Predicting the Movement and Retention of Pesticides in Soils: Physical and Chemical Nonequilibrium Modeling Approaches.

Liwang Ma
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/5655
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
Predicting the movement and retention of pesticides in soils: Physical and chemical nonequilibrium modeling approaches

Ma, Liwang, Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1993
PREDICTING THE MOVEMENT AND RETENTION OF PESTICIDES IN SOILS: PHYSICAL AND CHEMICAL NONEQUILIBRIUM MODELING APPROACHES

A Dissertation

Submitted to the Graduate Faculty of the 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

Liwang Ma
B.S. Beijing Agricultural University, P. R. China 1984
M.S. Beijing Agricultural University, P. R. China 1987
December 1993
I gratefully acknowledge my major professor, Dr. H. Magdi Selim for his advice throughout my Ph.D. program. It has been a great reward for me to work with him. This piece of work could not be accomplished without his guidance and support. I also enjoy my personal relationship with him and his family. They make my wife and me feel at home during our stay at Louisiana State University.

Special thanks are given to Drs. Lloyd M. Southwick and Guye H. Willis, USDA-ARS, who provided numerous suggestions to my program. My thanks also extend to the rest of my graduate committee, Dr. D. Dean Adrian, Civil Engineering, Dr. David C. Blouin, Experimental Statistics, and Dr. Ralph J. Portier, Environmental Studies, for their advice and suggestions to my graduate program.

I also would like to thank my colleagues, Drs. Lewis Gaston and Christoph Hinz and Ms. Janet Ardoin, for their introduction to soil physics facilities and laboratory techniques; the Department of Agronomy for providing research assistantship; and Ciba-Geigy Cooperation for providing $^{14}$C-labeled atrazine. This work was also funded by CSRS-USDA water quality project no. 903-09-6157 of the Louisiana Agricultural Experimental Station.

At last, not the least, I would like to acknowledge my wife, Qian Hong Wu, for her patience, support, and understanding. To her this piece of work is devoted.
4. **PREDICTING ATRAZINE TRANSPORT IN SOILS: SECOND ORDER AND MULTIREACTION APPROACHES** ...................................................... 110
   4.1 Introduction ...................................................................................... 110
   4.2 Model Formulation ....................................................................... 113
      4.2.1 Second-order two-site model .............................................. 115
      4.2.2 Multireaction and transport model .................................... 117
   4.3 Materials and Methods .................................................................. 119
      4.3.1 Column experiments ............................................................... 119
      4.3.2 Batch experiments ................................................................. 122
   4.4 Results and Discussion ................................................................. 123

5. **TORTUOSITY, MEAN RESIDENCE TIME AND DEFORMATION OF TRITIUM BREAKTHROUGHS FROM UNIFORM SOIL COLUMNS** ............................................. 150
   5.1 Introduction ...................................................................................... 150
   5.2 Material and Methods .................................................................... 158
   5.3 Results and Discussion ................................................................. 160
      5.3.1 Deformation of tritium BTCs ............................................. 160
      5.3.2 Superposition .......................................................................... 176
      5.3.3 Tortuosity and transport path length ...................................... 178

6. **EVALUATION OF CHEMICAL AND PHYSICAL NONEQUILIBRIUM IN ATRAZINE TRANSPORT IN A SHARKEY SOIL** ............................................................... 183
   6.1 Introduction ...................................................................................... 183
   6.2 Model Formulation ....................................................................... 187
      6.2.1 Model I ................................................................................... 188
      6.2.2 Model II ................................................................................... 198
   6.3 Results and Discussion ................................................................. 200
      6.3.1 Model parameter estimations .............................................. 200
      6.3.2 Model prediction ................................................................... 201
      6.3.3 Model sensitivity analysis ..................................................... 216

7. **SUMMARY AND CONCLUSION** ............................................................... 222

REFERENCES ................................................................................................................ 226

VITA ................................................................................................................................. 252
ABSTRACT

Atrazine retention and transport in a highly aggregated Sharkey clay soil were investigated through kinetic batch experiments, miscible displacement (column transport), and mathematical modeling. Batch results indicated that atrazine retention was kinetic and adsorption-desorption was hysteretic. Adsorption and desorption isotherms were well described using the Freundlich equation \( S = KC^N \). Fitted Freundlich K was a function of reaction time and initial atrazine input concentrations, whereas fitted N was only affected by reaction time. Desorption hysteresis was quantified by the maximum difference between adsorption and desorption isotherms, and showed a linear increase with reaction time.

Atrazine adsorption kinetics was successfully described by a modified second-order two-site (SOTS) approach which was incorporated into the convective-dispersive transport equation. Atrazine was assumed to be present in four phases: a soil solution phase, a noncatalytic (equilibrium) adsorption phase with low binding energy, a catalytic (kinetic) adsorption phase with strong interactions with matrix surfaces, and irreversible sorbed hydroxyatrazine or other physical irreversible adsorbed atrazine. Retention reactions between different phases were based on second-order kinetics and the vacant sites were assumed to be accessible to both equilibrium and kinetic reactions. The total amount of retention sites was assumed constant for a specific soil. Based on one set of independently estimated parameters, the model was capable of predicting atrazine adsorption kinetics and desorption hysteresis. The SOTS model was rigorously validated by predicting fourteen atrazine column transport (breakthrough)
results for different aggregate sizes, input concentrations, water flux, column lengths, and flow interruptions.

The SOTS model was further developed to a second-order two-site two-region model to examine the contribution of physical versus chemical nonequilibrium retention in this aggregated soil. Best model predictions were obtained by assuming that all the vacant adsorption sites of the dynamic and stagnant soil regions were considered accessible to solutes in the mobile and immobile phases. A major feature of the modified two-region model is that the fraction of sites, which is a difficult to measure parameter, need not be specified and the amount retained by each soil region is solely a function of reaction rates.
CHAPTER 1.

ATRAZINE IN SOIL ENVIRONMENT: A LITERATURE REVIEW

1.1 Introduction

As the world's need for food increases, pesticides become indispensable in agriculture as does fertilizer. 62% of the agricultural land in the U.S.A. is treated with pesticides, of which 69% is herbicides, 19% insecticides and 12% fungicides (Pimental et al. 1991). Without the use of pesticides, the total production of all crops and livestock in the United States would be reduced by 40% and the price of farm products to consumers would increase by 50-70% (Khan 1980). Since 1945, the use of synthetic pesticides in the United States has grown 33-fold (Pimental et al. 1991). According to a forecast (Green et al. 1987), pesticide usage is increasing exponentially, especially herbicides. Of the pesticides used in agriculture, only 0.1% actually reaches target pests, the rest (over 99%) moves into the ecosystem (Pimental and Levitan 1986). The latter may cause serious environmental problems, such as groundwater contamination, food contamination, air pollution, etc. (Pimental et al. 1991). In order to eliminate the detrimental effects, research is desperately needed on the quantitative determination of pesticides in the soil-water-air ecosystem.

Atrazine (6-chloro-N-ethyl-N'- (1-methylethyl)-1,3,5-triazine-2,4-diamine) has been used worldwide to control weeds in sugarcane and corn since 1952 (Frank and Sirons 1985, McEwen and Stephenson 1979, Anonymous 1990). U. S. farmers used 26,000 tons of atrazine in 1971 and 38,000 tons in 1985 (Green et al. 1987) and over
39,600 tons in 1990 (Periera and Rostad 1990). In the European Community Countries, an estimated amount of 8000 metric tons of active atrazine compound was applied during 1989 and 140 metric tons only in England and Wales (Durand and Barcelo 1992). Subsequent to this extensive use, numerous reports on groundwater contamination have been published (Helling and Gish 1986, Isensee et al. 1988, Pionke et al. 1988, Muir and Baker 1976). A survey of wells in Wisconsin showed contamination of 152 wells out of 752 wells and 4 out of 13 under normal agricultural practice (WNDR, 1988). Southwick et al. (1990) reported atrazine concentrations up to 3.53 μg/L in 1m depth tile-drain water samples in a Commerce clay soil 12 days after application. In a later study, Southwick et al. (1992) detected atrazine concentrations as high as 403 μg/L after 7 days of application in a Sharkey clay soil. Smith et al. (1990) observed atrazine concentration of 350 μg/L 12 days after application in a sandy soil. These reported concentrations are much higher than the safety drinking water lifetime advisory level of 3.0 μg/L recommended by the Environmental Protect Agency (EPA) (USEPA 1988). These widely reported contaminations of atrazine led to increased public pressure to regulate atrazine application due to its potential adverse effects on human health. Iowa, the first state to regulate atrazine, has limited the use of atrazine on certain soils. This practice will reduce the allowable application of atrazine by at least 25% statewide (News, 1990). On the other hand, scientific studies with atrazine has been continued for the last 40 years in many disciplines. As early as 1970, a special issue of Residue Reviews (Vol.32) on s-triazines was compiled. Hundreds of papers concerning atrazine or
related s-triazines are published worldwide every year. Atrazine studies were presented in most of the meetings related to environment and agriculture (Somasundaram and Coats 1991, Cheng 1990, Garner et al. 1986).

All of these works can be grouped into experimental research and mathematical modeling. The former includes batch experiment, column transport study, and field monitoring (Clay and Koskinen 1990a, b, Elrick et al. 1966, Rao et al. 1979, Southwick et al. 1990, 1992). However, mathematical modeling has its special place in transferring information from the laboratory to the field. Ideally, models should be able to predict atrazine spatially and temporally under varying weather, soil and topographic conditions. By using computer simulation, atrazine can be managed to maximize weed control and minimize environmental impacts.

Today, computer modeling is even more emphasized by both laboratory and field oriented scientists due to the following reasons (Hurle and Walker 1980, Wagenet and Rao 1990): (1) modeling can be used as a tool to combine experimental results obtained under different conditions, and as an ideal way to present the relationship between the affecting factors; (2) good models can be used to forecast the behavior of a soil system under different conditions, and to reduce the endless, time-consuming field trials; (3) even less than perfect models can be used to help the layout of field experiments and make field experiments more successful; (4) models play an important role in communication between laboratory and field workers; (5) models can be used in operational purposes, such as timing of pesticide application and sequence of crop rotation.
Pesticide simulation models can be classified as deterministic and stochastic (Wagenet and Rao 1990). Although stochastic models derived from the probability density function (pdf) have gained popularity recently, especially in modeling field scale experiments (Jury et al. 1982, Butters and Jury 1989, Jury 1982, Jury et al. 1982), Deterministic models of solute transport based on miscible displacement theory (Nielson and Biggar 1962) may be the most widely used model approach. These models presume that soil-water flow and solute transport processes operate such that the occurrence of a given set of physical and chemical events leads to a uniquely definable water or solute distribution in soil profiles, and can be described by the convection-dispersion equation (CDE) (Wagenet and Rao 1990). Pennell et al. (1990) evaluated five deterministic models with aldicarb and bromide under field conditions, e.g. Chemical Movement in Layer Soils (CMLS), Method Of Underground Solute Evaluation (MOUSE), Pesticide Root Zone Model (PRZM), Groundwater Loading Effects of Agricultural Management Systems (GLEAMS), and Leaching Estimation And Chemistry Model-Pesticides (LEACHMP). They concluded that none of the models accurately described measured solute concentration distributions. Many reasons have been attributed to the failure of predictive models, such as inaccuracy of kinetics of degradation (Hurle and Walker 1980), ignoring adsorption-desorption non-singularity and kinetics (Leistra 1980), and oversimplifying the soil system due to lack of input data (Wagenet and Rao 1990).

The CDE used in one dimension model can be expressed by the following equation (Wagenet and Rao 1990):
\[
\frac{\partial}{\partial t} (\rho C_s + \theta C_L + \xi C_G) = \frac{\partial}{\partial z} \left[ \theta D(\theta, q) \frac{\partial C_L}{\partial z} - q C_L + D_{OG} \frac{\partial C_G}{\partial z} \right] \pm \psi \tag{1.1}
\]

Where \( \rho \): bulk density (g/cm³)

\( \theta \): volumetric water content (cm³/cm³)

\( \xi = (\theta_s - \theta); \theta_s \) is saturated volumetric soil-water content (cm³/cm³)

\( C_s, C_L, \) and \( C_G \) are pesticide concentrations in solid, liquid and gas phases, respectively (µg/cm³)

\( q \): macroscopic soil-water flux (cm/hr)

\( D(\theta, q) \): effective diffusion coefficient (cm²/hr)

\( t \): time (hr)

\( z \): vertical distance (cm)

\( D_{OG} \): vapor diffusion coefficient (cm²/hr)

\( \psi \): sources or sinks for the pesticide (µg/cm³/hr), such as degradation, irreversible reactions, etc.

In the case of atrazine, the Henry's law constant is very low (2.45x10⁻⁷) (Jury et al. 1983), so \( C_G \) is negligible as compared to \( C_L \). Therefore, equation (1.1) can be simplified as:

\[
\frac{\partial}{\partial t} (\rho C_s + \theta C_L) = \frac{\partial}{\partial z} \left[ \theta D(\theta, q) \frac{\partial C_L}{\partial z} - q C_L \right] \pm \psi \tag{1.2}
\]

Under steady-state water flow, \( q \) and \( \theta \) are constants, then equation (1.2) can be further simplified as:
In order to solve the above equations, the following functions are prerequisite:

\[
\frac{\partial C_s}{\partial t} + \theta \frac{\partial C_L}{\partial t} = \theta D(\theta, q) \frac{\partial^2 C_L}{\partial z^2} - q \frac{\partial C_L}{\partial z} \pm \psi
\]  

(1.3)

In order to solve the above equations, the following functions are prerequisite:

\[
C_s = F_1(C_L, z, t, \theta, q)
\]  

(1.4)

and

\[
\psi = F_2(C_L, z, t, \theta, q)
\]  

(1.5)

All the deterministic models try to find the simple and reasonable formulas of \(F_1\) and \(F_2\). The simplest form of \(F_1\) is adsorption isotherms, such as the Freundlich and the Langmuir equations (Hamaker and Thompson 1972), and the commonly used \(F_2\) form is first-order degradation (Hamaker 1972a). However, \(F_1\) and \(F_2\) are usually more complicated and take implicit forms (Selim et al. 1976, Skopp and Warrick 1974, van Genuchten and Wierenga 1976).

Sharkey soil (very-fine, montmorillonitic, nonacid, vertic Haplaquept) is commonly found in the Mississippi alluvial plain and frequently used as corn or sugarcane fields. It has organic content of 1.73 %, pH of 6.45 (top soil), clay content of 61%, silt content of 36%. It is poorly drained with a seasonal high water table within 1-3 feet of the surface in most years. Slopes range from 0-3 percent. In dry season, cracks of 1-3 cm wide develop to a depth of 20 inches or more in most years (Schumacher et al. 1988). Due to its shallow water table and frequent atrazine application, as high as 400 ppb of atrazine has been reported in 1 m tile-drain water.
samples one week after application (Southwick et al. 1992). Since this soil-pesticide combination could be the worst scenario in terms of groundwater contamination, systematic study of atrazine in such a soil is valuable. The objectives of this study were (i) to evaluate the effects of incubation time on hysteretic behavior of atrazine adsorption-desorption in batch experiments; (ii) to predict atrazine adsorption-desorption kinetics and hysteresis in batch experiments; (iii) to predict atrazine transport in uniformly packed soil columns under different experimental conditions; (iv) to evaluate the importance of chemical and physical nonequilibrium in atrazine transport. In order to achieve these goals, batch equilibrium, batch kinetics and column transport studies were initiated based on knowledge gained from the literature. Several new approaches were also proposed and tested against experimental results.

1.2 Atrazine Adsorption and Desorption

Protonation of atrazine is considered the main mechanism of atrazine adsorption at low pH (Armstrong and Chesters 1968). The protonation can be carried out in the following ways: (1) at the soil surface by reaction of atrazine with the hydronium ion on the exchange site; (2) in the solution phase by H⁺, with a subsequent adsorption via ion exchange; and (3) by reaction with the dissociated protons from the residual water on the soil surface or on the exchangeable cations. However, hydrogen bonding and van der Waal’s forces could be the prime mechanism for the adsorption of unprotonated atrazine at neutral pH (Bailey et al. 1968, Armstrong and Chesters 1968, Obien 1970). Welhouse and Bleam (1993), using nuclear magnetic resonance (NMR) technique, demonstrated the formation of hydrogen-bond-complexes between atrazine and compounds commonly found in soil organic matter. They further measured the formation constants of the complexes and found that weak to moderately strong complexes are formed with amine, hydroxyl and carbonyl functional groups. However, strong complexation is observed with the carboxylic acid and amide function groups. Hydrophobic bonding is also considered as a mechanism for adsorption of s-triazines (Walker and Grawford 1968).

Higher atrazine adsorption is observed at lower pH on montmorillonite (Bailey et al. 1968, Armstrong and Chesters 1968), model absorbents (Armstrong and Chesters 1968), and humic fractions (Kalouskova 1989). Adsorption reaches its maximum when surface acidity is approximately equal to the dissociation constant of atrazine (pKa=1.68) (Armstrong et al. 1967, Bailey et al. 1968, Nearpass 1969, Armstrong and Chesters 1968). Similar results have been reported on natural soil
systems (Hayes et al. 1968, Obien 1970, Harris and Warren 1964). Hayes et al. (1968) studied the adsorption of atrazine onto untreated soils, H+-, and Ca++-saturated soils, and found that H+-saturated soils had highest adsorption, followed by untreated and Ca++-saturated soils. However, Obien (1970) treated four Hawaiian soils (Kaipoioi, Kapaa, Molokai and Lualualei) with Ca(OH)₂ or HCl to obtain a soil pH range of 3.5-8.0. He found that adsorption of atrazine increased with decrease in pH (or increase in protonation). From the study on bentonite and muck soils, Harris and Warren (1964) concluded that hydrogen ions caused two opposite effects on atrazine adsorption: enhancing adsorption due to increase in atrazine protonation and retarding adsorption due to the loss of exchange sites on the soil surface. So, at very low pH (lower than pKₐ), atrazine adsorption would decrease because of the competition on exchange sites from H⁺ (Armstrong and Chesters 1968).

Organic matter is the principal soil component influencing the adsorption of many herbicides (Rao and Jessup 1983, Hubbs and Lavy 1990). Talbert and Fletchall (1965) found that atrazine adsorption was highly related to organic matter contents (r=0.82), followed by clay (r=0.65) and CEC (r=0.63) in the 25 soils studied. Walker and Crawford (1968) obtained the correlation coefficients of 0.96, 0.91, and 0.08 between adsorption and percentage of carbon (% OC), CEC, and percentage of clay (%), respectively, in 36 soils. Brouwer et al. (1990) observed a linear increase of distribution coefficient (Kₐ) with organic matter content. Thus, $K_{oc} = K_d/(%OC)$ was proposed as a property of pesticides and was assumed to be independent of soil properties (Yaron et al. 1985). Partial removal of organic matter by hydrogen
peroxide showed a great decrease in atrazine adsorption (Walker and Crawford 1968, Huang et al. 1984). Besides the absolute amount of organic matter content, the stage of decomposition is also important in determining atrazine adsorption (Walker and Crawford 1968, Talbert and Fletchall 1965, Singh et al. 1989). This is because humic substances (specially humic acid) have higher affinities for atrazine than nonhumic substances (carbohydrates, proteins, waxes, etc.) (Dunigan and McIntosh 1971, Tompkins et al. 1968, Walker and Crawford 1968). Although fulvic acid has high catalytic activity for atrazine hydrolysis (Gamble and Khan 1985, Khan 1980) due to its high carboxylic acid group content and high total surface acidity, it only plays a minor role in atrazine adsorption by forming weak complexes with atrazine (Van der Waals and weak hydrogen bond) (Hayes et al. 1968). However, Barriuso et al. (1991) reported that 62% of the total bound residues was associated with the fulvic acids in the Brown soil studied, and that this percentage decreased with time.

