difference in concentration between the two regions.

5.5.4 Solid cylinder with axial pore - numerical model development

The modeling approach for horizontal diffusive exchange is exactly the same as that for the spherical model development. The only difference is that there are only two hydraulic regions, both of which may or may not be mobile, and we end up with a two by two matrix (i.e. the analog to Eq. 5.51). The mobile effects are addressed in the vertical solute transport routines. There are just two equations that govern the horizontal equilibration for the hollow cylindrical system given by Gerke and van Genuchten (1993).

$$\frac{\Delta c_f}{\Delta t} = \frac{D_{f,m} \theta_m}{(b-a)^2 F_{f,m}' \theta_f R_f} \left(\frac{V_f}{V_{i,f}} - 1 \right) (c_m - c_f) \quad (5.67)$$

$$\frac{\Delta c_m}{\Delta t} = \frac{D_{f,m}}{(b-a)^2 F_{f,m}' R_m} (c_f - c_m) \quad (5.68)$$

where all variables and the differencing scheme are as previously described in the section on spheres.

5.6 METHODS AND MATERIALS

The numerical model, Solute Transport in Multiple Porosity Media (STMP) was evaluated by comparison with analytical solutions and experimental data. STMP was compared to two analytical models of solute transport through structured soils. Firstly, solute transport through a medium consisting of uniformly distributed and sized spherical aggregates (the SPHERE model of van Genuchten (1985)), and secondly, solute transport through an immobile matrix consisting of a single, axial, uniform macropore of a given porosity (the PORE model of van Genuchten *et al* (1984)). Experimental data were obtained from both the literature and new experiments. The evaluation was based upon the ability of the model to describe transport related non-equilibrium solute transport. The model has the ability to describe sorbing chemicals, but this analysis dealt with a non-interacting solute (e.g. chloride).

5.6.1 Sources of data

Analytical models for solute transport through structured media were obtained from the U.S. Salinity Laboratory, Riverside, CA. The SPHERE model is described by van Genuchten (1985) and the PORE model is described in detail by van Genuchten *et al* (1984). The SPHERE and STMP models were applied to the data of Rao *et al* (1980b). The PORE and STMP models were compared for a series of pore radius ratios (ξ) and macropore pore-water velocities (Table 5.3). The assumptions inherent in the PORE model do not lead to easy experimental evaluation because the data are very hard to obtain (e.g. solute transport through an immobile soil matrix with an embedded macropore). However, the STMP was evaluated based upon its ability to predict similar breakthrough curves when operating under the conditions given by PORE.

5.6.2 Transport through columns consisting of a matrix and porous spherical aggregates

The data reported by Rao *et al* (1980a, 1980b) was utilized to evaluate the applicability of the STMP model to a real experimental system. A detailed description of the experiments can be found in their original work so only a brief review will be given here for reference purposes.

Their study consisted of steady-state solute transport experiments performed using homogeneously packed columns of glass beads in combination with randomly placed synthetic porous spheres (ceramic). The glass bead column represents a mobile region and the spheres were assumed to be an immobile region. Two different sized porous spheres were considered in experiments conducted at three different pore water velocities for each size sphere. The necessary parameters that were either derived or estimated

by Rao *et al* (1980a,b) for use in their experiments are listed in Table 5.4.

The relatively mobile (bead matrix) and immobile (porous spheres) water contents (Table 5.2) are given by θ_M and θ_A respectively. Relative water content is defined as the volume averaged water content of the particular region of interest divided by the total volume averaged water content, which itself is given by the sum of θ_M and θ_A ($\theta = \theta_M + \theta_A$). The parameter Φ is the ratio of relatively mobile water content to that of the total water content ($\Phi = \theta_M / \theta$). The average macroscopic mobile phase pore water velocity is given by V_m and the dispersion coefficient by D_M . The average number of spheres in a given unit of volume is N_s and from this we are able to determine the relative volume (RV) of spheres occupying the transport volume. This information is used in STMP and is given by

$$RV = \frac{4}{3} \pi r^3 N_s \quad (5.69)$$

The total amount of tracer applied is designated by PV and is given by qt_o/L , where t_o is the duration of the pulse, L is the column length (300 mm for all cases) and q is the surface flux density. The lateral diffusion coefficient was reported to be $28.8 \text{ mm}^2/\text{day}$ (i.e. the effective diffusion coefficient for the sphere).

The actual experimental data was obtained from the published research paper of Rao *et al* (1980b) by using a GIS software package. For each of the experiments considered in this study (i.e. experiments 1-3 and 5-7 of Rao *et al* (1980b), all four corners of the plots were digitized and used as reference points. These reference points were then used to obtain the coordinates of the actual data points which were then downloaded to a separate plot file. These plot files were used to evaluate STMP's ability to describe the measured BTC's using only the measured parameters reported in Table 5.4 and without any curve-fitting.

5.6.3 Transport through columns with an embedded axial pore of a given porosity

Column experiments were designed to evaluate STMP's ability to describe solute transport through a soil column of a uniform matrix in which a continuous axial pore of a given material was incorporated. The columns were packed with two different materials, each of which had unique hydraulic properties. The purpose of having two different media with widely different saturated hydraulic conductivities was so that one would behave as a preferential flow path (macropore). Hence, one of the matrix materials used was a Harford loam (coarse-loamy, mixed, mesic family of Aeric Fragiaquepts) and the other one was commercially available sand (washed, fine and uniform). The Harford soil was collected from the 5-30 cm depth from a site in Tompkins County, New York, then air-dried, and passed through a 2-mm sieve prior to use. The washed sand had a saturated conductivity that was approximately two orders of magnitude greater than that of the Harford soil. The Harford soil was chosen over other soils in order to reduce the time involved in conducting the experiments, i.e. the coarse-loamy texture had a reasonably high packed saturated conductivity ($\sim 320 \text{ mm/day}$).

The soil column body (Fig.5.12) was made of polycarbonate piping (76 mm dia.) and the bottom boundary cap was machined from 19.5 mm thick polycarbonate sheeting. The bottom cap was machined to the center at a 15° to allow for column effluent drainage into a common collection point. A port drilled through the bottom cap from the outside through to the machined cavity allowed atmospheric conditions

and free drainage at the lower boundary condition. At the top of the column body an overflow spout was attached to maintain a 1-mm head of solution at the soil surface. The soil column was supported on a perforated stainless steel plate. Fine particles were restricted from moving through the stainless steel support by a glass fiber filter with a pore size of $1.0\ \mu\text{m}$ that was sandwiched between the lower soil boundary and the support plate.

A system was designed to allow the systematic packing of the two regions. The matrix component of the column was packed first, during which time the soil preferential region was separated from the matrix region by use of a solid Teflon tube (6.15 mm dia.) located at the column center and extending through the entire length of the column. A packing tool was fabricated that would pass over the in-place Teflon tube, allowing for the light pressure of packing the Harford soil surrounding the pore. This allowed the matrix (Harford) soil to be packed in increments while the solid Teflon tube remained in place.

Prior to packing, the air-dry soil was moistened to a 5% gravimetric moisture content. The moistened soil was measured out in portions that would produce an approximate bulk density (BD) of $1.25\ \text{g/cm}^3$ when packed into increments of 1 cm. The column body was marked in 1 cm increments. Each portion of the previously weighed soil was sequentially added to the column body and packed to the correct height that was already marked on the column body. Between each portion of soil added, the surface of the most recently packed increment was scratched in an effort to establish a continuous and homogeneously packed column. Following the completion of the packing exercise, a 1.0 cm diameter, perforated, stainless steel plate was placed on the soil surface in an off-center position. This was done to disperse and minimize the force of the drops of supply solution on the soil surface.

The composite columns (with the Teflon tube still in place) were preconditioned in all experiments by saturating with a background solution of deaerated 50mM CaSO_4 solution. The saturation of the columns was initiated from the bottom at a slow application rate ($\sim 0.25\ \text{mL/min}$) using an HPLC pump. This was done to enhance the removal of entrapped air in the column. The wetting proceeded until a 1-mm standing head of solution appeared at the soil surface, at which point the input solution was diverted from the bottom to the top of the column. At all times during the experiment a 1-mm head of solution was maintained at the soil surface. The bottom of the column was then opened to the atmosphere and the column was allowed to drain freely. The application of the background solution to the soil surface continued until a steady-state water flow was reached, usually achieved within 24 hours.

