
Shikui Xue

Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation


https://digitalcommons.lsu.edu/gradschool_disstheses/6225

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
MODELING PHYSICAL AND CHEMICAL
NONEQUILIBRIUM TRANSPORT OF
HERBICIDE IN SOILS FROM DIFFERENT TILLAGE SYSTEMS

A Dissertation

Submitted to the Graduate School of
 Louisiana State University and
 Agricultural and Mechanical College
 in partial fulfillment of the
 requirements for the degree of
 Doctor of Philosophy

in

The Department of Agronomy

By
Shikui Xue
B.S. Huazhong Agricultural University, P.R. China 1984
M.S. Chinese Academy of Sciences, 1987

May, 1996
ACKNOWLEDGEMENTS

I would like to take this opportunity to thank the many people who gave advice and assistance while I was working on my Ph.D program. First, I would like to express my gratitude to my major professor, Dr. H. M. Selim for generously providing guidance by sharing his time, ideas, and experience with me throughout my graduate program.

In addition, I am grateful to Dr. Liwang Ma for his suggestions throughout my research, and to Mr. D. C. Johnson and Steven L. McGowen for their assistance in the field and laboratory.

I would also like to acknowledge Dr. Glenn V. Wilson from the University of Tennessee for his many invaluable suggestions, Dr. L.M. Southwick for providing standard compounds used in this study, Dr. Robert L. Hutchinson for providing the tillage experiment plots used in this study, and Dr. C. W. Lindau for providing the materials used for quick freezing of soil columns.

Finally, I wish to thank the members of my graduate committee: Dr. R. P. Gambrell, Dr. Richard M. Johnson, Dr. K. T. Valsaraj and Dr. David J. Longstreth for their advice and suggestions during my graduate program.

Last, but not the least, I appreciate the convenience provided by all faculty and staff members of the Department of Agronomy throughout my program.

Funding for this research was supported in part by a USDA-NRI grant under the supervision of Professor Selim.
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ................................................................. ii

ABSTRACT ........................................................................................... vi

CHAPTER

1 A REVIEW OF HERBICIDE BEHAVIOR IN SOILS OF DIFFERENT TILLAGE SYSTEMS .................................................... 1

1.1 Introduction .................................................................................. 1

1.2 Herbicide Transport in Soils .................................................... 4

1.2.1 Retention Mechanism ......................................................... 5

1.2.2 Equilibrium Retention Models ........................................ 6

1.2.3 Kinetic Retention Models ................................................ 7

1.2.4 Factors Affecting Retention Reactions ........................... 9

1.2.5 Hydrodynamic Dispersion .................................................10

1.2.6 Preferential Transport .........................................................13

1.2.7 Biological Decomposition ...................................................14

1.3 Modeling the Water and Herbicide Transport.........................16

1.3.1 Modeling Water Flow .........................................................16

1.3.2 Modeling Herbicide Transport ..........................................18

1.4 Alachlor Behavior in Soil ...........................................................23

1.5 Current Experimental Methods on the Fate
and Transport of Herbicide ...................................................25

1.5.1 Retention and Mobility Studies of Herbicides 25

1.5.2 Tracer Studies for Characterizing Preferential Flow 26

1.5.3 Herbicide Transport under Unsaturated Flow 29

1.6 Objectives ......................................................................................31

2 MODELING ADSORPTION-DESORPTION KINETICS
OF ALACHLOR IN SOILS OF DIFFERENT TILLAGE SYSTEMS .................................................... 33

2.1 Introduction ...................................................................................33

2.2 Methods .........................................................................................36

2.2.1 Soil ............................................................................................36

2.2.2 Batch Experiment .................................................................36

2.2.3 Multiple Reaction Modeling
and Statistical Analysis .....................................................37

2.3 Results and Discussions ..............................................................38

2.3.1 Adsorption-Desorption Kinetics .........................................38

2.3.2 Alachlor Hysteresis ..............................................................52

2.3.3 Validation ................................................................. 55
# PREFERENTIAL FLOW IN SOILS FROM NO-TILL AND CONVENTIONAL TILLAGE SYSTEMS

3.1 Introduction ................................................................. 59
3.2 Materials and Methods .................................................... 63
   3.2.1 Transport Experiments ........................................... 63
   3.2.2 Breakthrough Curve Analysis .................................. 65
   3.2.3 Superposition of Short Pulse ................................... 66
3.3 Results and Discussions .................................................. 67
   3.3.1 The Flow Paths in Undisturbed Columns .................... 68
   3.3.2 BTC Characteristics of Tritium ................................. 80
   3.3.3 Modeling BTCs of Tritium ...................................... 84
3.4 Conclusions ...................................................................... 85

# MODELING ALACHLOR TRANSPORT IN SATURATED SOILS FROM NO-TILL AND CONVENTIONAL TILLAGE SYSTEMS

4.1 Introduction ................................................................. 87
4.2 Materials and Methods .................................................... 90
   4.2.1 Batch Experiments .................................................. 90
   4.2.2 Miscible Displacement Experiments ......................... 90
   4.2.3 Equilibrium Retention Modeling .............................. 91
   4.2.4 Multireaction Modeling .......................................... 93
   4.2.5 Multireaction Transport Modeling ......................... 93
4.3 Results and Discussions .................................................. 95
   4.3.1 Soil Properties ...................................................... 95
   4.3.2 Modeling Alachlor Adsorption ................................ 95
   4.3.3 The tillage Effect on Alachlor Adsorption ............... 99
   4.3.4 Hydrodynamic Dispersion Coefficients .................. 105
   4.3.5 Alachlor BTCs in Soils from Different Tillage Systems 107
   4.3.6 Transport Modeling .............................................. 108
   4.3.7 Retention Parameters of Alachlor During Transport in Undisturbed Soil Columns 112
   4.3.8 Alachlor Recovery, Degradation and Irreversible Reaction 122
   4.3.9 Tillage Effect on Alachlor Transport ..................... 123
4.4 Conclusions ...................................................................... 124

# SUMMARY AND CONCLUSIONS

5 ................................................................. 126

REFERENCES .................................................................. 132
ABSTRACT

The physical and chemical nonequilibrium transport of alachlor were studied in a surface Gigger soil from different tillages through tracer studies, and batch and miscible displacement experiments. Batch experiments indicated initially fast reaction followed by slow adsorption. Adsorption and desorption results indicated time dependent hysteretic behavior and was best described by a multireaction model incorporating nonlinear equilibrium reaction, a reversible kinetic mechanism, and a consecutive irreversible mechanism. The model predicted alachlor hysteresis and adsorption-desorption kinetics satisfactorily based on parameters obtained from adsorption experiments.

Tracer (Eosin Y and Blue FCF dyes) studies showed non-uniformly stained areas in undisturbed soil cores (6.4 cm i.d, 15 cm length) and indicated more pronounced preferential flow and physical nonequilibrium solute transport in no-till than in conventional tillage. Tritium breakthrough curves (BTCs) indicated earlier breakthrough associated with bimodal peaks in short pulses for no-till. The shape of BTCs were also dependent on flow direction. The superimposed experimental data from short pulses well predicted the data of long pulses. The classical convective-dispersive equation was inadequate and there was no improvement in describing tritium BTCs using physical nonequilibrium models (mobile-immobile and stochastic models) for soils from no-till.

Miscible displacement results indicated that alachlor BTCs in soils of no-till were more asymmetrical, with earlier breakthrough and longer tailing than soils from conventional tillage. A multireaction transport model (MRTM) was not satisfactory for
alachlor prediction using independently measured parameters from batch experiments. However, MRTM successfully described alachlor BTCs in a calibration mode where physical and chemical nonequilibrium were dominant. Best-fit parameters indicated the dominance of kinetic reactions compared with parameters from batch experiments and may be attributed to soil heterogeneity. Although no-till increased alachlor retention in batch experiments, an overall estimation based on the sum of kinetic and equilibrium retention showed no significant influence on retention by tillage. High pressure liquid chromatography (HPLC) chromatograms, fitted transport parameters, flow interruptions and percent recoveries indicated a significant consecutive irreversible reaction in soils of conventional tillage. Moreover, no-till increased alachlor transport based on breakthrough time compared with conventional tillage.
1.1 Introduction

Conservation tillage practices are widely adopted in the United States. It was estimated that by the year 2010, 95% of all cropland in the United States will be farmed with conservation tillage practices (McWhorter, 1984). No-till is one of the most common conservation tillages. With no-till, there is effective control of erosion and surface water runoff (Shelton et al., 1983), however, it increases amount of water entering the soil and increases usage of pesticides to control enhanced weed and insect problems. In addition, no-till generally depends more on herbicides and less on cultivation to control weeds than conventional tillage. More herbicide may be needed also because surface residues intercept the spray (Crosson et al., 1986).

The effect of no-till on macropore development and the flow of water and chemicals through macropores has been shown to be significant (Tyler and Thomas, 1977; Edwards et al., 1988; Andreini and Steenhuis, 1990). There are various viewpoints regarding the fate and transport of applied agricultural chemicals in different tillage system. Because soil is left practically undisturbed under no-till, macropores (cracks between aggregates and biological continuous macropores towards the groundwater) increase the hydraulic conductivity (Mahboubi, et al., 1993) thus increase infiltration of water with decreased attenuation of dissolved chemicals due to low pore-
surface area. Under undisturbed flow conditions, there is a higher leaching under no-till than conventional tillage (Gish, 1991; Dick et al., 1986; Hall et al., 1989; Isensee et al., 1990). However, macropores may not be hydrologically active and transport of herbicides through smaller pores may result in greater reactivity in no-till than conventional tillage. Typically, in situ storm events are not of sufficient size or intensity to cause saturated flow in the vadose zone, unless perched water table or downslope convergent processes are prevalent (Wilson, et al., 1991). As a result, the no-till practice may not enhance the leaching of herbicides. Fermanich and Daniel (1991) reported greater carbofuran transport in tilled than in no-till in laboratory soil columns. The significance of unsaturated versus saturated flow conditions to preferential transport of herbicides is not well documented.

Conservation tillage practices may alter the chemical and biological properties of soils. Important soil changes take place with continuous no-till. Soil organic matter content increases and its distribution in the soil profile is changed. Plow-tillage buries organic debris, whereas that which accumulates on the surface of untilled soil may reduce herbicide effectiveness. Increased soil organic matter content causes increased adsorption of most herbicides, requiring increased rates of application. (Triplett and Worsham, 1985). No-till also increases the cation exchange capacity (CEC) of the surface soil compared to conventional tillage (Mahboubi, et al., 1993; Stearman et al., 1989; Phillips and Phillips, 1984). Although the formation of macropores may increase the potential for herbicide leaching through the vadose zone, changes in the soil chemical properties may enhance herbicide retention in the surface horizons of no-till.
soils. This was demonstrated by Levanon et al., (1993) who reported higher concentration of the herbicides occurred in the leachates of conventional column than the no-till columns. Shallow soil samples have revealed that pH decreases up to 1 unit after conservation tillage is practiced, due primarily to nitrogen fertilization (Blevin et al., 1982). Moreover, increased organic matter content in no-till results in reduced herbicide activity (i.e., concentration levels) and may result in greater herbicide retention. However, dissolved soil organic carbon may compete with soil organic matter for herbicide retention. This would result in increased herbicide solubility and mobility, and decreased retention of herbicide (Chiou and Manes, 1986; Chiou et al., 1987) and therefore alter the fate and transport of herbicides (Madhun et al., 1986; Lee and Farmer, 1989; McCarthy and Zachara, 1989; Abdul et al. 1990; Chin et al., 1990; Lee et al., 1990). Because dissolved organic matter is mobile in the soil environment (Jardine and Jacobs, 1990), herbicides are transported to greater soil depths. How these changes in chemical and biological properties due to tillage practices influence the retention of herbicides is not well verified.

Research plots at the West Tennessee Experiment Station (Jackson, TN), were established in 1981 under continuous no-tillage and conventional tillage cotton with wheat and hairy vetch cover crops. A similar long-term study was initiated at LSU Agricultural Center, Macron Ridge Research Station, Winnsboro, LA, in the Fall of 1986 (Hutchinson, et al., 1993) to evaluate the agronomic and economic feasibility of alternative tillage systems and winter cover crops for cotton on a highly erodible loess soil. Other goals of this study were to identify soil, environmental, and biotic factors
that influence cotton response to alternative tillage systems and winter cover crops. These plots include no-till and conventional tillage of cotton with wheat, crimson clover, and hairy vetch and no winter cover crops. The preemergence herbicides were used for controlling the weeds. These plots are ideal for studying long-term tillage effects on herbicide transport through highly erosive soils common to the southern region.

1.2 Herbicide Transport in Soils

The classical convection-dispersion equation that is generally acceptable for the description of dissolved chemicals in the soil solution is (Selim, 1992):

$$\theta \frac{\partial C}{\partial t} + \rho \frac{\partial S}{\partial t} = \theta D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \sum_i \psi_i$$

(1.1)

where \( C \) is solute concentration in solution (\( \mu g \ m^{-1} \)), \( \theta \) is the soil water content (cm\(^3\) cm\(^{-3}\)), \( \rho \) is the soil bulk density (g cm\(^{-3}\)), \( D \) is the hydrodynamic dispersion coefficient (cm\(^2\) h\(^{-1}\)), and \( v \) is Darcy’s water flux density (cm h\(^{-1}\)). In addition, \( S \) is the solute concentration associated with the solid phase of the soil (\( \mu g \ g^{-1} \) soil) and \( \psi_i \) are the rates of solute removal (or supply) from soil solution (\( \mu g \ cm^{-3} \ h^{-1} \)) and are not included in \( S \). The (\( \partial S/\partial t \)) term is a fully reversible process between the solution and the solid phases, and \( \psi_i \) are irreversible (sinks or sources) rates of reactions, i.e., transformation reactions. Processes governing the interactions of individual solute species must be identified if prediction of the fate of contaminants in the soil using the convection-dispersion equation (1.1) is sought. The transport equation indicates that chemical
retention, hydrodynamic dispersion, water flux and biological degradation may influence the fate of herbicides in soils of different tillage systems.

1.2.1 Retention Mechanism

Retention (i.e., sorption and desorption) reactions play a significant role in the transport of herbicides in different tillage systems. Sorption may be regarded as a partitioning of the herbicide between the bulk solution phase and the solid phase (soil matrix). (Greenland et al., 1965; Biggar and Cheung, 1973). The partition processes is characterized by a distribution coefficient ($K_o$) given by

$$K_o = \frac{a_s}{a_e} = \frac{\gamma_s C_s}{\gamma_e C_e}$$

(1.2)

where $a_s =$ activity of the adsorbed solute, $a_e =$ activity of the solute in the equilibrium solution, $C_s =$ micrograms of solute adsorbed per milliliter of solvent in contact with the adsorbent surface, $C_e =$ micrograms of solute per milliliter of solvent in equilibrium solution, $\gamma_s =$ activity coefficient of adsorbed solute, and $\gamma_e =$ activity coefficient of the solute in the equilibrium solution. It is assumed that $K_o$ is related to the standard differential Gibbs energy of adsorption ($\Delta G^\infty$) in the limit at infinitely dilute adsorbate solution. Thus,

$$\lim_{C_s \to 0} \frac{C_s}{C_e} = \frac{a_s}{a_e} = K_o$$

(1.3)

when the $\gamma$ terms approach unity, we have $\Delta G^\infty = -RT\ln K_o$. The value of $K_o$ is obtained by plotting $\ln(C_s/C_e)$ vs. $C_e$, and then extrapolating to zero $C_e$. The intercept
vary with time. Linear, Freundlich, and one-, and two-site Langmuir equations are perhaps most commonly used to describe equilibrium reactions. Since a sorption maximum is rarely observed, the Freundlich equation seems to be more applicable than the Langmuir. At low herbicide concentrations, the sorption can be described by a linear sorption isotherm that passes through the origin (Johnson and Farmer, 1993). Models assuming an equilibrium partitioning are less complex, require fewer parameters to be estimated, and their solution are more readily obtained. In certain cases, however, the equilibrium model may sacrifice accuracy relative to more appropriate nonequilibrium model. As a result, the first-order reversible kinetic reaction has been extended to include the nonlinear kinetic type (Mansell et al., 1977).

1.2.3 Kinetic Retention Models

For some solutes, retention reactions in the soil solution have been observed to be strongly time dependent (Selim, 1992). A number of empirical models have been proposed to describe kinetic retention reactions of solutes in the solution phase. The earliest model is the first-order kinetic reaction, which was first introduced into the convective-dispersive transport equation (1.1) by Lapidus and Amundson (1952).

Multiple Reaction Models

Multisite or multireaction models deal with the multiple interactions of one species in the soil environment. Such models are based on the assumption that a fraction of the total sites are highly kinetic whereas the remaining fraction of sites interact slowly or instantaneously with those in the soil solution. The earliest multireaction models is the two-site model proposed by Selim et al. (1976). Such a two-
site approach proved successful in describing observed extensive tailing of breakthrough results of herbicides.

A general multireaction model is presented by Selim (1992). In this model, the solute was considered in the solution phase (C) and in five phases representing solute retained by the soil matrix as $S_e, S_1, S_2, S_3,$ and $S_{irr}$, where $S_e, S_1$ and $S_2$ are in direct contact with the solution phase and are governed by concurrent-type reactions. $S_e$ as the amount of solute that is sorbed reversibly and is in equilibrium with C at all times. The governing equilibrium retention/release mechanism was that of the nonlinear Freundlich type. The retention/release reaction associated with $S_1$ and $S_2$ were considered to be direct contact with C as the two site reaction. The multireaction model also considers irreversible solute removal via a retention sink term Q in order to account for irreversible reactions such as precipitation/dissolution, mineralization and immobilization. The multireaction model also includes an additional retention phase ($S_3$) that is governed by a consecutive reaction with $S_2$. This phase represents the amount of solute strongly retained by the soil that reacts slowly and reversibly with $S_2$ and may be a result of further rearrangements of the solute retained on matrix surfaces. The reaction between $S_2$ and $S_3$ was considered to be of the kinetic first-order type.

**Second-Order Two-Site Models**

Considering the sites on the soil matrix that are accessible for retention of the reactive solutes in solution, a second-order two-site model was proposed (Selim, 1992). In this model, a fraction factor $F$ was introduced to denote type 1 and type 2 sites to the total amount of sites $S_T$, and $\phi$ as the amount of vacant sites in the soil. The
forward processes is controlled by the product of concentration (C) and vacant sites (φ),
by the reversible processes.

1.2.4 Factors Affecting Retention Reactions

**Organic Matter:** Laboratory studies have, in general, indicated that organic matter
plays a major role in the performance of soil applied herbicides. Such studies often
involved multiple correlation analyses for herbicide adsorption by a series of soils with
widely different properties, including organic matter content, clay content, clay mineral
type pH and CEC (Stevenson, 1982). Huang (1984) indicated that besides organic
matter, the noncrystalline to poorly crystalline Al and Fe components (extracted by the
sodium dithionite-citrate bicarbonate method) and other inorganic constituents present
in a series of particle size fractions of the soils, especially <20 μm fractions, provide
adsorption sites for atrazine. Several other researchers (Wood et al., 1987; Peter and
Weber, 1985) have found high correlations between metolachlor and metribuzin
sorption and organic matter content. Brouwer et al. (1990) reported a linear increase
of distribution coefficient $K_d$ with organic matter content. Thus, $K_{oc}$ ($K_d$ divided by
percent organic carbon, %OC) was proposed as a characteristic property of the
herbicide and was assumed to be independent of soil properties (Yaron et al. 1985).
The use of $K_{oc}$ showed less variability between soils. Groundwater contamination has
been frequently observed in regions where herbicides are applied to coarse-textured
soils with low organic carbon (OC) contents (Cohen et al., 1984). Because soil organic
matter is the primary sorbent for herbicides (Chiou, 1989), soils low in OC have a
lower capacity for retarding herbicide mobility.
Dissolved Organic Matter: Another important factor influencing the retention of herbicides in soils is dissolved organic carbon. As it influences herbicide retention in soils, the solubility of a compound is enhanced by a fraction of organic matter dispersed into water. The presence of high-molecular-weight humic material in water even at trace quantities can significantly enhance the apparent water solubility of some otherwise extremely insoluble organic compounds by partition-like interactions with the microscopic organic environment of the dissolved humic material (Chiou and Manes, 1986; Gschwend and Wu, 1985). Complexation of organic compounds such as herbicides with suspended and dissolved organic matter has been demonstrated in the laboratory (Stevenson, 1972). Several studies have shown that colloidal organic matter and soluble macromolecules may be mobile through aquifer material and soils (Jardine et al., 1992).