The surfaces of clay minerals have negative changes that are balanced by exchangeable cations, and thus, are important in adsorption of cationic and protonated herbicides (Yaron et al. 1985). The pH in the immediate vicinity of clay surface is much lower than that in the bulk solution. Therefore, clay can be a very strong proton donor and adsorb protonated atrazine (Yaron et al. 1985). Philen et al. (1970, 1971) found that paraquat and diquat adsorption by the external surfaces of vermiculite and mica are linearly related to the surface charge density. However, Laird et al. (1992) found that atrazine adsorption decreased with surface charge density (SCD) in pH range of 4.75-6.45 in 14 Ca-saturated smectites. Therefore, atrazine may be adsorbed
as neutral molecules in that pH range. The importance of clay on pesticide adsorption also decreases with increase in soil organic matter content (Hance 1969). Thus, the role of clay on atrazine adsorption is dependent on the type of clay as well as its surface coverage with organic matter. In soils with less than 5% of carbon content, clay makes some contributions to atrazine adsorption (Walker and Crawford 1968). Bailey and White (1970) demonstrated that the adsorption capacity of clay for herbicides followed the order of montmorillonite > illite > kaolinite.

The effects of temperature on atrazine adsorption are not consistent from laboratory to laboratory. Some researchers found a positive relationship between atrazine adsorption and temperature (Dao and Lavy 1978, McGlamery and Slife 1966, Dunigan and MacIntosh 1971, Yamane and Green 1972). A negative relationship, on the other hand, was obtained on bentonite (pH 8.5) by Harris and Warren (1964). Hayes et al. (1968) observed a higher atrazine adsorption at 20 °C than at 70 °C during the first eight hours of reaction with humic acid. However, Huang et al. (1984) did not find any temperature effect in the range of 5-25 °C in soils with neutral pH (6.0-7.6). These results suggest that temperature effects are dependent on the adsorption mechanisms of the adsorbates. Calvet (1980) concluded that the observed temperature effect depended on the response of both surface-solute and water-solute interactions to change in temperature.

Water content was shown to have effects on s-triazine protonation and adsorption by modifying the aggregation of adsorbents and by increasing or decreasing the accessibility of surface to the solute (Grover and Hance 1970). Dao and Lavy
(1978) found that an increase in soil:water ratio led to an increased adsorption of atrazine. However, Grover and Hance (1970) reported an increase in sorption of atrazine with decrease in soil:solution ratios from 4:1 to 1:10, which was explained as a result of decrease in ionic strength (Alva and Singh 1991). Nearpass (1967) also found an increase in atrazine adsorption as soil:water ratio decreased from 1:2 to 1:5. However, the distribution coefficients ($K_d$) are not affected by soil:water ratio. In a study with simazine, Singh et al. (1989) found that the soil:water ratio did not affect simazine desorption hysteresis. By using infrared spectra analysis, Brown and White (1969) found that reduction in water content caused an increase in protonation and adsorption of propazine. Green and Obien (1969) derived the following expression based on mass balance to reflect the effect of water content on atrazine concentration in soils:

$$C_w = \frac{Q}{m(W_e+K_d)}$$  \hspace{1cm} W_e > 0 \hspace{1cm} (1.6)

$$C_a = K_d \times C_w$$  \hspace{1cm} (1.7)

where $C_a$ and $C_w$ are the concentrations in solid and liquid phases ($\mu g/g$), respectively. $K_d$ is the adsorption distribution coefficient, $Q$ is the total atrazine applied to the system ($\mu g$), $m$ is the total soil weight on an oven-dry basis (g), and $W_e$ is the effective water content (g/g). $W_e$ is given by the following equation:

$$W_e = W - W_{15bar}$$  \hspace{1cm} (1.8)
where $W$ and $W_{15\text{bar}}$ are the total water content and water content at 15 bar (g/g), respectively, on the oven dry basis. Therefore, the effect of water content on adsorption is dependent on both $W_{15\text{bar}}$ and $K_d$. Equations (1.6) and (1.7) actually describe the dilution effect of water (Dao and Lavy 1978). However, $K_d$ itself is not a constant as water content changes, because decrease in water content increases surface acidity and reduces competition from water molecules (Bailey and White 1964, Brown and White 1969). Thus, due to differences in soil:water ratio, the conventional batch experiment may not yield partition coefficients applicable to field conditions (Hilton and Yuen 1963, Green and Obien 1969, Hance 1988).

Increase in the concentration of electrolytes in soil solution increases atrazine adsorption due to decrease in soil pH and atrazine water solubility (Dao and Lavy 1978, Hurle and Freed 1972, Swanson and Dult 1973). Similar results were reported with other pesticides (Alva and Singh 1991, Koskinen and Clay 1983). However, Armstrong and Chesters (1968) found that addition of NaCl decreased atrazine adsorption slightly. This decrease in adsorption was explained by competition between salts (cations) and protonated atrazine for adsorption sites (Dunigan and Macintosh 1971, Gilmour and Coleman 1971). Nearpass (1967) observed a decrease in atrazine sorption in a Bayboro clay soil with an increase in cation saturation (Ca, Mg, or Na). Gilmour and Coleman (1971) also found that an increase in effective CEC after Ca-saturation resulted in greater adsorption if pH and protonation are constant. Obien (1970) measured an increase in the efficiency of hydroxyatrazine extraction when CaCl$_2$ was added to nonacidified methanol, but Goswami and Green (1973) obtained
the opposite result using acidified methanol. This discrepancy was explained by the change in soil pH which, in turn, affects the protonation of atrazine. CaCl$_2$ increases pH in the soil with a net positive charge and decreases pH in the soil with a net negative charge (Mekara and Uehara 1972). Calvet (1980) summarized that cations affected herbicide adsorption by competing for adsorption sites with positively charged organic molecules, or by acting directly as adsorption sites through the formation of coordination bonds, or by forming hydroxides on the clay surface.

However, hydrolyzed product (hydroxyatrazine) does not affect atrazine adsorption (Armstrong and Chesters 1968, Obien 1970, Wang et al. 1990). This independent adsorption behavior indicates that these two compounds are adsorbed on different sites (Obien 1970). Since the pK$_a$ of atrazine is 1.68 and that of hydroxyatrazine is 5.1, their degrees of protonation are very different in soils. Therefore, the competition or interference between the two compounds should be minimal, if not negligible. But, the decrease in the total atrazine concentration due to hydrolysis increases the distribution coefficient ($K_d$) (Obien 1970).

Atrazine adsorption studies by use of mechanical shaking show that 98% of atrazine that was adsorbed within 24 hrs was adsorbed in the first two hours, and that the change in the amount of atrazine adsorbed between 24 and 48 hours was less than 1-2 % (Clay et al. 1988a, Clay and Koskinen 1990a,b). These results, along with others (Obien 1970, Wauchope and Myers 1985, Kalouskova 1989), shown that atrazine adsorption is composed of two phases: fast and slow adsorption phases. One explanation for the observed two phases is the two adsorption site theory (Selim et al.
Wauchope and Myers (1985) hypothesized labile and restricted absorption sites, and found an increase in atrazine adsorption on restricted sites accompanied with a concurrent decrease of atrazine on labile sites. Another explanation is the physical diffusion theory, in which the slow adsorption is caused by the diffusion of atrazine from accessible surfaces into the interspace of organic matter or the interlayer of clay minerals (Skopp and Warrick 1974, van Genuchten and Wierenga 1976, Hamaker 1972b, Brusseau and Rao 1989). However, the CDE's derived from both theories are mathematically identical when both chemical reaction and physical diffusion are linear (Rao and Jessup 1983, Nkedi-Kizza et al. 1984).

Atrazine adsorption at equilibrium is usually expressed as an adsorption isotherm. The commonly used isotherm is the Freundlich equation (Brouwer et al. 1990, Albanis et al. 1989, Clay et al. 1988a, Clay and Koskinen 1990a,b, Huang et al. 1984, Bailey et al. 1968):

\[ X = K_f \times C^N \]  

where \( X \) is the amount sorbed at equilibrium (\( \mu g/g \)), \( K_f \) is the Freundlich coefficient, \( C \) is the equilibrium concentration of the compound in the liquid phase (\( \mu g/ml \)) and \( N \) is the Freundlich exponent. \( K_f \) usually increases with decreasing soil pH (Clay and Koskinen 1990a). However, in a study with 14 Ca-saturated smectites, Laird et al. (1992) found that \( \log(K_f) \) is best correlated to surface charge density (SCD) and surface area. \( N \), on the other hand, is positively correlated to pH and SCD. The value of \( N \) for atrazine is usually less than or close to 1.0 (Clay et al. 1988a, Clay and
Koskinen 1990a,b, Brouwer et al. 1990, Calvet 1980, Burkhard and Guth 1981, McGlamery and Slife 1966). So, it is valid to use the following equation for a given soil-herbicide combination in the practical range of pesticide concentrations (Brouwer et al. 1990, Green and Obien 1969).

\[ X = K_d \times C \]  \hspace{1cm} (1.10)

where \( K_d \) is the distribution coefficient. It depends not only on pesticide properties, but also on soil properties. Among the soil properties, soil organic matter content has been shown to be the major determining factor. Therefore, the use of \( K_{oc} \) defined by the following equation may be more meaningful for a given pesticide:

\[ K_{oc} = \frac{K_d \times 100}{\% O.C.} \]  \hspace{1cm} (1.11)

The use of \( K_{oc} \) showed less variability between soils. Gerstl and Yaron (1983) found that the \( K_{oc} \) value of napropamide in six soils ranged from 249 to 450 (ml/g) while \( K_d \) from 0.27 to 2.94 ml/g. The other advantage of using \( K_{oc} \) is that it is a parameter of the pesticide itself and can be estimated from physical and/or chemical properties of the pesticide, such as solubility, octanol-water partition coefficient (\( K_{ow} \)), melting point, pure solute molar volume (Green and Karichhoff 1990, Mingelgrin and Gerstl 1983, Briggs 1981, Singh et al. 1989). Table 1.1 lists some of the physical and chemical properties of atrazine and hydroxyatrazine. The estimated \( K_{oc} \) could be used as a first approximation in modeling chemical transport and in establishing a reference data base in the literature (Green and Karichhoff 1990, Johnson and Farmer 1993).
Table 1.1 Physical and Chemical Properties of Atrazine and Hydroxyatrazine

<table>
<thead>
<tr>
<th></th>
<th>molecular Wt</th>
<th>pK_a</th>
<th>water solubility (ppm)</th>
<th>vapor pressure (mmHg)</th>
<th>K_{ow}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>216</td>
<td>1.68</td>
<td>33</td>
<td>3.0 \times 10^{-7}</td>
<td>160</td>
</tr>
<tr>
<td>Hydroxyatrazine</td>
<td>198</td>
<td>5.15</td>
<td>16</td>
<td>------</td>
<td>---</td>
</tr>
</tbody>
</table>

^a Jordan (1970); ^b Somasundaram et al. (1991); ^c Suntio et al. (1988).
However, it may be of little practical value in transport study, since a small difference in the distribution coefficient may greatly affect the mobility of a pesticide in soil (Singh et al. 1989, Mingelgrin and Gerstl 1983).

In order to fully understand the mechanisms of atrazine adsorption and desorption in soils, studies were conducted on pure clay (Weber 1970, Yamane and Green 1972, Bailey et al. 1968) and pure organic matter (McGlamery and Slife 1966, Weber et al. 1969, Gilmour and Coleman 1971, Li and Felbeck 1972a). Dunigan and MacIntosh (1971) and Huang et al. (1984) used another strategy by testing the adsorption capacity of the residual soil system after removing certain soil components. However, this technique still cannot present the real situation in soils, because organic matter, sesquioxides and clay minerals are closely interrelated to each other in soils. Therefore, these treatments do more than eliminate a constituent and affect the remaining materials by blocking or unblocking adsorption sites for atrazine (Dunigan and MacIntosh 1971, Calvet 1980).

Four methods have been used for the assessment of pesticide adsorption-desorption in the literature (Green et al. 1980, Hance 1988, Rao and Davidson 1980, Johnson and Farmer 1993). Method I is the widely used "batch" method in which a certain amount of adsorbent is suspended by agitation in a fixed volume of adsorbate solution. Method II involves continuous flow of a solution of known concentration into a flow cell in which the adsorbent is maintained in suspension. This method can be used to obtain an isotherm in a single flow cell by measuring the effluent frequently. Method III also involves continuous flow equilibration but utilizes a thin column or
pad of adsorbent in a flow cell rather than the adsorbent suspension cell of method II. Method IV involves the exposure of adsorbent in a column to a flowing solution of known concentration until adsorption equilibrates with the inlet solution, followed by displacement of the adsorbed pesticide with pesticide-free solution. This method directly measures the displaced pesticide. Each method has its advantages and disadvantages. Method I and II change the adsorbent by agitation. Method III is limited by long equilibrium time and is more useful for measuring the kinetics of adsorption-desorption reactions in soils. Method IV is restricted when the adsorbed pesticides are not desorbable by the solvent used. Choosing a method is based on the intended use of the data and the ease of measurement.

Sparks and Rechcigl (1982) compared batch and miscible displacement (flow system) techniques on potassium adsorption. They found that the batch method reached equilibrium sooner than miscible displacement. They also noticed that clay content did not affect the equilibrium time in batch experiments, but it increased the equilibrium time in miscible displacement. The faster equilibrium in batch experiments was also observed by Kookana et al. (1992b) in a pesticide study, which was attributed to mechanical shaking, vortex, and centrifuging involved in batch experiments. The sorption coefficients obtained from the continuous flow method are significantly lower than those calculated from batch experiments (Davidson et al. 1968, Kookana et al. 1992a). Therefore, the validity of the adsorption-desorption isotherms obtained by the batch technique is questionable in miscible column experiments. Rao and Jessup (1983) suggested that "batch slurry" methods were
insensitive and might be unsuitable for investigating sorption kinetics. However, Johnson and Farmer (1993) found that the sorption coefficients from the batch technique were not significantly different from the ones obtained from the continuous flow method at a flow rate of 2.7 cm/day. Thus, the validity of equilibrium in pesticide transport depends on the flow rate (van Genuchten et al. 1974, Davidson et al. 1968).

The Freundlich equation is also used for atrazine desorption isotherms. But, the N for desorption isotherms (N_d) is consistently lower than that of adsorption isotherms (N_a) (Clay et al. 1988a, Clay and Koskinen 1990a,b, Swanson and Dutt 1973). Therefore, less herbicide is desorbed from soils than predicted by the adsorption isotherm, which is often referred to as hysteresis (Selim et al. 1976, Swanson and Dutt 1973, van Genuchten et al. 1974, 1977). Swanson and Dutt (1973) found that N_d was independent of atrazine initial concentration, and that a N_a/N_d value of 2.3 was adequate in describing atrazine adsorption-desorption hysteresis. However, the K was concentration dependent. Similar results were reported on picloram (van Genuchten et al. 1974) and 2,4,5-T (van Genuchten et al. 1977).

However, Barriuso et al. (1992) proposed a two-compartment adsorption-desorption model, where atrazine adsorption has two components (linear and exponential adsorptions) as described by the following equation.

\[
\frac{X}{m} = K_1 C + \left(\frac{X}{m}\right)_n (1 - e^{-K_2 C})
\]  

(1.12)
where $C$ is solution concentration ($\mu g/ml$), $x/m$ is the amount of herbicide adsorbed ($\mu g/g$), $(x/m)_n$ is the maximum amount adsorbed in the exponential compartment ($\mu g/g$), and $K_1$ and $K_2$ are constants.

The non-singularity or hysteresis of atrazine adsorption-desorption isotherms has been observed in many laboratories (Harris and Warren 1964, Swanson and Dutt 1973, Koskinen and Harper 1990, Pignatello 1989, Hamaker and Thompson 1972, Clay et al. 1988a, Clay and Koskinen 1990a,b, Brusseau and Rao 1989), which means that for a given equilibrium solution concentration, more atrazine is retained on the soil during the desorption phase than during the adsorption phase. Hysteresis is more obvious under low soil pH, long equilibrium time, high organic matter content, frequent drying and rewetting, and high degradation rates (Hamaker and Thompson 1972, Best and Weber 1974, Clay and Koskinen 1990b, Pignatello and Huang 1991). Although there is no satisfactory explanation for this difference in adsorption-desorption isotherms, several causes may be responsible for the observed hysteresis (Brusseau and Rao 1989, Koskinen and Harper 1990, Rao and Davidson 1980):

1. nonequilibrium during adsorption and desorption processes. However, this cannot be overcome by increased equilibrium time. Koskinen et al. (1979) found that the hysteresis increased with incubation time.

Pesticides can form stable chemical linkages with organic substances in soil by direct chemical attachment to reactive sites on colloidal organic surfaces or by incorporation into the structures of newly formed humic and fulvic acid during the humification process (Stevenson 1976). The latter is enhanced by such processes as freezing and thawing, wetting and drying. In a study with linuron, Singh et al. (1989) found that the desorption hysteresis disappeared after the removal of organic matter.

(3) Chemical degradation of atrazine during adsorption. The degradation product, hydroxyatrazine, desorbs much more slowly compared to atrazine (Clay and Koskinen 1990a). Stevenson (1972) found that the hydrologs of atrazine were strongly bound to soil organic matter.

(4) artifacts resulting from experimental methods and pesticide measurements (Rao et al. 1978). Mechanical shaking in batch experiments may result in changes of the soil surfaces and the composition of the slurry (Koskinen and Cheng 1983, Gschwend and Wu 1985, Green and Obien 1969). Huang et al. (1984) showed that particle sizes in the range 2-5 μm produced the highest adsorption of atrazine. Repeated centrifuging of the slurry was also reported to be responsible in some way for the nonsingularity of pesticide adsorption (Bowman and Sans 1985). Green et al. (1980) suggested that maintenance of aggregate structure is important when independent adsorption measurements are to provide data for mathematical simulation.

Indirect measurement of atrazine adsorption from the disappearance of atrazine from liquid solution may exclude degradation and volatilization loss during experiments (Clay et al. 1988a, Singh et al. 1990a). Singh et al. (1990a) observed that
the Freundlich K-values calculated with the solution difference method are as much as 2.5 times higher than the mass-balance computed values for atrazine. On the other hand, in a study with napropamide and lindane, Johnson and Farmer (1993) found that the sorption coefficients derived from the solution difference method are not significantly different from those obtained from the mass balance method. However, the solution difference method may not be appropriate if the concentration change is relatively small compared to the error in pesticide measurement (Green and Yamane 1970, Boesten 1990, Johnson and Farmer 1993).

The hysteresis phenomenon has been incorporated into pesticide transport models by several authors (van Genuchten et al. 1974, 1977, Swanson and Dutt 1973). These investigators found that separating sorption process into adsorption and desorption considerably improved their model predictions. Selim et al. (1976) proposal a two-site model to explain the observed desorption hysteresis, in which two different adsorption sites were assumed. Both sites kinetically react with soil solutes. This model has been used often in the literature and is able to provide better predictions for reactive solute sorption and transport (Wauchope and Myers 1985, Van Genuchten et al. 1974, Rao et al. 1979).

Besides the hysteresis in adsorption-desorption isotherms, atrazine adsorbs onto soil irreversibly and becomes nonextractable even with organic solvents (e.g. methanol). This portion of atrazine is often referred to as bound residual and increases with incubation time. Sorenson et al. (1993) found that only 5% of $^{14}$C was unextractable immediately following application, but up to 18% was unextractable.
months after application in a sandy loam soil. Clay et al. (1988a) found that 20% of atrazine was nonextractable with methanol after 6 days. Schiavon (1988a) noticed that 60% of atrazine was not extractable by methanol solution one year after atrazine application. Capriel et al. (1985) found 50% ¹⁴C residues in the unextractable form nine years after ¹⁴C-ring labeled atrazine was applied to a mineral soil under field conditions. Barriuso et al. (1991) observed 15-40% of atrazine in bound form after six months of incubation. Durand and Barcelo (1992) reported a permanent level of atrazine of 20-25 ng/g (8% of applied atrazine) in soils. Clay and Koskinen (1990b) found that all atrazine was extractable with methanol after one extraction (1 day) with 0.01 M CaCl₂. However, up to 18% of atrazine applied was nonextractable after five extractions (5 days) with 0.01 M CaCl₂ in Ves clay loam. They also noticed that the percentage of methanol nondesorbable atrazine increased with the decrease in initial atrazine concentration. Similar results were reported by others (Gamble and Khan 1992, Johnson and Farmer 1993, Smith et al. 1992). The high percentage of bound residue at low atrazine concentrations is probably due to more adsorption to the restricted adsorption sites (Smith et al. 1992, Johnson and Farmer 1993). Bound atrazine residual, which may be parent compound or metabolites, is also dependent on the solvent and conditions of extraction (Kaufman 1976, Clay and Koskinen 1990b). However, the unextractable atrazine is not necessarily correlated with the lack of availability to plants, animals, and microorganisms (Hamaker and Goring 1976). Small amounts of the unextractable pesticide are still available to plants and microorganisms (Khan 1991).
First-order kinetics have been employed by many authors to describe pesticide adsorption-desorption (Calvet 1980, Hamaker and Thompson 1972) and non-equilibrium transport in the soil environment (Leistra 1980), which can be expressed as follows:

\[ \frac{dQ_a}{dt} = k_a(Q_\infty - Q_a) \]  

(1.13)

and

\[ \frac{dQ_d}{dt} = k_{des} * Q_a \]  

(1.14)

Where \( Q_a \) and \( Q_d \) are the amount of atrazine adsorbed and desorbed (\( \mu g \)), respectively. \( Q_\infty \) is the maximum amount adsorbed (\( \mu g \)), and \( k_a \) and \( k_{des} \) are the rate constants for adsorption and desorption, respectively.