Once at steady-state, the application of background solution was terminated and the 1-mm head was allowed to infiltrate until the solution level nearly disappeared into the soil surface. At this time a syringe was used to deliver a 1-mm head of 25 mM CaCl_2 (tracer) which had been prepared in the same background solution used to saturate the column. A pulse of tracer of approximately one pore volume (PV) was applied to the soil surface. The effluent from the column was collected (ISCO Inc. Fraction Collector, Lincoln, NE) following the addition of the tracer pulse. The 1-mm head was then allowed to infiltrate and the background solution was reinitiated at the column surface in a manner identical to the pulse application. The effluent was analyzed for chloride by a Haake-Buchler Digital Chloridometer (Haake-Buchler Instruments, Inc., Saddle Brook, NJ). Collections were continued until no measurable Cl^- appeared in the fractions.

On completion of the experiment, the soil column was allowed to drain until drainage had essentially ceased. The solid Teflon tube was slowly and non-destructively removed from the column. The moistened soil enabled the soil to maintain the structural integrity of the artificial pore. The exposed pore was then filled with washed sand in 1-cm increments. For each successive 1-cm layer a smaller diameter tube (3 mm dia) was used to pack the sand in an effort to limit the development of air pockets. Care was taken to limit disturbances caused to the pore wall from the packing. With the preferential region in place, the column was re-saturated (~ 0.25 mL/min) from the bottom to remove as much air as possible from the column. Once a 1-mm head had formed at the top of the column, the solution application was diverted from the bottom to the top and steady-state flow was established as previously. A one PV pulse of 25 mM CaCl_2 solution was then applied and the effluent was immediately collected in fractions in anticipation of the pulse moving quickly through the artificial preferential flow zone. The details of the pulse application and re-initiation of the background solution are the same as those for the non-composite column (Teflon tube in place).

Four solute transport experiments were performed, two each at lengths of 175 and 290 mm. For each length, one experiment was conducted with the solid Teflon tube in place (homogeneous column, HC) and the other with washed sand substituted for the tube (preferential column, PC). It was anticipated that the data from the HC's could be fitted to an analytical solution (Parker and van Genuchten, 1984) to obtain necessary transport parameters to be used in the STMP model for describing the data of the PC's.

5.7 RESULTS AND DISCUSSION

5.7.1 Spherical model evaluation (STMP)

The data taken from Rao *et al* (1980a, 1980b) and the analytic (SPHERE) and numerical (STMP) model simulations are plotted in Figs. 5.13-5.14. Figure 5.13 is a plot of the three velocity cases (low, medium, high; experiment 1, 2, and 3 of Table 5.4) for the small spherical size (5.5 mm) and Fig. 5.14 is a similar plot (experiment 5, 6, and 7 of Table 5.4) for the large spherical size (7.5 mm). The numerical model (STMP) was evaluated on its ability to describe the solute transport data, in terms of how closely the predicted BTC matched the measured data points and analytical model simulations, and whether or not the predicted BTC's had a shape consistent with that of the measured data points.

STMP described the measured data well and also matched fairly closely the simulations given by the analytical model. This was particularly true for the lower pore-water velocity cases (i.e. Fig. 5.13a,b, Table 5.4, expt's 1-2; Fig. 5.14a,b, Table 5.4, expt's 5-6). STMP was less successful on those parts of the BTC's in which the relative concentrations between regions were at the extremes of the fitted equation used for determining the shape factor (Eq. 5.27). For instance, if the relative concentration of the sphere is less than 0.01 or greater than 0.99 relative concentration units then the fitted equation (Eq. 5.27) and the resulting coefficients (Table 5.2-5.3) may not be valid because the regression of Eq. 5.27 on the data was performed only for data in which $0.01 \leq c' \leq 0.99$. Similarly, in diffusion from the sphere if the relative difference in concentration between regions is greater than 0.99 or less than 0.01 then the fitted equation (Eq. 5.27) may not be valid because the regression was based on data in which $0.01 \leq \Delta c \leq 0.99$. This effect is readily apparent if one carefully examines the portions of the BTC in which the relative

concentration effectively approaches these extremes (i.e. peaks and tails). On those sections of the BTC there is a slight difference between the analytical and STMP models. For example, when the flux concentration approaches unity ($c'=1$), such as when the sphere and mobile concentrations within the column begin to approach equilibrium with one another, then there is a noticeable difference between the SPHERE and STMP predictions. Also, on the tailing side of the BTC's there is also a slight difference between the models. This is probably due to the rapid movement of the tracer-free solution into the column that causes the relative concentration 'difference' between the sphere (immobile) and bead matrix (mobile) to be greater than 0.99. This effect is more apparent for the higher pore-water velocity cases (Figs. 5.13c and 5.14c). Also, STMP predictions are noticeably better for the smaller sphere sizes (5.5 mm) than for the larger spheres (7.5 mm). Again, this is probably related to the extreme values of relative concentration (or difference) used in the fitted equation (Eq. 5.27) for deriving an average shape factor over the time step.

The volume of the larger sphere is more than double ($\sim 2.5\times$) that of the smaller spheres. Hence, it would require a greater flux of solute from/into the large spheres compared to the small spheres in order to obtain a particular change in sphere concentration. This would have the effect of keeping the relative concentrations (or relative differences) between the spheres and mobile matrix at an extreme value (relative to the fitted equation Eq. 5.27) for a longer period of time. This could induce the more prevalent discrepancies between SPHERE and STMP seen in the results for larger spheres.

A simulation was performed to test the effects of aggregate size. The simulation consisted of the same two cases as in Fig. 5.13b,c except that the sphere radius ($r = 4.37$ mm) was chosen such that the volume would be half that of the 5.5 mm spheres. All of the parameters for the simulations are the same as those listed in Table 5.4 (expt's 2-3). The average number of spheres per unit volume was increased to maintain the same relative volume of spheres for the 5.5 mm sphere transport experiments (Table 5.4, expt's 2-3). The results are plotted in Fig. 5.15. For the medium flow rate (Fig. 5.15a), STMP simulated a near perfect fit to the SPHERE model. Figure 5.15b, on the other hand was less successful.

The inability of STMP to describe the tail of the BTC's in Figs. 5.13c, 5.14c and 5.15b is probably a result of the chosen time-step. If the time-step is too coarse then the model may over-predict the vertical solute flux or alternatively, an under-prediction may occur when the solute diffuses from the sphere. This results because the model prevents an adequate exchange of solute between the sphere and surrounding region when an inappropriate shape factor is employed. The shape factor used in the FO mass transfer coefficient is averaged over the time-step, and in cases where time-steps are large and water flux densities fairly high this may not be a very good approximation. This would be especially true when the difference in solute concentration between interacting regions is large. For instance, if one re-considers Figs. 5.4-5.6, (keeping in mind the FO nature of the model) then an average shape factor may not be appropriate because the time rate of change of average concentration of the sphere is large when the concentration difference between regions is large. For example, at a dimensionless time of $1E-7$ the average relative concentration of a sphere subjected to a constant concentration boundary source and initial concentration of zero is approximately 0.002 relative units. To describe accurately solute diffusion in/out of a sphere it is necessary to consider a sufficiently small time-step. In essence, the time rate of change of average concentration of the sphere is infinite when the concentration in the sphere is zero. The simulations reported here used a time-step of 0.0001 days, which translates into a dimensionless time-step of approximately 0.00013. If one considers the coarseness of the time-steps used for the simulations and the

fact that STMP performed well for all but the highest water flux densities, then it may be concluded that STMP performed well given the inherent approximations in determining an effective shape factor.

5.7.2 Cylindrical model evaluation: STMP and Pore

The soil-macropore simulations (Tables 5.5-5.6)) are plotted in Figs. 5.16-5.20. Included in the plots are simulations by PORE, STMP and TRANSMIT (Hutson and Wagenet, 1995). The TRANSMIT model was configured such that the FO mass transfer coefficient was equivalent to a mass transfer coefficient determined from STMP for the particular radius ratio (ξ) of the simulation and for an average relative concentration equal to 0.5 (van Genuchten, 1985). All other parameters for TRANSMIT were the same as those for STMP and PORE.

The simulation results indicate that for all ξ 's STMP predicted more closely the analytical model (PORE) than did TRANSMIT. The predictions by STMP approached those of PORE as one of/or two things occurred; 1) an increase in ξ and 2) an increase in flux density. For a ξ greater than 15, the simulations from PORE and STMP were very similar. TRANSMIT performed best when both the flux density and ξ were highest (Fig. 5.20c). The lack of a good prediction by STMP for low ξ (i.e. $\xi = 5$ and 10) is probably related to the concentration dependence of the shape factor (as was the case for the sphere) (Fig. 5.11).