1.2.5 Hydrodynamic Dispersion

The various mechanisms that may contribute to dispersion have been under investigation in several fields, including chemical engineering, chromatography, soil science and hydrology. These mechanisms include axial diffusion, hydrodynamic dispersion, boundary layer or film diffusion, and intraparticle diffusion. There are two general ways in which the effects of multiple sources of dispersion can be modeled. The first involves the use of an explicit terms and separate governing equations for each mechanism contributing to dispersion. The effect of intraparticle diffusion on herbicide transport, for example, is simulated with an appropriate equation describing flux in and out of porous particles. The hydrodynamic dispersion phenomena is due to the
nonuniform flow velocity distribution during fluid flow in the porous soil medium. This is responsible for the spreading of the herbicide pattern. When this spreading is considered to be a random processes, the equivalent flux can be taken to be proportional to the concentration gradient, with the dispersion coefficient $D$ being the proportionality constant.

The research of hydrodynamic dispersion into the nature and extent of its effect in agricultural soils has been reviewed by Biggar and Nielson (1967). Tritiated water was used in these investigations. The phenomenon is connected with differences in flow rate between various parts of the water phase. These differences exist both within a pore section and between different pores and pore sections. Values for the dispersion coefficient can be obtained from carefully controlled soil-column experiments. Amount of spreading in such an experiment is shown by concentration distribution with depth in the column or with times in the effluent. Average water-flow velocity in pores exerts an influence, as does degree of water saturation. Diffusion in the water phase has a two-fold effect: on the one hand there is a contribution to spreading in the flow direction, on the other hand the diffusion component perpendicular to the flow direction tends to eliminate concentration differences caused by hydrodynamic dispersion.

Generally, the hydrodynamic dispersion can be expressed as (Brusseau, 1993)

$$D = \frac{D_o}{\tau} + \alpha v$$

where $D_o$ is the molecular diffusion coefficient in water ($L^2/T$), $\tau$ is tortuosity, $\alpha$ is dispersivity (cm) and $v$ is pore water velocity. The molecular diffusion coefficient of

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
ionic species in free solution can be estimated by the Nernst-Einstein equation (Ibl, 1983)

\[ D_o = \frac{mRT}{|Z_i|F} \] (1.5)

where \( m = \) the mobility (i.e. the steady state velocity attained by the ion under action of unit force), \( R = \) universal gas constant, \( T = \) temperature, \( Z = \) charge of the ion, \( F = \) Faraday constant.

For liquid organic compounds, the Stock-Einstein equation has been shown to be adequate for describing the molecular diffusion coefficients (Thibodeaux, 1979). An approximate analytical relation of diffusion coefficient in cm\(^2\) s\(^{-1}\) for solute in water:

\[ D_o = 7.4 \times 10^{-8}(\Psi \times 18)^{1/2} T \mu V^{0.6} \] (1.6)

where \( V = \) the molar volume of the solute in cm\(^3\) mol\(^{-1}\) as liquid at its normal boiling point, \( \mu = \) the viscosity of the solution in centipoise (i.e. 0.01 g cm\(^{-1}\) s\(^{-1}\), \( \mu \) are 0.01787 and 0.01022 poise at 0\(^{\circ}\)C and 20\(^{\circ}\)C respectively), \( \Psi = \) the "association parameter" for water, and \( T = \) the absolute temperature in K. The recommended value of \( \Psi \) for water is 2.6. This equation is good only for dilute solutions of non-dissociating solute. It is noted that the molecular diffusion coefficients are generally in the order of 8-15x10\(^{-6}\) cm\(^2\) s\(^{-1}\) (Acar, et al., 1990).

Temperature corrections of molecular diffusion coefficients for liquids can be inferred from the above equation. Since viscosity is strongly temperature dependent, the following proportionality should be used:
where the subscripts 1 and 2 refer to different temperatures respectively.

The amount of herbicide diffusing through a unit area of soil at any point is the product of the gradient of concentration, and the apparent diffusion coefficient whose value is determined by the geometric factors and partition of a herbicide over the soil phases. The molecular diffusion mechanism is due to the random thermal motion of molecules in solution and is an active process regardless of whether there is net water flow in the soil. Herbicides diffuse more slowly in soil than in air or free solution because the pathway through the pores is restricted and tortuous and because part of the chemical may be retarded by sorption on the solids or because the chemical material may influence the solubility. Graham-Bryce (1969) reported that diffusion coefficients varied little with concentration for disulfoton and dimethoate in a silt loam soil, but increased rapidly with increase in moisture content for dimethoate from $3.31 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 10% volumetric moisture content to $1.41 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 43% moisture content. In contrast, for disulfoton which is more volatile, less soluble and more strongly sorbed than dimethoate, diffusion coefficients were smaller ($2.83 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 41% moisture content) but did not change much as the soil became drier ($2.74 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, at 8% moisture content).

1.2.6 Preferential Transport

There are two different processes which are involved in herbicide transport, one is the movement through the soil matrix and one is rapid downward movement through
macropores (Starr and Glotfelty, 1990). High water fluxes and flow through large pores between aggregates increases nonequilibrium between liquid and solid phase. Preferential transport has been cited as being responsible for the rapid movement of agricultural chemicals to lower soil depths (Czarap et al., 1992). It increases the dispersion coefficient $D$ and water flux $v$ and thus increases the transport. Preferential solute transport and water flow in tilled and untilled soils has been reported by Andreini and Steenhuis (1990). They used grid lysimeters to separate the water flowing through undisturbed soil columns from conventional and conservation tillage systems both temporally and spatially. They sprinkled two soil columns continuous with water (2 cm d$^{-1}$) for 10 days, applied a spike of bromide and blue dye for 24 h in the sprinkler water, and then watered the columns for an additional 30 days. At no time during the experiment did water accumulate on the soil surface. Following water application the columns were excavated to determine water flow paths. In both tillage systems, dye flow pathways led to areas where water and solutes exited the columns. In the no-till column, nearly the entire depth of the profile was short-circuited by preferential flow, but in the tilled column solute passed through the mixed, unstructured plow layer. By use of a soluble dye to denote flow pathways in soil, Trundgill et al. (1983) found only a small fraction of soil stained. Less than 3% of total soil volume was involved in the transport processes. Watson and Luxmoore (1988) found $<1\%$ of the soil volume was used in transport of 96% of the water flux in a forest soil.
1.2.7 Biological Decomposition

Decomposition is another main phenomenon influencing the fate of herbicide transport. Alachlor is primarily degraded microbially in soil. Degradation is a slow biological processes for alachlor and other acetanilide herbicides (Sharp, 1988), and only small amounts were mineralized in surface soils (Novick et al. 1986). It has been found that microbial degradation was of greater importance than volatilization and leaching for acetanilide herbicides (Zimdahl and Clark 1982). The half-lives of alachlor at 20°C and 80% saturated soil moisture, was 18 days in a clay loam soil (Zimdahl and Clark, 1982; Ivany et al., 1983; David, 1990). Microbial degradation of herbicides increases with increased soil moisture and soil temperature. A quantity is needed to express the decomposition-rate equation. Usually these rates are considerably higher in soil than in water at the same pH. So far the first-order rate equation has been used most frequently. It is assumed that the decomposition rate is proportional to the amount of herbicide remaining at time t

$$ \frac{dQ}{dt} = -K_r Q \quad (1.8) $$

where $K_r$ is the rate constant in day$^{-1}$. Equations of the hyperbolic type represent breakdown patterns with a comparatively high rate for lower amounts. For $C = C_0/2$, the half-life ($t_{1/2}$) can be calculated as

$$ t_{1/2} = \frac{0.693}{K_r} \quad (1.9) $$
1.3 Modeling the Water and Herbicide Transport

1.3.1 Modeling Water Flow

The flow through porous media depends primarily on the dimensions of the void fraction. Since the size of the pores is difficult to characterize, a dimension of the solid phase in the case of discrete particles and the surface area of the solid phase in the case of consolidate media are usually used for characterization. In one method, the packed theory is then developed by applying single straight tubes to the collection of crooked tubes. It is assumed that the medium is uniform and that there is no "channeling". According to Blake-Kozeny equation and Darcy's Law, the permeability of the column is (Bird et al. 1960)

\[ k = \frac{150 (1-\varepsilon)^2}{d^2 \varepsilon^3} \]  

(1.10)

where \( d \) is equivalent diameter of aggregate and \( \varepsilon \) is porosity of the soil column.

Another method of modeling water flow is to describe the characteristics of channel flow. Bouma and Dekker (1978) used a dilute solution of methylene blue in water (0.03% by weight) and stained walls of pores in the soil were observed and counted after subsequent excavation. The stain pattern in the entire soil mass on vertical ped faces and in channels had been observed for 10 cm depth intervals in terms of type (bands on ped faces or in tubular pores), sizes and quantities. Presence of stain on the wall of a soil pore is a clear indication of water movement. But lack of stain does not necessarily imply complete lack of movement. Stains are produced by complete or partial penetration of dye water from large pores into dry, fine porous peds. Leaving
a stain on the outside as de-colored water proceeds to penetrate the ped and dye water move further downward along the ped face. The number of the channel bands > 7.5 mm wide, and bands 2.5-7.5 mm wide were counted for every 10 cm interval in the profile. They reported that the number of pathways along large vertical pores that were involved in infiltration (as indicated by stains) was determined by the flow region. The number of colored bands increases with rain intensity. The morphological observations presented were transformed into diagrams showing the entire stained contact area for any given depth interval. The observed infiltration pattern resulted in a small vertical contact area between soil and infiltrating water through the large pores. Only a small fraction (2% or less) of potentially available contact area in a dry soil was used for vertical flow through the large pores). Bouma, et al., (1979) used Methylene blue to indicate flow patterns. A statistical planar and tubular void-interaction model was used to estimate sizes of "necks" in the flow systems, which were assumed to determine the saturated hydraulic conductivity. Two types of data, obtained from horizontal thin sections, (i) measured width distribution of stained planar voids (d_i, d_{i+1}, d_{i+2}...), and (ii) the number of measurements in each width class d_i (N_i, N_{i+1}, N_{i+2}...). The data were used to calculated hydraulic conductivities of the preferential flow based on observed geometry of voids. For a plane slit of unit length (perpendicular to the direction of the flow) it follows:

\[ \frac{Q}{t} = \frac{\rho g \pi r^4}{8 \eta} vH \]  

(1.11)

where \( Q/t \) = volume of liquid conducted per unit time and length (cm^3 sec^{-1}); \( \eta \) =
viscosity (g cm\(^{-1}\) sec\(^{-1}\)); \(\rho\) = liquid density (g cm\(^{-3}\)); \(g\) = gravitational constant (m s\(^{-2}\)); \(\nabla H\) = hydraulic gradient (m m\(^{-1}\)); and \(d\) = width of plane slit (cm). For a tubular void with radius \(r\) (cm) it follows:

\[
\frac{Q}{t} = \frac{\rho g \pi r^4}{8\eta} \nabla H
\]

1.3.2 Modeling Herbicide Transport

The traditional approach to modelling and predicting herbicide transport is to solve the convection-dispersion equation (1.1) analytically or numerically, depending on the problem addressed (van Genuchten and Alves, 1982). This equation is based on a differential mass balance of a control volume. Even though the solution to this equation will result in the knowledge of the herbicide distribution in space and time, in most cases only the concentration is monitored with time at a particular point. This is especially true for laboratory studies performed for the determination of solute behavior during transport in soil columns. The effluent versus time is referred to as the breakthrough curve (BTC). The BTCs are usually modelled using the CDE, e.g. the outflow is predicted by the determination of the solute distribution inside the control volume. When the soil is nonhomogeneous, physical nonequilibrium models are often proposed (van Genuchten, 1981).

Mobile-Immobile Transport Models

A mathematical model was proposed when apparent non-equilibrium condition in the system are attributed to large heterogeneities in microscopic pore-water velocities (Parker and van Genuchten, 1984). This approach assumes that the liquid phase can be
partitioned into mobile (dynamic or macro-porosity) and immobile (stagnant or micro-porosity) regions. Convective and dispersive transport is restricted to the mobile water phase, while transfer of solutes into and out of the immobile (non-moving) liquid phase is assumed to be diffusion-limited. The governing equation for this two-region model mobile-immobile model are

\[
(\theta_m + f_m \frac{\partial}{\partial t} C_m^m + [\theta_{im} + (1-f_m) \rho k] \frac{\partial}{\partial t} C_{im}^m) = \theta_m
\]  

(1.13)

\[
[\theta_{im} + (1-f_m) \rho k] \frac{\partial}{\partial t} C_{im}^m \alpha (c_m - c_{im})
\]

(1.14)

where \( c_m \) and \( c_{im} \) are the resident concentrations of the mobile and immobile liquid phases respectively; \( \theta_m \) and \( \theta_{im} \) are the mobile and immobile volumetric water contents such that \( \theta = \theta_m + \theta_{im} \). \( D_m \) is the hydrodynamic dispersion coefficient in the mobile water region, \( q \) is Darcy water flux and \( f_m \) represents the fraction of the sorption sites that equilibrated with the mobile liquid phase, and \( \alpha \) is a mass transfer coefficient that governs the rate of solute exchange between the mobile and immobile regions.

Applying reduced variable \( v_m = q/\theta_m \), equation (1.13) and (1.14) become

\[
\beta R \frac{\partial C_m^m}{\partial T} + (1-\beta) R \frac{\partial C_m^m}{\partial T} = \frac{1}{P} \frac{\partial C_{m}^{2m}}{\partial X^2} - \frac{\partial C_m^m}{\partial X}
\]

(1.15)
The model consists of equation (1.15) and (1.16) subject to the conditions

\[ C_m(X, T=0) = C_{im}(X, T=0) = 0 \]  
\[ C_m(X \to \infty, T) = C_{im}(X \to \infty, T) = 0 \]

\[ (c - \frac{1}{d} \frac{\partial C}{\partial x})|_{x=0} = A \delta(T) \]  

where \( \delta(T) \) is the Dirac Delta function and \( A = M/(\beta L) \), where \( M \) is the mass input per unit column cross-sectional area. The solution for the volume-averaged concentration \( c_r \) in terms of the reduced variables is

\[ c_r(X, T) = c_i + (c_o - c_i) A(X, T) \quad 0 < T < T_0 \]  
\[ c_r(X, T) = c_i + (c_o - c_i) A(X, T) - C_o A(X, T - T_0) \quad T > T_0 \]

where

\[ A(X, T) = \int_0^T g(X, \tau) f(a, b) d\tau \]  

\[ g(X, \tau) = \left( \frac{P}{\pi \beta R} \right)^{1/2} \exp \left[ -\frac{P(\beta RX - \tau)^2}{4 \beta R \tau} \right] - \frac{P}{2 \beta R} \exp(\beta RX) \text{erfc}\left( \frac{P}{4 \beta R \tau} \right) \]
\[ J(a, b) = 1 - e^{-b} \int_{0}^{a} e^{-\lambda} \text{I}_0(2\sqrt{b\lambda}) d\lambda \] (1.24)

where

\[ a = \frac{\omega \tau}{\beta R} \] (1.25)

and

\[ b = \frac{\omega (T - \tau)}{(1 - \beta)R} \] (1.26)

The function \( J(a, b) \) is refereed as Goldstei's J-function (Goldstein, 1953); \( \text{I}_0 \) in this function represents a zero-order Bessel function.

**Two-Site Mobile-Immobile Models**

When considering the reaction in heterogenous systems, a Second-Order Mobile-Immobile Model was proposed (Selim, 1992). In the model, the chemically controlled heterogeneous reaction is governed according to the Two-Site approach, in the meantime, the physically controlled reaction is chosen to be described by diffusion or mass transfer of the mobile-immobile concept (Coats and Smith, 1964; van Genuchten and Wierenga, 1976). Leaching of herbicide through macropores occurs as discrete pulses with each large storm while transport through smaller pores is assumed immobile. For such conditions, mobile-immobile transport models have been successfully used to predict transport of several ions in soil columns (Selim et al., 1987; Gaston and Selim 1990). In such models, equilibrium ion exchange reactions among competing ions are considered in the mobile and immobile water zones and transfer
between zones is by diffusion. It is further assumed that the inter-aggregate surfaces are those which are in contact with the immobile water; whereas, intra-aggregate or macropore surface are indirect contact with the mobile water phase. This model was extended to incorporate retention reaction of the equilibrium type as well as degradation reactions (van Genuchten and Wagenet, 1989). In addition, a kinetic second-order retention approach has been incorporated into the mobile-immobile concept by Selim and Amacher (1988).

**Stochastic Modeling of Herbicide Transport**

Early stochastic modeling of water flow in heterogenous porous media was proposed by Dagan (1982). It has become quite common to regard the medium as well as the flow variable as a random variable characterized by probability distributions rather than by well-defined deterministic values. The fractured medium were treated as an equivalent porous medium (Neuman et al., 1985). This is appropriate when the fractured media contains many inter-connecting fractures. In fact, there is much field evidence that the dispersivity is not a constant due to medium heterogeneities but depends on the travel distance and/or scale of the system. There have been many studies to incorporate the scale dependent dispersion in modeling studies (Gelhar et al., 1979; Hatton and Lightfoot, 1984).

Another approach was that fracture medium was assumed by means of a limited number of tortuous and intersecting channels (Tsang and Tsang, 1987). These channels have variable apertures along their lengths. The parameters that characterize the channels are (i) the aperture density distribution, which gives the relative probability
of the occurrence of a given aperture value, (ii) the effective channel length and width, and (iii) the aperture spatial correlation length, which gives the spatial range within which the aperture values are correlated.

Toride et al., (1995) used three stochastic variables including pore water velocity v, dispersion coefficient D and distribution coefficient K_d for linear adsorption or the first-order rate coefficient for nonequilibrium adsorption α. The three different pairs of random parameters are described with a bivariate lognormal joint probability density function for the one dimensional solute transport.

1.4 Alachlor Behavior in Soil

Alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide, a pre-emergence herbicide, is one of the most commonly used soil-active herbicides. It is extensively used to control annual grasses and certain broad leaf weeds in corn, cotton, soybean and sugarcane etc. About 37 million kilograms of alachlor is produced annually in the USA (Chesters et al., 1989). The molecular structure is shown in Fig. 1.1. Its molecular formula is C_{14}H_{20}ClNO_2 and it has a molecular weight of 269.77. Its solubility in water is 148-242 ppm at 25°C and with field half life of 14-49 days (Wauchope et al. 1992). It is photolytically stable and is chemically stable up to 105°C. The distribution coefficient varied with soils. A K_d of 1.1 and K_w of 157 was reported by Kladivko, et al. (1991). Due to its moderate retention by soil, some studies (Wu, 1980) reported that alachlor did not leach below 8 cm in field soil and not below 4 cm in a moist soil. However, residues of these herbicides are frequently found in environmental samples of soil and water due to their persistence and relatively high
Fig. 1.1 Alachlor Molecular Structure
water solubility and weak soil sorption (Cohen, 1984). Due to possible groundwater contamination and health effects, the U.S. EPA proposed Maximum Contaminant level Goals (MCLG) of zero ppb for alachlor (U.S. Environmental Protection Agency, 1989a). But so far, alachlor has been detected in ground water in many states including Iowa, Pennsylvania, Maryland, Nebraska, and Minnesota etc. (Roux et al., 1991; Cohen, 1992; Holden and Graham, 1990).

1.5 Current Experimental Methods on the Fate and Transport of Herbicide

1.5.1 Retention and Mobility Studies of Herbicides

Batch methods are widely used method for characterizing the retention of herbicides (Sparks, 1988) and for supporting product registration (US Environmental Protection Agency, 1982). Thin-layer Chromatography is another method used for degradation and mobility study of herbicide (Sharon and Koskinen, 1990). The study via TLC conducted by Sharon and Koskinen (1990) indicated that greater than 88% of the \(^{14}\)C in solution chromotographed with parent alachlor, the remaining 12% of the \(^{14}\)C in solution was distributed equally along the plate which may result from degradation.

Several researchers conducted transport experiments for dissolved chemicals using saturated soil columns (Selim and Ma, 1995; Czapar et al. 1992). It is a commonly used method to study herbicide mobility, which is required by the USEPA to support product registration (U.S. Environmental Protection Agency, 1982).
1.5.2 Tracer Studies for Characterizing Preferential Flow

Techniques to visualize macropores and cracks, and to measured their capacity of transporting water and solutes have been introduced by Bouma and Dekker (1978), and Bouma et al. (1978, 1979). These methods often involve the application of an amount of dye solution to the soil surface. The presence of the dye, which adsorbed at the walls of the cracks and macropores, can be studied. It can provide direct evidence for the presence of preferential flow channels in the soil and gives information on the nature and the extent of the flow channels involved.

Allen et al. (1989) proposed the mechanisms of dye adsorption in soils. The adsorption of a dye onto adsorbents follows three consecutive stages. First, dye migrates through the solution to the exterior surface of the adsorbent particles. Secondly, the dye moves within the pores of the particles. Then, thirdly, the dye is adsorbed at sites on the interior surface of the adsorbent particles. They proposed that the main resistance to the mass transfer occurs solely in the second stage, i.e., during the movement or diffusion of the dye in the pore structure of the adsorbent. Dubinin (1967) suggested that the pore structure of adsorbent particle consists of macropores, transitional pores, and micropores. The pore size distribution can be shown to be more important than the surface area.