Selim et al. (1976) proposed a two adsorption site model to explain adsorption kinetics and desorption hysteresis. The governing equations are:

\[ \frac{\partial S_I}{\partial t} = \frac{\theta}{\rho} k_1 * C^m - k_2 S_I \]  

(1.15)

\[ \frac{\partial S_{II}}{\partial t} = \frac{\theta}{\rho} k_3 * C^n - k_4 S_{II} \]  

(1.16)

where \( k_1, k_2, k_3 \) and \( k_4 \) are the rate constants (hr\(^{-1}\)). \( S_I \) and \( S_{II} \) are the concentrations on the \( S_I \) and \( S_{II} \) adsorption sites (ug/g), respectively. \( C \) is the concentration in soil solution phase (\( \mu g/ml \)), and \( m \) and \( n \) are reaction orders for site I and II, respectively.
Barriuso et al. (1992) described pesticide desorption as a function of dilution factor \( (d) \) based on a two compartment model:

\[
\frac{x}{m} = \left[ (\frac{x}{m})_0 - (\frac{x}{m})_{irr} \right] d^{-k} + (\frac{x}{m})_{irr}
\]  

(1.17)

where \( \frac{x}{m} \) is the amount of pesticide adsorbed (\( \mu g/g \)), \((\frac{x}{m})_0\) is the initial amount of herbicides adsorbed before the start of desorption, \((\frac{x}{m})_{irr}\) is the nondesorbable amount of pesticide, \(d\) is the dilution factor, and \(k\) is a coefficient related to the desorption efficiency.

1.3 Atrazine Hydrolysis

Much research has been conducted on atrazine hydrolysis. Atrazine hydrolysis to hydroxyatrazine is considered a chemical process catalyzed by soil surfaces (Best and Weber 1974, Obien 1970). In soils, hydrolysis of atrazine is favored by low soil pH, high organic matter content, low moisture content, high temperature, high clay content, etc. (Best and Weber 1974, Harris 1967, Obien 1970). This hydrolysis process is a primary pathway for atrazine detoxication (Armstrong et al. 1967, Armstrong and Chesters 1968, Harris 1967, Russell et al. 1968, Skipper et al. 1967, Muir and Baker 1978, Goswami and Green 1971, Obien and Green 1969, Roeth et al. 1969, Skipper 1970). Armstrong and Chesters (1968) demonstrated that the only detected degradation product of atrazine was hydroxyatrazine. They noticed that 43.5% of the applied atrazine converted to hydroxyatrazine during a 56 day experiment with Poygan soil at pH 4.5. Muir and Baker (1978) found considerable amount of hydroxyatrazine below the plough layer in a field experiment. In a field
study with a sandy loam soil, Sorenson et al. (1993) found that hydroxyatrazine was the predominant degradation product of atrazine. The proportion of $^{14}$C as hydroxyatrazine in the top 10 cm increased from 15% 2 months after application to 37% 16 months after application.

Armstrong et al. (1967) conducted an extensive study on atrazine hydrolysis in three soils with a wide range of organic matter content and pH (Poygan silt loam, Ella loamy sand and Kewaunee clay). They found that soil pH is a predominant factor in determining hydrolysis of atrazine over organic matter. Low pH promoted hydrolysis even if there was low organic matter content. At similar pH levels, the higher the organic matter content, the higher the atrazine hydrolysis rate (Li and Felbeck 1972b). The hydrolysis rate reaches its maximum when surface acidity equals pKa (1.68), which is explained by the highest adsorption of atrazine near pK$_a$ (Armstrong and Chesters 1968, Obien 1970). However, Hance (1979) found that degradation increased slightly in Boddington Barn soil and decreased in Triangle soil with pH increasing from 5.1 to 8.2. This was probably due to different responses of soil surfaces to pH (Harris and Warren 1964).

Atrazine hydrolysis rate is much higher in the presence of soil (Armstrong et al. 1967, Burkhard and Guth 1981, Bacci et al. 1989, Obien 1970). This is due to the following: (1) the adsorption of atrazine on soil surfaces decreases the electronegativity of the carbon of the C-Cl bond, therefore, it is easier for nucleophilic displacement of Cl to take place; and (2) the pH value of the soil surface is 2-4 units lower than that in the bulk solution (Armstrong et al. 1967, Albanis et al. 1989,
Bailey et al. (1968). Obien (1970) quantitatively measured the soil catalytic effects in terms of "catalytic pH", which was defined as the equivalent soil-free aqueous solution pH at the same hydrolysis rate. He found the catalytic pH ranging from 0.54 to 5.03 in the four Hawaiian soils. This catalytic pH increases with increasing soil pH.

The mechanisms for atrazine hydrolysis in soils and in aqueous soil-free solutions are different. Hydrolysis of atrazine in soils results from hydrogen bonding between the adsorbent carboxyl and atrazine ring nitrogen atom, which facilitates replacement of Cl from the C-Cl bond by H₂O (Russell et al. 1968, Armstrong and Chesters 1968). But, in soil-free solutions, alkaline hydrolysis of atrazine is likely to involve direct nucleophilic displacement of Cl by OH, while acid hydrolysis may result from protonation of a ring or chain N atom followed by cleavage of the C-Cl bond by H₂O (Armstrong et al. 1967, Skipper 1970).

Brown and White (1969) found, through infrared studies, that reduction in water content caused an increase in hydrolysis due to both the high dissociation of residual clay-water and less competition from water molecules. Skipper (1970) observed that dehydration of Ca-Coker clay soil at 75 °C enhanced atrazine hydrolysis as a result of increased surface acidity. However, very dry conditions will decrease the degradation rate, because water also acts as a reaction medium for both biological and non-biological processes, and a reagent in hydrolysis reactions (Hurle and Walker 1980, Obien 1970). Harris (1967), through bioassay studies, found that low water content, high temperature, and long atrazine-soil contact time reduced the inhibition of oat seedlings.
Hayes et al. (1968) observed a higher decomposition rate of atrazine at 70°C rather than at 20°C. Obien and Green (1969) found that atrazine degradation (mainly chemical hydrolysis) was accelerated as temperature increased from 30 to 50 °C in four Hawaiian soils. Zimdahl (1968) noticed a three-times increase of the first-order degradation rate constants as temperature increased from 13.2 to 31.2 °C. Similar results were reported by Huang and Pignatello (1990) who found that atrazine decomposition was higher at 95 °C than that at 75 °C. Since microbial degradation is negligible at this higher temperature range, the temperature effect is mainly due to the increase in chemical hydrolysis. This temperature effect can be expressed by the Arrhenius equation (Obien 1970, Burkhard and Guth 1981, Li and Felbeck 1972a, Zimdahl 1968, Bosetto et al. 1993):

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{\Delta H_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(1.18)

where $k_1$ and $k_2$ are the first-order hydrolysis rate constants at temperature $T_1$ and $T_2$ (°K), respectively. $\Delta H_a$ is the activation energy (cal/mol), and $R$ is the gas constant (1.978 cal/mol/°K).

By comparing the hydrolysis rates among the soils and artificial adsorbents, Armstrong and Chesters (1968) concluded that carboxylic groups in soils were the most effective catalysts for atrazine hydrolysis. Although phenolic resin and montmorillonite showed high atrazine adsorption ability, their hydrolysis rates were relatively low (Russell et al. 1968, Brown and White 1969). However, Skipper (1970)
demonstrated, by infrared studies, that acidified montmorillonite was able to hydrolyse atrazine, but "allophanic" and other amorphous materials would be relatively inert.


\[-\frac{dC}{dt} = K \times C\]  \hspace{1cm} (1.19)

Integrating equation (1.17) yields:

\[C = C_0 \times e^{-kt}\]  \hspace{1cm} (1.20)

For \(C = C_0/2\) the half-life \(t_{1/2}\) is defined as:

\[t_{1/2} = \frac{0.6932}{k}\]  \hspace{1cm} (1.21)

where \(k\) is the rate constant. \(t_{1/2}\) (in days) is widely used as an index for atrazine persistence in soils, although some reports disagree with the use of \(t_{1/2}\) (Hamaker 1972a, Junk et al. 1984).

The longest half-life of atrazine is observed in aqueous solution near neutral pH (Armstrong et al. 1967, Burkhard and Guth 1981). It can be expressed by the following equations in aqueous soil-free solutions (Armstrong et al. 1967):

For acidic solutions: \(\log(t_{1/2}) = 0.62pH - 0.1\)

For alkaline solutions: \(\log(t_{1/2}) = 5.64 - 0.91(pH - 7)\)

Similar pH effects were observed in soils (Burkhard and Guth 1981) and humic acid (Li and Felbeck 1972b). Hiltbold and Buchanan (1977) found that atrazine persisted
8-9 days, 9-13 days, and 29 days longer with each unit increase in soil pH from 5 to 7 in Mclaurin sandy loam, Hartsells sandy loam and Decatur silt loam, respectively. But at neutral pH (6.8-6.9), Junk et al. (1984) did not observe atrazine degradation during a 68 week period. Skipper (1970) found the hydrolysis of atrazine on H- or Al-montmorillonite, but he was unable to detect atrazine hydrolysis on Ca²⁺- and Cu²⁺-montmorillonite although there was an existence of atrazine-cation-clay complex. He further confirmed that hydrolysis involved the interactions of the chain-NH with the clay system, and that the hydrolytic product was in a protonated keto form of hydroxyatrazine.

In a study with a Poygan soil and model adsorbents (carboxylic resin, phenolic resin and cellulose acetate), Armstrong and Chesters (1968) observed a linear relationship between the hydrolysis rate constant and the extent (%) of atrazine adsorption. On the other hand, Burkhard and Guth (1981) found that adsorption and t₁/₂ in soils increase in the same direction, as shown by the following equation:

$$\log(Q)=a \times t_{1/2} + b$$  (1.22)

where Q=100*(K_f/OM) is the amount adsorbed per unit mass of organic matter, K_f is the Freundlich constant, OM is organic matter content (%), and a,b are regression parameters. However, Hance (1974) could not establish a relationship between the rate of atrazine decomposition and the extent of adsorption. Therefore, adsorption does not always protect a chemical from degradation, nor does it always lead to an increased rate of loss (Hurle and Walker 1980, Obien 1970). This inconsistent adsorption-
hydrolysis relationship may be understandable in view of the follow aspects: (1) The reported standard enthalpy change for adsorption ranges from 3.8 to 664.8 cal/mol (Dao and Lavy 1978) while that for hydrolysis is 19140 cal/mol at pH 2 (Obien 1970). (2) In a study with 12 s-triazines on soil clays, Brown and White (1969) found that protonation and adsorption are directly related to their dissociation constants (pKa), but hydrolysis has an inverse relationship.

If the rate constant (k) is proportional to the percentage of atrazine adsorbed on soil surfaces (Armstrong and Chesters 1968), then, according to the Freundlich adsorption equation, the rate constant can be expressed as:

\[ k \propto \frac{\rho X}{\rho X + \theta C} = \frac{K_f \rho C^N}{K_f \rho C^N + \theta C} \]  

or

\[ k \propto \frac{K_f}{K_f + \frac{\theta}{\rho} C^{1-N}} \]  

Therefore, the rate constant (k) is a constant only if N=1. Fortunately, N is very close to 1.0 (0.89-0.96) (Albanis et al. 1989, Brouwer et al. 1990). However, if N is far from 1.0, k or t_{1/2} is concentration dependent. Thus, hydrolysis is not first-order (Armstrong et al. 1967, Hance and McKone 1971). Hyperbolic or power-order equations would then be more appropriate (Hamaker 1972a). Hamaker and Goring (1976) proposed a mechanistic explanation for this non-first-order degradation by
dividing pesticides between available and unavailable fractions, with only the available fraction subjected to degradation.

Hydroxyatrazine is adsorbed more strongly on soils than atrazine (Clay et al. 1988a, Clay and Koskinen 1990a, Schiavon 1988a,b, Goswami and Green 1973, Helling 1971b, Obien and Green 1969, Green et al. 1968) due to its higher protonation at the same soil pH (pKa of hydroxyatrazine is 5.1 vs. 1.68 for atrazine) (Armstrong and Chesters 1968, Brouwer et al. 1990, Obien 1970). Goswami and Green (1973) proposed that protonated hydroxyatrazine was adsorbed on negative sites on clays (montmorillonite and halloysite), and that the adsorption became stronger as pH increased from 2 to 7. Clay and Koskinen (1990a) studied the adsorption and desorption of atrazine and hydroxyatrazine, and found that, although atrazine showed non-singularity, atrazine can be desorbed to some extent, whereas, the desorption of hydroxyatrazine was negligible. So, leaching of hydroxyatrazine in soils is not likely (Schiavon 1988a, Goswami and Green 1973, Clay and Koskinen 1990a, Somasundaram et al. 1991). The high adsorption of hydroxyatrazine by soil may also be attributed to its low solubility (Yaron et al. 1985), although the relationship between solubility and adsorption is not clear (Yaron et al. 1985, Weber 1967, Harris and Warren 1964).

1.4 Microbial Degradation of Atrazine and Hydroxyatrazine

Atrazine can be degraded by both fungal and nonfungal microorganisms. Kaufmann and Blake (1970) observed atrazine degradation by 12 different fungi in a basal salt medium supplemented with sucrose. Skipper et al. (1967) found four percent
of the ethylamino $^{14}$C in CO$_2$ evolved by *Aspergillus fumigatus*. Schocken and Speedie (1984) also observed atrazine degradation by a marine fungus, *Periconia prolifica*. Although fungi are the main microorganisms participating in atrazine biodegradation (Kaufmann and Blake 1970, Kaufmann and Kearney 1970), some nonfungal microbial species are also reported to be able to mineralize atrazine (Giardina et al. 1980, Behki and Khan 1986, Bernal-Cespedes 1990). Giardina et al. (1980) observed the degradation of atrazine by a soil bacterium belonging to *Nocardia* genus. Behki & Khan (1986) and Bernal-Cespedes (1990) found atrazine biodegradation by species of *Pseudomonas*.

The degradation pathways by microorganisms were reviewed by Erickson and Lee (1989), including dealkylation and ring cleavage. Generally, microbial degradation of atrazine is negligible compared to hydrolysis (Green et al. 1968). Goswami and Green (1971) and Skipper et al. (1967) found that hydroxyatrazine was more susceptible to ring cleavage than atrazine. Both ring cleavage and dealkylation of atrazine and hydroxyatrazine are enhanced by addition of an energy source, but are retarded under anaerobic conditions due to high pH, restricted aeration or fewer microorganisms (Goswami and Green 1971, Wolf and Martin 1975). Microbial degradation of the side chains of atrazine is much more rapid than that of ring cleavage, with the ease of deethylation over deisopropylation (McCormick and Hiltbold 1966, Skipper 1970, Goswami and Green 1973, Adams and Thurman 1991, Durand and Barcelo 1992). However, Schocken and Speedie (1984) found that deisopropylatrazine was the predominant biodegradation product over deethylatrazine.
by a marine fungus. Therefore, the pathways may be slightly different among microbes. Goswami and Green (1971) concluded that the degradation of atrazine was composed of chemical hydroxylation at the 2-position and microbial dealkylation with chlorine intact in the 2-position.

The microbial degradation products, deethylatrazine and deisopropylatrazine, have higher mobility than hydroxyatrazine (Schiavon 1988b, Adams and Thurman 1991, Sorenson et al. 1993). Sorenson et al. (1993) found that, although hydroxyatrazine was the predominant degradation product in the top 10 cm of a sandy loam soil, deethylatrazine was the predominant product at the 10-30 cm depth and accounted for up to 23% of the $^{14}$C present in the 10-20 cm depth. They also noticed that the proportion of deethylatrazine and deisopropylatrazine increased with depth while that of hydroxyatrazine decreased with soil depth. A detection of hydroxyatrazine below 10 cm depth was due to in situ degradation of atrazine rather than leaching from the top soil layers. Therefore, the microbial degradation products have higher potential to contaminate ground water compared to hydroxyatrazine.

Microbial degradation of atrazine is proportional to soil organic matter content, soil moisture content, and soil temperature (McCormick and Hiltbold 1966, Roeth et al. 1969, Skipper 1970). Roeth et al. (1969) observed a decrease in $^{14}$C evolution from atrazine treated soils with increasing soil depth. They further defined a factor to evaluate the significance of chemical and microbiological degradation of atrazine in soils, which is:
This factor was found to range from 33 to 194, depending on the soil studied. McCormick and Hiltbold (1966) found that addition of glucose promoted the release of $^{14}$CO$_2$ from $^{14}$C-atrazine incubated soils. Although there are some studies on the effects of pH on atrazine biodegradation, the pH effects are not consistent from laboratory to laboratory (Yaron et al. 1985).

First-order kinetics is also used for biological reactions due to the relatively small amount of pesticides in soils (Hamaker and Goring 1976). Therefore, the biological and nonbiological degradation processes are indistinguishable in terms of mathematical modeling. Phogat et al. (1984) found that atrazine degradation proceeded as first-order reactions in both sterilized and unsterilized soils, despite the half-life of 80 and 50 days, respectively. In a recent paper, Nash (1988) concluded that the overall dissipation of atrazine (a total loss from application, volatilization, bio- or chemical degradation, adsorption, etc.) followed pseudo first-order kinetics in the field, and that the dissipation rate constants ranged from 0.006 to 0.085/day. Southwick et al. (1990, 1992) observed a half-life of 35-36 days in the top 2.5 cm of a Commerce clay loam and 24 days in a Sharkey clay soil. Durand and Barcelo (1992) reported atrazine half live of 30 days in the Ebro Delta conditions. Ghadiri et al. (1984) found that atrazine dissipation was similar in conventional-till and no-till treatments with half-lives of 42 and 50 days respectively. Helling et al. (1988)
observed different half-lives in a no-till soil in different years. They further noticed that atrazine dissipation rate was not first-order in one of their experimental years. However, atrazine dissipation in aqueous solution is much slower compared to that in soils. Elint et al. (1993) found that atrazine was not degraded in groundwater during an incubation period of 539 days under 10 °C. Widmer et al. (1993) reported an average half-life of 4.5 yr±42 weeks in deionized and well water samples stored at 4°C and 30°C. Thus, they suggested that it might not be necessary to refrigerate water samples prior to analysis.

However, first-order degradation is not adequate in describing the overall dissipation rate of atrazine (Gustafson and Holden 1990). Obien and Green (1969) found that atrazine loss from four Hawaiian soils approached a first-order reaction rate at 30 °C and deviated from it at 50 °C. Richter et al. (1992) found that atrazine degradation may be better described by combining first-order degradation with a simultaneous first-order adsorption. Higher first-order half lives were observed at lower atrazine initial concentrations (Hance and McKone 1971, Singh et al. 1990b). Singh et al. (1990b) found that $t_{1/2}$ decreased with increasing soil moisture content. Gustafson and Holden (1990) proposed a first-order, nonlinear kinetic model based on the assumption of a spatially variable first-order rate constant.