5.7.3 Comparison with experimental column data

Two experiments were performed on each of two lengths, 175 mm and 285 mm. One of the solute transport experiments for each column length was conducted as a homogeneously packed column. The breakthrough curves from these columns were then fitted to the CDE (CXTFIT2, Toride *et al*, 1995) to determine the necessary transport parameters to be used in STMP (Table 5.7). This was also done to obtain an approximate value for the saturated conductivity of the Harford soil matrix. After obtaining these values, a preferential cylindrical region of 6.15 mm dia. was opened axially through the center of the column and then refilled with a medium-fine washed sand. This effectively mimicked a preferential region.

A solute experiment was then conducted on each of the soil columns. Using the values from the homogeneous columns, input files were established for the STMP to predict the measured breakthrough curves. The flow rates for the cylindrical mantle surrounding the pore, and the pore were adjusted so that the peak concentrations predicted by the STMP would match the measured BTC's on the basis of pore volume (Fig. 5.21). STMP simulated solute transport experiments reasonably well when compared to the analytical solutions under the same conditions.

Although not evaluated in this research, STMP has the ability to describe multiply interacting regions. For example, the numerical model is formulated such that a distribution of spherical sizes can be considered, or alternatively, the shape factor can be applied to a system consisting of other geometry and/or a mixture (ie. rectangular structures, solid cylinders). For natural porous media, in which many different aggregate shapes and sizes can reside, this may be a useful approach to describing the residence times of solute in these types of media.

Another consideration is that only steady-state flow was investigated. However, Gerke and Van Genuchten (1993) showed that a first-order transfer term could be derived that was similar to the first-order solute transfer term (ie. the water transfer coefficient was proportional to the effective hydraulic conductivity between interacting and a shape factor). This would be an interesting avenue for future work.

5.8 CONCLUSIONS

The basic premise of this study was that non-equilibrium models assume the soil matrix consists of independent fractions having different physical and chemical mass transfer mechanisms. These processes and their representation in fate and transport models have been discussed. In particular, processes affecting non-equilibrium transport due to chemical (sorption) interactions as well as physical (transport-related) non-equilibrium.

The multi-region water flow and solute transport model of Hutson and Wagenet (TRANSMIT) was modified so that it could better approximate the geometric properties of structured media (plates, spheres and cylinders). In this study only steady-state water flow was considered. The horizontal transfer routines developed here are significantly different to those in TRANSMIT and describe two situations: 1) diffusion into a sphere and 2) diffusion within a hollow cylinder containing a continuous axial pore. The resultant numerical model for Solute Transport in Multiple Porosity Media (STMP) was evaluated by comparison with two analytical models of solute transport through structured soils 1) solute transport through a medium of uniformly distributed and sized spherical aggregates (the SPHERE model of van Genuchten (1985)) and 2) solute transport through an immobile matrix consisting of a single, axial, uniform macropore of a given porosity (the PORE model of van Genuchten *et al* (1984)). Experimental data were obtained from both the literature and new experiments. The evaluation was based on the ability of the model to describe transport related (physical) non-equilibrium solute transport although the STMP model is capable of describing chemical sorption.

In the case of the spherical model evaluation, STMP described the measured data well and matched fairly closely the simulations given by the analytical model (SPHERE), especially when pore-water velocities were low. At high water flux densities STMP performed less well, but given the inherent approximations in determining the effective shape factor for the sphere the overall performance of STMP was considered to be acceptable.

In the cylindrical model evaluation simulation results from STMP matched the analytical model (PORE) more closely than did TRANSMIT. Predictions by STMP approached those of PORE as either the pore radius ratio or the flux density increased. TRANSMIT performed best when both the flux density and the pore radius ratio were highest. The absence of good predictions by STMP at low pore radius ratios is probably related to the concentration dependence of the shape factor (which was also the case for the sphere).

Table 5.1 Coefficients appearing in Eq. 5.27 obtained from fitting Eq. 5.27 to the data in Figs 5.3 and 5.9.

Geometry	A_1	A_2	A_3
<u>Sphere</u>	-4.02899	-1.56088	5.72028
<u>Cylinder</u>			
($\xi^\dagger=5$)	0.93915	-0.984708	0.0707348
($\xi=10$)	0.888736	-0.899708	0.0221183
($\xi=15$)	0.804747	-0.811278	0.0121811
($\xi=20$)	0.745888	-0.750352	0.00814699
($\xi=30$)	0.676967	-0.681588	0.00426995
($\xi=45$)	0.611851	-0.616022	0.00237950
($\xi=60$)	0.570932	-0.575044	0.00160396
($\xi=75$)	0.541891	-0.545966	0.00119167
($\xi=100$)	0.507208	-0.511053	0.000836922

$\dagger \xi$ = the relative radius of the cylinder and pore (i.e. $\xi = b/a$).

Table 5.2 Coefficients appearing in Eq. 5.28 obtained from fitting Eq. 5.27 to the data in Figs 5.3 and 5.9 and recombining coefficients. These coefficients describe the situation where solute fluxes are into the sphere.

Geometry	β_1	β_2	β_3	β_4
<u>Sphere</u>	-0.670265	-1.00595	3.0584	6.08064
<u>Cylinder</u>				
($\xi^\dagger=5$)	-0.475205	-1.02389	0.0701571	0.137040
($\xi=10$)	-0.542711	-1.012095	0.02429	0.048000
($\xi=15$)	-0.607315	-1.006863	0.0149123	0.0296214
($\xi=20$)	-0.659265	-1.004855	0.0108051	0.0215057
($\xi=30$)	-0.72901	-0.999488	0.00626792	0.0125423
($\xi=45$)	-0.808518	-0.997103	0.00387392	0.00777037
($\xi=60$)	-0.867059	-0.995650	0.00280137	0.00562721
($\xi=75$)	-0.913792	-0.994730	0.00219425	0.00441175
($\xi=100$)	-0.976755	-0.994122	0.00164732	0.00331412

$\dagger \xi$ = the relative radius of the cylinder and pore (i.e. $\xi = b/a$).

Table 5.3 Coefficients appearing in Eq. 5.28 obtained from fitting Eq. 5.27 to the data in Figs 5.3 and 5.9 and recombining coefficients. These coefficients describe the situation where solute fluxes are out of the sphere.

Geometry	β_1'	β_2'	β_3'	β_4'
<u>Sphere</u>	-0.203783	-4.0584	.00594814	.657822
<u>Cylinder</u>				
($\xi^\dagger=5$)	-.032561	-1.07016	0.023892	29.1885
($\xi=10$)	-0.0130250	-1.0249	0.0120946	83.3339
($\xi=15$)	-.00899475	-1.01491	0.00686272	135.038
($\xi=20$)	-0.007089	-1.01081	0.00485504	185.997
($\xi=30$)	-0.00457172	-1.00627	-0.000511817	318.922
($\xi=45$)	-0.00314123	-1.00387	-0.00289738	514.776
($\xi=60$)	-0.00243957	-1.0028	-0.00434981	710.832
($\xi=75$)	-.00201571	-1.00219	-0.00527024	906.670
($\xi=100$)	-0.00161854	-1.00165	-0.00587762	1206.96

$\dagger \xi$ = the relative radius of the cylinder and pore (i.e. $\xi = b/a$).

Table 5.4. Parameters for experiments of Rao *et al* (1980a,b)

Sphere Radius (mm)	Exp no.	θ_M	θ_A	Φ	v_M (mm/ day)	D_M (mm ² / day)	N_s (#/cm ³)	PV
5.5	1	0.227	0.159	0.589	461.52	2064.	0.628	2.721
5.5	2	0.227	0.159	0.589	4034.88	18067.2	0.628	2.306
5.5	3	0.227	0.159	0.589	20267.28	90748.8	0.628	2.486
7.5	5	0.238	0.160	0.598	448.08	2006.4	0.253	2.660
7.5	6	0.238	0.160	0.598	4016.88	17990.4	0.253	2.191
7.5	7	0.238	0.160	0.598	23187.36	103824	0.253	2.349

Table 5.5. Input data used to generate the STMP plots of Figs 5.15-5.19. The variable names are as defined in the text.

Data for figure #	V_g	θ_f	θ_{mi}	D_o (mm ² /day)	ξ	λ (mm)	$v_m = q_m / \theta_m$ (mm/day)	L (mm)
15(a)	0.2	0.5	0.5	160	5	4	10000	200
15(b)	0.2	0.5	0.5	160	5	4	50000	200
15(c)	0.2	0.5	0.5	160	5	4	150000	200
16(a)	0.2	0.5	0.5	160	10	4	10000	200
16(b)	0.2	0.5	0.5	160	10	4	50000	200
16(c)	0.2	0.5	0.5	160	10	4	150000	200
17(a)	0.2	0.5	0.5	160	15	4	10000	200
17(b)	0.2	0.5	0.5	160	15	4	50000	200
17(c)	0.2	0.5	0.5	160	15	4	150000	200
18(a)	0.2	0.5	0.5	160	45	4	10000	200
18(b)	0.2	0.5	0.5	160	45	4	50000	200
18(c)	0.2	0.5	0.5	160	45	4	150000	200
19(a)	0.2	0.5	0.5	160	100	4	10000	200
19(b)	0.2	0.5	0.5	160	100	4	50000	200
19(c)	0.2	0.5	0.5	160	100	4	150000	200

Table 5.6. Input data used to generate the Pore plots of Figs 5.15-5.19. The variable names are as defined by van Genuchten *et al* (1984).