Dyes Used in Tracer Studies

Many non-fluorescent dyes have been used to illustrate flow paths in soils. The choice of a dye is greatly restricted because soils often interact with the dye molecules (Corey, 1968). The study of Corey (1968) indicated Acid Red 1 had the highest
mobility among anionic dyes tested. Ghodrati and Jury (1990) used the dispersed Orange 3 dye to trace the preferential flow. However, it did not flow through the soil profile and was filtered out of the solution right at the soil surface, producing a crust because of its high concentration (80 g kg^{-1}). It penetrated only to a minimal depth of a few centimeters. van Ommen et al., (1988) proposed a method based on the formation of an intensely colored complex of iodine with starch. After application, horizontal cross-sections of the soil profile are obtained by removing slices of the soil. A whole soil profile can be excavated in order to obtain a series of two dimensional pictures of the phenomena. However, it is necessary that the starch and bleaching agent are uniformly applied onto the soil's cross section. Therefore, this approach is limited to non-structured soils (van Ommen et al., 1988).

Although methylene blue is readily visible, it is strongly adsorbed along the walls of conducting pores (Smettem and Collis-George, 1985; Steenhuis et al., 1990). Particularly in smaller pores, methylene blue is not a good indicator for water movement.

The Brilliant Blue FCF was considered to be the best compromise between mobility, visibility, and toxicity (Flury and Flühler, 1994; 1995). Brilliant Blue FCF has been used as tracer by Andreini and Steenhuis (1990) and Boll et al. (1992) in laboratory experiments, and by Pickering et al. (1988) and Steenhuis et al. (1990) in the field to stain flow pathways. The relative retardation was 1.2 for Brilliant Blue FCF compared with iodine. The Brilliant Blue FCF move a shorter distance compared with bromide.
Koch and Flühler (1994) used Brilliant Blue FCF as a point source in the center of the column or as a pulse over the entire surface. Lateral mixing of the point source was investigated visually by cutting the columns vertically into two halves immediately after the dye was detected in the outflow. The dye patterns along vertical profiles through the centers of columns were drawn. In the same paper, Koch and Flühler (1994) characterized the dye patterns for a layered column with three distinct layers.

Steenhuis et al. (1990) use a 0.6% solution of Rhodamine WT dye (moderately adsorbed), 1.0% FD&C blue #1 food coloring dye (weakly adsorbed), and 0.1% methylene blue dye (strongly adsorbed). The dyes were used to identify the primary solute-transport paths and to compare the flow mechanisms under the two tillage treatments. The staining pattern in the soil by the dye solutions indicated earthworm burrows are the most active flow conduits in the upper profile.

Ghodrati and Jury (1990) using an anionic water-soluble dye, Acid-Red 1 to characterize preferential flow. The observed vertical and horizontal distribution patterns of the water-soluble dye clearly indicated preferential flow patterns for each experimental condition. These include vertical fingering of dye tracers 5 to 20 cm wide, which extended more than twice as deep as the mean displacement of the dye, as well as isolated paths of dye indicating lateral flow. In addition to photographing, accurate traces of the stained dye patterns on the trench face were made at each site on clear plastic sheets. This processes was repeated by cutting the trench face successfully at 10 cm interval both vertically and horizontally. The representative vertical and horizontal flow patterns of the acid-Red 1 dye were produced directly from the photograph by re-
staining all colored regions with black ink. The relationship between the fraction of vertical and horizontal surfaces covered by the dye and the soil depth for these plots were obtained. The flow pattern are obviously three-dimensional, showing both lateral and vertical movement along tortuous paths. Characterization of preferential flow in soils through water tracer studies are, in most cases, inconclusive because of the inability of most solute sampling devices to detect the spatial pattern of preferential flow pathways.

1.5.3 Herbicide Transport under Unsaturated Flow

Under field conditions, macropores will empty as the soil water content decreases, while mesopores remain water-filled and hydrological active. Mesopores, which are capable of rapid infiltration (Wilson and Luxmoore, 1988), promote greater attenuation of chemicals due to increased pore-surface area (Luxmoore et al., 1990) and may be the key pore class to field-scale transport. To study the water and herbicide transport through pores, an unsaturated column method was used by Jardine and Jacobs (1990). They showed that while macropore transport is significant, solutes in smaller pores within aggregates are also highly mobile. Jardine and Jacob (1990) demonstrated, with undisturbed soil columns under steady-state flow conditions, significant differences in reactive solute transport as conditions were changed from saturated to just -1.0 Kpa pressure potential. For studying the transport of reactive Sr in undisturbed columns, Jardine et al. (1993) conducted miscible displacement experiments under unsaturated condition. Prior to the displacement experiments, soil column were slowly saturated with 0.05 M CaCl₂ from the bottom. The columns were then allowed to drain under
a desired pressure head in order to establish steady flow. The inlet pressure head was maintained with a Mariotte device and the outlet pressure head was maintained with a constant-vacuum source. A unit hydraulic head gradient was established within the column by placing the inlet and outlet the same pressure head. This resulted in a uniform matric potential and water content within the soil column. For most displacement experiments, a pressure head of -10 cm was selected because it allowed macro-pores (diameter < 1 mm) in the soil columns to remain empty. The results indicated that the application of -10 and -15 cm pressure heads resulted in five- and 40-fold decreases in the mean pore water flux, respectively, with relatively little change in soil water content relative to saturated conditions. They concluded that most of the water flux may be channeled through pores that hold water with tension < 10 cm (macropores). Selim et al. (1977) simulated solute transport through unsaturated multilayered soil profiles in which a steady, vertically downward water flow was considered. BTCs for the reactive solute show lower retardation factors for the soil profiles having a water table at z = 100 cm than at z → ∞. At steady state, a uniform soil water content can be used to represent each soil layer in order to simplify the solute transport problem. But for the transient water flow conditions of unsaturated multilayered soils, such a simplifying approach was not applicable (Selim, 1978).

Elrick et al. (1966) and Krupp and Elrick (1968) regulated the water content by placing a perforated sample holder in a pressure chamber, while the desired flow rate was obtained. Both ends of the sample were in close contact with a cellulose acetate membrane filter, supported by a porous screen and a stainless steel end cap containing
three plastic nipples. The sample and pressure chamber where placed on a balance to allow continuous monitoring of the sample weight and hence water content. A driving head, equal to the sample length, was established by increasing the pressure in the chamber (unit gradient). A constant water content was obtained throughout the sample. This meant that only one flow rate was possible for each water content.

The transport of chemicals in soil columns during a constant-flux, unsteady, unsaturated flow have been conducted by Mansell et al. (1993). Bond and Phillips (1990) gave an analytical solution of cation transport during unsteady, unsaturated soil water flow. Tan et al. (1992) conducted experiments using bacteria and calculated the position of bacteria front in flux-dependent unsteady state flow condition which is realistic in the field condition, but encountered difficulties in predicting the reactive bacteria change with space and time.

1.6 Objectives

In herbicide investigations, the increased demand for quantitative data is a stimulant to the use of computational models. There is a need to provide behavioral patterns of herbicide fate a toxicological value and to provide a discussion base for agricultural and environmental policy. A minimum requirement is that it must be possible to estimate and predict the concentration of herbicide as a function of time and position in the soil profile. The specific objectives of this study were:

(i) Examine the influence of chemical properties (organic matter) on the sorption and desorption kinetics of alachlor in soil of no-till and conventional tillage systems and characterize the retention behavior of alachlor;
(ii) Characterize the preferential flow and physical nonequilibrium transport of solute in undisturbed and saturated soils from no-till and conventional tillage systems;

(iii) Quantify physical and chemical nonequilibrium transport parameters of alachlor in undisturbed and saturated soils from no-till and conventional tillage systems; and

(iv) Model physical and chemical nonequilibrium transport of alachlor in undisturbed and saturated soils from no-till and conventional tillage systems.
CHAPTER 2

MODELING ADSORPTION-DESORPTION KINETICS OF ALACHLOR IN SOILS OF DIFFERENT TILLAGE SYSTEMS

2.1 Introduction

Alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide], a pre-emergence herbicide has been widely used for weed control for several agronomic crops (Lawruk et al., 1992). Alachlor has been classified by EPA as Group B2, a probable human carcinogen with a maximum contaminant level goal of zero in drinking water (U.S. EPA, 1989).

Adsorption and desorption (or retention) reactions of pesticides such as alachlor in soils play a significant role in their behavior and has been the subject of numerous investigations over the last three decades. Alachlor can be adsorbed by a coordination bond, through a water bridge, between the C=O groups and exchangeable cations on clay and organic matter (Bosetto et al., 1993). The coordination strength is directly correlated with the polarizing power of the exchangeable cation. X-ray diffraction analyses showed that alachlor penetrated the inter-layer space of montmorillonite (Bosetto et al., 1993). Alachlor may be characterized as a moderately nonpolar compound (Green and Karickhoff, 1990). Alachlor sorption has been associated with both hydrophilic and hydrophobic soil components. Consequently, adsorption of alachlor was found to be positively correlated with soil organic matter and clay content (Locke, 1992).
The dependence of pesticide retention on the concentration of pesticides in the soil solution has been observed by several investigators. Locke (1992) reported that a high percentage of alachlor applied to soils from no-till and conventional tillage experiments was adsorbed at low initial concentration. At low concentrations, Weber and Peter (1982) found that alachlor was adsorbed on Ca-organic matter and Ca-montmorillonite systems in similar amounts. However, at high concentrations, higher amounts of alachlor were adsorbed by Ca-montmorillonite than Ca-organic matter system. Senesi et al. (1994), through infrared analysis, indicated that the alachlor adsorption mechanism is concentration dependent, with H-binding and charge-transfer processes being the major mechanisms occurring at low concentrations. A hydrophobic binding of alachlor to the aliphatic parts of humic acid (HA) is dominant at high concentration. As a result of concentration dependant retention mechanism, a nonlinear isotherms or Freundlich isotherms was found for a wide range of concentration (Senesi et al. 1994).

The fate of pesticides and their potential mobility in soils are directly influenced by their retention mechanisms. In a kinetic study, Clay and Koskinen (1990) reported that alachlor retention was rapid and appeared complete within 24 h, with the first 2 h accounting for 88% of total retention. As a result, the validity of the local equilibrium assumption (LEA) is often invoked. For example, the Freundlich (equilibrium) approach was utilized to describe alachlor retention by Bosetto et al. (1993), Clay and Koskinen (1990), and Senesi et al. (1994). Although the Freundlich approach well described alachlor retention, the goodness of fit alone does not provide definite
information on the retention mechanisms. In addition, the rate at which "apparent" equilibrium is achieved, is influenced by limitations to diffusion through the sorbent as well as by specific sorbate-sorbent interactions. Nonequilibrium conditions may also be due to heterogeneity of sorption sites and slow diffusion to sites within the soil matrix, i.e. slowly accessible sites.

In a review of pesticide adsorption and desorption behavior, Calvet (1980) indicated that desorption is generally slower than adsorption. Based on adsorption-desorption kinetic results for alachlor over a 24 h period, Boesten and Van der Pas (1988) concluded that the evidence supporting the existence of hysteresis of alachlor is not convincing. In contrast, obvious hysteretic patterns were observed by Bosetto et al. (1993) and Helling et al. (1988). Hysteretic behavior along with increased irreversible alachlor retention with time were also reported by Clay and Koskinen, 1990) and Locke (1992). Incomplete recovery of applied alachlor and commonly observed hysteretic desorption phenomena were attributed to slower secondary sorption reactions. In fact, Locke (1992) applied with success a three-site multireaction model to describe alachlor adsorption versus time for soils under no-till and conventional tillage. No attempts were made to describe alachlor retention behavior during desorption, however.

The objectives of this study were: (i) to determine the kinetics of alachlor retention in two surface soil samples for a wide range of input concentrations, and (ii) to determine the hysteretic characteristics of alachlor adsorption-desorption in soils. The soils were Gigger silt loam collected from long term no-till and conventional tillage cotton plots. A third objective is to assess the capability of a nonlinear multireaction
model for the prediction of alachlor adsorption as well as desorption in soils based on independently derived model parameters.

2.2 Methods

2.2.1 Soil

Surface soils (0-15 cm) were sampled from long term no-till and conventional tillage cotton plots under wheat as winter cover, from the Macon Ridge Research Station, Winnsboro, LA. The soil used in this study was a Gigger soil and contained 22% sand, 66% silt and 12% clay. Organic matter content was 1.45% for the soil of no-till and 0.81% for the soil of conventional tillage. The pH (1:1 soil:water ratio) was 5.37 in the no-till and 5.23 in the conventionally tilled soil.

2.2.2 Batch Experiment

Alachlor retention in the two surface soils was carried out using batch methods as outlined by Ma and Selim (1994). The adsorption experiments were conducted by mixing 10 g of air-dry soil and 20 ml of alachlor solutions of varying concentrations in 40 ml Teflon tubes. Two batch experiments were conducted. In the first (data set I), three initial alachlor concentrations ($C_o = 1, 5, and 10 \text{ mg L}^{-1}$ in 0.01 N CaCl$_2$ solution) and 10 reaction times (1, 2, 4, 8, 16, 32, 64, 128, 256 and 512 h) were used in duplicate. In the second (data set II), eight alachlor initial concentrations ($C_o = 0.5, 1, 2, 5, 10, 20, 30$ and $50 \text{ mg L}^{-1}$ in 0.01 N CaCl$_2$ background solution) with 4 reaction times (24, 48, 120 and 528 hours) were carried out in duplicate. Samples were shaken for each reaction time, then were centrifuged, and the supernatants were withdrawn, and filtered for alachlor analysis by high performance liquid chromatography (HPLC).
Desorption of alachlor from the soil was carried out following sorption using successive dilution. Desorption was carried out in the first batch experiment (data set I) only. Desorption steps commenced following centrifugation and decanting of supernatant for HPLC analysis and weighing of sample tubes. The amount decanted was replaced by 20 ml of the background solution (0.01 N CaCl₂). The samples were then reweighed, vortex mixed, and returned to the shaker for the second desorption step (one day reaction time) for a total of six desorption steps in each desorption.

2.2.3 Multiple Reaction Modeling and Statistical Analysis

The two-site equilibrium-kinetic model of Selim et al. (1976) is perhaps one of the earliest multi-site or multireaction approaches for describing retention and transport behavior of reactive solutes in porous media. Basic to the multi-site approach is that the soil solid phase is made up of different constituents (soil minerals, organic matter, iron and aluminum oxides), and that a solute species is likely to react with various constituents (sites) by different mechanisms. This multiple or distributive reactivity approach was recently used by Weber et. al. (1992). As reported by Clay and Koskinen (1990) and Locke (1992), alachlor is assumed to react at different rates with different sites on matrix surfaces. Therefore, a multireaction kinetic approach may be considered to describe alachlor retention kinetics in soils.

The multireaction model used here considers several interactions of one reactive solute species (alachlor) within the soil environment. Specifically, the model assumes that a fraction of the total sites is highly kinetic whereas the remaining fraction interacts slowly or instantaneously with solute in the soil solution. As illustrated in Fig. 2.1, the
model accounts for reversible as well as irreversible (concurrent and consecutive) type reactions;

\[ S_e = k_e C^n \]  \hspace{1cm} (2.1)

\[ \frac{\partial S_1}{\partial t} = k_1 \frac{\theta}{\rho} C^m - k_2 S_1 - k_3 S_1 \]  \hspace{1cm} (2.2)

\[ \frac{\partial S_2}{\partial t} = k_3 S_1 \]  \hspace{1cm} (2.3)

\[ \frac{\partial S_{irr}}{\partial t} = k_{irr} \frac{\theta}{\rho} C \]  \hspace{1cm} (2.4)

where C is solute concentration in soil solution (mg L\(^{-1}\)), \( \rho \) is soil bulk density (g cm\(^{-3}\)), \( \theta \) is soil water content (cm\(^3\) cm\(^{-3}\)), and t is reaction time (h). The parameter \( k_e \) is Freundlich distribution coefficient (cm\(^3\) g\(^{-1}\)) and \( k_1, k_2, k_3 \) and \( k_{irr} \) are associated reaction rate coefficients (h\(^{-1}\)). The term \( S_e \) is the amount retained (reversibly) by equilibrium type sites (\( \mu g \) g\(^{-1}\) soil), \( S_1 \) is the amount retained (reversibly) by kinetic type sites (\( \mu g \) g\(^{-1}\) soil), and n and m are empirical parameters (dimensionless). In addition, \( S_2 \) is the amount irreversibly transferred from \( S_1 \), \( S_{irr} \) represents irreversible sites (\( \mu g/g \) soil). Transformation of \( S_1 \) to \( S_2 \) (eq. 2.3) as well as decomposition of alachlor in the solution phase (eq. 2.4) were assumed to follow a first-order reaction.

2.3 Results and Discussions

2.3.1 Adsorption-Desorption Kinetics

Different versions of the multireaction model of Fig. 2.1 represent different reactions from which one can deduce alachlor retention mechanisms.
Fig. 2.1. Schematic diagram of the nonlinear multireaction kinetic model.
Four variations were examined; (1) a two parameter model with $k_e$ and $k_{irr}$, (2) a three parameter model with $k_e$, $k_1$ and $k_2$, (3) a four parameter model with $k_e$, $k_1$, $k_2$ and $k_{irr}$, and (4) another four parameter model with $k_e$, $k_1$, $k_2$ and $k_3$. Each model variation was fitted to the experimental data using a nonlinear, least-squares, parameter optimization scheme (van Genuchten, 1981). Criteria used for estimating the goodness-of-fit of the model to the data were the $r^2$ and the root mean square (rms) statistics (Kinniburgh, 1986),

$$\text{rms} = \left[ \frac{\text{rss}}{N-P} \right]^{1/2}$$  \hspace{1cm} (2.5)

where rss is the residual sum of squares, $N$ is the number of data points and $P$ is the number of parameters.

In all subsequent model calculations, we assumed empirical coefficients $n$ and $m$ to be non-unity and $n = m$ (eq. 2.1-2.2). This assumption was used since there is no known method for estimating $n$ or $m$ independently. Estimated values were obtained from fitting isotherm (adsorption) results after 528 h to the Freundlich model, $S_T = k_f C^n$ where $S_T$ is the total amount retained. Estimates for $n$ were 0.608±0.028 for the soil from no-till and 0.660±0.013 for the soil from conventional tillage. Based on the extra sum of squares principle (Kinniburgh, 1986), there was a significant ($p<0.05$) improvement in the fitting of the Freundlich model as opposed to a linear model ($S_T = k_d C$). Therefore, these $n$ values were used in all model calculations.

The goodness-of-fit of these model variations was tested using alachlor adsorption-desorption (data set I) for initial concentration in solution ($C_0$) of 1, 5, and
10 mg L$^{-1}$. The results are listed in Table 2.1 for the no-till and conventional-till soil. Experimental data points and model predictions for the model variations are shown in Fig. 2.2 for the no-till soil with $C_0$ of 5 mg L$^{-1}$. The time-dependent behavior was well described by the various model variations indicating initial fast adsorption (closed circles) followed by slow adsorption where kinetic reactions appear dominant. Desorption results following 16, 128, 256, and 512 h of adsorption are shown by the open circles and were also well described by our model.

As indicated from estimates of the rate coefficients for the no-till and conventional-till soil (Table 2.1), model variation 4 with the consecutive irreversible reaction ($k_a$, $k_1$, $k_2$ and $k_3$) consistently provided lowest rms and highest $r^2$, and thus the best overall data fit. Alachlor concentrations versus time are given in Figs. 2.3 and 2.4, where the solid curves are fitted using model variation 4. Model variation 3 with the concurrent irreversible reaction ($k_a$, $k_1$, $k_2$ and $k_{irr}$) did not provide as good a fit as model variation 4 with the consecutive irreversible reaction. Therefore, one may assume that alachlor adsorption processes include a consecutive irreversible rather than a concurrent irreversible reaction. Consecutive irreversible type sites may represent "restricted" sites as reported by Locke (1992). Sorption may be reversible at some sites, but with time, alachlor may diffuse into clay or organic matrices where binding may be less reversible. Stronger retention by some clay and organic matter sites, together with slow diffusion from the clay surfaces, may result in the so-called "restricted" sorption phase. In addition, alachlor is known to be degradable under aerobic and anaerobic conditions and degradation was described by first-order kinetics (Pothuluri
Table 2.1. Comparison of goodness of fit of several variations of the nonlinear multireaction model for describing alachlor adsorption-desorption kinetics (data set I) for Gigger soil with no-till and conventional till. Overall fit is based on model variation 4 with all C_o's.