1.5 Quantitative Measurement of Atrazine.

The three primary requirements for chemical analysis of pesticides are efficient extraction, effective cleanup and sensitive determination (McGlamery et al. 1967). All of these procedures are empirical due to lack of knowledge on pesticide-adsorbent,
solvent-absorbent, and pesticide-solvent relationships (Chesters et al. 1974). Shaking, reflux and soxhlet are the commonly used methods in soil extraction. Mattson et al. (1970) found that the highest recovery of atrazine was obtained with either water-methanol (1:9) soxhlet extraction for 24 hours or water-acetonitrile (1:9) one-hour reflux extraction. Goswami and Green (1973) extracted atrazine and hydroxyatrazine simultaneously by shaking soil-acidified methanol (1:10) slurry for three hours at pH 2.5. 94% of hydroxyatrazine and 100% of atrazine were recovered in the two Hawaiian soils. Obien (1970) found that, although methanolic solution was able to recover atrazine completely in a fortified Kapaa soil, 0.05-0.10 N CaCl₂ methanolic salt solution improved hydroxyatrazine recoveries (81-87%). White et al. (1967) used chloroform (50g/100ml) to extract atrazine by soxhlet for four hours (75% of recovery). McGlamery et al. (1967) found that soxhlet extraction with methanol was more efficient than shaking (86% vs. 70% of recovery). Best and Weber (1974) extracted 100g of moist soil with 200ml methanol in a soxhlet apparatus for 18 hours and obtained recoveries of 95-98%. Ghadiri et al. (1984) soxhlet-extracted atrazine by mixing 30-50 g air-dry soil with 150 ml methanol for 3 hours (87% recovery). In recent work, Huang and Pignatello (1990) found that the maximum yield of atrazine was obtained by batch extraction at 75 °C for 2-4 hours with methanol-water (80:20) solution.

Two clean up methods, liquid-liquid partition and column separation, have been employed in atrazine studies. HCl (0.2-0.5 N) acidified chloroform was used as a liquid-liquid partition method to separate hydroxyatrazine from atrazine (Armstrong
et al. 1967, Armstrong and Chesters 1968, Obien 1970, Skipper 1970). This method is more efficient in triazine water solution (98.8% of recovery) than in methanolic solution (48.3% of recovery) (Obien 1970). However, Chesters et al. (1974) found that the basic alumina column method is more efficient than the liquid-liquid partition method. Many authors have used basic alumina column clean-up procedures (Mattson et al. 1970, White et al. 1967, Green et al. 1977, McGlamery et al. 1967, Zimdahl 1968). The solvents used to recover atrazine from the columns vary from laboratory to laboratory: 50ml chloroform:ether (95:5) by White et al. (1967); 150ml 3:1 benzene:hexane solution by Green et al. (1977); benzene:ether (60:40) by Zimdahl (1968); and methylene chloride:ethyl ether (95:5) by Mattson et al. (1970). Besides being used for clean-up purposes, alumina columns can also separate hydroxyatrazine from atrazine (Chesters et al. 1974).

The commonly used methods for quantitative measurement are bioassay, thin layer chromatography (TLC), high pressure liquid chromatography (HPLC), gas chromatography (GC), ultraviolet spectrometry, and liquid scintillation counting (LSC). The choice of methods depends on the availability of instruments, the purpose of the experiment, and the accuracy required. Bioassay is the best method to study atrazine phytotoxicity in the plant-soil-pesticide continuum. The basic idea is to obtain a standard curve between plant yield and atrazine application rate; then, according to the yield obtained in the test soil samples, atrazine concentration can be calculated. The disadvantage of bioassay is that the response of plant is slow and the result is a time-average. The accuracy of the method depends on seed activity, plant sensitivity
and soil conditions. Oat seedling (Hiltbold and Buchanan 1977) and cucumber (Libik and Romanowski 1976) have been used as indicator plants. This method can be most useful in ranking crop susceptibility to atrazine.

The ultraviolet spectrophotometry method was reviewed by Mattson et al. (1970). The principle of this method is to measure atrazine hydroxy-derivative (hydroxyatrazine) in stead of atrazine itself. The hydroxy-derivative is obtained by hydrolysis with, for example, 1 N HCl or 50% H₂SO₄. Hydroxyatrazine has an absorption maximum at 240nm and minima near 225 and 255 nm. Quantitative determination is based on a base-line technique:

\[
E = A^{240} - \frac{(A^{225} + A^{255})}{2}
\]

where \(E\) is net absorbance, \(A^{240}\), \(A^{225}\), and \(A^{255}\) are absorbency at 240, 225 and 255 nm, respectively. White et al. (1967) used wavelengths of 227, 241 and 257 nm. Kalouskova (1989) also used this method to determine atrazine, but he used a wavelength of 245nm and did not use the base-line technique. Li and Felbeck (1972a) used \(A^{240}\) to monitor atrazine hydrolysis.

Thin layer chromatography is the least expensive method. McGlamery and Slife (1966) used this method to check radiological purity of atrazine by developing \(^{14}\)C- atrazine on Whatman No. 1 filter paper with isopropanol:ammonium hydroxide:water (8:1:1) solution \((R_f =0.97)\). Obien and Green (1969) differentiated atrazine and hydroxyatrazine by using silica gel developed with chloroform-acetone mixture (9:1 v/v) for 45 min \((R_f =0.92-0.94\) for atrazine and 0-0.05 for
hydroxyatrazine). Alhajjar et al. (1990) used a solvent mixture of benzene:acetic acid:water (60:40:3) to develop atrazine on silica gel. Best and Weber (1974) used two solvent mixtures to separate atrazine on silica gels: Petroleum ether:CHCl₃:C₂H₅OH (95%) (5:3:2 v/v) and CHCl₃:CH₃NO₂ (1:1 v/v). Clay et al. (1988a) developed atrazine on TLC plates for 13cm with benzene:acetic acid:water (50:50:3) to determine atrazine and its metabolites. In a later study, atrazine was developed with butanol:acetic acid:water (11:5:4) to a height of 14cm on a silica gel plate (Clay and Koskinen 1990a,b).

Gas chromatography has been widely used in pesticide measurements. Durand and Barcelo (1992) used a 15mx0.15mm i.d. fused silica capillary column coated with chemically bound cyanopropylphenyl DB 225. The injector and detector temperatures were held at 300 and 320°C respectively. The column temperature was programed from 70 to 220°C at 6 C/min. Atrazine was detected with a nitrogen-phosphorus detector (NPD). Widmer et al. (1993) also used NPD and a capillary column of 25mx0.2mmx0.33μm film thickness of 5% diphenyl and 95% dimethylpolysiloxane. Basta and Olness (1992) used dual-column gas chromatography with NPD to determine and confirm pesticides (atrazine, alachlor and metribuzin). The two GC capillary columns (30mx0.25mm i.d) were DB-5 (5% phenyl-95% methyl) and DB-1701 (14% cyanopropylphenyl-86% methyl). Injector temperature was 250 °C. Column temperature programming was employed: 45°C for 1 min, followed by 40°C/min to 150 °C and 5 °C/min to 220 °C with 5 min hold at 220 °C. Southwick et al. (1990) used an electrolytic conductivity detector in their atrazine measurements.
GC/MS (mass spectrometry) has also been used to analyze atrazine by several authors (Kolpin and Kalkhoff 1993, Squillace et al. 1991, Thurman et al. 1991).

HPLC has been increasingly used in recent years in atrazine measurement (Bouchard 1987, Brouwer et al. 1990, Clay et al. 1988a, Gamble and Khan 1988). Bouchard (1987) used a 4μm particle size Nova-Pak C_{18} Column (N=6500) with a mobile phase of methanol:acetonitrile:water (41:7:52 v/v). The wavelength he used was 222 nm for atrazine. Clay et al. (1988a) used a ODS-Hypersil column (100x2.1mm) with a mobile phase of methanol:water (60:40 v/v) for atrazine, and wavelength of 220 nm. The column used by Brouwer et al. (1990) was packed with Chrompack CM-tm-Spher C_{18}. Both atrazine and hydroxyatrazine were measured at 223 nm but eluted with different mobile phases (45:55 of acetonitrile:water for atrazine and 59.8:0.2:40 of methanol:acetic acid:water for hydroxyatrazine). Gamble and Khan (1988) used a Altex Ultrasphere-ODFS column with 5μm particle size, 4.6 mm IDx25 cm length. A 2 cm guard column of same diameter and packing was mounted in front of the column. The injected samples were leached with a mobile phase consisting of 50% acetonitrile-H_{2}O containing 1.58x10^{-3} M HCl, and with flow rate of 1.0 cm/min. Atrazine and hydroxyatrazine were detected at wavelengths of 222 and 240 nm, respectively.

1.6 Atrazine Movement in Soils

Atrazine is transported mainly in the water phase (Rodgers 1967, Lavy 1968, Green et al. 1968). Due to its low vapor pressure (Jordan et al. 1970), volatilization loss is negligible for atrazine (Goswami and Green 1971, Alhajjar et al. 1990, Bacci
et al. 1989). Elling et al. (1987) only detected trace amounts of atrazine on a thin layer chromatograph hanging in the atmosphere for three weeks after atrazine application. Glotfelty et al. (1989) measured atrazine volatilization losses from fallow field and found that only 2.4% of the applied atrazine was lost after 24 days. Although Wienhold et al. (1993) reported a 14% loss from volatilization after 35 days under optimum evaporation conditions in a laboratory chamber, atrazine movement in soils is mainly affected by water flow and adsorption-desorption processes (Leistra 1980).

Many methods have been used to measure atrazine movement in soil, such as soil thin layer chromatography (Helling 1971a,b,c, Hubbs and Lavy 1990, Somasundaram et al. 1991), packed soil column experiments (Elrick et al. 1966, Bouchard 1987), unperturbed-structure soil column (Schiavon 1988a,b), field tile-drain sampling (Southwick et al. 1990, 1992, Muir and Baker 1978, Von Stryk and Bolton 1977), and lysimeters (Adams and Thurman 1991, Kordel et al. 1992). In a field study, Troiano et al. (1993) found that atrazine movement was affected by both irrigation methods (sprinkler, basin and furrow) and percolation treatments (low, medium and high). Atrazine was leached to a deeper soil profile under higher level of percolation rate and furrow irrigation. They also observed a prominent second peak lower in the soil profile. Sadeghi and Isensee (1992) compared atrazine movement under conventional tillage and no-tillage conditions. They found that more atrazine was leached beyond 10 cm under no-till plots than under conventional till plots. They
further noticed a correlation between rainfall pattern and atrazine movement. Similar observations were reported by Isensee et al. (1990).

Hysteresis behavior of atrazine sorption results in column breakthrough curves (BTCs) with steep fronts and extensive tailing (Leistra 1980, Rao et al. 1979, Elrik et al. 1966). Better prediction in pesticide movement has been reported after considering the kinetics of sorption (Swanson and Dutt 1973, Cameron and Klute 1977, Hornsby and Davidson 1973). Physical and chemical nonequilibrium models in describing pesticide adsorption-desorption have been reviewed by several authors (Brusseau and Rao 1989, Pignatello 1989, Rao and Jessup 1983, Leistra 1980).

High water fluxes and large aggregate size increase nonequilibrium between liquid and solid phases. Davidson and Chang (1972) applied herbicide solution to soil columns consisting of either small or large aggregates, and found that at high liquid fluxes, the non-equilibrium effects were more marked in highly aggregated soils than in less aggregated soils. This was explained by the longer time needed for the solute in the flowing liquid to equilibrate by diffusion with the interior of the large aggregates. This sorption nonequilibrium has been reported to be the most significant factor influencing pesticide transport (Rao and Jessup 1983, Van Genuchten et al. 1974, 1977).

However, non-equilibrium is not the only reason for the asymmetrical breakthrough curves (BTC) observed (Brusseau and Rao 1989). Other factors, such as irreversible adsorption or degradation, also affect the shape of BTC. Hydroxyatrazine has been detected in the tailing phase of BTCs (Green et al. 1968).
This hydroxy-derivative is much less mobile than atrazine (Somasundaram et al. 1991). Gamble & Khan (1992) and Gamble & Ismaily (1992) observed a very fast atrazine adsorption period, followed by a slow adsorption period and a even slower adsorption period thereafter. These results may suggest the existence of heterogenous adsorption sites and/or degradation processes. Thus, there could be a coexistence of chemical and physical nonequilibrium in pesticide transport (Brusseau et al. 1989b).

Atrazine movement under field conditions is much less than that in soil columns after the same amount of water leached, because evaporation of water from the soil surface reduces downward movement and enhanced upward movement of capillary water in the field (Leistra 1980, Hubbs and Lavy 1990). The increased adsorption on soil surface due to daily wetting and drying may also retard atrazine movement (White 1976). Starr and Glotfelty (1990) found that a larger proportion of atrazine was on the surface horizon after leaching with 10 cm of chloride solution. Von Stryk and Bolton (1977) monitored atrazine from tile drains at a depth of 0.7m in a clay soil, and found that the total amount of atrazine leached per year was about 0.8% or less of the annual dosage. Muir and Baker (1978) estimated the loss of atrazine beyond 1.2-1.6m from April to December to be about 0.22% of the annual dosage in loamy soils. The movement in the field is even less if atrazine is applied as solid powder. Calvet et al. (1975) observed that at 10 °C it took a few days before atrazine concentration reached half of its water solubility (33ppm). So atrazine granules can stay on the surface several days before they are totally dissolved.
On the other hand, small amounts of atrazine can reach a deeper depth than predicted due to preferential flow through cracks or large pores. This preferential flow carries pesticides to deeper layers before the top layers are completely moistened (Leistra 1980, Rao et al. 1988, Kladivko et al. 1991, Gish et al. 1991, Smith et al. 1992, Edwards et al. 1993). Atrazine movement through preferential paths depends on storm intensity, initial soil moisture content, and timing of storm after application (Edwards et al. 1993). Therefore, two quite different processes are involved in atrazine movement: one-dimensional movement through the soil matrix and rapid downward movement through macropores (Starr and Glotfelty 1990).

1.7 Mathematical Modeling of Pesticide Transport in Soils.

The earliest approach to modeling pesticide movement in laboratory soil columns was the local equilibrium assumption (LEA) (Elrick et al. 1966, van Genuchten et al. 1974, Kay and Elrick 1967), where a linear adsorption isotherm, \( S = K_d C \), was used. Therefore, a retardation factor \( R = 1 + K_d \rho / \theta \) was introduced. This approach usually provided poor description of solute transport (van Genuchten et al. 1974, Davidson et al. 1968, Davidson and Chang 1972). Therefore, more sophisticated assumptions were introduced, such as nonequilibrium sorption (Rao et al. 1979, Lee et al. 1991, Brusseau et al. 1991), non-first-order degradation (Rao and Jessup 1982), and nonsingularity of adsorption-desorption isotherms (Hornsby and Davidson 1973, Swanson and Dutt 1973, van Genuchten et al. 1974). These models are used as a tool to explore the mechanisms of each process, and to quantitatively express the effects of the interacted experimental factors (e.g. water content, water
flux, temperature, soil structure, and soil texture) on pesticide movement. Selim et al. (1976) proposed a two-site chemical reaction model based on chemical heterogeneity of soils. This model improved the predictability of pesticides in soils (Selim et al. 1976, Rao et al. 1979, Wauchope and Myers 1985, Gamerdinger et al. 1990, 1991). Gamble and Khan (1990, 1992) used a second-order kinetic approach in atrazine modeling, where atrazine adsorption sites in the soil matrix were assumed to be limited (Selim and Amacher 1988). Although models based on physical heterogeneity were also proposed (Skopp and Warrick 1974, Van Genuchten and Wierenga 1976), they are mathematically equivalent to the models based on chemical nonequilibrium (Nkedi-Kizza et al. 1984). Recently, a multiprocess model was proposed by Brusseau et al. (1989b) to account for both chemical and physical nonequilibrium.

The effect of water flow velocity on pesticide movement is the least known area in pesticide transport studies. The use of adsorption-desorption kinetics and nonsingularity of sorption isotherms did not improve model prediction at higher pore-water velocities (water-flow rate divided by soil water content) (Davidson and McDougal 1973, van Genuchten et al. 1974, Hornsby and Davidson 1973). Less adsorption of pesticides and left-shift of BTC at high water flux were observed in several studies (Davidson and McDougal 1973, van Genuchten et al. 1974, Rao et al. 1979). van Genuchten et al. (1974) was able to obtain better prediction of pesticide movement under all the water fluxes by assuming that the fraction of the soil participating in the adsorption processes was a function of the average pore-water velocity.
In field studies, several models have been applied. Troiano et al. (1993) applied LEACHM to explain the difference in atrazine transport under different irrigation pattern and percolation levels. Utermann et al. (1990) used a transfer function model to evaluate atrazine migration in tile-drained soils. Sauer et al. (1990) evaluated the PRZM on atrazine mobility under two tillage systems. They found that PRZM yielded better simulation in the early growing season while it overpredicted pesticide penetration at later sampling dates.
CHAPTER 2
HYSTERETIC CHARACTERISTICS OF ATRAZINE
ADSORPTION-DESORPTION BY A SHARKEY SOIL

2.1 Introduction

Atrazine adsorption and desorption studies have been conducted over the last 40 years since these processes are necessary in understanding atrazine retention behavior and its potential mobility within the soil. Batch equilibration has been extensively used in several investigations. The Freundlich (equilibrium) model is a commonly used approach for describing atrazine distribution between soil and solution for both sorption processes. The Freundlich equation is perhaps the oldest of the nonlinear sorption equations and may be expressed as

\[ S = KC^N \] (2.1)

where \( S \) is the amount of solute retained by the soil (\( \mu g \ g^{-1} \)), \( C \) is the solution concentration (\( \mu g \ ml^{-1} \)), \( K \) is the distribution coefficient (\( cm^3 \ g^{-1} \)) and \( N \) is a dimensionless parameter commonly less than unity. Although adsorption and desorption isotherms can be described equally well by the Freundlich model, desorption isotherms often provide significantly different model parameters in comparison to those associated with adsorption isotherms (Clay and Koskinen 1990a,b, Clay et al. 1988a). For a desorption step, the amount of atrazine desorbed or released to the soil solution is overpredicted when adsorption parameters are used.
Specifically, for a given concentration in soil solution, the amount of atrazine retained by the soil was always lower based on adsorption isotherm results in comparison to desorption isotherms. This phenomenon is commonly referred to as desorption hysteresis and is characteristic of retention behavior of several solutes in soil (Selim et al. 1976, Swanson and Dutt 1973, van Genuchten et al. 1974, van Genuchten et al. 1977).

Several factors influence significantly the amount of atrazine adsorbed and desorbed in soil including organic matter content, soil pH, extracting solvent, temperature, and incubation (or reaction) time (Capriel et al. 1985, Clay and Koskinen 1990b, Khan 1991, Obien and Green 1969, Schiavon 1988a, Talbert and Fletchall 1965). Ease of atrazine desorption has been quantified by its desorbability in different solvents. According to its water and methanol extractability, the amount of atrazine retained by soil can be divided into three categories: water extractable, water nonextractable but methanol extractable, and methanol nonextractable (Clay and Koskinen 1990a, Obien and Green 1969). In terms of its energy status in soils, the methanol-extractable atrazine exhibits stronger interaction with soil organic matter and clay than water-extractable fractions, and the methanol-nonextractable atrazine forms the strongest bonds in soil and is referred to as soil-bound residues. The latter, which may be parent material or degradation products, increase with incubation time (Capriel et al. 1985, Clay and Koskinen 1990a, Khan 1991, Schiavon 1988a).

Water desorbability best characterizes the mobility of atrazine within the soil profile, and has been widely studied under different environmental conditions (Clay
and Koskinen 1990a,b, Clay et al. 1988a). However, few studies have investigated effects of incubation time on atrazine behavior during desorption. The purpose of this study was to determine the influence of incubation time on atrazine desorption hysteresis for a Sharkey clay soil. Capability of the Freundlich approach in describing atrazine adsorption and desorption isotherms for different times of incubation was also investigated. Another objective of this study was to relate Freundlich model parameters (K and N) to incubation time during atrazine desorption. These parameters are seldom available from desorption data sets and are necessary for predicting the fate of atrazine retention and potential movement in the soil profile.