Data for figure #	β	θ	D_a (mm ² /day)	ξ	D_m (mm ² /day)	P_m	γ	L (mm)
15(a)	0.2	0.5	63.643	5	4.01e4	49.921	6.364	200
15(b)	0.2	0.5	63.643	5	2.0e5	49.984	1.273	200
15(c)	0.2	0.5	63.643	5	6.0e5	49.995	0.424	200
16(a)	0.2	0.5	63.643	10	4.01e4	49.921	6.364	200
16(b)	0.2	0.5	63.643	10	2.0e5	49.984	1.273	200
16(c)	0.2	0.5	63.643	10	6.0e5	49.995	0.424	200
17(a)	0.2	0.5	63.643	15	4.01e4	49.921	6.364	200
17(b)	0.2	0.5	63.643	15	2.0e5	49.984	1.273	200
17(c)	0.2	0.5	63.643	15	6.0e5	49.995	0.424	200
18(a)	0.2	0.5	63.643	45	4.01e4	49.921	6.364	200
18(b)	0.2	0.5	63.643	45	2.0e5	49.984	1.273	200
18(c)	0.2	0.5	63.643	45	6.0e5	49.995	0.424	200
19(a)	0.2	0.5	63.643	100	4.01e4	49.921	6.364	200
19(b)	0.2	0.5	63.643	100	2.0e5	49.984	1.273	200
19(c)	0.2	0.5	63.643	100	6.0e5	49.995	0.424	200

Table 5.7. The measured and fitted transport parameters for the HC's.

Exp	L (mm)	ρ (g/cm ³)	θ	$v=q/\theta$	t_{pv}	R^*	D^* (mm ² /day)	R^2
1	175	1.241	0.537	387.6	0.9668	0.946	2006.8	.99
2	285	1.210	0.528	414.2	0.8796	0.961	1517.7	.99

*Indicates a fitted variable.

D =effective dispersion coefficient= $D_o + \lambda v$, ρ =soil bulk density, t_{pv} =time of pulse in effective pore volumes, v is pore water velocity, L is the soil column length and θ is the volumetric water content.

Figure 5.1 The average concentration (c') of a sphere and first-order (FO) model as a function of dimensionless time (T)

Figure 5.2 The time rate of change of the average concentration in the sphere as a function of dimensionless time (T).

Figure 5.3 The time rate of change of the concentration in the sphere as a function of the concentration in the sphere (c_s'). The approximation of the data is shown as a solid line..

Figure 5.4 A comparison of the exact and approximate models for the average concentration in a sphere as a function of dimensionless time (T).

Figure 5.5 Two cases for the average concentration in a sphere as a function of dimensionless time (T); i) sphere/in – initial sphere concentration equals 0 and outside source is constant at 1.0; ii) sphere/out – the opposite of i).

Figure 5.6 Two cases for the time rate of concentration as a function of concentration; i) sphere/in – solute is diffusing from a constant concentration source into an initially solute free sphere, ii) sphere/out – the opposite case to (i) where the value plotted is the absolute value of the derivative.

Figure 5.7. The average concentration in a hollow cylinder and the FO diffusion model. The cylindrical model was plotted for a series of outside-inside radius ratios (ie. a is the pore radius and b is the surrounding cylinder radius).

Figure 5.8 The time rate of change of concentration as a function of dimensionless time (T) for a series of hollow cylinders with varying geometry. (ie. b is the cylinder radius and a is the pore radius).

Figure 5.9. The plots of the various coefficients appearing in Table 5.2 (B_i) as a function of the radius ratio (R). Fitted regression equations are also plotted.

Figure 5.10. The plots of the various coefficients appearing in Table 5.3 (B_i) as a function of the radius ratio (R). Fitted regression equations are also plotted.

Figure 5.11. The time rate of change of concentration plotted as a function of concentration for a series of cylinders with varying geometry (ie. a is the pore radius and b is the surrounding cylinder radius).

Figure 5.12. Diagram for the column apparatus used for the macropore column studies.

Figure 5.13 The plots of experiments 1-3 from Table 5.4. Included are the measured data of Rao *et al* (1980b) (symbols), STMP (solid) and the analytical sphere model (dashed line); (a) experiment 1, (b) experiment 2, and (c) experiment 3.

Figure 5.14 The plots of experiments 5-7 from Table 5.4. Included are the measured data of Rao *et al* (1980b) (symbols), STMP (solid) and the analytical sphere model (dashed line); (a) experiment 5, (b) experiment 6, and (c) experiment 7.

Figure 5.15 Simulations for solute transport through a soil column consisting of randomly located 4.37 mm spheres. The necessary parameters are listed in Table 5.4 with the following modifications: a) experiment 2 with sphere radius now equal to 4.37 mm and b) experiment 3 with sphere radius now equal to 4.37 mm.

Figure 5.16. Plots of BTC's from a continuous pulse application of a solution through a soil-macropore system in which the relative radius (ξ) was 5 and relative volume of macropores was 0.2; (a) slow application rate, (b) medium, and (c) fast.

Figure 5.17. Plots of BTC's from a continuous pulse application of a solution through a soil-macropore system in which the relative radius (ξ) was 10 and relative volume of macropores was 0.2; (a) slow application rate, (b) medium, and (c) fast.

Figure 5.18. Plots of BTC's from a continuous pulse application of a solution through a soil-macropore system in which the relative radius (ξ) was 15 and relative volume of macropores was 0.2; (a) slow application rate, (b) medium, and (c) fast.

Figure 5.19. Plots of BTC's from a continuous pulse application of a solution through a soil-macropore system in which the relative radius (ξ) was 45 and relative volume of macropores was 0.2; (a) slow application rate, (b) medium, and (c) fast.

Figure 5.20. Plots of BTC's from a continuous pulse application of a solution through a soil-macropore system in which the relative radius (ξ) was 100 and relative volume of macropores was 0.2; (a) slow application rate, (b) medium, and (c) fast.

Figure 5.21 Measured and predicted BTC's (CXTFIT2, Toride *et al* (1995)) for the homogeneous and preferential soil columns (HC's); a) 175-mm length column, b) 285-mm length column, c) 175-mm length column with preferential region and d) 285-mm column with preferential region. Soil column parameters and fitted values for the homogeneous soil columns are listed in Table 5.7. Measured data points are symbols and simulated data are lines.

CHAPTER 6

CONCLUDING DISCUSSION

This project focussed on the observations and description of non-equilibrium transport of atrazine and alachlor in soil. Two chapters concentrated on laboratory column experiments which studied the transport of atrazine and alachlor through columns of soil which had been amended with several types of organic matter, manure, sludge and in the case of alachlor, alfalfa residue. Chapter four showed that a modified numerical model could produce the same shaped breakthrough curves as analytical solutions, and chapter five described modifications to the TRANSMIT multi-region model that enabled it to be applied to a wide range of soil geometries.

As far as the behaviour of atrazine and alachlor in organically-amended soils was concerned, we showed that sludge sorbed atrazine to a greater extent than manure, and that alachlor was sorbed most strongly by sludge, to a lesser extent by manure and very slightly by alfalfa. Under flowing conditions, apparent K_d values were greater when concentrations of amendment were high, perhaps owing to less masking by clay and other mineral particles.

Degradation of alachlor, however, was highest in alfalfa-amended soil, and slowest in sludge-amended soil. Degradation was higher in manure amended soil than in unamended soil. This suggests that while sorption tends to slow degradation, other factors, such as the presence of nutrients in manure and alfalfa, combine to determine degradation rate.

Back-calculation of K_{oc} values for each of the amendments shows that the relative K_{oc} values for unamended soil, manure and sludge (calculated from their individual contribution to sorption), was similar.