<table>
<thead>
<tr>
<th>C_o</th>
<th>Model Variation</th>
<th>r^2</th>
<th>rms</th>
<th>k_e</th>
<th>k_1</th>
<th>k_2</th>
<th>k_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1</td>
<td>0.969</td>
<td>0.0262</td>
<td>1.4506±0.1144 0.0150±0.0023</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.978</td>
<td>0.0224</td>
<td>1.4600±0.1006</td>
<td>-</td>
<td>0.0107±0.0018 0.0027±0.0012</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.978</td>
<td>0.0225</td>
<td>1.4604±0.1010 0.0000±0.0028</td>
<td>0.0107±0.0018 0.0027±0.0012</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.979</td>
<td>0.0221</td>
<td>1.4404±0.1052</td>
<td>-</td>
<td>0.0083±0.0028 0.0067±0.0069</td>
<td>0.0034±0.0026</td>
</tr>
<tr>
<td>5.0</td>
<td>1</td>
<td>0.985</td>
<td>0.1377</td>
<td>1.9698±0.1498 0.0024±0.0004</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.991</td>
<td>0.1113</td>
<td>1.8420±0.1338</td>
<td>-</td>
<td>0.0076±0.0020 0.0043±0.0018</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.991</td>
<td>0.1120</td>
<td>1.8422±0.1350 0.0000±0.0002</td>
<td>0.0075±0.0020 0.0043±0.0018</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.992</td>
<td>0.1098</td>
<td>1.8038±0.1462</td>
<td>-</td>
<td>0.0079±0.0037 0.0109±0.0106</td>
<td>0.0017±0.0012</td>
</tr>
<tr>
<td>10.0</td>
<td>1</td>
<td>0.991</td>
<td>0.2356</td>
<td>2.1438±0.1472 0.0011±0.0002</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.996</td>
<td>0.1643</td>
<td>1.8880±0.1214</td>
<td>-</td>
<td>0.0102±0.0028 0.0095±0.0031</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.998</td>
<td>0.1546</td>
<td>1.7282±0.1424 0.0007±0.0002</td>
<td>0.0216±0.0095 0.0372±0.0183</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.998</td>
<td>0.1478</td>
<td>1.7252±0.1386</td>
<td>-</td>
<td>0.0230±0.0101 0.0406±0.0192</td>
<td>0.0014±0.0004</td>
</tr>
<tr>
<td>Overall</td>
<td>4</td>
<td>0.995</td>
<td>0.1252</td>
<td>1.8370±0.0966</td>
<td>-</td>
<td>0.0179±0.0056 0.0313±0.0114</td>
<td>0.0017±0.0008</td>
</tr>
</tbody>
</table>

(Table 2.1 continued)
<table>
<thead>
<tr>
<th>Cg (mg L⁻¹)</th>
<th>k</th>
<th>Cg (mg L⁻¹)</th>
<th>k</th>
<th>Cg (mg L⁻¹)</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1</td>
<td>0.972</td>
<td>0.0313</td>
<td>1.1418±0.1036</td>
<td>0.0067±0.0011</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.978</td>
<td>0.0281</td>
<td>1.1368±0.0962</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.978</td>
<td>0.0283</td>
<td>1.1382±0.0980</td>
<td>0.0000±0.0009</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.980</td>
<td>0.0276</td>
<td>1.1054±0.1054</td>
<td>-</td>
</tr>
<tr>
<td>5.0</td>
<td>1</td>
<td>0.980</td>
<td>0.1614</td>
<td>1.7464±0.1620</td>
<td>0.0019±0.0004</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.987</td>
<td>0.1351</td>
<td>1.5858±0.1530</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.989</td>
<td>0.1351</td>
<td>1.5066±0.1734</td>
<td>0.0010±0.0007</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.991</td>
<td>0.1287</td>
<td>1.2120±0.2928</td>
<td>-</td>
</tr>
<tr>
<td>10.0</td>
<td>1</td>
<td>0.993</td>
<td>0.2127</td>
<td>1.7266±0.1198</td>
<td>0.0011±0.0002</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.997</td>
<td>0.1407</td>
<td>1.5392±0.0914</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.997</td>
<td>0.1411</td>
<td>1.5248±0.0978</td>
<td>0.0080±0.0021</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.998</td>
<td>0.1333</td>
<td>1.5222±0.0960</td>
<td>-</td>
</tr>
<tr>
<td>Overall 4</td>
<td>1</td>
<td>0.996</td>
<td>0.1117</td>
<td>1.5078±0.0696</td>
<td>-</td>
</tr>
</tbody>
</table>

Cg is alachlor concentration in soil solution; r² is correlation coefficient; rms is the root mean square error; k_e is Freundlich distribution coefficient; k_irr is reaction rate coefficient from solution to irreversible sites S_j irr. k_1 and k_2 are forward and backward reaction rate coefficients for reversible kinetic site S_1 and k_3 is rate coefficient irreversibly transformed from sites S_1 to S_2.
Fig. 2.2 Measured alachlor concentration versus time during adsorption (closed circles) and desorption (open circles) for Gigger soil with no-till with initial concentration \( C_0 \) of 5 mg L\(^{-1} \). Desorption results followed 16, 128, 256, and 512 h of adsorption. Solid and dashed curves are fitted results using four variations of the nonlinear multireaction model.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Fig. 2.3. Experimental results of alachlor adsorption (closed circles) and desorption (open circles) in Gigger soil with no-till. Initial concentrations ($C_o$) were 1, 5 and 10 mg L$^{-1}$. The solid curves are based on individual fitting for each $C_o$ (model variation 4) and dashed curves are based on the overall set of model parameters of Table 2.1.
Fig. 2.4. Experimental results of alachlor adsorption (closed circles) and desorption (open circles) in Gigger soil with conventional tillage. Initial concentrations ($C_0$) were 1, 5 and 10 mg L$^{-1}$. The solid curves are based on individual fitting for each $C_0$ (model variation 4) and dashed curves are based on the overall set of model parameters of Table 2.1.
et al. 1990). Although model variation 4 provided the best fit, model parameters were significantly different for different C_o's. As indicated in Table 2.1, estimated k_e at C_o = 1 mg L^{-1} was significantly lower than that for higher C_o's. However, there was no significant difference in k_e values for C_o of 5 and 10 mg L^{-1} for no-till and conventional-till soils. In addition, for both soils, there was some increase in k_3 as C_o decreased, which is indicative of a high fraction of irreversible sites at low concentrations. It may be assumed that irreversible sites are surface limited. At low concentrations, alachlor was highly accessible to the irreversible sites and vice-versa. Conversely, the kinetic backward rate constants k_2 was higher at high C_o's. The overall shape of experimental and model fitted curves are flatter at the higher initial concentrations compared with lower concentrations (Figs. 2.3 and 2.4).

Based on parameter estimates given in Table 2.1 for data set I, k_e values for no-till soil were significantly higher (p=0.05) than those of conventional-till soil, regardless of initial concentrations. This finding is also consistent with the results from data set II (Table 2.2). No significant differences were found for k_1, k_2 and k_3 between the two soils. This result is consistent with the report of Locke (1992) where the Freundlich parameter K_f was found to be higher in no-till than in conventional till soils due to increased organic matter content. Locke (1992) also reported that their instantaneous adsorption coefficient (k_e) for no-till was greater than that of conventional till.

To test whether adsorption-desorption mechanisms based on model descriptions were concentration dependent, the entire data set for all C_o's was used in the nonlinear
Table 2.2. Comparison of goodness of fit of the nonlinear multireaction model (variation 4) for describing alachlor adsorption kinetics for $C_0$ of 0.5 to 50 mg/L (data set II) for Gigger soil.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>No-Till</th>
<th>Conventional-Till</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>0.608±0.028</td>
<td>0.660±0.013</td>
</tr>
<tr>
<td>$k_e$ (cm$^3$/g)</td>
<td>2.330±0.208</td>
<td>0.926±0.278</td>
</tr>
<tr>
<td>$k_1$ (h$^{-1}$)</td>
<td>0.0043±0.0030</td>
<td>0.0130±0.0090</td>
</tr>
<tr>
<td>$k_2$ (h$^{-1}$)</td>
<td>0.0059±0.0048</td>
<td>0.0137±0.0107</td>
</tr>
<tr>
<td>$k_3$ (h$^{-1}$)</td>
<td>0.0000±0.0004</td>
<td>0.0001±0.0001</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.9999</td>
<td>0.9999</td>
</tr>
<tr>
<td>rms</td>
<td>0.1415</td>
<td>0.0488</td>
</tr>
</tbody>
</table>

$C_0$ is alachlor concentration in soil solution; n is Freundlich nonlinear empirical parameter; $k_e$ is Freundlich distribution coefficient; $k_1$ and $k_2$ are forward and backward reaction rate coefficients for reversible kinetic sites $S_1$; $k_3$ is rate coefficient of irreversibly transformed from sites $S_1$ to $S_2$; $k_{irr}$ is reaction rate coefficient from solution to irreversible sites $S_{irr}$; rms is the root mean square error and $r^2$ is correlation coefficient.
least-square parameter estimation procedure. As a result, a set of model parameter estimates, hereafter referred to as the overall set of parameters, were also obtained (see Table 2.1). The dashed curves of the time dependent alachlor adsorption-desorption shown in Figs. 2.3 and 2.4, were obtained based on these overall set of parameters. There were considerable discrepancies in predicting alachlor concentrations during adsorption, especially at the low $C_0$ in both soils used in this study. The deviation was less pronounced at high $C_0$. At high $C_0$ the overall set of parameters described both adsorption and desorption versus time behavior equally well and is considered an added credence to the capability of our multireaction model. Moreover, this concentration dependent alachlor observation is consistent with that reported by Locke (1992). Senesi et al. (1994) also indicated that alachlor retention may be governed by concentration dependent adsorption mechanisms. As a result, the extent of kinetic reactions became concentration dependent. H-binding and charge-transfer processes may be irreversible and time dependent. A similar analogy may be advanced for higher concentrations.

Results of alachlor retention behavior during adsorption from data set II are shown in Figs. 2.5 and 2.6 for no-till and conventional-till soils, respectively. The solid curves shown in the Figures were obtained based on the overall set of parameters (model variation 4) and are given for both soils in Table 2.2.

Based on the goodness of fit and their statistics, adsorption results of data set II were well described by the model as illustrated by the low rms and high $r^2$s. Moreover, the use of an overall set of parameters was successful except for data from
Fig. 2.5. Experimental results of alachlor in Gigger soil with no-till and for a wide range of initial concentration ($C_0$'s). The solid curves are based on overall set of model parameters in Table 2.2.
Fig. 2.6. Experimental results of alachlor in Gigger soil with conventional tillage and for a wide range of initial concentration ($C_0$'s). The solid curves are based on overall set of model parameters in Table 2.2.
low \( C_0 \) (<1). This finding illustrates the dependence on \( C_0 \) and is consistent with our previous finding based on adsorption-desorption of data set I.

2.3.2 Alachlor Hysteresis

Adsorption-desorption results (data set I) are presented as isotherms in the traditional manner in Figs. 2.7 and 2.8. These isotherms clearly indicate considerable hysteresis in both soils. This hysteretic behavior resulting from discrepancy between adsorption and desorption isotherms was not surprising in view of the kinetic retention behavior of alachlor in our soils. Selim et al. (1976) showed that observed hysteresis in batch experiments may be explained by using a two-site equilibrium-kinetic model. They showed that lack of equilibrium conditions may be responsible for observed desorption hysteresis. It has been shown that desorption protocol (artifact) also may be a cause for such a discrepancy (Clay and Koskinen, 1990; Locke, 1992). Bowman and Sans (1985) reported that a substantial amount of observed hysteresis is caused by centrifugation of the suspension. This artifact may partially explain the discrepancy between model prediction and measured data as discussed in the next section.

Adsorption-desorption isotherms (Figs. 2.7 and 2.8) indicate that the amount of irreversible or nondesorbable phase increased with time of reaction. Alachlor may be retained by heterogeneous type sites having a wide range of binding energies. At trace alachlor concentrations, binding may be irreversible. The amount of nondesorbable herbicide almost always increased with time (Wauchope and Myers, 1985). In terms of its energy status in soils, methanol-extractable alachlor exhibited stronger interaction (H-bounding and charge transferring) with soil organic matter and clay than did water-
Fig. 2.7. Experimental and predicted alachlor adsorption-desorption isotherms for Gigger soil with no-till. The solid curves are based on overall set of model parameters (Table 2.1) and dashed curves are predictions using parameters from data set II (Table 2.2).
Fig. 2.8. Experimental and predicted alachlor adsorption-desorption isotherms for Gigger soil with conventional tillage. The solid curves are based on overall set of model parameters (Table 2.1) and dashed curves are predictions using parameters from data set II (Table 2.2).
extractable fractions. Methanol-nonextractable alachlor forms the strongest bonds in soil and is referred to as soil bound residues. Lack of complete recovery has been reported by others. For example, Helling et al., (1988) found that alachlor recovery (1 d after application) was 57% of that surface broadcasted as an emulsifiable concentrate. Bosetto et al. (1993) reported only 50% recovery was obtained after several washings in distilled water.

Decomposition may also contribute to the observed alachlor hysteresis shown in Figs. 2.7 and 2.8. Alachlor is primarily degraded microbially in soil. Degradation of alachlor and other acetanilide herbicides is a slow biological processes, and only small amounts were mineralized in surface soils (Novick et al. 1986). Microbial degradation was reported to be greater than volatilization or leaching for acetanilide herbicides (Zimdahl and Clark, 1982). Alachlor was 50 times more persistent in a sterile than in non-sterile soil (Beestman and Deming, 1974). The half-life of alachlor in a clay loam soil was reported as 18 d (Zimdahl and Clark, 1982).

2.3.3 Validation

A prerequisite for the validation of a model, such as the multireaction model proposed here, is that necessary model parameters must be estimated independently. Such a validation should be carried out prior to model adoption for prediction of retention and mobility of pesticides in the soils. This validation is also necessary for the use of a model for different soils and for a wide range of conditions. This requirement is not always achieved because independent parameters are not often available, however. As a result, evaluation of a model is sometimes restricted to goodness of fit.
of the model results to experimental measurements such as the solid curves of adsorption-desorption isotherm results of Figs. 2.7 and 2.8. In addition, efforts to describe adsorption-desorption often result in two significantly different sets of parameters; one for adsorption and another for desorption (e.g. Ma et al, 1993; Locke, 1992). In contrast, for all calculations presented in this study, only one set of model parameters was used to describe both adsorption and desorption. We are not aware of efforts to describe alachlor adsorption-desorption kinetics based on only one set of model parameters as was carried out in this study.

Validation of our proposed kinetic model is illustrated by the dashed curves shown by the isotherms of Figs 2.7 and 2.8 and the solid curves of alachlor concentration versus time for selected $C_0$'s shown in Fig. 2.9. Here all model parameters ($n$, $k_e$, $k_1$, $k_2$ and $k_3$) were obtained independently from experimental measurements (i.e., from data set II). With the exception of $\rho$ and $\theta$, initial conditions for this initial-value problem were the only input required. Based on these predictions, we can conclude that the model predicted the overall alachlor adsorption and desorption (hysteresis) behavior satisfactorily. However, predictions of desorption isotherms were not considered adequate at longer time periods. In addition, the model underpredicted experimental adsorption isotherms which directly influences subsequent predictions for the desorption isotherms. Discrepancies between experimental and predicted are expected if the amounts of alachlor in the various phases ($C$, $S_e$, $S_1$, and $S_2$) at each desorption step were significantly different. These underpredictions also may be due to the inherent assumptions of the model. Specifically, the model may not account for all
Fig. 2.9. Experimental and predicted alachlor concentration versus time during adsorption (closed circles) and desorption (open circles) for initial alachlor concentration ($C_0$) of 5 and 10 mg L$^{-1}$ for Gigger soil with no-till. The solid and dashed curves are predictions using parameters from data set II (Table 2.2).
retention or provide incomplete description of alachlor reactions in soils. In addition, we recognize that our parameter estimates were based on the nonlinear least-square procedure where high concentrations are emphasized. We also assumed that the reversible reactions had the same nonlinearity \((n=m)\). The model allows for \(n \neq m\) but we are not aware of experimental method for determining \(n\) and \(m\) independently.

Finally, based on literature review, most retention experiments were designed for adsorption measurements where desorption data were not always sought. Therefore, kinetic retention models, such as the one proposed in this study, which are capable of predicting desorption behavior of pesticides in soils based solely on adsorption parameters are of practical importance. Based on our results, the overall goodness of our model predictions, except for large desorption times, are considered adequate and provides added credence to the applicability of our proposed model approach.
CHAPTER 3

PREFERENTIAL FLOW IN SOILS FROM NO-TILL AND CONVENTIONAL TILLAGE SYSTEMS

3.1 Introduction

Preferential transport has been cited as being responsible for the rapid movement of agricultural chemicals in structured soils (Czarap et al., 1992). Because soils remain essentially undisturbed under no-till, macropores are developed and thus enhance infiltration of water (Ehlers, 1975). As a result, under undisturbed flow conditions there is a higher leaching of pesticides under no-till (Isensee et al., 1990). Dyes are widely used to stain the travel paths of water and solutes to provide direct evidence for the presence of preferential flow channels in soils.

Techniques to visualize macropores and cracks, and their capacity of transporting water and solutes have been introduced by Bouma and Dekker (1978), and Bouma et al. (1978, 1979). These often involve the application of an amount of dye solution to the soil surface. The presence of a dye, which is adsorbed on the walls of cracks and macropores, can be thus investigated. Preferential solute transport and water flow in tilled and untilled soils has been reported by Andreini and Steenhuis (1990). A blue dye was used to trace the water flow path. In no-till columns, nearly the entire depth of the profile was short-circuited by preferential flow, but in the tilled column solute passed through the mixed, unstructured plow layer.
Steenhuis et al. (1990) used dyes to identify the primary solute-transport paths and to compare the flow mechanisms under two tillage treatments. The staining pattern in the soil by the dye solutions indicated earthworm burrows were the most active flow conduits in the upper profile. Ghodrati and Jury (1990) used an anionic water-soluble dye to characterize preferential flow in field soils. The observed vertical and horizontal distribution patterns of the water-soluble dye clearly indicated preferential flow patterns under either ponding or daily sprinkler irrigation. These include vertical fingering of dye tracers 5 to 20 cm wide, extending more than twice as deep as the mean displacement, as well as isolated paths of the dye which is indicative of lateral flow. In most cases, characterization of preferential flow in soils based on tracer studies are inconclusive. This is mainly due to the inability of most solute sampling devices to detect the spatial pattern of preferential flow pathways in the soil over time.

Transport studies in soil columns have commonly been conducted with sieved, dried and repacked soil materials. The soil structure is destroyed through such a pretreatment. This shortcoming can be overcome by use of undisturbed soil columns. Solute transport studies with undisturbed soil cores have been proven to be useful in characterizing macropore flow (White et. al., 1984). Several theoretical models, including the convection-dispersion (CDE) equation (Parker and van Genuchten, 1984), mobile-immobile model (van Genuchten and Wierenga, 1976), two-region transport models (Parker and van Genuchten, 1984; Selim and Ma, 1995) and stochastic models (Bresler and Dagan, 1982) have been developed to describe one dimensional solute transport in laboratory and field conditions. Several authors found that their
experimental data could be explained equally well by a two-region model as well as by
the simple CDE model (Schulin et al., 1987), and they could not decide whether a
distinction into macropore region and micropore region was justified. Steenhuis, et al.,
(1994) proposed that solute transport consisted of preferential flow and matrix flow with
little modification through the soil channels (preferential path) to the deep soil. The
solute concentration in matrix flow obey the convective-dispersive equation.

Coats and Smith (1964) introduced a transport model to account for diffusion-
limited mass transfer into immobile soil regions and to explain the observed large
dispersion coefficients found for structured soils. By using flow interruption, the large
impact of micropore diffusion was observed and the contributions of macro- and
micropore transport mechanisms can be separated (Oren et al., 1996).

The soil can also have a distinct bimodal pore size distribution, water-filled
macropores are considered to contribute to the convective transport, whereas transport
into and out of the micropores is by diffusion only. During interruption, diffusion in
the column continues and may have induced a change of concentration in the effluent
when flow resumes. Solute transport in structural soil is therefore characterized by an
early arrival of solutes displaced through the macropores and a slow approach to the
final concentration caused by the slow diffusion within soil matrix. When modeling
flow interruption, convection is ignored and the dispersion coefficient D reduces to the
macropore diffusion coefficient, which is equal to molecular diffusion coefficient
divided by tortuosity. The experimental data needed to validate existing solute transport
models are limited and development of more refined approaches for modeling solute preferential flow is also hindered due to the lack of experimental data (Butters and Jury, 1989).