2.2 Materials and Methods

2.2.1 Batch studies

The soil used in this study was a Sharkey clay (very-fine, montmorillonitic, nonacid, thermic Vertic Haplaquept) from Iberville Parish, Louisiana. The soil was from the Ap horizon and contained 61% clay, 36% silt, and 3% sand. Organic matter content was 1.7% and soil pH was 6.48 (2:1 soil:water ratio). The retention of atrazine by Sharkey soil was studied using the batch method. Here, initial (input) concentrations of atrazine (C_i or C_initial) in the solutions reacted with the soil were 0.54, 1.05, 2.08, 4.10, and 10.46 \mu g ml^{-1}. Nine incubation periods (0, 1, 2, 4, 8, 12, 16, 20, 24 d) between adsorption and desorption were used to study incubation time effects on atrazine desorption isotherms. Background solution composition for the atrazine solutions was 0.01 N Ca(NO_3)_2. Radioactive atrazine (^{14}C-UL-ring-labeled) was diluted to 7.7x10^4 Bq ml^{-1} and used as a tracer to monitor the extent of
retention. The validity of the use of one sample for each treatment was investigated in a separate experiment which is discussed in the subsequent section (see also Figure 2.1). Atrazine adsorption was initiated by adding 5 g of air-dry soil in each 40-ml Teflon centrifuge tube. Ten milliliters solution, for a range of atrazine concentrations, was added to each tube. Nine replicates were used for each $C_i$ and corresponded to the nine incubation periods. The slurries were shaken for 24 hours and then centrifuged at 540 g (2000 rpm) for 10 min. The supernatant were decanted (6.39±0.15 ml) and collected for analysis, and the soil residuals were incubated with caps on. During incubation, the tubes containing the soil and entrained solution were stored at 21±1 C for prescribed periods.

One set of the above replicates was taken for a desorption step immediately after the 24 h adsorption time (without an incubation period). The remaining eight sets were used for desorption experiments after they were incubated for periods of 1, 2, 4, 8, 12, 16, 20 and 24 d. Six consecutive desorption steps over 6 d were conducted for each set. A desorption step was carried out as following; add 10 ml of atrazine-free 0.01 N Ca(NO$_3$)$_2$ into the tubes containing soil residuals followed by mixing, shaking for 24 h, centrifuging, and decanting the supernatant (9.95±0.24 ml). As a result, total reaction time of atrazine with soil varied depending on the incubation period. Minimum reaction time was for the no incubation case, where 1 d of adsorption was followed by 6 d of desorption for a total of 7 d and a maximum reaction time was 31 d where the incubation period was 24 d. The supernatants were
Figure 2.1. The effects of soil:water ratio on atrazine adsorption-desorption isotherms for a Sharkey soil. Desorption was conducted after 4 d of incubation for $C_i$ of 11.33 $\mu$g ml$^{-1}$. No significant differences were obtained between soil:water ratio of 1:2 and 1:3 during adsorption ($p=0.294$), and among replicates during either adsorption ($p=0.817$) or desorption ($p\geq0.152$). Solid and dashed curves are (Freundlich) model predictions for adsorption and desorption, respectively.
analyzed using liquid scintillation counting (LSC). Several samples were also analyzed using high pressure liquid chromatography (HPLC) to validate agreements between LSC results and atrazine concentrations as measured using HPLC.

During desorption we used a soil to water ratio of 1:3 compared to a ratio of 1:2 for the adsorption step. Nearpass (1967) found that such a difference in soil:water ratio did not affect atrazine adsorption-desorption isotherms. In this study, we carried out a separate experiment with soil:water ratios of 1:2 and 1:3 for atrazine adsorption and desorption. One day adsorption was carried out as described above. Desorption was conducted after 4 d of incubation. Based on analysis of covariance, adsorption isotherms for both soil:water ratios were not significantly different (p=0.294). As shown in Figure 2.1, three replicates were used to test the validity of the use of a single sample for each treatment as mentioned above. No significant differences were obtained among replicates for either adsorption (p = 0.817) or desorption (p ≥ 0.152).

2.2.2 Sterilized system

Atrazine adsorption and desorption as described above were carried out on sterilized Sharkey soil to evaluate the contribution of microbial degradation on atrazine adsorption and desorption isotherms. One kg of soil was sterilized by exposure to $^{60}$Co for 58 h with a total radiation of 7 megarads in the Nuclear Science Center at Louisiana State University. Atrazine solution was sterilized by passing it through a 0.2-μm filter, and the 0.01 N Ca(NO$_3$)$_2$ solution was autoclaved. A sterilizing hood was used throughout the experiment to prevent contamination. Two concentration treatments (3.39 and 8.39 μg ml$^{-1}$) and two incubation times (12 and 24 d) were used.
with duplicates. Atrazine desorption (or release) was carried out following the 24 h adsorption step (shaking), decanting of supernatant, and an incubation period. Once again, six consecutive desorption steps over 6 d were carried out for each set. Along with the sterilized soil samples, adsorption-desorption studies with nonsterilized soil samples were also conducted with duplicates at the same time under the same experimental conditions. Paired t-test was used to evaluate the sterilization effects.

2.2.3 Atrazine analysis

For the LSC method, 0.5 ml of supernatant was mixed with 5 ml of scintillation cocktail and counted for 10 min on LSC. No quench correction was made and the radioactivity was recorded as counts per minute (CPM). Atrazine concentration was calculated as relative to atrazine initial concentrations. Atrazine initial concentrations were measured by HPLC method. Before HPLC analysis, the supernatants were filtered and a 200-μl aliquot was injected into a silica base column via a built-in loop. The sample was then eluted with a 70:30 by volume methanol:water mobile phase at a velocity of 1.0 ml min⁻¹. Atrazine was detected by a UV detector at a wavelength of 230 nm. The measured retention time was 6.2 min. The detectable limit under this condition was 0.01 μg ml⁻¹.

Amounts of atrazine adsorbed onto or desorbed from the soil were calculated from the concentration differences in the supernatants and that of initial (applied) solutions. This method attributes the amount of atrazine sorbed by the soil matrix equivalent to that removed from the soil solution. Desorption isotherms were generated by plotting atrazine concentration (C) versus the amount sorbed (S) for the
six consecutive desorption steps, for each $C_i$ and incubation time. Both adsorption
and desorption isotherms were fitted to the Freundlich equation [2.1] using non-linear
least squares optimization. Analysis of covariance was used to evaluate the
significance between treatments.

2.3 Results and Discussion

Atrazine adsorption results (Figure 2.1) were well described by the Freundlich
model (equation 2.1) with $K$ of $3.576 \pm 0.076 \text{ cm}^3 \text{ g}^{-1}$ and $N$ of $0.900 \pm 0.014$ with $r^2$
of 0.998. For the desorption isotherm of Figure 2.1, the respective values for $K$ and
$N$ were $8.419 \pm 0.305$ and $0.387 \pm 0.029$ with $r^2$ of 0.978. The Freundlich model was
also capable of describing the adsorption isotherm (solid curve) and the family of
desorption isotherms (dashed curves) at different incubation time (Figure 2.2). Fitted
model parameters for the adsorption and desorption isotherms of Figure 2.2 are given
in Table 2.1. The fitted $K$ values for desorption isotherms were consistently higher
than that associated with the adsorption isotherm (Table 2.1). The opposite trend was
observed for the parameter $N$. The results of Figure 2.2 also indicated that desorption
results deviated significantly from the adsorption isotherm. Such a deviation between
adsorption and desorption isotherms is referred to as hysteresis. These results
suggested that incubation resulted in a hysteretic behavior of atrazine. The extent of
atrazine hysteresis was more pronounced as the incubation time increased. Since the
incubation effect on hysteresis is highly significant ($p=0.0001$), the observed
hysteresis cannot be attributed to sample variances.
Table 2.1. Best-fit parameter values and goodness of fit of the Freundlich model for describing atrazine adsorption and desorption by Sharkey soil for different times of incubation and two initial concentrations ($C_i$'s).

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>$K^a$</th>
<th>$N^a$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption:</td>
<td>--- cm$^3$ g$^{-1}$ ---</td>
<td>Dimensionless</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.963±0.031</td>
<td>0.877±0.006</td>
<td>0.999</td>
</tr>
<tr>
<td>Desorption ($C_i = 10.46 \mu g$ ml$^{-1}$):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>no-incubation</td>
<td>6.244±0.127</td>
<td>0.555±0.020</td>
<td>0.999</td>
</tr>
<tr>
<td>4 day-incubation</td>
<td>7.863±0.273</td>
<td>0.382±0.036</td>
<td>0.994</td>
</tr>
<tr>
<td>12 day-incubation</td>
<td>8.863±0.182</td>
<td>0.308±0.022</td>
<td>0.996</td>
</tr>
<tr>
<td>24 day-incubation</td>
<td>10.113±0.315</td>
<td>0.220±0.033</td>
<td>0.983</td>
</tr>
<tr>
<td>Desorption ($C_i = 4.10 \mu g$ ml$^{-1}$):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>no-incubation</td>
<td>4.449±0.161</td>
<td>0.607±0.053</td>
<td>0.995</td>
</tr>
<tr>
<td>4 day-incubation</td>
<td>4.550±0.182</td>
<td>0.453±0.046</td>
<td>0.993</td>
</tr>
<tr>
<td>12 day-incubation</td>
<td>4.965±0.163</td>
<td>0.322±0.032</td>
<td>0.992</td>
</tr>
<tr>
<td>24 day-incubation</td>
<td>5.181±0.286</td>
<td>0.232±0.046</td>
<td>0.970</td>
</tr>
</tbody>
</table>

$^a$ value ± 95% confidence limits
Figure 2.2. Atrazine adsorption and desorption isotherm for a Sharkey clay soil for initial concentrations of 4.10 µg ml\(^{-1}\) (A) and 10.46 µg ml\(^{-1}\) (B). Solid and dashed curves are (Freundlich) model predictions for adsorption and desorption, respectively. The Freundlich parameters are listed in Table 2.1.
The desorption isotherms in Figure 2.2 relate the amount of atrazine retained by the soil matrix (S) to atrazine concentration in the solution (C) at each desorption step. The latter represents the amount of atrazine which was desorbed from the soil system, and is susceptible to movement in the soil. The total amount of atrazine recovered (in percent) versus incubation time for selected C_i's are shown in Figure 2.3. The results indicate that atrazine recovery decreased with incubation time (Figure 2.3). Such a finding was reported by Obien and Green (1969), where atrazine treated soil was incubated up to 60 d. In addition, atrazine recovery was lowest (56%) for C_i of 0.54 \( \mu g \) ml\(^{-1}\) and highest (67%) for C_i of 10.46 \( \mu g \) ml\(^{-1}\). The decrease in (percent) recovery as the C_i's decreased agrees with other studies including Clay and Koskinen (1990a) and Koskinen et al. (1979). Analysis of covariance indicated atrazine recoveries between C_i's at zero incubation time are not significantly different (\( p = 0.152 \)). However, the decreasing recoveries with incubation time are significantly different between C_i's (\( p = 0.039 \)) with highest decrease for C_i of 0.54 \( \mu g \) ml\(^{-1}\).

Based on our batch results, the lack of complete atrazine recovery and the existence of hysteresis were not completely understood. Since our desorption method was carried out over a 24 h time period, incomplete recovery may not be attributed to lack of instantaneous equilibration in this soil (Clay and Koskinen 1990a,b, Clay et al. 1988a). It is conceivable that other reactions such as slowly reversible and irreversible reactions are responsible for incomplete recovery and hysteresis (Clay and Koskinen 1990a,b, Clay et al. 1988a, Khan 1991, Obien and Green 1969). There are
Figure 2.3. Total atrazine recovery following six desorption steps versus incubation time. Significant differences were obtained among different $C_i$'s ($p=0.039$).
two possible mechanisms responsible for reversible and/or irreversible atrazine sorption in soils. One is due to the formation of atrazine-soil complexes which are not easily desorbable into the soil solution (Clay and Koskinen 1990a, Obien and Green 1969). In fact, atrazine can strongly bind to soil organic matter by either chemical or physical means (Khan 1991). Other mechanisms include chemical (nonbiological) and microbial degradation of atrazine (Obien and Green 1969, Swanson and Dutt 1973). Chemical degradation of atrazine by hydrolysis to hydroxyatrazine has been shown to be the primary pathway (Goswami and Green 1971, Obien and Green 1969, Skipper and Volk 1972, Skipper et al. 1967). Obien and Green (1969) detected hydroxyatrazine in methanol and water extractions from four atrazine treated Hawaiian soils by thin layer chromatography (TLC) after 34 d of incubation. Thus, chemical hydrolysis may be responsible for the observed atrazine hysteresis (Clay and Koskinen 1990a, Swanson and Dutt 1973). The contribution of hydrolysis to the observed hysteresis may be further inferred from the fact that atrazine hydrolysis is catalyzed by atrazine adsorption (Armstrong and Chesters 1968, Armstrong et al. 1967, Russell et al. 1968). However, hydroxyatrazine could not be confirmed in soil water solution in this study based on HPLC and LSC data sets (Table 2.2). A paired t-test showed that there was no significant difference between the concentration measured by HPLC and LSC (p≥0.342). It is possible that hydroxyatrazine is difficult to desorb from the soil complex into water solution (Clay and Koskinen 1990b, Clay et al. 1988a, Obien and Green 1969, Schiavon 1988a). Clay and Koskinen (1990b) obtained Freundlich K for
Table 2.2. Comparison of atrazine concentrations (C) for three C_i's as measured using HPLC and LSC for Sharkey soil following adsorption and six sequential desorption steps after 24 d of incubation. No significant difference between concentrations measured by HPLC and LSC (p ≥ 0.342).

<table>
<thead>
<tr>
<th>Initial Concentration (C_i)</th>
<th>μg ml⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.54  2.08  10.46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Final Atrazine Concentration (C)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th>LSC</th>
<th>HPLC</th>
<th>LSC</th>
<th>HPLC</th>
<th>LSC</th>
<th>HPLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>adsorption</td>
<td>0.161</td>
<td>0.164</td>
<td>0.699</td>
<td>0.741</td>
<td>4.025</td>
<td>4.158</td>
</tr>
<tr>
<td>1st desorption</td>
<td>0.058</td>
<td>0.058</td>
<td>0.289</td>
<td>0.282</td>
<td>1.676</td>
<td>1.688</td>
</tr>
<tr>
<td>2nd desorption</td>
<td>0.048</td>
<td>0.067</td>
<td>0.195</td>
<td>0.201</td>
<td>1.036</td>
<td>1.080</td>
</tr>
<tr>
<td>3rd desorption</td>
<td>0.032</td>
<td>0.040</td>
<td>0.134</td>
<td>0.136</td>
<td>0.700</td>
<td>0.676</td>
</tr>
<tr>
<td>4th desorption</td>
<td>0.029</td>
<td>0.022</td>
<td>0.094</td>
<td>0.095</td>
<td>0.477</td>
<td>0.473</td>
</tr>
<tr>
<td>5th desorption</td>
<td>0.019</td>
<td>0.014</td>
<td>0.069</td>
<td>0.070</td>
<td>0.330</td>
<td>0.323</td>
</tr>
<tr>
<td>6th desorption</td>
<td>0.017</td>
<td>0.007</td>
<td>0.058</td>
<td>0.052</td>
<td>0.241</td>
<td>0.234</td>
</tr>
</tbody>
</table>
hydroxyatrazine desorption ranging from 17.8 to 19.0 and N from -0.02 to 0.05 for spiked Plano and Waukegan soils. As a result, it may not be appropriate to confirm hydroxyatrazine based on the difference between LSC and HPLC measured concentrations. Therefore, methods for directly measuring hydroxyatrazine should be employed (Obien and Green 1969).

An attempt was made to evaluate biological degradation of atrazine by comparing atrazine concentrations measured at each adsorption-desorption step for sterilized and non-sterilized soils. Since atrazine concentrations from duplicate samples were consistently in agreement, only averaged results are shown in Figure 2.4. A paired t-test showed that there was a consistent agreement in atrazine concentrations during the desorption process for sterilized and non-sterilized soils (p > 0.367). These results reveal that the extent of atrazine hysteresis was not influenced by soil sterilization. Based on this finding, one may conclude that biological degradation is not responsible for the hysteresis phenomena shown in Figures 2.1 and 2.2. The increase of hysteresis with incubation time in this study may reflect an increase in the percentage of irreversibly adsorbed or chemical degraded atrazine with time (Obien and Green 1969).

A plot of the dimensionless parameter N of equation [2.1] versus incubation time is shown in Figure 2.5. The fitted N for the various desorption isotherms decreased with increasing incubation (or reaction) time. Moreover, there were no significant differences between treatments having different atrazine C_i's (p=0.635). This strongly suggests that N is primarily a function of reaction time. Lack of
Figure 2.4. Atrazine concentration in soil solution versus desorption step for sterilized (open symbols) and nonsterilized soils (closed symbols) for incubation periods of 12 d (A) and 24 d (B). The lines are averaged values. No significant differences were obtained between the sterilized and nonsterilized soil systems (p ≥ 0.367).
Figure 2.5. Fitted Freundlich N for desorption versus incubation time for several initial concentrations (C_i's). The solid line is fitted curve \[ N = 0.561 \exp(-0.044t) \] where t is incubation time in days. No significant differences among C_i's (p=0.635) were obtained.
dependency of fitted N values for different C_i's has also been reported by several authors (Clay and Koskinen 1990a, Swanson and Dutt 1973, van Genuchten et al. 1974, van Genuchten 1977). Results of N versus time t (in days) were fitted to an arbitrarily selected exponential model. The empirical formulation \[ N = 0.561 \exp(-0.044t) \] provided a good description of the results shown in Figure 2.5 with \( r^2 \) of 0.914. The fitted-distribution coefficient K was significantly dependent on both incubation (or reaction) time as well as C_i as depicted in Figure 2.6. Increased K values were consistently observed as C_i increased with a two-fold increase in K corresponding to an order of magnitude increase in C_i. The dependency of K on time of reaction was less consistent for the various C_i's. For low C_i's, K decreased somewhat with incubation time from 0 to 4 d whereas the opposite trend was observed for the higher C_i's (4.10 and 10.46 \( \mu \)g ml\(^{-1} \)). Clay and Koskinen (1990a) also obtained low K values for low initial concentration treatments, but they did not report changes of K with reaction time. The dependency of K and N on time and of K on C_i implies that the Freundlich model is an over simplification of atrazine retention mechanisms in the soil environment. Thus, it is essential to follow the history of atrazine adsorption and desorption sequences so that the appropriate K and N can be selected for prediction of the amount of atrazine sorbed at a given atrazine concentration.

Due to the presence of a significant atrazine hysteresis behavior (Figures 2.1 and 2.2) attempts were made to quantify this phenomena using a simplified approach. We propose to define hysteresis as the difference between adsorption and desorption
Figure 2.6. Fitted Freundlich K for desorption versus incubation time for several initial concentrations (C_i's).
isotherms. Therefore, we quantify hysteresis based on the maximum differences between an adsorption isotherm and a desorption isotherm such that:

\[
\omega = \frac{Max(S_d - S_a)}{S_a} \times 100
\]  

(2.2)

where \( \omega \) in percent is a measure of hysteresis and \( S_d \) and \( S_a \) are the amounts of atrazine sorbed based on desorption and adsorption isotherms (\( \mu g \ g^{-1} \)), respectively.