K_{oc} VALUE FOR INDIVIDUAL SOIL ORGANIC COMPONENTS, CALCULATED FROM MEASURED BATCH SORPTION (CHAPTERS 2 AND 3)

	Alachlor	Atrazine
Humus	93	53
Manure	84	52
Sludge	172	97
Alfalfa	22	-

From a sorption point of view, these results suggest that the effect of organic amendment is about the same as increasing the soil organic matter by an equivalent amount. This was certainly true of manure. It is expected that as the added organic material decomposes, and the residue becomes more similar to soil humus, then the K_{oc} values will approach more closely to that of humus, especially if the material is not too concentrated. Variability of K_{oc} between soils is at least as much as the variability between humus, sludge and manure.

Degradation is slowed as sorption increases, but this is offset by a supply of nutrients,

which could increase microbial activity. The variation of half life values for alachlor is summarized in the following table.

HALF-LIFE VALUES (DAYS) FOR ALACHLOR MEASURED UNDER CONDITIONS OF EQUILIBRIUM SORPTION (INCUBATION), AND SLOW AND FAST COLUMN FLOW (CHAPTER 3).

	Unamended	Sludge	Manure	Alfalfa
Incubation	24	32	21	15
Slow flow	10	15	9	7
Fast flow	7	nd	4	6

From an environmental viewpoint, the incubation half-life would be a conservative value for use in pesticide leaching risk assessments. The higher rates of degradation seen under faster flow conditions, where sorption was not able to proceed to equilibrium, operate for only short periods of time so the amount of alachlor degraded will not be high. Also, under natural field conditions, higher flow rates are associated with leaching to depths at which microbial activity may be lower.

The uneluted or sequestered mass of alachlor is interesting, since it raises the question as whether this is true sequestration, in which the chemical is so tightly sorbed that it will not be released under normal conditions (i.e. without degrading or removing soil humus), or if is merely a kinetic process. If the rate of sorption of the chemical is faster than the rate of desorption, and if, in addition, the chemical diffuses into a volume of organic matter, then we may expect to see behavior of this type. Classical column breakthrough experiments, which use easily-measured breakthrough concentrations to infer transport parameters and degradation, are flawed if sequestration is assumed to represent degradation, since the chemical does not appear in the leachate, or is at concentrations below the detectable limit. Taking sequestration or very slow desorption into account is one of the objectives of models such as that described in Chapters 4 and 5.

Detailed models of pesticide behavior and transport will not evolve into easy-to-use decision support tools, partly because the major factors which determine pesticide fate depend upon weather, soil properties and commonly-measured chemical properties, and partly because these models are often complicated and conjectural. These models are useful for assessing a specific process, given a defined flow regime and soil geometry, and whether or not this process is likely to be important relative to other processes and flow and reaction possibilities. During the course of this project much effort was devoted to model improvement, for both LEACHM and its multi-region derivative (TRANSMIT).

Chapter 5 describes the theoretical aspects of describing multi-region flow for a wide range of soil geometries. Preferential flow through channels of various shapes and dimensions are included here. While preferential flow is one application of this model, another, equally important, is the description of sorption, desorption and diffusion processes in a multi-region, multi-component soil, where flow pathways depend on soil pore geometry, and sorption and diffusion of pesticide molecules depend upon the shapes and volumes of the sorbing medium. In the experiments described in chapters 2 and 3, all we know about the nature of soil humus and the added amendment is their mass fraction. Unless more is known about geometry, diffusion path lengths and how these factors change during decomposition and with water content, we will not be able to predict pesticide behavior more accurately, nor will we be able to interpret the results of experiments with certainty.

For example, consider the organic amendments used in this work. The amount added (50 ton ha^{-1}) could be present in soil in many ways. That amount corresponds approximately to the amount of soil humus to a depth of 20 cm in that particular soil. At one extreme, soil humus is distributed fairly uniformly over soil mineral and aggregate surfaces. For a soil having a surface area of about $10 \text{ m}^2 \text{ g}^{-1}$, this corresponds to a 'thickness' of organic matter of about 1.3 nm. Under these conditions we would expect kinetic sorption rates to be higher and sequestration lower than if greater organic matter thicknesses were involved. At the other extreme, the amendment could be in the form of macro-aggregates consisting only of organic matter, with correspondingly high diffusion path lengths and low external surface area. The transmit model can be set up to reflect a spectrum of situations between these extremes, but unless we have more experimental and descriptive evidence as to the real nature of soil organic matter, the simulations remain conjectural.

This project has demonstrated, that from a qualitative point of view, the effects of organic amendments on the fate of pesticides are similar to merely increasing the soil humus level, but from a detailed quantitative viewpoint there are issues relating to diffusion, kinetic sorption processes and degradation that will only be resolved once we improve our ability to define and describe soil organic matter. We have, however, developed some sophisticated modelling tools which can be used for evaluating a range of scenarios, and which should become even more valuable in the future.

REFERENCES

- Addiscott, T.M. 1977. A simple computer model for leaching in structured soils. *J. Soil Sci.* 28:554-563.
- Ahuja, L. R., Johnsen, K. E., and G. C. Heathman. 1995. Macropore transport of a surface-applied bromide tracer: Model evaluation and refinement. *Soil Sci. Soc. Am. J.* 59:1234-1241.
- Alexander, M. 1995. How toxic are toxic chemicals in soil. *Environ. Sci. Technol.* 29:2713-2717.
- Anderson, M. P. 1979. Using models to simulate the movement of contaminants through ground water flow systems, *CRC Crit. Rev. Environ. Control.* 9:97-156.
- Angley, J.T., M.L. Brusseau, W.L. Miller and J.L. Delfino. 1992. Nonequilibrium sorption and aerobic biodegradation of dissolved alkylbenzenes during transport in aquifer material: Column experiments and evaluation of a coupled-process model. *Environ. Sci. Technol.* 26:1404-1410.
- Aris, R. 1958. *Proc. Royal Soc. London* A245: 268-277.
- Bahr, J. M. 1990. Kinetically influenced terms for solute transport affected by heterogeneous and homogeneous classical reactions. *Water Resour. Res.* 26:21-34.
- Ball, W. P., and P. V. Roberts. 1991. Long-term sorption of halogenated organic chemicals by aquifer material: 2 Intraparticle diffusion. *Environ. Sci. Tech.* 25:1237-1249.
- Barry, D.A. and Parker, J.C. 1987. *Transport in Porous Media* 2: 65-82.
- Barry, D.A.; Parlange, J-Y.; Rand, R. and Parker, J.C. 1988. *Transport in Porous Media*, 2: 421-423.
- Bear, J., 1988. *Dynamics of fluids in porous media*. Dover, New York. Ch.10.
- Beestman, G.B. and J.M. Deming. 1974. Dissipation of acetanilide herbicides from soils. *Agron. J.* 66:308-311.
- Beven, K.J. 1991. Modeling preferential flow: An uncertain future? *In Preferential flow*, edited by T.J. Gish and A. Shirmohammadi, pp. 1-11. American Soc. of Agric. Engin., St. Joseph, Mich.
- Beven, K.J. and P. Germann. 1981. Water flow in soil macropores. II. A combined flow model. *J. Soil Sci.* 32:15-29.
- Beven, K.J. and P. Germann. 1982. Macropores and water flow in soil. *Water Resour. Res.* 18:1311-1325.
- Biggar, J.W. and Nielsen, D.R. 1967. *Agron. J.*, 11: 254-274.
- Booltink, H. W. G. and J. Bouma. 1991. Physical and morphological characterization of bypass flow in a well-structured clay soil. *Soil Sci. Soc. Am. J.* 55:1249- 1254.
- Booltink, H. W. G., Hatano, R., and J. Bouma. 1993. Measurement and simulation of bypass flow in a structured clay soil: a physico-morphological approach. *J. Hydrol.* 148:149-168.
- Bresler, E. 1973. Simultaneous transport of solutes and water under transient unsaturated flow conditions. *Water Resour. Res.* 9: 975-986.
- Bruch, J.C. 1970. *Water Resour. Res.* 6: 791-800.