The tillage effect on tracer (such as tritium) transport properties are fundamental in understanding non-reactive solute behavior such as chloride, nitrate and other ions which are not adsorbed onto soil organic matter and clays. Different solute application methods have been investigated and the breakthrough curves (BTCs) were reported to be dependent on the pulse concentration and pulse duration (Kluitenberg and Horton, 1990). However, little work has been done to examine the effect of flow direction on preferential flow of solute in addressing the structuralization influence on solute transport. Moreover, few attempts have been made on relating the flow paths to solute BTC characterization and physical nonequilibrium solute transport of the tillage effect in undisturbed soil columns. This information is pertinent to tillage management strategies as well as to the formulation and validation of transport models describing preferential flow.

The purpose of this study was (i) to examine flow paths and preferential characteristics to determine the extent of heterogeneity of solute transport in undisturbed columns under different tillage systems; (ii) to investigate the influence of pulse duration and flow direction on tritium breakthrough in undisturbed soil columns of no-till and conventional tillage; (iii) to examine transport models for describing nonreactive solute in undisturbed soil columns.
3.2 Materials and Methods

3.2.1 Transport Experiments

A hydraulic coring device mounted on a tractor was used to obtain 15 cm acrylic cylinders (6.4 cm i.d.) of the surface undisturbed soil in two tillage systems (no-till vs. conventional tillage) of wheat (*Triticum aestivum* L.), hairy vetch (*Vicia villosa* Roth) and no winter cover, in Gigger silty loam (silt mixed thermic Typic Fragiudalf). The soil consists of 22% sand, 66% silt and 12% clay. Six treatments including no-till with wheat as a winter cover crop (NTW), no-till with hairy vetch as a winter cover crop (NTV), no-till with no winter cover crop (NNC); conventional tillage with wheat as a winter cover crop (CTW), conventional tillage with hairy vetch as a winter cover crop (CTV) and conventional tillage with no winter cover crops (CNC) were studied in duplicate. The field site was located at the LSU Agricultural Center, Macron Ridge Research Station, Winnsboro, LA, and details were described in Chapter 2.

To eliminate the wall effect, the pedestal of soil was pushed out the column, and then carved around to 3-4 mm, slightly smaller than column diameter. A large portion of pararifin wax was placed on an electric hot plate until it was fully melted (56°C), and then filled the column annulus continuously. This wax coating was only performed on 2 of 12 columns, namely NTV2 and NNC2. The undisturbed columns were assembled with end plates and were equilibrated with CO₂ for 30 minutes to improve water saturation. Each soil column was saturated with a 0.005 M CaCl₂ solution using a stainless steel pump (piston and liner of variable speed pump, QG6 RH1, Fluid Metering Inc., Oyster Bay, NY) which was adjusted for the desired velocity. After
steady flow was reached, the weights of saturated soil columns were recorded and a small tritium pulse (duration of 10 minutes) and high concentration (25.0 M Bq L\(^{-1}\), i.e., 2 \(\mu\)Ci/mL) was applied from the bottom of the column (upward). After completing the elution of the tritium pulse with 0.005 M CaCl\(_2\), the inflow tubing was switched to allow the flow direction to be reversed. To carry out this switch in flow direction from upward to downward, flow was interrupted by stopping the flow pump for a few seconds. A second small tritium pulse with the same concentration and duration was then applied, from the top to the bottom of the column (i.e., downward). After elution of the downward pulse, a long tritium pulse of about 1 pore volume with lower concentration (0.35 M Bq L\(^{-1}\), i.e., 0.028 \(\mu\)Ci/mL) was subsequently applied in the downward direction. This large pulse was thereafter eluted with 0.005 M CaCl\(_2\) solution. A 0.5 mL aliquot of effluent solution was mixed with 5 mL of cocktail in a 6 mL plastic vial, were counted using Beckman LS 7500 Liquid Scintillation Counter for counting \(\beta\) radiation of tritium.

After completing the leaching of tritium, one pore volume pulse (initial concentration of \(C_0 = 2\) g L\(^{-1}\) prepared in 0.005 M CaCl\(_2\)) of weakly reactive Eosin Yellowish dye (Eosin Y; 2\(^{'}\),4\(^{'}\),5\(^{'}\),7\(^{'}\),-Tetrabromofluorescein Disodium salt: \(C_{20}H_{6}Br_{4}Na_{2}O_{5}\), Mr691.88, color index 45380, solubility 100 g L\(^{-1}\), dark red) was applied in the upward direction. This dye was used by Selsted and Becker (1986) for reversible staining of peptides and proteins. Immediately after the termination of the upward pulse, a downward pulse (\(\approx 1.0\) \(V_o\)) of Brilliant Blue FCF, (\(C_{37}H_{38}N_{3}NaO_{9}S_{3}\), Mr787.91, color index 42090, solubility of 200 g L\(^{-1}\). \(k_d\) of 0.19, \(-5.78\) cm\(^2\) g\(^{-1}\)) with
a concentration of 2 g L\(^{-1}\) was applied to the soil column in an attempt to stain the flow path. After termination of the displacement experiments, the columns were weighed and put in a container for quick freezing with liquid N\(_2\). Columns was thereafter sectioned with an electric saw at 2 cm intervals. The stained areas in each section were photographed and drawn and the stained pattern were obtained. The dye concentration in the effluent solution were also measured for 4 soil columns (NTV2, NNC2, CTV2, and CNC2) with a spectrophotometer (HITACHI Model 100-20) at a wavelength of 630 nm for Blue FCF and 430 nm for Eosin Yellowish dye.

3.2.2 Breakthrough Curve Analysis

For non-reactive solutes, their transport through a homogeneous porous medium can be written as

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{3.1}
\]

where \(C\) is concentration (\(\mu\text{g mL}^{-3}\)), \(x\) is depth below the soil surface (cm), \(t\) is time (h), \(v\) is the average pore-water velocity (cm h\(^{-1}\)), and \(D\) is the hydrodynamic dispersion coefficient (cm\(^2\) h\(^{-1}\)) which can be expressed as (Brusseau, 1993)

\[
D = \frac{D_o}{\tau + \alpha \nu} \tag{3.2}
\]

where \(D_o\) is the molecular diffusion of solute in water (cm\(^2\) h\(^{-1}\)), \(\tau\) is tortuosity, \(\alpha\) is dispersivity (cm) and \(\nu\) is pore water velocity (cm h\(^{-1}\)).

The above equation (3.1) was subject to the initial condition

\[
C(x,0) = C_i \quad 0 < x < L \tag{3.3a}
\]
and the boundary conditions

\[ \nu C - \theta D \frac{\partial C}{\partial x} = \nu C_0; \quad x=0, \quad t<t_p \]  

(3.3b)

\[ \nu C - \theta D \frac{\partial C}{\partial x} = 0, \quad x=0, \quad t>t_p \]  

(3.3c)

\[ \frac{\partial C}{\partial x} (L,t) = 0 \]  

(3.3d)

where \( C_i \) is the initial concentration of solute in soil (mg kg\(^{-1}\) soil), \( L \) is the column length (cm), \( C_o \) is the pulse concentration (mg mL\(^{-1}\)), \( t_p \) is pulse duration (h) and \( \theta \) is soil moisture content (cm\(^3\) cm\(^{-3}\)). Equation (3.1) with boundary conditions (3.3a) to (3.3d) were solved numerically. The relative pore volume \( (T = V/V_0) \) and relative concentration \( C/C_0 \) were used to express the results of BTCs. Equation (3.1) was fitted to the breakthrough data to obtain the hydrodynamic dispersion coefficients by use of non-linear least inversion method of Parker and van Genuchten (1984).

3.2.3 Superposition of Short Pulses

For input concentration of a short pulse (with duration \( \delta \) pore volume), one can express the pulse concentration as

\[ I_j(t) = C_{oj}, \quad 0 \leq t < \delta \]

\[ = 0, \quad t \geq \delta \]  

(3.4)

where \( I_j \) is the pulse with \( C_{oj} \) as a constant concentration, and resulting relative concentration as \( C_j/C_{oj} \). For the input having \( n \) tritium pulses at \( x=0 \), each of duration
δ, then the relative concentration at the effluent (x=L) becomes

\[ \frac{C}{C_0} = \sum_{j=1}^{n} \frac{C_j(t-(j-1)\delta)}{C_{oj}} \]  

(3.5)

Since the relative effluent concentration at any time t is the result of the total pulses occurring up to that time but not subsequent to it, equation (3.5) must be modified as

\[ \frac{C}{C_0} = \sum_{j=1}^{t} \frac{C_j(t-(j-1)\delta)}{C_{oj}} \]  

(3.6)

the time t can be taken as a discrete variable taking value at δ time interval. The experimental data of short pulse with duration δ (≈ 0.015 V ω) were superimposed into duration t (≈ 1.0 V ω) to calculate the BTCs of long pulses. The principle of superposition can thus be used to characterize the behavior of soil column by unit (pulse duration δ) BTC and to predict the response BTC of an arbitrary input (pulse duration t). BTCs of long pulse were predicted with small pulse at the same experimental condition using the principle of superposition.

3.3 Results and Discussions

The experimental conditions for the transport experiments are given in Table 3.1. The pore-water velocity v, was taken as the flux (cm/h) divided by saturated moisture content θ (cm³/cm³). The saturated moisture content were higher in soil columns of no-till (≈ 0.5 cm³/cm³) compared with that of conventional tillage (≈ 0.46 cm³/cm³).
3.3.1 The Flow Paths of Undisturbed Columns

The advantage of using dyes is that one can relate observed preferential flow to structural features or macropores in soil. The stained areas and flow paths of three cross sections at 4, 8 and 12 cm below the soil surface of each column are shown in Fig 3.1. and Fig. 3.2. They indicate that there were considerable unstained areas for the no-till soils whereas the soils were somewhat uniformly stained in soils of conventional tillage. The only exception is the conventional tillage with no cover crop (replicate 2, i.e. CNC2) where significant wall effects were observed. These results revealed that water and solute was transported only through a portion of the pore space. Li and Ghodrati (1995) reported that only a small fraction of dye penetrated the soil matrix while the major fraction of dye entered through earthworm holes at the surface. In contrast, conventional tillage homogenizes and destroys part of the structure of the top soil and continuous macropores are disrupted. To characterize preferential flow in undisturbed soil columns, possible wall effects should be eliminated. Attempts were made for two columns (NTV2 and NNC2) to eliminate the wall effect. As shown in Fig. 3.1, there was no dye flow through the wall in the columns sealed by wax. It indicates the wall effect was partially eliminated therefore preferential flow paths can be more clearly demonstrated with the stained areas of the two dyes. The paths were irregular in soil of no-till. In the cross sections near the soil surface, the entire area was stained which indicate that the dye diffused and connected the flow paths; whereas for cross sections at lower depths, a discontinuous flow paths were observed which is indicative of preferential flow. Preferential paths can develop as a consequence of
Table 3.1 Experimental condition in tritium and dye transport study for soils from different tillage treatments

<table>
<thead>
<tr>
<th>Column Number</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\theta$ (cm$^3$ cm$^{-3}$)</th>
<th>v (cm h$^{-1}$)</th>
<th>Short pulse Duration</th>
<th>Long Pulse Duration</th>
<th>Eosin Y</th>
<th>Blue FCF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CTW1</td>
<td>1.47</td>
<td>0.468</td>
<td>1.33</td>
<td>0.0148</td>
<td>1.108</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>CTW2</td>
<td>1.39</td>
<td>0.475</td>
<td>0.98</td>
<td>0.0109</td>
<td>1.489</td>
<td>21.9</td>
</tr>
<tr>
<td></td>
<td>CTV1</td>
<td>1.44</td>
<td>0.462</td>
<td>1.35</td>
<td>0.0150</td>
<td>1.364</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>CTV2</td>
<td>1.47</td>
<td>0.496</td>
<td>0.94</td>
<td>0.0105</td>
<td>1.331</td>
<td>21.1</td>
</tr>
<tr>
<td></td>
<td>CNC1</td>
<td>1.45</td>
<td>0.457</td>
<td>1.36</td>
<td>0.0151</td>
<td>1.125</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>CNC2</td>
<td>1.46</td>
<td>0.464</td>
<td>1.00</td>
<td>0.0110</td>
<td>1.339</td>
<td>20.7</td>
</tr>
<tr>
<td></td>
<td>NTW1</td>
<td>1.40</td>
<td>0.509</td>
<td>1.21</td>
<td>0.0134</td>
<td>1.348</td>
<td>21.3</td>
</tr>
<tr>
<td></td>
<td>NTW2</td>
<td>1.43</td>
<td>0.495</td>
<td>0.94</td>
<td>0.0100</td>
<td>1.654</td>
<td>25.1</td>
</tr>
<tr>
<td></td>
<td>NTV1</td>
<td>1.41</td>
<td>0.507</td>
<td>1.22</td>
<td>0.0136</td>
<td>1.646</td>
<td>25.1</td>
</tr>
<tr>
<td></td>
<td>NTV2#</td>
<td>1.43</td>
<td>0.503</td>
<td>1.08</td>
<td>0.0133</td>
<td>0.699</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>NNC1</td>
<td>1.42</td>
<td>0.501</td>
<td>1.23</td>
<td>0.0137</td>
<td>1.025</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>NNC2</td>
<td>1.40</td>
<td>0.510</td>
<td>1.22</td>
<td>0.0137</td>
<td>1.434</td>
<td>18.0</td>
</tr>
</tbody>
</table>

$^+$CNC, conventional tillage-no cover; CTV, conventional tillage-vetch; CTW, conventional tillage-wheat; NNC, no-till-no cover; NTV, no-till-vetch; NTW, no-till-wageat. $\rho$ is bulk density of soil (g cm$^{-3}$); $\theta$ is soil moisture content (cm$^3$ cm$^{-3}$); v is pore water velocity (cm h$^{-1}$); V/V$_o$ is pore volumes of pulse duration; t$_p$ is the time of pulse duration. NTV2# is the column with flow interruption.

$^@$ Retardation factor was set to 1.0 in fitting tritium BTCs.

$^\S$ 10 min duration of tritium input; $^\S$ 15 hours duration for dye input.

$^{\S\S}$ R = fitted retardation factor (see solid and dashed lines of Fig. 3.3)
The stained areas by red and blue dyes for undisturbed soils from no-till with wheat (NTW2), vetch (NTV2) and no winter cover crop (NNC2) at 4, 8 and 12 cm depth below the soil surface.
The stained areas by red and blue dyes for undisturbed soils from conventional tillage with wheat (CTW2), vetch (CTV2) and no winter cover crop (CNC2) at 4, 8 and 12 cm depth below the soil surface.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Fig. 3.3 The BTCs of dye transport in undisturbed columns of (a) no-till with vetch as a winter cover crop (NTV2); (b) no-till with no winter cover crops (NNC2); (c) conventional tillage with vetch as a winter cover crop (CTV2) and (d) conventional tillage with no winter cover crop (CNC2).
Fig. 3.4  Short pulse BTCs of tritium in undisturbed soil columns of (a) and (b) no-till; (c) and (d) conventional tillage with wheat as a winter cover crop.
Fig. 3.5  Short pulse BTCs of tritium in soil columns of (a) and (b) no-till, (c) and (d) conventional tillage with vetch as a winter cover crop.
Fig. 3.6 Short pulse BTCs of tritium in soil columns of (a) and (b) no-till, (c) and (d) conventional tillage with no winter cover crop.
Fig. 3.7 Long pulse BTCs of tritium in soil columns of (a) and (b) no-till, (c) and (d) conventional tillage with wheat as a winter cover crop.
Fig. 3.8  Long pulse BTCs of tritium in soil columns of (a) and (b) no-till, (c) and (d) conventional tillage with vetch as a winter cover crop.
Fig. 3.9  Long pulse BTCs curves of tritium in soil column of (a) and (b) no-till, (c) and (d) conventional tillage column with no winter cover crop.
Fig. 3.10  Modeling long pulse BTCs of tritium in soil column of (a) no-till with wheat as a winter cover crop, (b) no-till with vetch as a winter cover crop and (c) no-till with no cover crop with three models (CDE, MIM and SM).
abandoned root channels, burrows and fissures. On a very local scale, pore spaces between soil structure peds may also be preferential flow paths.

The breakthrough curves of dyes are shown in Fig. 3.3. There was a higher concentration of dyes in effluent of no-till than that of conventional tillage, which can be explained by the flow paths stained in Fig. 3.1 and Fig. 3.2. The fitted parameters R is given in Table 3.1 and it ranged from 1.3 to 2.35 for both dyes in 4 columns where the BTCs of dyes were measured. This indicated the dyes were retarded by the soils. Flury and Flühler (1995) reported the retardation was 1.2 for Brilliant Blue FCF compared with Iodide. Andreini and Steenhuis (1990) found retardation factor of Brilliant Blue FCF ranged from 1.5 to 7 in soil columns of a fine sandy loam.

3.3.2 BTC Characteristics of Tritium

As shown from Fig. 3.4a to Fig. 3.9d, the breakthrough times were earlier in soil columns of no-till than that of conventional tillage in all cover crops. One exception was found in soil of conventional tillage with no cover (CNC2), where significant wall effect was observed (Fig. 3.2) and an early (0.2 V₀) tritium breakthrough was detected in effluent. The tritium was detected after only 0.2 V₀ following application in soils of no-till. In contrast, the tritium was detected after 0.4 V₀ for the conventional tillage. All results consistently indicated no-till reduced breakthrough time. Singh and Kanwar (1991) proposed the existence of rapid flow through macropores if the pore volume reaches 0.5 relative concentration (C/C₀) in the effluent was well before one pore volume. Based on this criterion, preferential flow were dominant in all soil columns of no-till. In addition to an early breakthrough, a sudden jump to peak concentrations was
followed by a precipitous drop to low concentration in all soil columns of no-till. These characteristics are similar to that of soils with earth worm holes as reported by Li and Ghodrati (1995).

Some BTCs in short pulse from no-till columns showed double or bimodal peaks in both upward and downward flow (Figs 3.4a, 3.5a, 3.6a and 3.6b). These bimodal peaks were independent of the direction of flow. This is an indication of the intrinsic preferential flow paths in the undisturbed soil columns. The first peak is perhaps caused by macropores and the second by the less permeable matrix-pore system. BTCs under preferential flow conditions show consistently early breakthrough of solutes with bimodal concentration peaks in other studies (Butters and Jury, 1989; Hornberger et al., 1990; Jury et al., 1986). Several investigators attributed preferential flow and bimodal peaks to flow heterogeneities in soils (Ma and Selim, 1994; Skopp et al., 1981; Hornberger et al., 1990). Observed double peaks may be attributed to the presence of multiple flow domains in some soils (Skopp et al., 1981), although chemical heterogeneities with reaction sites of different mass transfer rates and thus various breakthrough time can also lead to double peaks (Villermanx, 1974). This is not the case in this study since tritium is considered a non-reactive tracer. In soil with two distinct flow domains, there may be two separate or distinct BTCs. One has shorter travel time (preferential flow path), and another has a longer travel time. Ward et al., (1994) reported bimodal BTCs at three different values of fluxes. As flux decreased, the relative amount of solute associated with the slow peak of the BTC increased, while the time to first arrival of solute increased.
All BTCs in column of no-till showed some degree of tailing of the desorption (elution) side (Figs. 3.4 - 3.8). Such tailing or asymmetry has been postulated by van Genuchten and Wierenga (1976) to be due to the presence of immobile water. Convective solute transport in these models was assumed to occur only in the mobile soils water region, while adsorption in a stagnant region of the soil which is controlled by diffusion through the immobile (non-moving) fraction of the soil-water region. Extreme tailing under saturated condition, is an indication of cracks, or macropores in soil. Solute transport between mobile (flowing) and immobile (stagnant) soil-water regions is diffusion controlled. Thus excessive tailing and asymmetry indicate possible existence of nonequilibrium mass exchange between regions of different mobilities. Unlike the BTCs of soils from no-till, the BTCs of soils from conventional tillage (Figs. 3.4 - 3.9) were relatively symmetric, indicating little or no preferential flow was taking place in these columns. For the no-till with vetch as a winter cover crop in replicate 2 (NTV2) shown in Fig. 3.8b, two flow interruptions were carried out during tritium transport experiments. One is during the tritium pulse input (0.7 V_o), and another was during leaching or elution at 2.7 V_o. There was no concentration change due to flow interruption, which is consistent with the results of Koch and Flüeler (1993) in packed porous beads. These observations contrasts to that of Oren et al. (1996) where a significant change of outflow concentration was observed when flow was interrupted in undisturbed soil columns. Both diffusion in macropores and diffusion into micropores may explain the change, but the two processes may compensate each other if the transfer in each direction is equal each other. The influence of the two diffusion
processes depend on the concentration gradients and the mass transfer coefficient between macro and micropores.