We now invoke the validity of the equilibrium model where \( C \) and \( S \) are related by the Freundlich equation [2.1]. Therefore, the maximum difference between adsorption and desorption isotherms is at some concentration (\( C' \)). This can be obtained by taking the derivative of Freundlich equation for both desorption and adsorption isotherms at \( C' \) which yields:

\[
C' = \left( \frac{K_d N_d}{K_a N_a} \right) \frac{1}{N_a - N_d}
\]  

(2.3)

where \( K_d, N_d, K_a, \) and \( N_a \) are the corresponding Freundlich parameters for desorption and adsorption isotherms respectively. Upon Substitution of equation [2.3] in [2.2] a generalized hysteresis expression is obtained:

\[
\omega = \left( \frac{N_a}{N_d} - 1 \right) \times 100
\]  

(2.4)

indicating that for a given set of adsorption and desorption isotherms, hysteresis as measured by the parameter \( \omega \) can be determined provided that \( N_a \) and \( N_d \) are known.
The ratio Na/Nd has also been used as a parameter to describe adsorption-desorption hysteresis by others (Swanson and Dutt 1973, van Genuchten et al. 1974, 1977). Swanson and Dutt (1973) used a Na/Nd ratio of 2.3 to predict atrazine breakthrough curves in column leaching studies with two soils. van Genuchten et al. (1974) found that Na/Nd was a function of the maximum adsorbed concentration in their studies with picloram in a Norge loam soil. They obtained Na/Nd values ranging from 2.3 to 3.1 in their concentration range. The use of these ratios improved their model prediction considerably. In another study with 2,4,5-T, van Genuchten et al. (1977) used a Na/Nd ratio of 2.3 in their two-region transport model. They also noticed that this value was independent of the initial 2,4,5-T concentrations, which is in agreement with our results. However, our results further revealed that Na/Nd increases with the incubation time. The obtained Na/Nd ratios range from 1.56 at 0 d incubation to 4.52 at 24 d incubation. Based on equation [2.4], we calculated \( c_j \) for different incubation times and \( C_j \)'s. As Figure 2.7 indicates, the hysteresis \( (\omega) \) increased linearly with reaction time \( (r^2=0.929) \). Moreover, as we expected from the independency of N on \( C_j \)'s, there was no effect of \( C_j \) on \( \omega \) \( (p=0.690) \). Results based on equation (2.4) shown in Figure 2.7 are consistent with earlier results indicating N for desorption is independent of initial concentration (Figure 2.5).

It is recognized that the use of Freundlich isotherms assumes equilibrium between C and S. Such equilibrium is seldom achieved since atrazine adsorption continues for several days or months (Obien and Green 1969, Talbert and Fletchall 1965). Thus, isotherm-derived parameters for fitted data are time dependent as
Figure 2.7. Calculated hysteresis $\omega$ (percent) versus incubation time for several initial concentrations ($C_i$'s). No significant differences among $C_i$'s (p=0.690) were obtained.
illustrated in Figure 2.5 and 2.6. This time dependency reflects the inadequacy of the isotherm in describing adsorption and desorption processes, and should be recognized when equilibrium models are utilized. Other models including the two-site; two-site/two region and multisite kinetic model have shown promise in predicting kinetic behavior of adsorption-desorption for different C_i’s (Selim 1989, Selim et al. 1976, van Genuchten and Wagenet 1989). Due to their complexity, several of these models have not been fully validated.

In conclusion, we quantified the extent of hysteresis during adsorption and desorption of atrazine as a function of incubation time for a Sharkey soil. Our results clearly illustrated the dependence of the amount of atrazine retained by the soil on incubation time between adsorption and desorption. We also proposed a simplified approach for quantifying extent of hysteresis of atrazine retention in soils. Based on this approach, we found that hysteresis can be easily quantified provided that Freundlich N from adsorption and desorption isotherms are known.
CHAPTER 3
PREDICTING ATRAZINE ADSORPTION-DESORPTION IN SOILS:
A MODIFIED SECOND ORDER KINETIC MODEL

3.1 Introduction

The amount of desorption or release of pesticides from soils is commonly recognized to be less than that predicted by adsorption isotherms. This phenomenon is often referred to as desorption hysteresis. Hysteresis is perhaps responsible for the poor prediction capability of models dealing with pesticide transport in soils (van Genuchten et al. 1974, Selim et al. 1976). In order to explain the hysteresis phenomenon, several hypotheses were proposed based on chemical and physical nonequilibrium and the heterogeneity of adsorption sites (Selim et al. 1976, Selim and Amacher 1988, van Genuchten and Wierenga 1976, van Genuchten and Wagenet 1989). Selim et al. (1976), among others, first developed a two-site model based on chemical heterogeneity of soil adsorption sites. Application of the two-site model for pesticide modeling can be found in the literature (Cameron and Klute 1977, Rao et al. 1979, Wauchope and Myers 1985, Gamerdinger et al. 1990, 1991). This two-site (equilibrium-kinetic) model was later extended to the second-order two-site model (Selim and Amacher 1988) and the multireaction transport model (Amacher et al. 1988, Selim et al. 1989). At the same time, a mobile-immobile two-region approach based on physical nonequilibrium was also proposed in the literature (Skopp and
Warrick 1974, van Genuchten and Wierenga 1976). Analogies between the two-site approach and the two-region model have been discussed by several authors (e.g., Selim and Amacher 1988, van Genuchten and Wagenet 1989). Nkedi-kizza et al. (1984) presented a discussion of the equivalence of the mobile-immobile and the equilibrium kinetic two-site models.

Selim et al. (1976) showed that observed hysteresis in a batch experiment may be explained using the two-site equilibrium-kinetic model. In fact, they showed that lack of equilibrium conditions may be responsible for observed desorption hysteresis. Little effort has been made to test such an approach for the analysis of observed hysteresis of pesticide retention by soils. Rather, equilibrium is often assumed for batch experiments when adsorption and desorption isotherms are fitted to either a Freundlich or a Langmuir equation. However, fitted parameters from adsorption results were found to be significantly different from that based on desorption processes (Clay and Koskinen, 1990a and 1990b, Chapter 2). Van Genuchten et al. (1974) obtained an improved prediction of a kinetic model by dividing retention into adsorption and desorption periods with the use of their corresponding fitted isotherm parameters to describe pesticide mobility in soils. Similar approaches were used by Swanson and Dutt (1973) for atrazine and by van Genuchten et al. (1977) for 2,4,5-T.

Attempts to predict batch results using kinetic approaches are sparse, however. Amacher et al. (1988) applied a nonlinear kinetic multireaction model to explain chromium (VI) and cadmium adsorption in soils during batch experiments. However, the fitted parameters were significantly different between initial concentration
treatments, which implies that the model did not completely simulate the behavior of chromium and cadmium in soils. Similar results were reported by Selim and Amacher (1988) when a proposed second-order kinetic model was used. Jardine et al. (1992) was successful in predicting dissolved organic carbon (DOC) breakthrough results from soil columns based on the second-order model. Model parameters were not independently measured, rather they were based on best-fitting of the breakthrough data. Recently, Locke (1992) and O'Dell et al (1992) fitted the sorption kinetics of pesticides using two-reaction-sites model. They found a dependency of model-fitted parameters on initial pesticide concentrations. This dependency not only limits the interpretability but also nullifies the predictability of the obtained parameters.

In this paper, we present a kinetic model for describing pesticide adsorption-desorption behavior in soils. Specifically, our objectives were (1) to describe atrazine adsorption and desorption isotherms (hysteresis) under different experimental conditions, and (2) to predict atrazine sorption kinetics at different initial concentrations. The model is based on the second-order approach where nonequilibrium conditions were assumed dominant. Physical nonequilibrium was not considered here and only chemical heterogeneity of the retention sites were assumed in this approach. In southern Louisiana, Sharkey clay soil is extensively planted to sugarcane and receives routine applications of atrazine (Southwick et al. 1990, 1992), thus resulting in an intensive and repeated exposure of this soil to atrazine. Thus, results from models such as that presented here are necessary so that the parameters needed to describe pesticide transport in soils are independently measured. This work
should also provide improved understanding and insight into the pesticide adsorption-desorption mechanisms.

3.2 Model Formulation

Several investigations suggested the presence of at least two types of sorption sites for atrazine retention by the soil matrix (Clay and Koskinen 1990a,b, Wauchope and Myers 1985, Gamble and Ismaily 1992). One type of sites is of the equilibrium type. Whereas the other is of the kinetic type. A third type that results from surface catalyzed hydrolysis has also been proposed and referred to as irreversible sites (Armstrong et al. 1967, Russell et al. 1968, Gamble and Khan 1990, 1992). Gamble and Ismaily (1992) suggested the presence of three types of sites for atrazine adsorption based on monitoring atrazine concentration in soil solution. They observed that an early drop in atrazine concentration was too fast to monitor, followed by an 8-day slowly decreasing and an even slower linear decrease thereafter. Gamble and Khan (1992) also suspected that adsorption sites had a mixture of structural and chemical properties. They noticed a change of kinetic parameters with sorption site saturation, but they did not speciate the sites in their model. Rather they calculated overall equilibrium and kinetic adsorption-desorption constants and a first-order kinetic hydrolysis rate coefficient from measured atrazine and hydroxy atrazine concentrations in both soil and solution phases.

In this paper, three processes were incorporated into a three-site reaction model as shown in Fig. 3.1. This model is similar to other models except for the irreversible reaction catalyzed by soil surface (Selim et al., 1976, van Genuchten et
Figure 3.1  A schematic of the proposed second-order model.
al., 1974, Cameron and Klute, 1977). This surface catalyzed reaction has been first incorporated into modeling cadmium adsorption on goethite by Theis et al. (1988). In a formulation similar to the hypothetical model of Gamble and Khan (1990), we assume that atrazine in the soil is present in four phases (see Fig. 3.1). Here C is the soil solution phase, $S_e$ is assumed to represent the amount retained on noncatalytic sites and has low binding energy with soil, $S_k$ is the amount retained on catalytic sites which form strong interactions with the soil matrix; and $S_i$ represents irreversible sites occupied by hydroxyatrazine following hydrolysis reaction or other physical irreversible sites. We further assumed that the reactions among the various atrazine phases are governed based on the second-order kinetic approach (Selim and Amacher 1988, Gamble and Khan 1990, 1992). According to second-order formulation, the rate of reaction is a function of not only that present in solution but also on the amount of available (or vacant) sites on matrix surfaces. It is also assumed that the total retention capacity or the total amount of sites on matrix surfaces $S_{\text{max}}$ ($\mu\text{g/g soil}$) is time invariant and consists of two types of sites (see eq. 2 to 5 of Selim and Amacher, 1988).

A major difference in our formulation presented here and that of the second-order two-site model of Selim and Amacher (1988) is that we assume that vacant sites are equally accessible and can thus be occupied by either $S_e$ or $S_k$. That is $S_e$ and $S_k$ can compete for the unoccupied adsorption sites regardless of whether they are of type-1 or type-2 sites. Therefore, we assume that adsorption sites are related and affected by each other and adsorption of one species may block the adsorption sites
of the other type. In contrast, adsorption sites of the irreversible type $S_i$ are assumed to be independent of $S_e$ and $S_k$, since adsorption of hydroxyatrazine does not affect the adsorption of atrazine (Armstrong and Chesters 1968, Wang et al. 1990). Therefore, based on the above, we defined $\phi$ (\(\mu g \ g^{-1}\)) as the amount of vacant sites which is dependent on the amount of sites occupied by $S_e$ and $S_k$ such that;

$$S_{\text{max}} = \phi + S_e + S_k \quad (3.1)$$

where $S_{\text{max}}$ (\(\mu g \ g^{-1}\)) represents the total atrazine adsorption capacity in the soil and is treated as a constant for a specific soil.

The governing kinetic expressions of the rate of reactions for atrazine present in the soil solution phase ($C$) and that in the reversible and irreversible phases ($S_e$, $S_k$, and $S_i$) may be written as,

$$\frac{\partial S_e}{\partial t} = k_1 \theta \ C \ \phi - k_2 \ S_e \quad (3.2)$$

$$\frac{\partial S_k}{\partial t} = k_3 \theta \ C \ \phi - (k_4 + k_5) \ S_k \quad (3.3)$$

$$\frac{\partial S_i}{\partial t} = k_5 \ S_k \quad (3.4)$$

$$- \theta \frac{\partial C}{\partial t} = \rho \left[ \frac{\partial S_e}{\partial t} + \frac{\partial S_k}{\partial t} \right] \quad (3.5)$$

where $C$ is atrazine solution concentration (\(\mu g/\text{ml}\)); $S_e$ and $S_k$ are the amounts of atrazine sorbed reversibly, and $S_i$ is the amount irreversibly retained, respectively (\(\mu g\))
g⁻¹). In addition, θ is the water content of the system (ml ml⁻¹); ρ is soil bulk density (g ml⁻¹) and t is time (h). In eq. (3.1), k₁ and k₃ ((ml μg⁻¹ h⁻¹) are the forward reaction rate coefficients associated with Sₑ and Sₖ, respectively. Whereas, k₂ and k₄ (h⁻¹) are the corresponding backward rate coefficients associated with Sₑ and Sₖ, respectively. In addition, k₅ (h⁻¹) is the rate coefficient associated with the irreversible phase Sᵢ of eq. (3.4).

The presence of the irreversible reaction between Sₖ and Sᵢ results in that equilibrium can not be achieved as long as Sₖ > 0. However, if k₅ is close to zero, quasi-equilibrium may be reached at large times where ∂C/∂t approaches zero. Under such conditions, for Sₑ we have at t → ∞,

\[ Sₑ = \frac{k₁}{k₂} \theta C \phi = Kₑ \theta C \phi \]  \hspace{1cm} (3.6)

and using eq (3.1) to rearrange eq (3.6) yields,

\[ Sₑ = \frac{Kₑ \theta C}{1 + Kₑ \theta C} (S_{max} - Sₖ) \]  \hspace{1cm} (3.7)

where Kₑ (=k₁/k₂) is the equilibrium constant (μg/ml⁻¹) associated with type 1 sites. Similarly, for Sₖ at t → ∞, we have,

\[ Sₖ = \frac{Kₖ \theta C}{1 + (Kₖ + Kₑ) \theta C} S_{max} \]  \hspace{1cm} (3.8)

where Kₖ = k₃/k₄. Equation (3.8) when substituted in eq. (3.7) yields,
\[ S_e = \left( \frac{K_k \theta C}{1 + (K_k + K_e) \theta C} \right) S_{\text{max}} \]  

Therefore, the total amount retained on matrix surfaces (S) at large times is,

\[ S = (S_e + S_k) = \frac{S_{\text{max}} \omega C}{1 + \omega C} \]  

Equation (3.10) is the standard Langmuir equation where \( \omega \) is a Langmuir constant (ml \( \mu \text{g}^{-1} \)),

\[ \omega = (K_k + K_e) \theta \]  

Moreover, the Langmuir eq. (3.10) is a convenient form for obtaining independent estimate of the adsorption capacity \( S_{\text{max}} \) and will be discussed in a later section.

The system of equations (3.2)-(3.6) is a nonlinear one and was thus solved by finite difference (explicit-implicit) iteration method (Selim et al. 1976, Selim et al. 1990), and used to predict atrazine adsorption and desorption isotherms. It was also necessary to use the numerical solution of the system of equations along with a nonlinear least squared optimization scheme to obtain estimates of model parameters which provide best fit of the experimental results (van Genuchten 1981).

3.3 Materials and Methods

3.3.1 Adsorption

Atrazine adsorption was carried out using the batch equilibration technique. \(^{14}\text{C}-\text{UL-ring labeled atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine)} \) was supplied by CIBA-Geigy Corp. The soil used was a Sharkey clay soil
(very-fine, montmorillonitic, nonacid, thermic, vertic Haplaquept) collected from the Ap horizon. The soil contained 61% clay, 36% silt, 3% sand, and organic matter content of 1.7% with a soil pH of 6.48 (2:1 soil:water ratio). Two soil:water ratios (1:6 and 1:15) and six $^{14}$C-atrazine spiked atrazine solutions having concentrations ($C_i$) of 2.95, 5.91, 11.94, 17.73, 23.48, and 29.45 $\mu$g/ml in 0.01 N $\text{Ca(NO}_3\text{)}_2$ were used. Duplicates were used for each initial concentration ($C_i$) and soil/water ratio. Adsorption was initiated by mixing 2 or 5g soil with 30 ml of the various atrazine solutions in a 40 ml Teflon tube. The slurries were shaken for 15 min every hour and centrifuged at 2000 rpm for 5 min after specific reaction (sampling) times. A 0.5 ml aliquot was sampled from the supernatant at reaction time of 2, 8, 24, 96, 192, 288 and 504 hours. The slurries were vortexed and returned to the shaker after each sampling. The collected samples were analyzed using Liquid Scintillation Counting (LSC). Additional details of the batch technique are available elsewhere (Amacher et al., 1986).

3.3.2 Adsorption capacity

Atrazine adsorption capacity ($S_{\text{max}}$) was quantified using the batch technique by repeatedly replacing the supernatants with atrazine (input) solutions having $C_i$ values of 11.94, 17.73, 23.48 and 29.45 $\mu$g/ml. All applied solutions were spiked with $^{14}$C-ring labeled atrazine in 0.01 N $\text{Ca(NO}_3\text{)}_2$ background solution. Five g of soil and 10 ml of atrazine solution were mixed in a 40 ml Teflon tube. Four replicates were used for each atrazine concentration. After 2 h of shaking, the slurries were centrifuged and the supernatants were replaced by 10 ml of their corresponding
atrazine (input) solutions. The new slurries were returned to the shaker and the process of shaking, centrifuging, decanting of supernatants, etc., was repeated six times for a total reaction time of 12 h. The two-hour interval between replacements of atrazine solutions was based on previous reports that 98% of adsorption occurred during the first two hours (Clay and Koskinen 1990a,b). Following the sixth decanting, a seventh replacement was performed where the reaction time was 12 hours (rather than 2 h) with the slurries shaken for 15 min every hour for a total reaction time of 24 h. Subsequent to this 24-h step, three additional replacements were conducted after reaction times of 8, 13, and 22 days. Atrazine concentration in decanted solutions was measured using LSC.

3.3.3 Desorption

The batch method was utilized to generate atrazine desorption isotherms for a range of $C_i$'s and reaction times. First, a-24 h adsorption step was carried out for atrazine $C_i$ of 0.54, 1.05, 2.08, 4.10, and 10.46 $\mu$g/ml as described above except with soil:water ratio of 1:2 (5 g soil and 10 ml solution). Incubation times were 0, 1, 2, 4, 8, 12, 16, 20 and 24 days. Following incubation, atrazine desorption using successive dilutions was carried out. Six consecutive desorption steps (6 days) were conducted for each set. A desorption step was carried out as follows; add 10 ml of atrazine-free 0.01 N Ca(NO$_3$)$_2$ into the tubes containing soil residuals which was followed by mixing, shaking for 24 hours, centrifuging, and decanting the supernatants. As a result, total reaction time of atrazine with the soil varied depending on the incubation period. Minimum reaction time was for the no-
incubation case, where 1 day of adsorption was followed by 6 days of desorption for a total of 7 days and a maximum reaction time was 31 days where the incubation period was 24 days. Additional details of the desorption technique are available elsewhere (Chapter 2).

3.4 Results and Discussion

3.4.1 Kinetics

An examination of our adsorption results shown in Fig. 3.2 clearly indicates that an adsorption capacity $S_{\text{max}}$ for atrazine was not attained. In fact, amounts of atrazine adsorption continued to increase with time and no adsorption plateau was observed for the various $C_i$'s used. These adsorption results were directly measured using our repeated replacement technique where we attempted to saturate the sites on matrix surfaces by maintaining high atrazine concentration in solution (11.94, 17.73, 23.48 or 29.45 $\mu$g/ml). Obviously, atrazine sorption capacity was not reached during our reaction time (22 d) and applied concentrations ($C_i$'s). Since $C_i$ is limited by atrazine solubility (29.45 $\mu$g/ml in our case), it appears that it is not possible to measure the adsorption capacity by use of the batch saturation technique utilized here.