- Brusseau, M. L. 1992. Nonequilibrium transport of organic chemicals: the impacts of pore water velocity. *J. Contam. Hydrol.* 5:215-234.
- Brusseau, M. L. and P. S. C. Rao. 1990. Modeling solute transport in structured soils: A review. *Geoderma*. 46:169-192.
- Brusseau, M.L. 1992. *J. Contam. Hydrol.* 9: 353-368
- Brusseau, M.L., Larsen, T and Christensen. T.H. 1991. Rate-limited sorption and nonequilibrium transport of organic chemicals in low organic carbon aquifer materials. *Water Resour. Res.* 27:1137-1145.
- Brusseau, M.L., R.E. Jessup, and P.S.C. Rao. 1989. Modeling the transport of solutes influenced by multiprocess nonequilibrium. *Water Resour. Res.* 25:1971-1988.
- Brusseau, M.L., R.E. Jessup, and P.S.C. Rao. 1990. Sorption kinetics of organic chemicals: evaluation of gas-purge and miscible-displacement techniques. *Environ. Sci. Technol.* 24:727-735
- Brusseau, M.L., Z. Gerstl, D. Augustijn and P.S.C. Rao. 1993. Simulating solute transport in aggregated soil with the two-region model: Measured and optimized parameter values. Prepared for Soil Sci. Soc. of America.
- Brusseau, M.L.; Jessup, R.E. and Rao, P.S.C. 1991. Non-equilibrium sorption of organic chemicals: elucidation of rate-limiting processes. *Environ. Sci. Technol.* 26: 134-142.
- Carsel, R.F., C.N. Smith, L.A. Mulkey, J.D. Dean, and P. Howise. 1984. User's manual for the pesticide root zone model (PRZM), release 1. USEPA-600/3-84-109. USEPA Washington, DC.
- Carlsaw, H. S. and J. C. Jaeger. 1959. *Conduction of heat in solids*. Oxford University Press, Oxford.
- Chen, C, and R. J. Wagenet. 1992a. Simulation of water and chemicals in macropore soils: Part 1. Representation of the equivalent macropore influence and its effect on soil-water flow. *J. Hydrol.* (Amsterdam) 130:105-126.
- Chen, C., and R. J. Wagenet. 1992b. Simulation of water and chemicals in macropore soils. Part 2: Application of linear filter theory. *J. Hydrol.* (Amsterdam) 130:127-149.
- Chen, W. and R.J. Wagenet. 1997. Analysis of pesticide long-term leaching behavior during transport in heterogeneous porous media. *Soil Sci. Soc. Amer. J.* 61:360-371.
- Chen, W., and R. J. Wagenet. 1995. Solute transport in porous media with sorption-site heterogeneity. *Environ. Sci. Technol.* 29:2725-2734.
- Chesters, G., G.V. Simsiman, J. Levy, B.J. Alhajjar, R.N. Fathulla and J.M. Harkin. 1989. Environmental fate of alachlor and metolachlor. *Rev. Environ. Contam. Toxicol.* 110:1-74.
- Chiou, C.T. 1989. Ecological Studies 73; Gerstl, Z., Chen, Y., Mingelgrin, U., Yaron, B., Eds.; Springer-Verlag: New York, NY, pp 163-175.
- Chiou, C.T.; Porter, P.E. and Schmedding, D.W. 1983. Partition equilibria of non-ionic organic compounds between soil organic matter and water. *Environ. Sci. Technol.* 17:227-231.
- Clapp, C.E.; Larson, W.E.; Harding, S.A. and Titus, G.O. 1980. Utilization of Sewage Wastes on Land; Research Progress Report; Agricultural Research Service, U.S. Dep. of Agric.; Univ. of Minn. St. Paul, MN, pp D1-D23.
- Coats, K. H., and B. D. Smith. 1964. Dead-end pore volume and dispersion in porous media. *Soc. Pe. Eng. J.* 4:73-84.

- Comfort, S.D., W.P. Inskeep and R.E. Macur. 1992. Degradation and transport of dicamba in a clay soil. *J. Environ. Qual.* 21:653-658.
- Crank, J. 1975. The mathematics of diffusion. Oxford University Press, Oxford.
- Czapar, G. F., Horton, R., and R. S. Fawcett. 1992. Herbicide and tracer movement in soil columns containing an artificial macropore. *J. Environ. Qual.* 21:110-115.
- Dao, T. H., and T. L. Lavy. 1978. Atrazine adsorption on soil as influenced by temperature, moisture content and electrolyte concentration. *Weed Sci.* 26:303-308.
- Darcy, H. 1856. Les fontaines publiques de la ville de Dijon. Paris: Dalmont.
- Davidson, J. M., Rieck, C. E., Santleman, P. W. 1968. Influence of water flux and porous material on the movement of selected herbicides. *Soil Sci. Soc. Am. Proc.* 32:629-633.
- Davidson, M.R. 1985. Numerical calculation of saturated-unsaturated infiltration in a cracked soil. *Water Resour. Res.* 21:709-714.
- Doyle, R.C., D.D. Kaufman, and G.W. Burt. 1978. Effect of Dairy manure and sewage sludge on ¹⁴C-pesticide degradation in soil. *J. Agri. Food Chem.* 26:987-989.
- Edwards, W.M., R.R. van der Ploeg, and W. Ehlers. 1979. A numerical study of the effects of non-capillary size pores upon infiltration. *Soil Sci. Soc. Am. J.* 43:851-856.
- Elrick, D. E., Erh, K. T., and H. K. Krupp. 1966. Application of miscible displacement techniques to soils. *Water Resour. Res.* 2:717-727.
- Felsot, A.S. and Dahm, P.A. 1979. *J. Agri. Food Chem.* 27: 557-563.
- Flury, M. 1996. Experimental evidence of transport of pesticides through field soils - a review. *J. Environ. Qual.* 25:25-45.
- Flury, M., Fluhler, H., Jury, W. A., and J. Leuenberger. 1994. Susceptibility of soils to preferential flow of water: a field study. *Water Resour. Res.* 30:1945-1954.
- Gaber, H. M., Comfort, S. D., Inskeep, W. P., and H. A. El-Attar. 1992. A test of the local equilibrium assumption for adsorption and transport of picloram. *Soil Sci. Soc. Am. J.* 56: 1392-1400.
- Gaber, H.M., W.P. Inskeep, S.D. Comfort, and J.M. Wraith. 1995. Nonequilibrium transport of atrazine through large intact soil cores. *Soil Sci. Soc. Am. J.* 59:60-67.
- Gamerding, A. P., Lemley, A. T., and R. J. Wagenet. 1991. Nonequilibrium sorption and degradation of three 2-chloro-s-triazine herbicides in a soil-water system. *J. Environ. Qual.* 20:815-822.
- Gamerding, A. P., R. J. Wagenet, and M. Th. vanGenuchten. 1990. Application of two-site/two-region models for studying simultaneous nonequilibrium transport and degradation of pesticides. *Soil Sci. Soc. Amer. J.* 54:957-963.
- Gamerding, A.P., A.T. Lemley, and R.J. Wagenet. 1991. Nonequilibrium sorption and degradation of three 2-chloro-s-triazine herbicides in soil-water systems. *J. Environ. Qual.* 20:815-822.
- Gerke, H. H., and M. T. van Genuchten. 1993. A dual porosity model for simulating the preferential movement of water and solutes in structured porous media. *Water Resour. Res.* 29:305-319.
- Grisak, G. E., and J. F. Pickens. 1980. Solute transport through fractured media 1. The effect of matrix diffusion. *Water Resour. Res.* 16:719-730.
- Gwo, J. P., Jardine, P. M., Wilson, G. V., and G. T. Yeh. 1996. Using a multiregion model to study the effects of advective and diffusive mass transfer on local physical

- nonequilibrium and solute mobility in a structured soil. *Water Resour. Res.* 32:561-570.
- Haggerty, R., and S. M. Gorelick. 1995. Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. *Water Resour. Res.* 31:2383-2400.
- Hamaker, J.W.; Goring, C.A.I. and Youngson, C.R. 1966. *Organic Pesticides in the Environment*; Gould, F.F., Ed.; Adv. Chem. Ser. No. 60; American Chemical Society: Washington, DC, pp 23-37.
- Heathman, G. C., Ahuja, L. R., Timlin, D. J., and K. E. Johnsen. 1995. Surface Aggregates and macropore effects on chemical transport in soil under rainfall. *Soil Sci. Soc. Am. J.* 59:990-997.
- Huang, P. M., Grover, R., and R. B. Mckercher. 1984. Components and particle size fractions involved in atrazine adsorption in soil. *Soil Sci.* 138:20-24.
- Hutson, J. L. and R. J. Wagenet. 1992. *LEACHM -Leaching estimation and chemistry model*. Version 3 Res. Ser. 92-3. Dep. of Soil, Crop and Atmos. Sci., Cornell Univ., Ithaca, NY.
- 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.* 59:743-751.
- Jardine, P. M., Wilson, G. V., and R. J. Luxmoore. 1990. Unsaturated solute transport through a forest soil during rain storm events. *Geoderma.* 46:103-118.
- Jaynes, D. B., Bowman, R. S. and R. C. Rice. 1988. Transport of a conservative tracer in the field under continuous flood irrigation. *Soil Sci. Soc. Am. J.* 52:618-624.
- Jury, W. A., Grover, R., Spencer, W. F., and W. J. Farmer. 1983. Behavior assessment model for trace organics in soil. 1. Model description. *J. Environ. Qual.* 12:558-664.
- Jury, W.A. and Roth, K. 1990. Transfer functions and solute movement through soil: theory and applications; Birkhäuser Verlag Basel, pp 85-104.
- Jury, W.A. and Utermann, J. 1992. *Transport in Porous Media* 8: 277-297.
- Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983. Behavior assessment model for trace organics in soil: I. Model description. *J. Environ. Qual.* 12:558-564.
- Jury, W.A.; Focht, D.D. and Farmer, W.J. 1987. Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and degradation. *J. Environ. Qual.* 16, 422-428.
- Jury, W.A.; Gardner, W.R.; and Gardner, W.H. 1991. *Soil Physics*; John Wiley & Sons: New York, NY, pp 243-254.
- Jury, W.A.; Sposito, G. and White, R.E. 1986. A transfer function model of solute transport through soil 1 Fundamental concepts. *Water Resour. Res.* 22: 243-247.
- Karickhoff, S.W. 1984. *J. Hydraul. Eng.* 110: 707-735.
- Kookana, R. S., Aylmore, L. A. G., and R. G. Gerriste. 1992. Time-dependent sorption of pesticides during transport in soils. *Soil Sci.* 154:214-225.
- Koskinen, W.C. and Harper, S.S. 1990. *Pesticides in the Soil Environment: Processes, Impacts, and Modeling*; Cheng, H.H., Bailey, G.W., Green, R.E., Spencer, W.F., (Eds.); Soil Science Society of America Book Series no. 2; Soil Science Society of America: Madison, WI, pp 51-78.
- Kreft, A. and Zuber, A. 1978. *Chem. Eng. Soc.* 33, 1471-1480.
- Lafolie, F. 1993. One-dimensional solute transport modelling in aggregated porous media. 2. Effects of aggregate size distribution. *J Hydrol.* 143: 85-107.