To further examine the flow characteristics in the undisturbed columns of no-till and conventional tillage, BTCs of the short pulse were used to predict the BTCs of long pulse at the same experimental condition using principle of superposition (Ma and Selim, 1994). The predicted results are shown by dash curves in Fig. 3.7 - 3.9. These BTCs were calculated using equation (3.7) by a repeated summation of several successive short pulse BTCs until the desired pulse duration was achieved. The superimposed BTCs were consistent with observed BTCs of the long pulse (Figs. 3.7 - 3.8). Such predictions of measured results are confirmation of the intrinsic nature of the flow paths in the soil columns. Poor predictions for the two replications from no-till with wheat cover crop (NTW1 and NTW2 of Fig 3.7) may be attributed to possible changes in the flow paths during transport. Possible changes in the flow paths during transport may have occurred in the column with cracks and channels as a result of structural changes. Water-unstable aggregates may cause a change in flow paths due to their collapse during water saturation. Additionally, macropore geometry may change with time.

The direction of flow (i.e., upward or downward) influenced the shape of tritium breakthrough results as shown in Figs. 3.4 -3.6. The BTCs in soils of no-till were distinctly different for each flow direction, which may be due to the structuralization of soil of no-till. The direction of flow had little effect on tritium breakthrough in the soils of the conventional tillage. The only exception is that of conventional tillage with
no winter cover crops (Fig. 3.6c). Conventional tillage homogenizes and destroys part of the structure of the topsoil and continuous macropores are disrupted. Furthermore, we are not aware of previous studies where upward versus downward flow was investigated for various soils from no-till and conventional tillage.

3.3.3 Modeling BTCs of Tritium

As shown from Fig. 3.4 - Fig. 3.9, the CDE (equation 3.1) adequately described the tritium BTCs in soils under conventional tillage. The CDE did not adequately describe the experimental data of soils from no-till, especially for the short pulse (Figs 3.4a, 3.5a, 3.6a and 3.6b). This inadequacy is expected because the CDE (equation 3.1) is based on assumption of homogeneous pore distribution. However, the model description was improved for the long pulse (Figs 3.7a, 3.8a and 3.9a). As indicated by dye staining, the soil columns from no-till was heterogenous.

It is perhaps conceivable to describe such BTCs based on two region or two domain flow approaches (Skopp et al., 1981), mobile and immobile model (MIM) as proposed by van Genuchten and Wierenga (1976) and stochastic model (SM) as proposed by Bresler and Dagan (1982). To test the physical nonequilibrium models in describing tritium BTCs in undisturbed soil columns, the MIM and SM models of Parker and van Genuchten (1984) were used to describe the long pulse BTCs of soils from no-till (Fig 3.10). There was no improvement in data description. The same result was reported by Hiroshi et al., (1994) where the BTCs of bromide were not adequately described by either CDE or MIM models. Increasing the number of model parameters created more uncertainty of parameter estimation. Li and Ghodrati (1995) did not obtain
a satisfactory fitting when using CDE, MIM, and SM for NO$_3^-$ transport in soil columns with earthworm macropores. They concluded that MIM did not seem to apply to solute transport in soil columns containing earthworm macropores and the partition of soil water into mobile and immobile is not sufficient to account for the range of pore water velocities encountered. In addition, the CDE, MIM and SM could not describe the double peaks of BTCs. Skopp et al. (1981) proposed a two-domain transport model to explain early breakthrough and bimodal peaks in solute transport. Another alternative is use a stochastic model (or transfer function model) to predict the bimodal BTCs by superposition of two probability density function. Utermann et al. (1990) successfully predicted double peaks using a bimodal probability density function.

3.4 Conclusions

The dye study indicated that the heterogeneous solute transport which characterized the preferential flow in undisturbed soil columns from no-till with earlier breakthrough time, longer tailing, and double peaks, compared with the BTCs from undisturbed soil columns of conventional tillage. Such observations implies that preferential flow was pronounced and thus enhanced the transport of non-reactive solute in soils of no-till compared to that of conventional tillage. The flow direction altered shape of tritium BTCs which is indicative to structural formation for the no-till. Double peaks were observed for short pulses whereas excessive tailing was observed for the long pulse in soil of no-till, suggesting that the double peak effect was integrated with pulse duration. The direction and the pulse duration had little influence on tritium BTCs in soil of conventional tillage. The consistency between the experimental data and
the prediction of BTCs of long pulse using superposition from short pulse experimental data can be used as a confirmation in the flow paths of soil columns. The preferential flow in undisturbed soil columns may be attributed to macropores and cracks between aggregates. The CDE for BTCs of soil columns from no-till where preferential flow is pronounced, may not be strictly applicable, especially for the pulse of high concentration and short duration. Mobile-immobile transport model (MIM) and stochastic model (SM) did not improve the fitting. Thus at present we are not aware of modeling approaches that can predict solute transport in the no-till soils which displayed preferential characteristics.
CHAPTER 4

MODELING ALACHLOR TRANSPORT IN SATURATED SOIL FROM NO-TILL AND CONVENTIONAL TILLAGE SYSTEMS

4.1 Introduction

Alachlor, a pre-emergence herbicide, is one of most commonly used soil-active herbicides. It has been extensively used to control annual grasses and certain broad leaf weeds in corn, cotton, soybean and sugarcane fields. About 37 million kilograms of alachlor are produced annually in the USA (Chesters et al., 1989). According to the criteria of Green and Karickhoff (1990), alachlor is a nonionizable, moderately nonpolar compound. It has water solubility of 148-242 mg L$^{-1}$ at 25°C, and field half life of 14-49 days (Wauchope et al. 1992). It has been considered a human carcinogen (U.S. EPA, 1989). Because of groundwater contamination and possible health effects, EPA proposed zero μg L$^{-1}$ for alachlor as a Maximum Contaminant Level Goal (U.S. EPA, 1989). But so far, alachlor have been detected in ground water in many states including Iowa, Pennsylvania, Maryland, Nebraska, and Minnesota etc. (Cohen, 1992).

Preferential transport has been cited as being responsible for the rapid movement of agricultural chemicals (Czapar et al., 1992). Preferential solute transport and water flow in tilled and untilled soils has been reported by Andreini and Steenhuis (1990). The authors used grid lysimeters to separate the water flowing through undisturbed soil columns from conventional and conservation tillage systems both temporally and spatially. They found that dye flow pathways led to areas where water and solutes exited the columns. In the no-till column, nearly the entire depth of the profile was
short-circuited by preferential flow; but in the tilled column, dye passed uniformly through the mixed, unstructured plow layer. Watson and Luxmoore (1986) found < 1% of the soil volume was used in the transport of 96% of water flux in a forest soil. Because of preferential flow, Isensee et al. (1990) detected alachlor in shallow groundwater shortly after application in soil of no-till.

Although the formation of macropores and preferential flow may increase the potential for herbicide leaching through the vadose zone, changes in the soil chemical properties may enhance herbicide retention in the surface horizons of no-till soils, thus, higher concentration of the herbicides occurred in the leachates of conventional than no-till soils (Levanon et al., 1993). Adsorption reactions play a large role in the fate of alachlor transport under different tillage systems. Increased sorption to soil organic carbon may reduce leaching. Sorption provides a mean to quantify and characterize the potential for alachlor binding and mobility in soil. No-till was reported to increase organic carbon content and thus increase cation exchange capacity (Lal, et al., 1994). Cover crop was reported to influence the soil organic carbon content and clover cover caused significantly higher soil C levels compared with fallow, even after 1 year (Kumwenda, et al., 1993). However, the greater amount of crop residue in the conservation tillage systems did not appear to affect the amount of alachlor retained on the soil or its dissipation rate (Gaynor et al., 1987). Soil organic matter content is a major factor for alachlor adsorption, and appears to occur primarily on the humic acid and fulvic acid and to a lesser extent on clay colloids (Chesters et al., 1989). By studying infrared spectra of free alachlor and herbicide-clay complexes, Bosetto et al.
(1993) concluded that alachlor is adsorbed on homoionic montmorillonite by coordination bond, through a water bridge, between the \( \text{C}=\text{O} \) group and the exchangeable cation of the clay. Senesi et al., (1994) studied the infrared spectra of pure alachlor and adsorbed alachlor and indicated the interaction occurred between \( \text{C}=\text{O} \) and \( \text{C-} \text{N} \) group by H-bound formation. Generally, the retention of alachlor in soil has been described by either (instantaneous) equilibrium (Locke, 1992) or kinetic reactions whereby concentrations in solution and sorbed phases vary with time (Xue and Selim, 1995).

There are limited data and contradictory conclusions regarding the fate of agrochemicals and their transport in soils under different tillage systems (Levanon, 1993). The influence of tillage and cover crops on alachlor mobility are not well understood. There is also a lack of knowledge of the mechanisms involved in rapid transport processes of adsorbing chemicals. In alachlor investigations, the increased demand for quantitative data has acted as a stimulant to the use of computational models. These are needed to give the behavioral pattern of a toxicological value. A minimum requirement of the model is that it must predict the concentration of alachlor as a function of time and depth in the soil profile. The objectives of this study were (i) to investigate alachlor mobility in soils of different tillage and cover crops based on adsorption kinetics and (ii) to determine the influence of tillage and winter cover crops on alachlor mobility based on transport characteristics and parameters of breakthrough results.
4.2 Materials and Methods

A long-term study was initiated at LSU Agricultural Center, Macron Ridge Station, Winnsboro, LA, in the Fall of 1986 to study the effects of several tillage systems and winter cover crops on cotton (*Gossypium hirsutum* L.) cultivation. The soil was a Gigger silt loam (fine silty, mixed, thermic Typic Fragiudalf). Among these, six treatments were chosen for this study. We focused our investigation on conventional and no-till tillage systems under three winter cover crop treatments namely; wheat (*Triticum aestivum* L.), hairy vetch (*Vicia villosa* Roth) and no cover crop.

4.2.1 Batch Experiments

Surface soil samples from six treatments were taken and passed through a 2 mm sieve. Adsorption of alachlor in all surface soils were carried out using kinetic batch methods. Alachlor adsorption experiments were commenced by mixing 10 g of soil and 20 mL of different alachlor solutions in Teflon centrifuge tubes. Eight initial alachlor concentrations (0.5, 1, 2, 5, 10, 20, 30 and 50 μg mL⁻¹) were used and four reaction times (1, 2, 5, and 22 day) were studied in duplicates. At the end of each reaction time, the samples were centrifuged for 10 minutes at 5000 rpm, the supernatants were withdrawn, and filtered for analysis.

4.2.2 Miscible Displacement experiments

A Giddings hydraulic coring device mounted on a tractor was used to obtain undisturbed soil column of 15 cm acrylic cylinders (6.4 cm i.d.) from the six treatments. The acrylic cylinders were pushed into soil and then were carefully lifted from the ground and the excess soil in the bottom of the cylinder was shaved off. The
columns were used for saturated flow experiments and direct parameter estimation. The undisturbed columns were carefully assembled with glass beads on the soil surfaces to ensure contact with both ends of column. The flow parts were connected with Teflon tubes. The soil columns were firstly equilibrated with CO₂ for 30 minute to replace the air trapped in soils; then the columns were saturated using a 0.005 M CaCl₂ solution by adjusting the stainless pump (piston and liner of variable speed pump, QG6 RH1, Fluid Metering Inc., Oyster Bay, NY) to a desired velocity until a steady flow velocity was reached. One pore volume (V₀) tritium pulse of 1.0 M Bq L⁻¹ (0.028 μCi mL⁻¹), followed by about 6 pore volume alachlor (10 mg L⁻¹ in 0.005 M CaCl₂) were applied and then leached with 0.005 M CaCl₂ solution for about 20 V₀s. A 0.5 mL aliquot of the supernatant was mixed with 5 mL of "ULTIMA GOLD" cocktail was mixed in a 6 mL plastic vial. The β radiation of tritium was measured by liquid scintillation counter (Beckman LS 7500 Liquid Scintillation Counter). Alachlor concentration was determined by high performance liquid chromatograph (HPLC) using a UV detector at a wavelength of 220 nm. A Supeclco LC-18 reversed column (25 cm x 4 mm i.d.) was used with 70:30 acetonitrile:water as the mobile phase at a flow rate of 1 mL min⁻¹. The lower detection limit for alachlor was 5 μg L⁻¹. The breakthrough curve (BTC) were expressed as relative concentration C/C₀ vs. number of pore volumes (T=V/V₀).

4.2.3 Equilibrium Retention Modelling

Linear and Freundlich models are the most widely used model for describing herbicide adsorption. In the linear model
where $S$ is adsorption (µg g$^{-1}$ soil), $k_d$ is the concentration-independent distribution constant (cm$^3$ g$^{-1}$) and $C$ is the concentration at equilibrium (mg L$^{-1}$). The partitioning coefficient of organic matter was calculated as

$$k_{oc} = 100k_d/OC\%$$

(4.2)

where OC\% is the soil organic carbon content expressed as a percent of the soil mass.

In the Freundlich model

$$S = k_f C^N$$

(4.3)

where $N$ is nonlinear equilibrium parameter. $k_f$ is Freundlich distribution constant (cm$^3$ g$^{-1}$), $C$ and $S$ are as defined in linear model.

The adjusted $r^2$ ($r_{adj}^2$) were used to test the goodness-of-fit of models and was calculated as

$$r_{adj}^2 = 1 - \frac{(n-1)(1-r^2)}{(n-p)}$$

(4.4)

where $n$ is the sample size and $p$ is the number of parameters in the model. $r$ is correlation coefficient.

The adsorption data for one day and 22 day were fitted using the NONLIN procedure of SAS (1985) to obtain equilibrium parameters of linear and Freundlich models.
4.2.4 Multireaction Modeling

The following multireaction model was presented by Selim (1992),

\[ S_e = k_e C^N \]  \hspace{1cm} (4.5)

\[ \frac{\partial S_1}{\partial t} = k_1 \frac{\theta}{\rho} C^N - k_2 S_1 - k_3 S_1 \]  \hspace{1cm} (4.6)

\[ \frac{\partial S_2}{\partial t} = k_3 S_1 \]  \hspace{1cm} (4.7)

\[ S_T = S_e + S_1 + S_2 \]  \hspace{1cm} (4.8)

where \( C \) is the solute in soil solution (mg L\(^{-1}\)), \( \rho \) is the soil bulk density (g cm\(^{-3}\)), \( \theta \) is the water content (cm\(^3\) cm\(^{-3}\)), \( t \) is the reaction time in hour, \( k_e \) is distribution constant (g cm\(^{-3}\)), \( k_1, k_2 \) and \( k_3 \) are associated rate coefficient (hr\(^{-1}\)), \( S_e \) is the amount retained by equilibrium sites, \( S_1 \) is the amount retained by kinetic sites, \( S_2 \) represented amount retained by irreversible sites and \( S_T \) is the total amount of solute retained by the soil matrix (\( \mu g \) g\(^{-1}\) soil). The parameter \( N \) was obtained from fitting adsorption data after 22 days of reaction using the Freundlich equilibrium equation (4.5). The above reactions (4.5-4.8) represent initial-value problems that were solved numerically using finite-difference approximations.

4.2.5 Multireaction Transport Modeling

The BTCs for reactive solutes are usually described using the convective-dispersive transport equation (Selim, 1992)
where $D$ (cm$^2$ h$^{-1}$) is hydrodynamic dispersion coefficient as expressed by Brusseau (1993):

$$D = \frac{D_0}{\tau} + \alpha \nu$$  (4.10)

where $D_0$ is the diffusion in water (cm$^2$ h$^{-1}$), $\tau$ is tortuosity (dimensionless), $\alpha$ is dispersivity (cm) and $\nu$ is pore water velocity (cm h$^{-1}$), $\rho$ is bulk density (g cm$^{-3}$), $\theta$ is volumetric saturated moisture content (cm$^3$ cm$^{-3}$), $S$ is concentration of the solute in the adsorbed phase ($\mu g$ g$^{-1}$ soil), $C$ is the solute concentration in the liquid phase ($\mu g$ mL$^{-1}$), and $z$ is depth (cm).

The initial condition used was

$$C(x,0) = C_i \quad 0<x<L$$  (4.11a)

and the boundary conditions were

$$\nu C - \theta D \frac{\partial C}{\partial x} = \rho C_0; \quad x=0, \quad t<t_p$$  (4.11b)

$$\nu C - \theta D \frac{\partial C}{\partial x} = 0, \quad x=0, \quad t>t_p$$  (4.11c)

$$\frac{\partial C}{\partial x}(L,t)=0$$  (4.11d)

where $C_i$ is the initial concentration of solute in soil (mg kg$^{-1}$ soil), $L$ is the column length (cm), $C_0$ is the pulse concentration (mg L$^{-1}$), $t_p$ is pulse duration (hrs).
Dispersion coefficients was estimated based on tritium BTC data using nonlinear least-squares inversion methods (Parker and van Genuchten, 1984). The above equations were solved using explicit-implicit finite difference approximations.

4.3 Results and Discussions

4.3.1 Soil Properties

Selected soil properties for the surface soil from different tillage systems are showed in Table 4.1. The average organic matter content was 1.37±0.439 in soils of no-till and 0.96±0.348 in that of conventional tillage. There was a significant (p=0.05) difference using t-test, which indicated no-till increased organic matter content. It is consistent with the report of Lal et. al. (1994). However, the soil pH was not affected by tillage which is consistent with report of Lal et. al. (1994).

4.3.2 Modeling Alachlor Adsorption

The goodness-of-fit for the linear and Freundlich equilibrium model after one day and 22 day adsorption are listed in Table 4.2. In all tillages and cover crops, the \( r^2_{adj} \) were higher for Freundlich model compared with the linear model especially for the 22 day adsorption. For all soils studied, the nonlinear parameter N of Freundlich model varied from 0.6532 to 0.9353. That N was less than unity indicated availability of sorption sites decreased as initial concentration increased. The Freundlich model accounts in a certain way for surface heterogeneity. The alachlor adsorption isotherm under no-till and conventional tillage under wheat as a cover crop is shown in Fig. 4.1. It is obvious that Freundlich model improved the fitting of the data compared with the linear model.
Table 4.1 Selected soil properties for the surface soils from different tillage and winter cover crops

<table>
<thead>
<tr>
<th>Sample§</th>
<th>Organic matter content</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>CTW</td>
<td>0.81</td>
<td>4.7</td>
</tr>
<tr>
<td>CTV</td>
<td>0.98</td>
<td>4.9</td>
</tr>
<tr>
<td>CNC</td>
<td>1.09</td>
<td>4.2</td>
</tr>
<tr>
<td>Conventional Tillage</td>
<td>0.96*</td>
<td>4.6</td>
</tr>
<tr>
<td>NTW</td>
<td>1.45</td>
<td>5.7</td>
</tr>
<tr>
<td>NTV</td>
<td>1.48</td>
<td>4.4</td>
</tr>
<tr>
<td>NNC</td>
<td>1.16</td>
<td>5.5</td>
</tr>
<tr>
<td>No-Till</td>
<td>1.36*</td>
<td>5.2</td>
</tr>
<tr>
<td>t</td>
<td>3.093*</td>
<td>1.32</td>
</tr>
<tr>
<td>t (p=0.05, n=4)</td>
<td>2.776</td>
<td>2.776</td>
</tr>
</tbody>
</table>

§ CTW, conventional tillage-wheat; CTV, conventional tillage-vetch; CNC, conventional tillage-no cover; NTW, no-till-wheat; NTV, no-till-vetch; NNC, no-till-no cover.

* These values are significantly different at the 0.05 level using t-test.
Table 4.2. The goodness-of-fit and parameters of equilibrium and multireaction model in fitting alachlor adsorption in soils of no-till and conventional tillage under different cover crops.