Gamble and Ismaily (1992) attempted to quantify atrazine adsorption capacity but actually measured the amount of atrazine adsorbed at quasi-equilibrium conditions rather than $S_{\text{max}}$. As shown in Fig. 3.2, different $C_i$'s produced different retention result. This is consistent with eq. (3.8) and (3.9) indicating that the amount of atrazine adsorbed is a function of $C$. 
Figure 3.2. Amount of atrazine sorbed versus time from the adsorption capacity experiments for a Sharkey soil. Replacements of supernatants were carried out with atrazine solutions of $C_i$ of 11.94, 17.73, 23.48 and 29.45 $\mu g/ml$. Solid and dashed lines connect experimental data points.
Atrazine adsorption results as a function of reaction time are shown in Fig. 3.3 and 3.4 for data sets having soil:solution ratios of 1:6 and 1:15 (g/ml), respectively. The adsorption pattern indicates initial fast adsorption reactions which occurred within the first 24 hours. This was followed by kinetic adsorption where slow reaction appears to be the dominant process. These observations are consistent with those of Gamble and Ismaily (1992) and lend credence to the concepts suggested by our proposed model. Due to our failure to estimate \( S_{\text{max}} \) from repeated replacement (adsorption capacity) data as discussed above, attempts were made to utilize the adsorption data of Figs. 3.3 and 3.4 to estimate the Langmuir parameters \( (S_{\text{max}} \text{ and } \omega) \) of eq. (3.10). Equation (3.10) is only valid if irreversible reactions are negligible. Based on such an assumption, one can follow Sposito (1989) to estimate these two parameters by plotting experimental data of \( S/C \) against \( S \). Specifically, multiplying both sides of eq. (3.10) by \( 1/C + \omega \), yields,

\[
K_d = \frac{S}{C} = S_{\text{max}} \omega - \omega S
\]

(3.12)

where \( K_d \) is the (Freundlich) distribution coefficient (ml\(^{-1}\) g). Since \( S \) cannot be measured experimentally, we assumed that the contribution from irreversible reaction (3.4) was small at reaction time of 192 hours. Thus, \( S \) may be approximated by the total amount of atrazine adsorbed. Figure 3.5 shows the relationship between \( K_d \) and \( S \) from the above adsorption data after 8 days of reaction. No specific patterns for the data sets of soil:water of 1:6 and 1:15 are apparent. A linear regression line \((r^2=0.94)\) provided parameter estimates for the coefficient \( S_{\text{max}} \) of 184.62 (µg g\(^{-1}\)) and
Figure 3.3  Atrazine sorbed versus time from the adsorption kinetic experiments having soil:solution of 1:6 and for several $C_i$'s. Solid and dashed curves are model calculations using the overall set of model parameters given in Table 3.1.
Figure 3.4 Atrazine sorbed versus time from the adsorption kinetic experiments having soil:solution of 1:15 and for $C_i$'s. Solid and dashed curves are predictions using the overall set of model parameters given in Table 3.1.
Figure 3.5  Distribution Coefficient ($K_d$) versus total amount of atrazine sorbed ($S$). Regression line ($r^2 = 0.94$) provided estimates for $S_{\text{max}} = 184.62$ $\mu$g/g and $\omega = 0.0261$ ml/$\mu$g.
ω of 0.02613 (ml μg⁻¹). Standard errors of estimates were 6.18 and 0.00217 for $S_{\text{max}}$ and ω, respectively. This linear behavior indicates that our method for estimating these parameters is acceptable.

The time dependent behavior of atrazine retention in Sharkey soil was well described by our second-order model (Tables 3.1 and 3.2 and Figures 3.3 and 3.4). The version of the model utilized in these calculations assumed an equilibrium rather than a kinetic reaction governing the noncatalytic sites ($S_e$) as illustrated by the observed rapid concentration decrease at early contact times. Therefore, only four additional model parameters; namely $K_e$, $k_3$, $k_4$, and $k_5$ were needed to describe our atrazine results. The previously estimated value of $S_{\text{max}}$ (= 184.62 μg g⁻¹) was used throughout this study. Other parameters such ρ, θ and $C_i$ were provided based on experimental conditions for each data set. For the data set of soil:solution ratio of 1:6, the model described the data adequately as indicated by the high $r^2$ values and low parameter standard errors (see Table 3.1). For each $C_i$, a set of model parameters that provided best-fit of the data, were independently obtained using nonlinear least-squares. It is obvious that the parameters were not highly dependent on initial concentrations ($C_i$'s). Such a finding is significant and raises the question whether one set of model parameters is capable of describing an entire data set for all initial concentrations. To address this, the entire data set for all $C_i$'s was used in the nonlinear least-square procedure. As a result, a set of parameter estimates, thereafter referred to as overall set of parameters, was also obtained (last line of Table 3.1). The solid and dashed curves of the time dependent atrazine sorption shown in Fig. 3.3
Table 3.1  Goodness of fit, model parameters values and their standard errors (SE) for the kinetic adsorption experiments (soil:water of 1:6) using the second order model.

<table>
<thead>
<tr>
<th>$C_i$ (µg/ml)</th>
<th>$r^2$</th>
<th>$S_{max}$ (µg/g)</th>
<th>$K_e$ (µg/ml)</th>
<th>SE</th>
<th>$k_3$ (µg/ml)$^{-1}$</th>
<th>SE</th>
<th>$k_4$ (µg/ml)$^{-1}$</th>
<th>SE</th>
<th>$K_k$ (µg/ml)$^{-1}$</th>
<th>SE</th>
<th>$k_5$ (µg/ml)$^{-1}$</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.95</td>
<td>0.997</td>
<td>184.62</td>
<td>0.016764</td>
<td>0.000368</td>
<td>0.000097</td>
<td>0.000020</td>
<td>0.006715</td>
<td>0.003096</td>
<td>0.0145</td>
<td>0.001570</td>
<td>0.001006</td>
<td></td>
</tr>
<tr>
<td>5.91</td>
<td>0.990</td>
<td>184.62</td>
<td>0.016222</td>
<td>0.000626</td>
<td>0.000085</td>
<td>0.000032</td>
<td>0.006118</td>
<td>0.005642</td>
<td>0.0138</td>
<td>0.001570</td>
<td>0.002005</td>
<td></td>
</tr>
<tr>
<td>11.94</td>
<td>0.986</td>
<td>184.62</td>
<td>0.015756</td>
<td>0.000704</td>
<td>0.000090</td>
<td>0.000037</td>
<td>0.007058</td>
<td>0.006111</td>
<td>0.0127</td>
<td>0.001170</td>
<td>0.001514</td>
<td></td>
</tr>
<tr>
<td>17.73</td>
<td>0.997</td>
<td>184.62</td>
<td>0.015709</td>
<td>0.000342</td>
<td>0.000112</td>
<td>0.000024</td>
<td>0.011776</td>
<td>0.004262</td>
<td>0.0095</td>
<td>0.001963</td>
<td>0.000605</td>
<td></td>
</tr>
<tr>
<td>23.48</td>
<td>0.982</td>
<td>184.62</td>
<td>0.015359</td>
<td>0.000874</td>
<td>0.000102</td>
<td>0.000056</td>
<td>0.006036</td>
<td>0.008880</td>
<td>0.0169</td>
<td>0.000355</td>
<td>0.003962</td>
<td></td>
</tr>
<tr>
<td>29.45</td>
<td>0.990</td>
<td>184.62</td>
<td>0.017076</td>
<td>0.000685</td>
<td>0.000098</td>
<td>0.000039</td>
<td>0.007243</td>
<td>0.006148</td>
<td>0.0135</td>
<td>0.001149</td>
<td>0.001168</td>
<td></td>
</tr>
<tr>
<td>overall</td>
<td>0.999</td>
<td>184.62</td>
<td>0.016040</td>
<td>0.000307</td>
<td>0.000107</td>
<td>0.000019</td>
<td>0.009465</td>
<td>0.003175</td>
<td>0.0113</td>
<td>0.001628</td>
<td>0.000486</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2  Goodness of fit, model parameters values and their standard errors (SE) for the kinetic adsorption experiments (soil:water of 1:15) using the second order model.

<table>
<thead>
<tr>
<th>C_i</th>
<th>r^2</th>
<th>S_max</th>
<th>K_e</th>
<th>SE</th>
<th>k_3</th>
<th>SE</th>
<th>k_4</th>
<th>SE</th>
<th>K_k</th>
<th>k_5</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>μg/ml</td>
<td>μg/g</td>
<td>(ml μg(^{-1}))</td>
<td>(μg/ml)(^{-1})hr(^{-1})</td>
<td>-----hr(^{-1})-----</td>
<td>(μg/ml)(^{-1})</td>
<td>-----hr(^{-1})-----</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.95</td>
<td>0.995</td>
<td>184.62</td>
<td>0.015654</td>
<td>0.000746</td>
<td>0.000500</td>
<td>0.000204</td>
<td>0.077870</td>
<td>0.030323</td>
<td>0.064</td>
<td>0.003352</td>
<td>0.000590</td>
</tr>
<tr>
<td>5.91</td>
<td>0.976</td>
<td>184.62</td>
<td>0.016135</td>
<td>0.001314</td>
<td>0.000216</td>
<td>0.000165</td>
<td>0.030223</td>
<td>0.026621</td>
<td>0.0072</td>
<td>0.003053</td>
<td>0.001464</td>
</tr>
<tr>
<td>11.94</td>
<td>0.998</td>
<td>184.62</td>
<td>0.017678</td>
<td>0.000315</td>
<td>0.000077</td>
<td>0.000014</td>
<td>0.004263</td>
<td>0.002446</td>
<td>0.0181</td>
<td>0.000555</td>
<td>0.001271</td>
</tr>
<tr>
<td>17.73</td>
<td>0.986</td>
<td>184.62</td>
<td>0.016662</td>
<td>0.000690</td>
<td>0.000078</td>
<td>0.000024</td>
<td>0.004986</td>
<td>0.003473</td>
<td>0.0159</td>
<td>0.000534</td>
<td>0.001376</td>
</tr>
<tr>
<td>23.48</td>
<td>0.989</td>
<td>184.62</td>
<td>0.014989</td>
<td>0.001170</td>
<td>0.000068</td>
<td>0.000025</td>
<td>0.002081</td>
<td>0.001601</td>
<td>0.0326</td>
<td>0.000076</td>
<td>0.000417</td>
</tr>
<tr>
<td>29.45</td>
<td>0.971</td>
<td>184.62</td>
<td>0.014603</td>
<td>0.001125</td>
<td>0.000081</td>
<td>0.000021</td>
<td>0.003689</td>
<td>0.007426</td>
<td>0.0221</td>
<td>0.000331</td>
<td>0.004285</td>
</tr>
<tr>
<td>overall</td>
<td>0.999</td>
<td>184.62</td>
<td>0.015420</td>
<td>0.000358</td>
<td>0.000078</td>
<td>0.000011</td>
<td>0.003994</td>
<td>0.001594</td>
<td>0.0195</td>
<td>0.000325</td>
<td>0.000582</td>
</tr>
</tbody>
</table>
Table 3.3  Goodness of fit, model parameters values and their standard errors (SE) for the adsorption capacity experiments using the second order model.

<table>
<thead>
<tr>
<th>C_i (µg/ml)</th>
<th>r^2</th>
<th>S_max</th>
<th>K_e</th>
<th>SE (µg/ml)</th>
<th>k_3</th>
<th>SE (µg/ml/hr)</th>
<th>k_4</th>
<th>SE (µg/ml/hr^2)</th>
<th>K_k</th>
<th>SE (µg/ml/hr^3)</th>
<th>K_k</th>
<th>SE (µg/ml/hr^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.94</td>
<td>0.995</td>
<td>184.62</td>
<td>0.017146</td>
<td>0.000667</td>
<td>0.000318</td>
<td>0.000082</td>
<td>0.030850</td>
<td>0.008372</td>
<td>0.0103</td>
<td>0.002060</td>
<td>0.000471</td>
<td></td>
</tr>
<tr>
<td>17.73</td>
<td>0.996</td>
<td>184.62</td>
<td>0.017482</td>
<td>0.000708</td>
<td>0.000277</td>
<td>0.000084</td>
<td>0.026927</td>
<td>0.008397</td>
<td>0.0103</td>
<td>0.001982</td>
<td>0.000490</td>
<td></td>
</tr>
<tr>
<td>23.48</td>
<td>0.996</td>
<td>184.62</td>
<td>0.018302</td>
<td>0.000797</td>
<td>0.000305</td>
<td>0.000104</td>
<td>0.030671</td>
<td>0.010769</td>
<td>0.0099</td>
<td>0.002039</td>
<td>0.000528</td>
<td></td>
</tr>
<tr>
<td>29.45</td>
<td>0.994</td>
<td>184.62</td>
<td>0.017931</td>
<td>0.000990</td>
<td>0.000384</td>
<td>0.000137</td>
<td>0.032094</td>
<td>0.011306</td>
<td>0.0120</td>
<td>0.001571</td>
<td>0.000465</td>
<td></td>
</tr>
<tr>
<td>overall</td>
<td>0.999</td>
<td>184.62</td>
<td>0.017928</td>
<td>0.000366</td>
<td>0.000324</td>
<td>0.000048</td>
<td>0.029945</td>
<td>0.004404</td>
<td>0.0108</td>
<td>0.001804</td>
<td>0.000208</td>
<td></td>
</tr>
</tbody>
</table>
were obtained based on this overall set of parameters. The corresponding simulated and experimental time dependent atrazine concentrations are shown in Figure 3.6. Model calculations shown in Figure 3.6 were obtained based on the same overall set of parameters. Therefore, we conclude that one set of parameters can be successfully used to describe atrazine behavior over this $C_i$ range.

The estimated irreversible rate coefficient ($k_5$) in Table 3.1 is one order of magnitude greater than the hydrolysis constant for a mineral soil ($1.72 \times 10^{-4}$ hr$^{-1}$) as reported by Gamble and Khan (1992). The reason for this discrepancy may be due to the assumption that this irreversible coefficient is a "lumped" constant which accounts for both chemical degradation as well as possible irreversible reactions. The amount of atrazine which was not recovered by Gamble and Khan (1992) (mass balance loss) was incorporated into the irreversible reaction (3.4) in our model, and is perhaps responsible for such high calculated $k_5$ values. By substituting the estimated overall parameters (from Table 3.1) and an estimate of $\theta$ (0.96 cm$^3$/cm$^3$) for our experiment into equation (3.11), we calculated an $\omega$ value of $0.02625$ (µg/ml)$^1$. Such a value is in close agreement to that ($0.02613$ (µg/ml)$^1$) obtained from equation (3.12). This surprising agreement supports our assumption that 192 h is sufficient for the equilibration of reactions (3.2) and (3.3) without significant contribution from reaction (3.4). It also suggests that the proposed two-site model is a reasonable approach. The consistency of experimental kinetic and equilibrium data has been reported by Jardine et al. (1992) for the two-site second-order model when used to describe dissolved organic carbon (DOC) transport in soils.
Figure 3.6  Atrazine concentration in soil solution versus time from the adsorption kinetic experiments having soil:solution of 1:6 and for several $C_i$'s. Solid and dashed curves are calculations using the overall set of model parameters given in Table 3.1.
Simulated results of the amount of atrazine sorbed on the various sites (S_e, S_k, and S_i) are shown in Fig. 3.7 for the case C_i of 11.94 μg ml\(^{-1}\). The simulations were calculated using the overall model parameters of Table 3.1. S_e is in equilibration with atrazine in solution and reached a maximum after a relatively short contact time and was followed by a gradual decrease with time. S_k increased at a much higher rate compared to S_i and reached apparent equilibrium after about 8 days. S_i increased linearly with time and was thus responsible for the continued slow (kinetic) atrazine adsorption. This is consistent with our experimental observations. Moreover, S_i accounted for 22% of the total sorbed after 504 h and only 7% in the first 192 h.

For the data set of soil:solution of 1:15, the second-order model described the data well as indicated by the high \( r^2 \) values and low parameter standard errors (see Table 3.2). Once again, parameter values were not dependent on C_i and an overall set of parameters was capable of providing best-fit of the entire data set in a similar fashion to that of the previous data set (soil:solution of 1:6). Comparison of Tables 3.1 and 3.2 reveals the similarity of parameter estimates for the two data sets. Our hypothesis here is that a major criterion for the validity of a model is that parameter values should be independent of experimental conditions. In this study, having two different soil:solution ratios, which resulted in our two data sets, constitute different experimental conditions. Differences in parameter values for \( k_3, k_4 \) and \( k_5 \) between the two data sets were small and did not generally exceed one order of magnitude. For \( K_e \), the values were also similar and ranged from 0.0153 to 0.0171 for the first data set (Tables 3.1) and from 0.0150 to 0.0177 ml μg\(^{-1}\) for the second data set.
Figure 3.7  Simulated atrazine in the sorbed phases ($S_e$, $S_k$, $S_i$, and $S$) versus time having soil:solution of 1:6 and $C_i = 11.94 \, \mu g/ml$. Parameters used are the overall set of model parameters given in Table 3.1.
(Tables 3.2). Similarities for $K_k$ were also observed and their values were 0.0095-0.0169 for the first data set and 0.0064-0.0195 ml $\mu g^{-1}$ for the second data set.

Additional evaluation of the second-order model was carried out by testing its capability to predict a different data set using an independent set of model parameters. Specifically, we examined the capability of the overall set of parameters from Table 3.1 to predict atrazine concentration versus time for the second data set having a soil:solution of 1:15. The solid and dashed curves in Fig. 3.4 are model predictions where one set of parameters was used to predict all six initial concentration ($C_i$) treatments. Figure 3.8 shows the corresponding atrazine concentrations and their corresponding predictions using our model. From Figures 3.4 and 3.8, good model predictions were obtained for all treatments. Once again, none of the model predictions in Figures 3.4 and 3.8 were obtained as a result of curve fitting of the experimental data shown. Rather, these predictions were based on the overall set of model parameters of Table 3.1 which were obtained independently of this data set. Therefore, these independent predictions suggest that this model is capable of describing atrazine adsorption for different $C_i$'s and soil-to-water ratios.

Attempts were also made to predict atrazine behavior for the adsorption capacity data set where the supernatants were replaced frequently with atrazine solution. Parameters used with the model were the overall set of parameters from Table 3.1. The model generally underestimated the amount of atrazine adsorbed as shown in Fig. 3.9. Failure to predict this data set is not well understood. Nevertheless, we attempted to describe the results using our model along with
Figure 3.8 Atrazine concentration in soil solution time from the adsorption kinetic experiments having soil:solution of 1:15 and for several $C_i$'s. Solid and dashed curves are model predictions using the overall set of model parameters given in Table 3.1.
nonlinear least-squares to obtain best-fit of the adsorption versus time results. Fig. 3.10 shows fitted atrazine adsorption calculations as a function of time where an overall set of best-fit model parameters was used. This overall set of parameters along with $r^2$ values is given in Table 3.3. Comparison of this set of parameters and the overall set of parameters from Table 3.1 indicates their similarities except for $k_3$ and $k_4$. The $k_3$ and $k_4$ were three fold that from Table 3.1. However, values for $K_k$ for the two data sets were similar (0.0113 versus 0.0108). Large rate coefficients for reaction (3.3) suggests that the replacement of the supernatants affects mostly the extent of kinetic reaction by forcing a steep concentration gradient between soil and solution phases. Therefore, from these model simulations, early equilibrium of reaction (3.3) is achieved for the adsorption capacity experiment (Fig. 3.10) in comparison to the retention experiment (Fig. 3.3).

The validity of the overall set of parameters of Tables 3.1, 3.2 and 3.3 was further tested using the generalized least-square F-test. The calculated F-statistics were 1.1205, 0.5728, and 0.2632 for the soil:solution ratios of 1:6, 1:15 and adsorption capacity data set, respectively. These values were considerably lower than their corresponding critical $F^*$ values (of 2.191, 2.191, and 2.183, respectively), at $\alpha$ level of 0.05. Therefore, there was no significant difference between the overall fitted parameters and those obtained for each $C_i$. In addition, the overall set of parameters indicated least variability as indicated by the smallest standard errors due to the large degree of freedom in model fittings (Table 3.1, 3.2, and 3.3). Based on
Figure 3.9  Amount of atrazine sorbed versus time from the adsorption capacity experiments. Solid and dashed curves are model predictions using the overall set of model parameters given in Table 3.1.
Figure 3.10  Amount of atrazine sorbed versus time from the adsorption capacity experiments. Solid and dashed curves are calculations using the overall set of model parameters given in Table 3.3.
these findings, we conclude that one set of parameters can be successfully used to
describe atrazine behavior over this wide range of concentrations.