- Lapidus, L. and N.R. Amundson. 1952. Mathematics of adsorption in beds. VI. The effect of longitudinal diffusion in ion exchange and chromatographic columns. *J. Phys. Chem.* 56:984-988.
- Lee, L.S., P.S.C. Rao, M.L. Brusseau, and R.A. Ogwada. 1988. Nonequilibrium sorption of organic contaminants during flow through columns of aquifer materials. *Envir. Toxicol. Chem.* 7:779-793.
- Leistra, M. 1973. Computation models for the transport of pesticides in soil. In *Residue Reviews*. 49:87-130.
- Li, L., Barry, D. A., Culligan-Hensley, P. J., and K. Bajracharya. 1994. Mass transfer in soils with local stratification hydraulic conductivity. *Water Resour. Res.* 30:2891-2900.
- Li, Y., and M. Ghodrati. 1994. Preferential transport of nitrate through soil columns containing root channels. *Soil Sci. Soc. Am. J.* 58:653-659.
- Ma, L., and H. M. Selim. 1996. Atrazine retention and transport in soils. p. 129-172. In *Reviews of environmental contamination and toxicology*, Vol. 145. Springer-Verlag, New York.
- Millington, R. J. and J. P. Quirk. 1960. Transport in porous media. p. 97-106. In *Trans. 7th Inter. Congr. Soil Sci.*, Madison, WI.
- Montgomery, J.H. 1993. *Agrochemicals desk reference: Environmental data*; Lewis Publishers: Chelsea, MI, pp 31-38.
- Moranville, M.B.; Kessler, D.P. and Greenkorn, R.A. 1977. *Am. Inst. Chem. Eng. J.* 23, 786-794.
- Nielsen, D. R., M. Th. van Genuchten, and J. W. Biggar. 1986. Water flow and solute transport processes in the unsaturated zone. *Water Resour. Res.* 22:89S- 108S.
- Nkedi-Kizza, P., J. W. Biggar, H. M. Selim, M. Th. van Genuchten, P. J. Wierenga, J. M. Davidson, and D R. Nielsen. 1984. On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol. *Water Resour. Res.* 20:1123-1130.
- O'Connor, G.A.; Wierenga, P.J.; Cheng, H.H. and Doxtader, K.G. 1980. Movement of 2,4,5-T through large soil columns. *Soil Sci.* 130, 157-162.
- Oddson, J.K., J. Letey, and L.V. Weeks. 1970. Predicted distribution of organic chemicals in solution and adsorbed as a function of position and time for various chemical and soil properties. *Soil Sci. Soc. Amer. Proc.* 34:412-417.
- Olsen, S.R. and Kemper, W.D. 1968: Movement of nutrients to plant roots. *Adv. Agron.*, 20: 91-151.
- Omoti, U., and A. Wild. 1996. Use of fluorescent dyes to mark the pathways of solute movement through soils under leaching conditions. 2 Field experiments. *Soil Sci.* 128:98-104.
- Parker, J. C., and M. Th. van Genuchten. 1984. Determining transport parameters from laboratory and field tracer experiments. *Virg. Agric. Exp. Stn. Bull.* no. 84-3.
- Parker, J.C. and Valocchi, A.J. 1986. Constraints on the validity of equilibrium and first-order kinetic transport models in structured soils *Water Resour. Res.* 22, 399-407.
- Pignatello, J. J. 1989. Sorption dynamics of organic compounds in soils and sediments. In *Reactions and movement of organic chemicals in soil. SSSA Special Publ No.22*, Madison, WI. p.45-80.

- Pignatello, J. J., Ferrandino, F. J., and L. Q. Huang. 1993. Elution of aged and freshly added herbicides from a soil. *Environ. Sci. Technol.* 27:1563-1571.
- Pignatello, J.J. and B. Xing. 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environ. Sci. Technol.* 30:1-11.
- Pivetz, B.E., J.W. Kelsey, T.S. Steenhuis and M. Alexander. 1996. A procedure to calculate biodegradation during preferential flow through heterogeneous soil columns. *Soil Sci. Soc. Am. J.* 60:381-388.
- Porro, I., Wierenga, P. J. and R. G. Hills. 1993. Solute transport through large uniform and layered soil columns. *Water Resour. Res.* 29:1321-1330.
- Pothuluri, J.V., T.B. Moorman, D.C. Obenhuber and R.D. Wauchope. 1990. Aerobic and anaerobic degradation of alachlor in samples from a surface-to groundwater profile. *J. Environ. Qual.* 19:525-530.
- Radulovich, R., Sollins, P., Baveye, P., and E. Solorzano. 1992. Bypass water flow through unsaturated microaggregated tropical soils. *Soil Sci. Soc. Am. J.* 56:721-726.
- Rao, P. S. C., Davidson, J. M., Jessup, R. E., and H. M. Selim. 1979 Evaluation of conceptual models for describing non-equilibrium adsorption-desorption of pesticides during steady-flow in soils. *Soil Sci. Soc. Am. J.* 43:22-28.
- Rao, P. S. C., Jessup, R. E., Rolston, D. E., Davidson, J. M., and D. P. Kilgrea. 1980a. Experimental and mathematical description of nonadsorbed solute transfer by diffusion in spherical aggregates. *Soil Sci. Soc. Am. J.* 44:684-688.
- Rao, P. S. C., Jessup, R. E., Rolston, D. E., Davidson, J. M., and D. P. Kilgrea. 1980b. Solute transport in aggregated porous media: Theoretical and experimental evaluation. *Soil Sci. Soc. Am. J.* 44: 139-146.
- Rao, P.S.C. and Jessup, R.E. 1983. *Chemical Mobility and Reactivity in Soil Systems*; Nelson, D.W., Elrick, D.E., and Tanji, K.K., Eds.; Soil Science Society of America: Madison, WI, 1983; pp 183-201.
- Rao, P.S.C., C.A. Bellin and M.L. Brusseau. 1993. Coupling biodegradation of organic chemicals to sorption and transport in soils and aquifers: Paradigms and paradoxes. In: *Sorption and degradation of pesticides and organic chemicals in soil. SSSA Special Publ.*, no. 32. pp.1-26.
- Rao, P.S.C.; Jessup, R.E. and Addiscott, T.M. 1982. Experimental and theoretical aspects of solute diffusion in spherical and nonspherical aggregates. *Soil Sci.* 133: 342-349.
- Rappoldt, C. 1990. The application of diffusion models to an aggregated soil. *Soil Sci.* 150:645-661.
- Rasmuson, A., and I. Neretnieks. 1980. Exact solution for diffusion in particles and longitudinal dispersion in packed beds. *Am. Inst. Chem. Eng. J.* 26:686-690.
- Richards, L.A. 1931. Capillary conduction of liquids through porous mediums. *Physics* 1:318-333.
- Rubin, J. 1983. Transport of reacting solutes in porous media: Relationship between mathematical nature of problem formulation and chemical nature of reactions. *Water Resour. Res.* 19:1231-1251.
- Scow, K.M. 1993. Effect of sorption-desorption and diffusion processes on the kinetics of biodegradation of organic chemicals in soil. In: *Sorption and degradation of pesticides and organic chemicals in soil. SSSA Spec. Publ.*, no. 32. pp.73-114.
- Selim, H. M., Davidson, J. M., and R. S. Mansell. 1976. Evaluation of a two-site