<table>
<thead>
<tr>
<th>Sample §</th>
<th>1 day—</th>
<th>22 day—</th>
<th>Kinetic—</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Linear)</td>
<td>(Freundlich)</td>
<td>(Linear)</td>
</tr>
<tr>
<td>CTW</td>
<td>r_{adj}</td>
<td>k_f</td>
<td>N</td>
</tr>
<tr>
<td>CTV</td>
<td>0.959</td>
<td>1.04</td>
<td>0.763</td>
</tr>
<tr>
<td>CNC</td>
<td>0.997</td>
<td>0.50</td>
<td>0.935</td>
</tr>
<tr>
<td>NTW</td>
<td>0.975</td>
<td>0.99</td>
<td>0.834</td>
</tr>
<tr>
<td>NTV</td>
<td>0.980</td>
<td>1.64</td>
<td>0.796</td>
</tr>
<tr>
<td>NNC</td>
<td>0.988</td>
<td>1.74</td>
<td>0.853</td>
</tr>
</tbody>
</table>

§ CTW, conventional tillage-wheat; CTV, conventional tillage-vetch; CNC, conventional tillage-no cover; NTW, no-till-wheat; NTV, no-till-vetch; NNC, no-till-no cover.
Fig. 4.1 Alachlor adsorption isotherms for (a) one day adsorption and (b) 22 day adsorption of soils from no-till (NTW) and conventional tillage (CTW).
The fit of the multireaction model (MRM) to the batch results of a wide range of initial concentrations ($C_0 = 0.5 - 50\ \text{mg L}^{-1}$) was achieved using the four parameter model ($k_s, k_1, k_2$ and $k_3$) consisting of one equilibrium reaction, one reversible reaction and one irreversible reaction. The goodness-of-fit for MRM are listed Table 4.2. For all soils, the $r^2_{adj}$ were higher than respective equilibrium models in soils of all tillages and cover crops, which indicated that multireaction model improved the fitting compared equilibrium models, especially for long adsorption times. Model parameters for MRM are listed in Table 4.3. The nonlinear parameter $N$ in equation was based on the equilibrium Freundlich parameter $N$ of 22 days (Table 4.2). Concentration as a function of time for no-till and conventional tillage under different cover crops are presented from Fig. 4.2 to Fig. 4.4 for various $C_0$s. Retention of alachlor by soil was rapid during initial stages of reaction and was then followed by slow and continuous alachlor retention. The solid lines are model fitting using MRM. The reversible kinetic reaction constants $k_1$ and $k_2$ were significantly different from zero except in soil of conventional tillage of vetch as winter cover crop. Slow diffusion to sites within the soil/organic matrix probably contributed to the apparent nonequilibrium behavior.

4.3.3 The Tillage Effect on Alachlor Adsorption

The overall contribution from both organic and inorganic sorbents is often described with a distribution coefficient of herbicide partitioning between solution and solid phase ($k_d$). As showed in Table 4.3, the equilibrium constant $k_d$, in all soils of no-till were significantly ($p=0.05$) higher than that of soils from respective conventional
Fig. 4.2  Alachlor concentration as a function of time for (a), no-till and (b) conventional tillage of wheat as a winter cover. All symbols represented measured concentration and all lines represented fitted concentration.
Fig. 4.3 Alachlor concentration as a function of time for (a), no-till and (b) conventional tillage of vetch as a winter cover. All symbols represented measured values and all lines represented fitted values respectively.
Fig. 4.4 Alachlor concentration as a function of time for (a), no-till and (b) conventional tillage of no winter cover. All symbols represented measured concentration and all lines represented fitted concentrations.
tillage. There were no significant differences within the same tillage, under different cover crops. As shown in Table 4.3, the equilibrium adsorption constants $k_e$ of the multireaction model in all no-till treatments were significantly ($p=0.05$) higher than that of conventional tillages. There was no clear trend on $k_e$ by winter cover crops. The influence of tillage and winter cover crop on kinetic parameters $k_1$ and $k_2$ were not consistent. The irreversible reaction constant $k_3$ were relatively small and there was no consistent trend on tillage and winter cover crops. The no-till increased alachlor adsorption can be clearly illustrated by $C$ vs. time in Fig. 4.2, Fig.4.3 and Fig.4.4, where alachlor concentration were lower in soils of no-till than that of the respective conventional tillage in all cover crops and different concentrations.

Alachlor sorption has been associated with both hydrophilic and lipophilic (hydrophobic) soil components and thus can be characterized by sorption per unit of organic carbon ($k_{oc}$, Locke, 1992). As shown in Table 4.3, the $k_{oc}$ was relatively stable compared with $k_4$ in soils of both no-till and conventional tillages. No-till increased the $k_{oc}$ in vetch and no cover crops compared with conventional tillage. There were no significant difference in $k_{oc}$ between no-till and conventional tillage with wheat as the cover crop. Therefore no consistent influence on $k_{oc}$ was resulted from tillage treatments. This indicated that increases in organic matter content and/or changes in its composition contributed to increasing alachlor adsorption. As shown in Table 4.3, $k_{oc}$ was variable and ranging from 90.6 to 143.4 for the soils studied.

The $k_{oc}$ characterizes partitioning between aqueous solution and organic phases in soil, but does not take into account composition characteristics of the organic phase,
Table 4.3 Equilibrium and kinetic parameters for different tillages and winter cover crops in batch experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_d$</th>
<th>$k_{oc}$</th>
<th>$k_e$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm$^3$ g$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTW</td>
<td>0.47±0.06</td>
<td>99.2±9.2</td>
<td>0.926±0.278</td>
<td>0.0130±0.0090</td>
<td>0.0137±0.0107</td>
<td>0.0001±0.0001</td>
</tr>
<tr>
<td>CTV</td>
<td>0.55±0.02</td>
<td>95.3±3.1</td>
<td>0.896±0.312</td>
<td>0.0022±0.0088</td>
<td>0.0160±0.0404</td>
<td>0.0002±0.0001</td>
</tr>
<tr>
<td>CNC</td>
<td>0.57±0.06</td>
<td>90.6±9.2</td>
<td>0.638±0.602</td>
<td>0.0318±0.0171</td>
<td>0.0693±0.0235</td>
<td>0.0001±0.0001</td>
</tr>
<tr>
<td>NTW</td>
<td>0.92±0.08</td>
<td>109.6±9.9</td>
<td>2.330±0.208</td>
<td>0.0043±0.0030</td>
<td>0.0059±0.0048</td>
<td>0.0000±0.0004</td>
</tr>
<tr>
<td>NTV</td>
<td>1.10±0.07</td>
<td>129.7±8.5</td>
<td>1.784±0.146</td>
<td>0.0034±0.0027</td>
<td>0.0162±0.0175</td>
<td>0.0004±0.0002</td>
</tr>
<tr>
<td>NNC</td>
<td>0.96±0.12</td>
<td>143.4±7.1</td>
<td>2.480±0.582</td>
<td>0.0087±0.0071</td>
<td>0.0448±0.0290</td>
<td>0.0001±0.0001</td>
</tr>
</tbody>
</table>

$^\dagger$ CTW, conventional tillage-wheat; CTV, conventional tillage-vetch; CNC, conventional tillage-no cover; NTW, no-till-wheat; NTV, no-till-vetch; NNC, no-till-no cover; $k_d$ is Freundlich parameter for the equilibrium model; $k_{oc}$ is obtained from $k_d$ values divided by organic carbon content; $k_e$ is distribution constant, $k_1$, $k_2$ and forward and backward rate coefficients for $S_1$, $k_3$ is rate coefficient for consecutive irreversible reaction from $S_1$ to $S_2$. 


which can vary widely among soils (Locke, 1992). Thus, organic composition could be responsible for the widely varied $k_{oc}$ values reported in the literature, e.g., 170 by Wauchope et al. (1992) and 342 as by Locke (1992). As result of its hydrophobic and hydrophilic nature, alachlor sorption is significantly correlated to organic matter and clay (Weber and Peter, 1982). Soil organic-matter content was one of the soil characteristics most highly correlated with adsorption of alachlor. Soil organic matter content increases and its distribution in the soil profile is altered in no-till. Plow-tillage buries organic debris, whereas that which accumulated on the surface of no-till soil may reduce alachlor mobility.

4.3.4 Hydrodynamic Dispersion Coefficients

The BTCs of tritium and alachlor transport in soil columns of different tillage systems are showed from Fig. 4.5 to Fig 4.10, with their corresponding experimental conditions given in Table 4.4. Two replicates were carried out for each treatment. Tritiated water was employed as a conservative tracer to investigate the hydrodynamic dispersion in each undisturbed column. The details of tritium transport study was reported in Chapter 3, and the hydrodynamic dispersion coefficients obtained from long pulse (duration about 1.0 $V_o$) were used in describing alachlor transport as described in later sections. We found good agreement among replicated columns for tritium BTCs except CNC2 where significant wall effect was observed in dye experiment. The hydrodynamic dispersions $D$ for each different column are given in Table 4.4. There was a tendency of a larger $D$ values in all soils of the no-till than that of respective
Table 4.4 Experimental condition and parameters in transport study for different tillages and winter cover crops.

<table>
<thead>
<tr>
<th>Sample§</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\theta$ (cm$^3$ cm$^{-3}$)</th>
<th>v (cm h$^{-1}$)</th>
<th>V/V$_0$</th>
<th>$t_p$ (h)</th>
<th>D (cm$^2$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTW1</td>
<td>1.47</td>
<td>0.468</td>
<td>1.33</td>
<td>6.65</td>
<td>75</td>
<td>1.62±0.09</td>
</tr>
<tr>
<td>CTW2</td>
<td>1.39</td>
<td>0.475</td>
<td>0.98</td>
<td>4.71</td>
<td>75.3</td>
<td>1.06±0.16</td>
</tr>
<tr>
<td>CTV1</td>
<td>1.44</td>
<td>0.462</td>
<td>1.35</td>
<td>6.75</td>
<td>75.0</td>
<td>1.82±0.23</td>
</tr>
<tr>
<td>CTV2</td>
<td>1.47</td>
<td>0.496</td>
<td>0.94</td>
<td>4.80</td>
<td>75.8</td>
<td>1.06±0.14</td>
</tr>
<tr>
<td>CNC1</td>
<td>1.45</td>
<td>0.457</td>
<td>1.36</td>
<td>6.80</td>
<td>75.0</td>
<td>0.92±0.12</td>
</tr>
<tr>
<td>CNC2</td>
<td>1.46</td>
<td>0.464</td>
<td>1.00</td>
<td>5.57</td>
<td>80.7</td>
<td>9.00±0.40</td>
</tr>
<tr>
<td>NTW1</td>
<td>1.40</td>
<td>0.509</td>
<td>1.21</td>
<td>6.05</td>
<td>75.0</td>
<td>14.6±2.6</td>
</tr>
<tr>
<td>NTW2</td>
<td>1.43</td>
<td>0.495</td>
<td>0.94</td>
<td>5.29</td>
<td>82.13</td>
<td>19.0±1.5</td>
</tr>
<tr>
<td>NTV1</td>
<td>1.41</td>
<td>0.507</td>
<td>1.22</td>
<td>6.10</td>
<td>75.0</td>
<td>10.36±2.7</td>
</tr>
<tr>
<td>NTV2</td>
<td>1.43</td>
<td>0.503</td>
<td>1.23</td>
<td>6.76</td>
<td>81.0</td>
<td>1.41±0.32</td>
</tr>
<tr>
<td>NNC1</td>
<td>1.42</td>
<td>0.501</td>
<td>1.23</td>
<td>6.15</td>
<td>75.0</td>
<td>1.53±0.12</td>
</tr>
<tr>
<td>NNC2</td>
<td>1.40</td>
<td>0.510</td>
<td>1.22</td>
<td>4.90</td>
<td>58.7</td>
<td>0.91±0.25</td>
</tr>
</tbody>
</table>

§ CTW, conventional tillage-wheat; CTV, conventional tillage-vetch; CNC, conventional tillage-no cover; NTW, no-till-wheat; NTV, no-till-vetch; NNC, no-till-no cover; $\rho$ is bulk density; $\theta$ is moisture content; v is pore water velocity; V/V$_0$ is the pulse duration in pore volume; $t_p$ is the pulse duration in hours; D is hydrodynamic dispersion coefficient.
conventional tillage. This is consistent with results from Singh and Kanwar (1991) where D values for no-till columns were about 2.5 times higher than average values from conventional tillage. Wheat as a winter cover crop in no-till (NTW) increased D compared with conventional tillage and had the highest D value among all tillage treatments. This is probably because of root channels which existed in the undisturbed column. Experiments conducted by Gish and Jury (1982, 1983) showed that wheat roots increased D values by 3 times. The dispersion coefficient is related to molecular diffusion and flow velocity as defined in equation (4.10). Molecular diffusion is much smaller than dispersion and usually ignored in saturated flow condition with relatively high velocity. Therefore the dispersion coefficient obtained from tritium BTC can be used to characterize the solute dispersion. Dispersion is a result of differences in flow rates in the various portions of the soil pore space. The flow in each portion of the soil pore space and its connectiveness to others determine the flow characteristics and the extent of dispersion in soils. As discussed in chapter 3, there was preferential flow paths in soils from no-till. When preferential flow exists, the dispersion coefficient will increase (Skopp and Gardner, 1992; Li and Ghodrati, 1995).

4.3.5 Alachlor BTCs in Soils from Different Tillage Systems

As shown from Fig. 4.5 to 4.10, there was considerable retardation of alachlor BTCs compared with tritium. The earlier breakthrough and longer tailing were observed in soils from no-till compared with that of conventional tillage, where higher peak concentrations were also observed (Fig 4.5 to Fig 4.10). Alachlor BTCs in soils of no-till were more asymmetrical than that of soils from conventional tillage. The early
breakthrough and asymmetrical shape of BTCs may be attributed to preferential flow in macropores and large dispersion (van Genuchten and Cleary, 1979). The early breakthrough and tailing are characteristics of physical nonequilibrium (Brusseau et al., 1989). If one assumes a wide range of pore size distribution in the no-till soil, a solute BTCs is more likely to be asymmetrical along with large dispersion. The tailing may also be a result of alachlor in stagnant regions of soil transversely diffused back into accessible or the mobile phase of the dynamic soil region. The early breakthrough in soils from no-till compared with that from conventional tillage is consistent with several reports (Hall et al., 1989; Pivetz and Steenhuis, 1989; Isensee et al., 1990; Gish et al., 1991; Isensee and Sadeghi, 1994). However, in other studies, there was no apparent effect of tillage on herbicide nonequilibrium transport (Starr and Glotfelty, 1990; Steenhuis et al., 1990; Gaynor et al., 1992; Ghodrati and Jury, 1992; Gaynor et al., 1995). In uniformly packed soil columns, Gaston and Locke (1994) observed a lack of physical nonequilibrium transport and greater retardation for alachlor in soils of no-till than conventional tillage.

4.3.6 Transport Modeling

The asymmetrical shape of tritium BTCs indicates that there was physical nonequilibrium in the transport of solutes in these undisturbed soil columns. Although the columns may be considered heterogenous, especially for soils of no-till, this heterogeneity can be assumed to be random in space, and dispersion may account for such heterogeneity. As discussed in Chapter 3, there was no improvement using physical nonequilibrium models to describe the tritium BTCs compared with using the
classical CDE. In addition to physical nonequilibrium, Gaston and Locke (1994) found chemical nonequilibrium as the dominant transport mechanism of alachlor in uniformly packed soil columns where physical nonequilibrium was assumed absent.

Although nonequilibrium sorption of organic compounds is often formulated in terms of chemically based retention models, such models have been shown (Nkedi-kizza et al., 1984) to be equivalent to simplified, physical models based on diffusive mass transfer (e.g., the two-region model of van Genuchten and Wierenga, 1976). The inclusion of a rate coefficient was adequate for characterizing time-dependent sorption and diffusion-controlled transport (e.g. Rao and Davidson, 1979). The multireaction transport model (MTRM) of Selim (1992) with one equilibrium reaction, one kinetic reversible reaction and one consecutive irreversible reaction was used in describing the alachlor transport (equation 4.5 - 4.8). The diffusion controlled adsorption can be accounted for by rate coefficients of different sites in the multireaction model. This model has been found to be most successful in describing the adsorption-desorption kinetics of alachlor retention as described in Chapter 2 (Xue and Selim, 1995). Selim et al. (1976) found that MRTM with one equilibrium and one fully reversible processes improved predictions of the excessive tailing of the desorption or leaching side and the sharp rise of the adsorption side of BTCs for picloram in comparison to single-reaction equilibrium or kinetic models.

Attempts were made to describe the transport of alachlor in the various columns based on the multireaction model (MRTM) described in equation 4.9-4.11. Hence, we used parameters which were independently obtained from the retention batch results
discussed in the previous section as well as in chapter 2. The specific MRTM model version used for transport prediction included one equilibrium, one kinetic reversible, and one consecutive irreversible reactions. Specifically model parameters used are given in Table 4.3. The predicted BTCs are shown in Figs. 4.5a - 4.10b. The correlations coefficients \( r^2 \) and mean square error (MSE) between the prediction and experiments are listed in Table 4.5 of this Chapter and Table 2.2 in Chapter 2. These predictions, in most case, were considered not adequate. The \( r^2 \) was 0.8917 for the NTW2 to 0.3815 for CTW2; the MSE was 0.1426 for NTW2 to 0.3141 for CTW2. Unsatisfactory predictions of alachlor BTCs using parameters from batch data have been reported in several other studies. There are currently no models available that can a priori predict leaching processes in soil under a variety of soil conditions without some calibration or fitting. For example, Gaston and Locke (1994) found there were considerable discrepancy between predicted and measured alachlor BTCs using two-site and three site equilibrium/kinetic sorption models. They used parameters which were independently derived from batch experiments. In some cases, pesticide leaching in the field was overestimated when parameters based on predictions from laboratory measurements were used (Rao et al., 1974; Burgard et al., 1993; Yen et al., 1994). Rao et al., (1974) explained this behavior due to micropore retention through saturated soil columns. However, in other cases, solutes moved deeper in soil profile than predicted.

Since the multireaction model was not successful in predicting alachlor BTCs when independently derived batch parameters were utilized, the capability of MRTM
in describing the BTC in a calibration mode was evaluated. Specifically, the MRTM was used along with a nonlinear parameter optimization scheme of Marquart (1963) to describe the alachlor BTCs. Calculated (fitted) BTCs are shown in Figs 4.6 - 4.11. and the best-fit parameter estimates along with $r^2$ and mean square error for individual column are given in Table 4.6. The multireaction model accurately described the BTCs in soil columns of different tillage systems. As indicated by Table 4.6, high $r^2$ (0.9836 to 0.9981) and low MSE (0.022 to 0.057) were obtained for all BTCs using the multireaction model. Best-fit parameters estimated based on nonlinear optimization from transport experiments (Table 4.6) were different from measured batch parameters (Table 4.3). The instantaneous distribution coefficient ($k_0$) was significantly lower than that from batch experiments for all cases. This may be because a significant fraction of sorption sites did not participate in instantaneous or fast retention reaction in the undisturbed soil columns. Traditional batch techniques that use high solution : soil ratios and agitation to obtain equilibrium may not obtain the essential kinetic information necessary to model solute mobility in undisturbed soils (O’Dell, et al., 1992). Brusseau et al., (1989) separated the processes responsible for nonequilibrium transport into two general classes: physical nonequilibrium and sorption-related nonequilibrium. Physical nonequilibrium results from the existence of mobile and immobile domains within the porous medium and affects both sorbing and nonsorbing solutes. Sorption related nonequilibrium involves only sorbing solutes and arises from chemical non-equilibrium and intra-sorbent diffusion. Although both physical and chemical nonequilibrium may be significant in undisturbed soils from different tillage
systems, the MRTM in calibration mode successfully described alachlor transport. This adds the credence to the capability of MRTM in describing the multiple retention processes during transport in soils.

4.3.7 Retention Parameters of Alachlor During Transport in Undisturbed Soils Columns

As indicated in Table 4.6, the fitted parameters demonstrated the dominance of the kinetic component of the multireaction model compared with batch parameters (Table 4.3 and 4.6). This may be attributed to heterogeneity of the undisturbed columns. The kinetic reaction is diffusion controlled and is extremely sensitive to flow or mixing effects. The dependence of kinetic reaction rate coefficients for atrazine transport in undisturbed soil cores were reported by several investigators (Gaber et al., 1995; Gamerdinger et al., 1991). Gaston and Locke (1994) found that model parameters for alachlor transport depend on pore water velocity. Specifically, best-fit parameters for alachlor BTCs not only differed from those determined from their batch data but also revealed dependency on pore water velocity or residence time. Since the rate coefficients varied with experimental conditions, an overall retention should be compared with estimates based on the sum of contributions from both kinetic and equilibrium retention, i.e., $K = k_e + \theta k_1 / \rho k_2$ (Selim et al., 1995). The overall retention $K$ is listed in Table 4.6. Based on Duncan's multiple range test, there was no significant difference ($p=0.05$) for the overall retention parameter $K$ between the no-till and conventional tillage treatments. The average $K$ was 1.53 for conventional tillage and 1.58 for the no-till. The critical range for significant difference was 0.276 ($p=0.05$). This could be due to the effects of heterogeneity in no-till where the retention sites were
Fig. 4.5 BTCs of alachlor in soil columns of no-till with wheat as a winter cover crop for (a) replication 1 and (b) replication 2.
Fig. 4.6 BTCs of alachlor in soil columns of conventional tillage with wheat as a winter cover crop for (a) replication 1 and (b) replication 2.
BTCs of alachlor in soil columns of no-till with vetch as a winter cover crop for (a) replication 1 and (b) replication 2.