- adsorption-desorption model for describing solute transport in soils. p.448-449. In Proc. Summer Simul. Conf, Washington, DC. 12-14 July.
- Selim, H.M.; Davidson, J.M. and Rao, P.S.C. 1977. Transport of reactive solutes through multi-layered soils. *Soil Sci. Soc. Am. J.* 41: 3-10.
- Shamir, U.Y. and Harleman, D.R.F. 1967. *Pro. Am. Soc. Civil Eng. Hydr. Div.* 93: 236-260.
- Shea, P.J. 1985. Detoxification of herbicide residues in soil. *Weed Sci. Suppl.* 33: 33-41.
- Skopp, J., and A. W. Warrick. 1974. A two-phase model for the miscible displacement of reactive solutes through soils. *Soil Sci. Soc. Am. Proc.* 38:545-550.
- Steenhuis, T. S., Staubitz, W., Andreini, M., Surface, J., Richard, T. L., Paulsen, R., Pickering, N. B., J. R. Hagerman, and L. D. Geohring. 1990a. Preferential movement of pesticides and tracers in agricultural soils. *J. Irr. Drain. Eng.* 116:50-66.
- Steenhuis, T.S. and J.-Y. Parlange. 1991. Preferential flow in structured and sandy soils, *In Preferential Flow*, pp. 12-21, edited by T.J. Gish and A. Shirmohammadi, Am. Soc. of Ag. Eng., St. Joseph, Mich.
- Steenhuis, T.S., J.-Y. Parlange, and M.S. Andreini. 1990. A numerical model for preferential solute movement in structured soils. *Geoderma* 46:193-208.
- Toride, N., F.J. Leij, and M.T. van Genuchten. 1993. A comprehensive set of analytical solutions for nonequilibrium solute transport with first-order decay and zero-order production. *Water Resour. Res.* 29:2167-2182.
- Toride, N.; Leij, F.J. and van Genuchten, M.Th. 1995. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments; Version 2.0; U. S. Salinity Laboratory, Agricultural Research Service, U.S. Department of Agriculture: Riverside, CA.
- Valocchi, A. J. 1985. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. *Water Resour. Res.* 21:808-820.
- Valocchi, A. J. 1990. Use of temporal moment analysis to study reactive solute transport in aggregated porous media. *Geoderma.* 46:233-247.
- van der Zee, S.E.A.T.M. and J.J.T.I. Boesten. 1991. Effects of soil heterogeneity on pesticide leaching to groundwater. *Water Resour. Res.* 27:3051-3063.
- van Genuchten, M. Th. and P. J. Wierenga. 1976. Mass transfer studies in sorbing porous media I. Analytical solutions. *Soil Sci. Soc. Am. J.* 40:473-480.
- van Genuchten, M. T., and P. J. Wierenga. 1977. Mass transfer studies in sorbing porous media. II. Experimental evaluation with tritium ($^3\text{H}_2\text{O}$). *Soil Sci. Soc. Am. J.* 41:272--278.
- van Genuchten, M. T., Tang, D. H., and R. Guennelon. 1984. Some exact solutions for solute transport through soils containing large cylindrical macropores, *Water Resour. Res.* 20:335-346.
- van Genuchten, M. Th. 1985. A general approach for modeling solute transport in structured soils. In Proc., Hydrogeology of Rocks of Low Permeability, Mem. Int. Assoc. Hydrogeol. 17:513-526.
- van Genuchten, M. Th., and F. N. Dalton, 1986. Models for simulating salt movement in aggregated field soils. *Geoderma.* 38:165-183.

- van Genuchten, M. Th., Davidson, J. M., and P. J. Wierenga. 1974. An evaluation of kinetic and equilibrium equations for the prediction of pesticide movement through porous media. *Soil Sci. Soc. Am, Proc.* 38:165-183.
- van Genuchten, M.Th. 1981. Non-equilibrium transport parameters from miscible displacement experiments. Res. Rep. 119. Riverside, California: U.S. Salinity Lab., USDA-ARS.
- van Genuchten, M.Th. and Alves, W.J. 1982. Analytical solutions of the one-dimensional convective-dispersive solute transport equation; *U.S. Dep. of Agric., Tech. Bull.* no. 1661.
- van Genuchten, M.Th. and R.J. Wagenet. 1989. Two-site/two-region models for pesticide transport and degradation: Theoretical development and analytical solutions. *Soil Sci. Soc. Am. J.* 53:1303-1310.
- van Genuchten, M.Th., and P.J. Wierenga. 1986. *Methods of Soil Analysis, Part I. Physical and Mineralogical Methods*; Agronomy Monograph no.9 (2nd Edition), Soil Science Society of America: Madison, WI, pp 1025-1054.
- Villermanx, J. 1990: Dynamics of linear interactions in heterogeneous media: a systems approach. *J. Petrol. Sci. and Eng.*, 4(1), 21
- Wagenet, R. J. 1985. Measurement and interpretation of spatially variable soil leaching processes. pp. 209-230. In D.R. Nielsen and J. Bouma (Eds.), *Soil Spatial Variability*, Centre for Agricultural Publishing and Documentation (PUDOC), Wageningen, The Netherlands.
- Wagenet, R. J. 1983. Salt movement in soils. p. 123-140. In Nelson, D. W., Elrick, D. E., and K. K. Tanji (ed.) *Chemical mobility and reactivity in soil systems*. SSSA Spec. Publ. 11. ASA and SSSA, Madison, WI.
- Wagenet, R. J. 1990. Quantitative prediction of the leaching of organic and inorganic solutes in soil. *Phil. Trans. R. Soc. London.* 329:321-330.
- Wagenet, R. J. and J. L. Hutson. 1986. Predicting the fate of non-volatile pesticides in the unsaturated zone. *J. Env. Qual.* 15:315-322.
- Wagenet, R. J. and P. S. C. Rao. 1990. Modeling Pesticide Fate in Soil. pp. 351-399 (Ch. 10) In: H. H. Cheng et al. (Eds.) *Pesticides in the Soil Environment*, SSSA Book Series, no. 2, Soil Science Society of America, Madison, WI.
- Wagenet, R. J. and P. S. C. Rao. 1990. Modeling pesticide fate in soil. pp.351-399 (Ch. 10). In *Pesticides in the Soil Environment*. Cheng, H. H. (ed.). SSSA Book Series, no. 2. Soil Science Society of America. Madison, WI.
- Wagenet, R. J., and P. F. Germann. 1989. Concepts and models of water flow in macropore soils. *Conn. Agric. Exp. Stn, Bull.* no. 876.
- Wagenet, R.J. and J.L. Hutson. 1989. *LEACHM: A finite difference model for simulating water, salt and pesticide movement in the plant root zone*. Continuum. Vol.2. Version 2.0. New York State Water Resour. Inst., Cornell Univ., Ithaca, New York.
- Walker, A., Y.H. Moon and S.J. Welch. 1992. Influence of temperature, soil moisture and soil characteristics on the persistence of alachlor. *Pest. Sci.* 35:109-116.
- Wilson, G. V., Jardine, P. M., O'Dell, J. D., and M. Collineau. 1993. Field-scale transport from a buried line source in variably saturated soil. *J. Hydrol.* 145:83-109.
- Wilson, G.V., Jardine, P. M., and J. P. Gwo. 1992. Modeling the hydraulic properties of a multi-region soil. *Soil Sci. Soc. Am. J.* 56:1731-1737.

- Yen, P.Y., W.C. Koskinen and E.E. Schweizer. 1994. Dissipation of alachlor in four soils as influenced by degradation and sorption processes. *Weed Sci.* 42:233-240.
- Yimin, L., and M. Ghodrati. 1995. Transport of nitrate in soils as affected by earthworm activities. *J. Environ. Qual.* 24:432-438.
- Zhang, R. 1995. Prediction of solute transport using a transfer function model and the convection-dispersion equation. *Soil Sci.* 160:18-27.
- Zhong, W.Z., A.T. Lemley, and R.J. Wagenet. 1986. Quantifying pesticide adsorption and degradation during transport through soil to ground water. p.61-77. In W.Y. Garner et al. (ed.) *Evaluation of pesticides in groundwater*. ACS Symp. Ser. no. 315. ACS, Washington, DC.