Fig. 4.7BTCs of alachlor in soil columns of no-till with vetch as a winter cover crop for (a) replication 1 and (b) replication 2.
Fig. 4.8 BTCs of alachlor in soil columns of conventional tillage with vetch as a winter cover crop for (a) replication 1 and (b) replication 2.
Fig. 4.9 BTCs of alachlor in soil columns of no-till with no winter cover crop for (a) replication 1 and (b) replication 2.
Fig. 4.10 BTCs of alachlor in soil columns of conventional tillage with no winter cover crop for (a) replication 1 and (b) replication 2.
Fig. 4.11 HPLC chromatogram of effluent in 4 days after alachlor application during transport experiment in soil from no-till with vetch as a winter cover crop.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Table 4.5 The alachlor recovery, goodness of prediction for BTCs using kinetic parameters of batch experiment in soils from different tillages and winter cover crops

<table>
<thead>
<tr>
<th>Sample 6</th>
<th>Recovery (%)</th>
<th>$r^2$</th>
<th>MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTW1</td>
<td>91.7</td>
<td>0.6363</td>
<td>0.298</td>
</tr>
<tr>
<td>CTW2</td>
<td>89.0</td>
<td>0.3818</td>
<td>0.314</td>
</tr>
<tr>
<td>CTV1</td>
<td>88.7</td>
<td>0.6994</td>
<td>0.274</td>
</tr>
<tr>
<td>CTV2</td>
<td>83.5</td>
<td>0.5444</td>
<td>0.291</td>
</tr>
<tr>
<td>CNC1</td>
<td>93.4</td>
<td>0.7276</td>
<td>0.256</td>
</tr>
<tr>
<td>CNC2</td>
<td>80.0</td>
<td>0.8982</td>
<td>0.174</td>
</tr>
<tr>
<td>NTW1</td>
<td>94.3</td>
<td>0.7909</td>
<td>0.215</td>
</tr>
<tr>
<td>NTW2</td>
<td>92.6</td>
<td>0.8917</td>
<td>0.143</td>
</tr>
<tr>
<td>NTV1</td>
<td>88.7</td>
<td>0.6994</td>
<td>0.274</td>
</tr>
<tr>
<td>NTV2</td>
<td>98.0</td>
<td>0.7815</td>
<td>0.235</td>
</tr>
<tr>
<td>NNC1</td>
<td>99.8</td>
<td>0.7749</td>
<td>0.271</td>
</tr>
<tr>
<td>NNC2</td>
<td>95.8</td>
<td>0.7800</td>
<td>0.200</td>
</tr>
</tbody>
</table>

6 CTW, conventional tillage-wheat; CTV, conventional tillage-vetch; CNC, conventional tillage-no cover; NTW, no-till-wheat; NTV, no-till-vetch; NNC, no-till-no cover.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Table 4.6 Fitted kinetic parameters of BTCs in soils from different tillages and winter cover crops in transport experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_e$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
<th>$K$</th>
<th>$r^2$</th>
<th>rms</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTW1</td>
<td>0.001±0.160</td>
<td>4.7701±3.6430</td>
<td>0.8993±0.6707</td>
<td>0.0070±0.0031</td>
<td>1.7</td>
<td>0.9924</td>
<td>0.045</td>
</tr>
<tr>
<td>CTW2</td>
<td>0.257±0.802</td>
<td>0.7707±0.6668</td>
<td>0.1817±0.1008</td>
<td>0.0066±0.0024</td>
<td>1.7</td>
<td>0.9932</td>
<td>0.034</td>
</tr>
<tr>
<td>CTV1</td>
<td>0.456±0.535</td>
<td>0.4899±0.4626</td>
<td>0.1338±0.0752</td>
<td>0.0092±0.0025</td>
<td>1.6</td>
<td>0.9968</td>
<td>0.030</td>
</tr>
<tr>
<td>CTV2</td>
<td>0.518±0.164</td>
<td>0.1982±0.0740</td>
<td>0.0693±0.0192</td>
<td>0.0108±0.0018</td>
<td>1.5</td>
<td>0.9966</td>
<td>0.022</td>
</tr>
<tr>
<td>CNC1</td>
<td>0.509±0.116</td>
<td>0.1628±0.0517</td>
<td>0.0581±0.0155</td>
<td>0.0040±0.0017</td>
<td>1.4</td>
<td>0.9965</td>
<td>0.031</td>
</tr>
<tr>
<td>CNC2</td>
<td>0.817±0.106</td>
<td>0.0261±0.0139</td>
<td>0.0155±0.0196</td>
<td>0.0138±0.0051</td>
<td>1.3</td>
<td>0.9958</td>
<td>0.025</td>
</tr>
<tr>
<td>NTW1</td>
<td>0.478±0.568</td>
<td>0.5451±0.5022</td>
<td>0.1432±0.0812</td>
<td>0.0023±0.0024</td>
<td>1.9</td>
<td>0.9960</td>
<td>0.030</td>
</tr>
<tr>
<td>NTW2</td>
<td>0.646±0.325</td>
<td>0.1469±0.1139</td>
<td>0.0524±0.0318</td>
<td>0.0015±0.0029</td>
<td>1.7</td>
<td>0.9933</td>
<td>0.031</td>
</tr>
<tr>
<td>NTV1</td>
<td>0.511±0.600</td>
<td>0.4899±0.4626</td>
<td>0.1338±0.0752</td>
<td>0.0092±0.0025</td>
<td>1.8</td>
<td>0.9969</td>
<td>0.030</td>
</tr>
<tr>
<td>NTV2</td>
<td>0.676±0.080</td>
<td>0.0929±0.0285</td>
<td>0.0552±0.0143</td>
<td>0.0008±0.0017</td>
<td>1.3</td>
<td>0.9981</td>
<td>0.023</td>
</tr>
<tr>
<td>NNC1</td>
<td>0.0004±0.02</td>
<td>0.8938±0.2194</td>
<td>0.2110±0.0568</td>
<td>0.0001±0.0037</td>
<td>1.5</td>
<td>0.9904</td>
<td>0.057</td>
</tr>
<tr>
<td>NNC2</td>
<td>0.0004±0.08</td>
<td>0.5163±0.2082</td>
<td>0.1432±0.0655</td>
<td>0.0026±0.0058</td>
<td>1.3</td>
<td>0.9836</td>
<td>0.057</td>
</tr>
</tbody>
</table>

8 CTW, conventional tillage-wheat; CTV, conventional tillage-vetch; CNC, conventional tillage-no cover; NTW, no-till-wheat; NTV, no-till-vetch; NNC, no-till-no cover; $k_e$ is distribution constant; $k_1$, $k_2$ and forward and backward rate coefficient for $S_1$, $k_3$ is rate coefficient $(h^{-1})$ for consecutive irreversible reaction from $S_1$ to $S_2$; $r^2$ is adjustable correlation coefficients; rms is the root mean square error, $K = k_e + \theta k_1 / \rho k_2$ is overall retention coefficient.
less accessible than that of soils from conventional tillage. In addition, for the transport of adsorbing chemicals, earthworm burrows are different from other macropores in soils, such as cracks or root channels. Edwards et al., (1992) found a higher attenuation of atrazine and alachlor in night crawlers burrows than unlined, artificial burrows. They suspected that organic and microbial lining of the burrows increased the adsorption of atrazine. In a transport experiment, dicamba and primisulfuron were more retarded than expected from batch studies (Stehouwer et al., 1994).

4.3.8 Alachlor Recovery, Degradation and Irreversible Reaction

Gaston and Locke (1994) showed a thin layer chromatogram for $^{14}$C recovery in column effluent as a function of pore volumes collected. They observed little degradation of alachlor even after 17 pore volumes (16 days). In this study, an analysis of the effluent by HPLC chromatograms (Fig. 4.11) gave no major peaks other than alachlor, which indicated that there was no metabolites in the column effluent. As shown in Table 4.6, the fitted transport model indicated that there was a considerable irreversible reaction in all six soil columns of conventional tillage and in one soil column of no-till (NTV1). In these columns, the rate coefficients $k_3$ for irreversible reaction were significantly different from zero ($p=0.05$) using a t-test. This result is consistent with mass recovery of alachlor in the effluent as listed in Table 4.5. The mass recovery of alachlor was varied with a tendency of higher recovery in soils of no-till than conventional tillage. Gaston and Locke, (1996) where they found 88% recovery of bentazon in effluent of no-till whereas 78% in conventional tillage. These differences may be attributed to the dissolved organic carbon which may activate the
alachlor in irreversible sites in undisturbed soils of no-till. This result was further confirmed by Figs 4.7b and 4.9b where flow interruption was conducted. There was no alachlor concentration change following flow interruptions during leaching in soil columns of no-till with vetch as cover crop (Fig. 4.7b). This could be the result of compensation between irreversible bonding reaction and reversible kinetic reaction. Irreversible bonding reaction may cause a decrease whereas reversible kinetic reaction may increase the alachlor concentration. Selim et al., (1995) reported that there was a significant concentration decrease of TNT after flow interruption during leaching when irreversible reaction or degradation occurred during transport experiments. Alachlor concentration showed an increase of 0.05 in C/C₀ following flow interruption (Fig. 4.9b) during leaching for soil of no-till with no winter cover crop. This is consistent with the result of atrazine in uniformly packed soil columns containing aggregates (Ma and Selim, 1994). It is an indication of dominance of reversible reaction and lack of irreversible bonding reaction or degradation.

4.3.9 Tillage effect on Alachlor Transport

As discussed in section 4.3.3, no-till increased alachlor retention in batch experiments of all cover crops. Increased hydrodynamic dispersion resulted in preferential flow in no-till and led to early alachlor breakthrough and thus reduced alachlor retardation. Increased heterogeneity of no-till caused the physical nonequilibrium transport and reduced values of diffusion-controlled equilibrium and kinetic parameters. The compensation between increasing adsorption due to high organic matter contents and reducing adsorption by diffusion-limited mechanisms led
to a non-significant difference of overall retention in undisturbed soils between no-till and conventional tillage. No-till may reduce the bound alachlor residue as a result of increased dissolved organic carbon (DOC). Although the overall alachlor retention was not affected by tillage, the no-till reduced the retardation and the shape of alachlor BTCs compared with conventional tillage based on alachlor breakthrough in this study.

4.4 Conclusions

No-till increased the retention of alachlor in completely mixed batch experiments, especially for instantaneous equilibrium reaction, whereas no-till may result in preferential flow and physical nonequilibrium transport in undisturbed soils. Alachlor transport was constrained by both physical and chemical nonequilibrium processes. Based on breakthrough which is affected by preferential flow or physical nonequilibrium, no-till reduced alachlor retardation compared with conventional tillage. Although the physical and chemical nonequilibrium were significant in undisturbed soil columns from no-till, the MRTM in a calibration model adequately described alachlor transport in those soils. This would indicate that the MRTM can describe the physical and chemical nonequilibrium transport of alachlor in this study where chemical nonequilibrium (i.e., kinetic reaction parameters) were affected by physical nonequilibrium (heterogeneity). No-till increased alachlor retention in completely mixed batch experiments compared with conventional tillage whereas it did not affect the alachlor overall retention in undisturbed columns based on parameters fitted from alachlor BTCs in transport experiments. As discussed in Chapter 3, there was more pronounced physical nonequilibrium solute transport in soils from no-till compared with
conventional tillage. This indicated that physical nonequilibrium affected chemical nonequilibrium and thus reduced the retardation of alachlor during transport. The difference in rate coefficients may explain the variation of shape of alachlor BTCs. The higher recovery and lack of irreversible reaction indicated that no-till may increase dissolved organic carbon (DOC) in soil and thus reduced bond alachlor residue during transport.
CHAPTER 5

SUMMARY AND CONCLUSIONS

The fate and transport of herbicide have been cited to be affected by tillage practices. However, there are various viewpoints regarding the overall effect of tillage. The controversy stems from the observed heterogeneity of the soil and its constituents as influenced by tillage. The heterogeneity of soils leads to physical and chemical nonequilibrium transport of herbicides in the soil profile. This study was designed to quantify and describe the transport of alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide] as affected by physical and chemical nonequilibrium in a Gigger soil (Typic Fragiudalf) from no-till and conventional tillage systems.

A batch study was conducted to characterize the chemical nonequilibrium reactions, i.e., kinetics of alachlor adsorption and desorption in surface soil samples collected from long term no-till and conventional tillage plots. A batch method was used to determine alachlor adsorption with time up to 528 h for a range of input concentrations from 0.5 to 50 mg/L. Successive dilution was used to quantify desorption kinetics following 16, 32, 64, 128, 256, and 512 h of adsorption.

Alachlor time-dependent results indicated initially fast adsorption followed by slow or kinetic type reactions. Adsorption-desorption results showed extensive hysteretic behavior resulting from discrepancies between adsorption and desorption isotherms. Hysteresis was more pronounced with increased reaction time of adsorption. Four variations of a nonlinear multireaction kinetic model successfully described retention results. However, adsorption and desorption were best described by a model
version incorporating nonlinear equilibrium, a kinetic reversible mechanism, and a consecutive irreversible mechanism. The model was successfully used in describing alachlor adsorption and desorption results. The model predicted the overall alachlor hysteresis satisfactorily except that, at long times, desorption isotherms were not considered adequate. The model was also capable of predicting alachlor desorption kinetics based solely on parameters obtained from adsorption experiments.

Tracer studies were conducted with two dyes (Eosin Y and Brilliant Blue FCF) and tritium to stain the flow paths and determine physical nonequilibrium characteristics including soil heterogeneity, as well as the preferential flow in undisturbed soils. The stained areas and flow paths revealed that solute transport occurred only through a portion of the pore space in soil from no-till, whereas the soil was somewhat uniformly stained and breakthrough curves (BTCs) displayed little preferential flow in soil from conventional tillage. The higher concentration of dyes in the effluent of no-till than that of conventional tillage may be explained by the stained flow paths observed.

The tritium breakthrough times was earlier in soil columns of no-till than that of conventional tillage in all cover crops. To examine the influence of pulse characteristics on tritium BTCs, pulses with two durations (long and short pulses) were applied. Most BTCs of short pulses of the no-till soil showed bimodal peaks when upward or downward flow was maintained. These bimodal peaks indicated intrinsic preferential flow paths in the undisturbed soil. All BTCs in columns of no-till showed some degree of tailing of the desorption (elution) side. The excessive tailing and
asymmetry indicated possible existence of nonequilibrium mass exchange between soil regions having different mobilities.

Tritium BTCs for the conventional tillage were relatively symmetric, which indicate little or no preferential flow in these soil columns. Flow interruption was carried out during tritium transport experiments and no concentration change due to flow interruption was observed.

The BTCs of short pulse were used to predict tritium BTCs of the long pulse using the principle of superposition. For most soils, the superimposed BTCs were consistent with observed BTCs of long pulse. These predictions are confirmation of the intrinsic flow paths in soil columns whereas poor predictions in soil of no-till with wheat cover crop may be attributed to change in the flow paths during the experiments. The BTCs in soils of no-till were distinctly different depending on the flow directions, which may be due to thestructuralization of soil after no-till practice. The direction of flow had little effect on tritium breakthrough in soils of conventional tillage.

The convection-dispersion equation (CDE) adequately described tritium BTCs of soils under conventional tillage. The description was not adequate for the experimental data of soils from no-till, especially for the short pulse. The physical nonequilibrium models including mobile-immobile model (MIM) and stochastic model (SM) were used to describe the long pulse BTCs of soils from no-till. There was no improvement in the description of the data. In addition, the CDE, MIM and SM were not capable of describing the double peaks of BTCs. The partition of mobile-immobile fraction may not sufficiently represent the reality of the structure of these undisturbed
soils where preferential flow occurred. Thus at present we are not aware of modeling approaches that can predict solute in the no-till soils which displayed preferential characteristics.

Miscible displacement experiments of alachlor were conducted in undisturbed soil columns of no-till and conventional tillages to quantify and model its physical and chemical nonequilibrium transport in soil. The no-till significantly increased the magnitude of equilibrium but not the kinetic parameters compared with conventional tillage. This effect may be a result of increasing organic matter content in no-till compared with conventional tillage. Similar to tritium BTC, an early breakthrough time and long tailing were observed for alachlor BTCs. This is perhaps due to preferential flow in all soils of no-till compared with conventional tillage, where higher peak concentrations, less retention and dispersion were observed. There was a tendency of increase hydrodynamic dispersion coefficients in soils of no-till compared with that of conventional tillage.

In an attempt to model the alachlor transport, a multireaction transport model (MTRM) with one equilibrium reaction, one kinetic reversible reaction and one consecutive irreversible reaction was used for describing the alachlor transport. Model predictions in most cases, were considered inadequate when independently measured model parameters from batch experiments were used. Since the multireaction model was not successful in alachlor prediction when batch parameters were utilized, the MRTM in a calibration mode was carried out to describe the BTCs in all soil columns of different tillage systems. High r² and low mean square error (MSE) were obtained for
all BTCs when a nonlinear parameter optimization scheme was used to describe alachlor BTCs. The successful description of alachlor BTCs with the MRTM added credence to its capability to describe both physical and chemical nonequilibrium transport of herbicides.

The values of fitted parameters from transport experiments indicated a dominance of kinetic reactions compared with parameters measured in batch experiments. In contrast, the instantaneous distribution coefficients were significantly lower than that from batch experiments. These effects may be caused by a significant fraction of the sorption sites not participating in retention reactions. Due to variation of kinetic parameters, an overall retention was compared with estimates based on the sum of contributions from kinetic and equilibrium retention, i.e., $K = k_e + \theta k_1/\rho k_2$. Based on Duncan's multiple range test, there was no significant difference ($p=0.05$) for $K$ between the no-till and conventional tillage treatments. This could be due to the effects of heterogeneity in no-till where the retention sites were perhaps less accessible than that of soils from conventional tillage.

Analysis of the effluent by HPLC chromatograms gave no major peaks other than alachlor, which indicated that there was no detectable metabolites in the effluent of the columns and no degradation occurred during transport experiments. Moreover, parameters from fitted BTCs indicated considerable irreversible reaction in all soil columns of conventional tillage and in one no-till soil column. In these columns, the rate coefficients $k_3$ for irreversible reaction were significantly different from zero ($p=0.05$) using a t-test. This result is consistent with mass recovery of alachlor in the
effluent where alachlor recovery in the effluent was higher in soils without irreversible reactions than those with irreversible reactions.

There was a tendency of higher recovery in soils of no-till than conventional tillage. The difference may attribute to the dissolved organic carbon which may activate alachlor in irreversible sites in undisturbed soils of no-till. This result was further confirmed by experiments where flow interruption was conducted. There was no alachlor concentration change after flow interruptions during leaching for the soil of no-till with vetch as a cover crop whereas there was somewhat of an increase of alachlor concentration in soil of no-till with no cover crop. Although the no-till increased alachlor retention in completely mixed batch experiments because of high organic matter content compared with conventional tillage, no-till increased the alachlor transport in term of breakthrough due to soil heterogeneity and preferential flow.
REFERENCES


Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.


Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.


Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.


Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.


van Ommen, H. C. 1985. The 'mixing cell' concept applied to transport of non-reactive and reactive components in soils and groundwater. J. Hydrol. 78:201-213


Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.


American Society of Agronomy,
677 S. Segoe Rd., Madison, WI 53711.
Fax 608-273-2021

Dear Editor:

I am writing to you to request for permission to reproduce the paper "Modeling Adsorption-Desorption Kinetics of Alachlor in a Typic Fragiudalf" in Journal of Environmental Quality (24:896-903) by S.K. Xue and H.M. Selim for using in my dissertation. It will be greatly appreciated if you can fax me the permission.

Sincerely

S.K. Xue

3/27/96

Permission granted

Dore M. Keat
Asst. Exec. Vice Pres.
VITA

Shikui Xue was born on June 18, 1963, in The People's Republic of China. He received his Bachelor's degree of Science from Huazhong Agricultural University in 1984 in Soil Science and Agrochemistry, and Master of Science degree from Institute of Soil Science, Academia Sinica in 1987 in Department of Soil Geography. As a research associate, he worked in Soil Geography, Institute of Soil Science, Academia Sinica from 1987 to 1990. He took the Advanced Course of irrigation from October to December, 1990 at Volcani Center, Agricultural Research Organization, Israel. As a visiting scholar, he worked in Soil Physics and Irrigation from 1991 to 1992 at ARAVA Research Station, Israel. As a research assistant, he worked in Soil Physics, Department of Agronomy, Louisiana State University for Doctor degree of Philosophy. He is the author and coauthor of 14 scientific papers in refereed journals, book chapters and proceedings on the subject of Solute Transport, Irrigation, Nutrient Cycling and Soil Geography.
Candidate: Shikui Xue

Major Field: Agronomy

Title of Dissertation: Modeling Physical and Chemical Nonequilibrium Transport of Herbicide in Soils From Different Tillage Systems

Approved:

[Signature]
Major Professor and Chairman

[Signature]
Dean of the Graduate School

EXAMINING COMMITTEE:

Richard M. Johnson

[Signature]

Darryl Foylott

[Signature]

Robert P. Dambell

[Signature]

Kalleid T. Valky

Date of Examination:

March 21, 1996