3.4.2 Hysteresis

Isotherm results from the adsorption-desorption experiment are presented in
Fig. 3.11. The desorption isotherms relate the amount of atrazine retained by the soil
matrix to atrazine concentration in soil solution at each desorption step. The latter
represents the amount of atrazine which was desorbed from the soil system, and is
thus susceptible to movement in the soil. The desorption isotherms shown in Fig.
3.11 are associated with atrazine initial concentration ($C_i$) of 10.46 $\mu$g/ml. These
results clearly indicated that desorption results deviated significantly from the
adsorption isotherm. Such a deviation between adsorption and desorption isotherms
is referred to as hysteresis. These results suggest that incubation resulted in a
hysteretic behavior of atrazine where the extent of atrazine hysteresis was more
pronounced as the incubation (or reaction) time increased. Similar hysteretic behavior
for atrazine adsorption-desorption was obtained by Swanson and Dutt (1973) for two
soils. An attempt to describe atrazine hysteretic adsorption-desorption was carried out
using the Freundlich (equilibrium) approach. They found that Freundlich parameters
for adsorption were significantly different from that for desorption. We also found
(Chapter 2) that adsorption and desorption isotherms were well described by the
Freundlich model ($S=K_dC^N$). Fitted $K_d$ parameter values for desorption isotherms
were consistently higher than that associated with adsorption and the opposite trend
was observed for the exponential parameter $N$. 
Figure 3.11  Experimental (symbols) and predicted (curves) atrazine adsorption-desorption isotherms for Sharkey soil. Solid and dashed curves are predictions of adsorption and desorption isotherms, respectively, using the overall set of model parameters given in Table 3.1. Desorption isotherms were for \( C_i \) of 10.46 \( \mu g/ml \).
Attempts to describe atrazine adsorption and desorption isotherms of Fig. 3.11 using our proposed model were carried out in two different ways. Our hypothesis was that model validation and thus its capability to describe output results are based on whether necessary model parameters were independently obtained. Such a stringent requirement is not only necessary but desirable for model evaluation and use for different soils and/or conditions. However, it is recognized that such a requirement is not often met since parameter estimates are often difficult to obtain and model evaluation is based solely on goodness-of-fit of model results to the data. Our first attempt was to utilize model parameters ($K_e$, $k_3$, $k_4$, and $k_5$) based on the overall fit of the adsorption data (Table 3.1). Use of these parameters along with $\Theta$ and $\rho$ in our model resulted in the solid and dashed curves shown Fig. 3.11. The model predicted the overall behavior of atrazine retention during adsorption and desorption (hysteresis) and gave satisfactory description of desorption isotherms. However, model predictions were not considered adequate at advanced desorption steps and for low atrazine concentrations. In fact, the prediction of the adsorption isotherm (solid curve) deviated considerably by underpredicting the experimental isotherm. Such deviations directly influence subsequent model predictions for the desorption isotherms. Continued deviations are expected to dominate model predictions if the amounts of atrazine in the various phases ($C$, $S_e$, $S_k$, and $S_l$) at each desorption step were significantly different from experimental conditions. However, one can argue that such predictions are indeed satisfactory based on model parameters which were obtained independent of the data set being described. Moreover, we are not aware of
modeling efforts which attempted to describe adsorption and desorption using the same set of parameters as was performed here.

In an effort to improve model predictions of adsorption and desorption (hysteresis) results a different set of model parameters was used. This is because it is conceivable that model deviations shown in Fig. 3.11 was due to the fact that different sets of experimental conditions prevailed for the adsorption-desorption experiment (successive dilutions) from that of the kinetic batch experiments. As can be seen from Fig. 3.12 improved prediction was obtained when the model parameters used were from the atrazine capacity ($S_{\text{max}}$) experiment. Specifically, parameter values used were $K_e = 0.017928$ (ml$^{-1}$/μg), $k_3 = 0.000324$ (μg/ml)$^{-1}$hr$^{-1}$, $k_4 = 0.029945$ hr$^{-1}$, $k_5 = 0.001804$ hr$^{-1}$. This improvement may be partially attributed to the similarity in experimental methodologies between capacity measurement and desorption studies (i.e., replacement of supernatants and same soil/water ratios) where retention may be closer to that for equilibrium conditions as discussed previously.

Experimental and predicted adsorption-desorption isotherms for initial atrazine concentration ($C_i$) of 4.1 μg ml$^{-1}$ is shown in Fig. 3.13. Model parameters were those of $C_i$ of 10.1 μg ml$^{-1}$ of Fig. 3.12. Based on adsorption-desorption isotherms of Figs. 3.12 and 3.13, the prediction capability of the model was adequate. However, other small differences between adsorption and desorption studies may still exist, as shown by the underestimation of the amount of atrazine adsorbed at late stage of desorption (Fig. 3.11 and 3.12). The decrease in predictability at low C’s may also be partially attributed to the difficulty in measurement of low concentration (Johnson and Farmer...
Figure 3.12  Experimental (symbols) and predicted (curves) atrazine adsorption-desorption isotherms forSharkey soil. Solid and dashed curves are predictions of adsorption and desorption isotherms, respectively, using an overall set of model parameters given in Table 3.3. Desorption isotherms were for \( C_i \) of 10.46 \( \mu g/ml \).
Figure 3.13  Experimental (symbols) and predicted (curves) atrazine adsorption-desorption isotherms for Sharkey soil. Solid and dashed curves are predictions of adsorption and desorption isotherms, respectively, using an overall set of model parameters given in Table 3.3. Desorption isotherms were for $C_i$ of 4.10 $\mu g/ml$. 
1993). The standard error increases as LSC counts decrease. Since the solution was only spiked with \(^{14}\text{C}\)-atrazine, this larger error at low \(^{14}\text{C}\) counts was amplified when the counts were translated into atrazine concentration, and was propagated through the calculation of \(S\) from \(C\). Because of the opposite error directions in \(C\) and \(S\), the error was further exaggerated in desorption isotherm presentation.

The underprediction of atrazine adsorption at low \(C\) shown in Figs 3.11-3.13 reflects the shortcomings of our proposed model. This may be due to the failure to account for adsorption and desorption mechanisms and/or to incomplete description of atrazine reactions. Since parameter estimates were based on the nonlinear least-square procedure high atrazine concentrations are emphasized. Therefore, it is not easy from our data base to achieve a set of model parameters which can fully describe atrazine adsorption-desorption over a wide concentration range. In fact, Gamble and Khan (1992) found that values for atrazine adsorption-desorption rate coefficients decreased as the amount of the atrazine adsorption sites approached saturation. They also found that a mass balance loss, referred to as bound residue, increased as atrazine concentration decreased. Similar results were also observed by Smith et al. (1992) as well as in our laboratory when we extracted atrazine from Sharkey soil with 100 ml of methanol/water (80/20) subsequent to the last desorption step. Rao et al. (1979) found that in an attempt to model atrazine and 2-4,D transport in Cecil and Eustis soils, model parameters were highly input concentration dependent. The modeling approach used was the equilibrium-kinetic two-site approach of Selim et al. (1976). Recently, Locke (1992) and O'Dell et al. (1992) found that, based on different
modeling approaches, parameter estimates for adsorption-desorption for alachlor and imazethapyr were dependent on input concentrations. Similar results have also been observed by Jardine et al. (1992). Such dependency on input concentration may be attributed to changes in reaction mechanism or the failure to account for adsorption sites. Jardine et al. (1992) found that a one-site model was appropriate for low DOC concentrations and a two-site model best described the transport of DOC at high concentrations. Thus, the dependency of model or model parameters on input concentration is a major drawback in model applications. Further studies are needed in order to improve the versatility of models.
CHAPTER 4
PREDICTING ATRAZINE TRANSPORT IN SOILS:
SECOND-ORDER AND MULTIREACTION APPROACHES

4.1 Introduction


\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} - \left( \frac{\rho}{\theta} \right) \frac{\partial S}{\partial t} \tag{4.1}
\]

where \( C \) represents the aqueous solute concentration (\( \mu g/ml \)), \( S \) is the sorbed solute concentration (\( \mu g/g \)), \( \theta \) is the soil water content (\( cm^3 \ cm^{-3} \)), \( D \) is the dispersion
coefficient (cm²/h), \( v \) is the average pore water velocity (cm/h), \( \rho \) is the bulk soil density (g cm⁻³), \( x \) is the spatial coordinate (cm), and \( t \) is time (h).

The application and modification of equation (4.1) are mainly on the sorption term (\( \frac{\partial S}{\partial t} \)). The simplest form of the sorption term is derived from the local equilibrium assumption (LEA) where solute adsorption is assumed to be instantaneous and can be expressed by sorption isotherms, such as the Freundlich and Langmuir equations. Although this assumption simplifies the mathematical solutions of the CDE, it usually gives poor description of the breakthrough curves, especially at high velocities (van Genuchten et al. 1974, Kay and Elrick 1967, Elrick et al. 1966, Davidson and Chang 1972). Thus, kinetic adsorption-desorption was proposed, but did not adequately predict the tailing of breakthrough curves (Davidson and McDougal 1973, van Genuchten et al. 1974). Selim et al. (1976) proposed a two-site retention model based on chemical heterogeneity of soils. This model improved the predictability of pesticides in soils (Selim et al. 1976, Rao et al. 1979, Wauchope and Myers 1985) and was developed to a multireaction model (Amacher et al. 1988, Selim 1989). Later, a second-order kinetic two-site model was proposed by Selim and Amacher (1988) to account for maximum sorption sites on matrix surfaces. Although models which are based on physical heterogeneity were proposed at the same time (Skopp and Warrick 1974, van Genuchten and Wierenga 1976), they were equivalent mathematically to models based on chemical nonequilibrium (Nkedi-Kizza et al. 1984). In addition, the real rate-limiting processes in soil-solute reactions are not well-
known. Therefore, models based on chemical nonequilibrium were developed on experimental evidence as is the case in this paper.

Elrick et al. (1966) modeled atrazine transport based on the validity of the linear equilibrium assumption. Swanson and Dutt (1973) improved atrazine transport prediction by dividing sorption into adsorption and desorption processes and modeling them separately. Recently, the application of the two-site adsorption model has been reported (Rao et al. 1979, Gamerdinger et al. 1990, 1991). However, these models are thus far in the stage of "curve-fitting" and their potential has not been fully utilized to "predict" atrazine movement under different experimental conditions. For example, essential model parameters obtained by curve-fitting are often sensitive to experimental conditions and are not unique to experimental data sets (Brusseau et al. 1989a). Since most models were developed from a conceptual abstract of a soil system, direct measurement of model parameters is often not feasible.

Other attempts to model atrazine behavior in soils were also made. By assuming that atrazine adsorption follows a second-order process, Gamble and Khan (1990, 1992) measured atrazine adsorption capacity and adsorption rate coefficients for organic and mineral soils. They found a change of the rate coefficients with atrazine concentrations, which was attributed to heterogeneity of atrazine adsorption sites. However, no efforts were made to speciate the adsorption sites in their model.

In this paper, we present an evaluation of two models, a second-order two-site model (SOTS) and a multireaction transport model (MRTM) for describing atrazine transport in miscible displacement experiments. Since validation requires testing of
a model based on data sets obtained under various experimental conditions, our overall objective was to carry out a validation study of the two models based on independently measured model parameters. The data sets used were experimentally measured BTCs for column transport studies under conditions of different (a) input concentrations $C_0$, (b) column lengths $L$, (c) pore water velocities $\nu$, (d) multiple pulse applications, and (f) flow interruption (incubation).

4.2 Model Formulation

Two atrazine adsorption sites and one irreversible reaction site have been proposed in the literature (Clay and Koskinen 1990a,b, Wauchope and Myers 1985, Armstrong et al. 1967, Gamble and Khan 1990, 1992, Gamble and Ismaily 1992). The two adsorption sites are the equilibrium ($S_e$) and kinetic ($S_k$) adsorption-desorption sites. The irreversible reaction ($S_i$) includes both hydrolysis sites catalyzed by the soil surface and possible physically irreversible adsorption sites. The three types of sites are related to each other as shown in Fig. 4.1 and have successfully predicted atrazine adsorption kinetics and desorption hysteresis in batch experiments (Chapter 3). Two mathematical models based on different assumptions are presented in this paper. One is the second-order model with the assumption that the adsorption sites on the soil are limited (Selim and Amacher 1988). Therefore, the reaction rates are affected not only by solute concentrations but also by the availability of adsorption sites. The second approach is a multireaction model, in which adsorption sites were not limiting. Thus, the reaction rates are only functions of solute concentrations (Amacher et al. 1988, Selim 1989).
Figure 4.1  A schematic of the proposed second-order model
4.2.1 Second-order two-site model (SOTS)

The second-order kinetic model has been applied to predict atrazine retention in batch experiments in Chapter 3, and is similar to the one used by others (Selim and Amacher 1988, Gamble and Khan 1990, 1992) except for the assumption that all vacant or unoccupied sites are equally accessible to $S_e$ and $S_k$. The model is described as follows (by using unity activity coefficient) (Chapter 3):

$$S_e = K_e \theta C \phi$$

$$\frac{\partial S_k}{\partial t} = k_3 \theta C \phi - [k_4 + k_5] S_k$$

$$\frac{\partial S_i}{\partial t} = k_5 S_k$$

$S_e$ and $S_k$ are the amount sorbed ($\mu g/g$) on equilibrium and kinetic sites, respectively, whereas $S_i$ is the amount of irreversibly sorbed atrazine ($\mu g/g$). The parameter $\phi$ is the amount of unoccupied sorption sites on matrix surfaces ($\mu g/g$); $K_e$ is the equilibrium constant ($\mu g/ml)^{-1}$; $k_3$ is the forward reaction rate coefficients of the kinetic reaction ($\mu g/ml)^{-1}h^{-1}$; $k_4$ is the corresponding backward reaction rate coefficients ($h^{-1}$), and $k_5$ is the irreversible rate coefficient ($h^{-1}$). Here $\phi$ can be expressed as a function of $S_e$ and $S_k$ based on previous assumptions as follows:

$$S_{\text{max}} = \phi + S_e + S_k$$

$S_{\text{max}}$ ($\mu g/g$) represents the atrazine sorption capacity of the soil (sorption maxima) and is assumed constant for a specific soil. Thus, $S_e$ can be rewritten as
\[ S_e = \left[ \frac{K_e \theta C}{1 + K_e \theta C} \right] (S_{\text{max}} - S_k) \] (4.6)

The presence of the irreversible reaction between \( S_k \) and \( S_i \) results in that equilibrium can not be achieved as long as \( S_k > 0 \). However, if \( k_5 \) is close to zero, quasi-equilibrium may be reached at large times where \( \partial C/\partial t \) approaches zero. Under such conditions, for \( S_e \) we have at \( t \to \infty \), the amount atrazine sorbed on both adsorption sites \( S (= S_e + S_k) \) can be expressed as;

\[ S = \frac{\omega C S_{\text{max}}}{1 + \omega C} \] (4.7)

or

\[ K_d = \frac{S}{C} = \omega S_{\text{max}} - \omega S \] (4.8)

where

\[ \omega = (K_k + K_e) \theta \] (3.9)

where \( K_k = k_3/k_4 \). The adsorption term \( \partial S/\partial t \) can be expressed as:

\[ \frac{\partial S}{\partial t} = K_e \theta \phi \frac{\partial C}{\partial t} + k_3 \theta C \phi - k_4 S_k \] (4.10)

Therefore, incorporation of (4.10) into the CDE (4.1) yields:

\[ R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} + \left( \frac{\rho}{\theta} \right) (k_3 \theta C \phi - k_4 S_k) \] (4.11)

where \( R = 1 + K_e \omega \phi \) is the retardation factor.
4.2.2 Multireaction and transport model (MRTM)

The multireaction model was based on the assumption that the amount of sorption sites is not limited. Gamble and Khan (1992) showed that this assumption is valid for low atrazine concentrations in mineral soils. Therefore, the retention reactions are a function of atrazine concentration such that (Selim et al. 1976, Amacher et al. 1988, Selim 1989)

\[
S_e = \frac{\kappa_1}{\kappa_2} \left[ \frac{\theta}{\rho} \right] C^n = K_f \left[ \frac{\theta}{\rho} \right] C^n
\]

\[
\frac{\partial S_k}{\partial t} = \kappa_3 \left[ \frac{\theta}{\rho} \right] C^m - \left[ \kappa_4 + \kappa_5 \right] S_k
\]

\[
\frac{\partial S_i}{\partial t} = \kappa_5 S_k
\]

where \( K_f \) is an equilibrium constant (dimensionless), \( \kappa_3 \) and \( \kappa_4 \) are the forward and backward reaction rate coefficients of the kinetic sites (h\(^{-1}\)), and \( \kappa_5 \) is the irreversible rate coefficient (h\(^{-1}\)), respectively. The parameters \( n \) and \( m \) are the reaction orders associated with \( S_e \) and \( S_k \) respectively. In this paper, we assumed \( m = n \). In the absence of irreversible reaction (i.e., \( \kappa_5 = 0 \)), \( S_k \) approaches equilibrium at large adsorption time and the total amount of atrazine adsorbed on both adsorption sites \( S (=S_e+S_k) \) can be expressed in the following Freundlich formulation;

\[
S = \eta C^n
\]

where \( \eta \) is the overall distribution coefficient
\[ \eta = \frac{\theta}{\rho} \left( K_f + \frac{\kappa_3}{\kappa_4} \right) \]  

(4.16)

Incorporation of reactions (4.12), (4.13) and (4.14) into the CDE (4.1) yields;

\[ R' \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} + \kappa_3 C^n - \frac{\rho}{\theta} \kappa_4 S_k \]  

(4.17)

where \( R' = 1 + n K_f C^{-1} \) is referred to as the Freundlich retardation factor of the MRTM model. The CDEs for SOTS model (4.11) and the MRTM model (4.17) were solved subject to the following initial and boundary (third type) conditions (Selim and Mansell 1976, van Genuchten and Parker 1984);

\[ C = C_i \quad t=0, \quad 0 < x < L_e \]  

(4.18)

\[ S_e = S_k = S_i = 0 \quad t=0, \quad 0 < x < L_e \]  

(4.19)

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

(4.20)

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

(4.21)

\[ \frac{\partial C}{\partial x} = 0 \quad x=L_e, \quad t > 0 \]  

(4.22)

where \( t_p \) is the duration of an applied atrazine pulse and \( L_e \) is the solute transport length. The CDEs subject to the above conditions were solved numerically using the implicit-explicit finite difference (Crank-Nicholson) method (Selim et al. 1990). All
parameters for the two models were determined independent of the data sets from the transport (column) experiments. Specifically, $S_{\text{max}}$ and $n$ were estimated from batch adsorption isotherms and $K_e$, $k_3$, $k_4$ and $k_5$ for the SOTS model and $K_f$, $\kappa_3$, $\kappa_4$ and $\kappa_5$ for MRTM were calculated from kinetic batch data sets. The dispersion coefficient (D) and solute path length ($L_e$) were obtained from tritium breakthrough results for each column experiment. Other input parameters such as $t_p$, $\nu$, $\theta$ and $\rho$ were determined experimentally.

4.3 Materials and Methods

4.3.1 Column experiments

Sharkey top soil (very-fine, montmorillonitic, nonacid, Vertic Haplaquept) was chosen in this study because of its highly stable structure feature. It contained 61% of clay, 36% of silt, 3% of sand, organic matter of 1.7% and a pH of 6.48 (2:1 soil:water). Three particle size ranges (<2mm, 2-4mm and 4-6mm) were selected in the atrazine transport (column) experiments. Two input atrazine concentrations ($C_0$) of 5 and 10 mg/L in 0.01 N Ca(NO$_3$)$_2$ background solution were used. $^{14}$C-UL-ring labeled atrazine was utilized as a tracer throughout the study. Acrylic columns with lengths of 10 or 15cm (6.4 cm ID) were used after we ascertained that this material was not active in atrazine adsorption. Uniformly packed soil columns were purged with CO$_2$ before saturation. Column saturation was carried out upward with 0.01 N Ca(NO$_3$)$_2$ atrazine-free solution for one week prior to atrazine pulse applications. Input velocity was controlled by a piston pump, and the effluent was collected by a fraction collector. Eight individually packed soil columns were
investigated under different experimental conditions with a total of 14 BTCs generated. Table 4.1 summarizes the experimental conditions for each column. Each BTC was obtained by introducing an atrazine pulse followed by several pore volumes of leaching with 0.01 N Ca(NO$_3$)$_2$ atrazine-free solution. Two atrazine pulses were introduced into column I to study the effect of input concentrations on effluent results. Single pulse application was introduced in columns II, III and IV which differed in aggregate sizes and column lengths. In column V we introduced four consecutive atrazine pulses. The first two were under similar conditions. The third pulse followed by an 8 d incubation period (flow interruption) at the end of the pulse. In the fourth pulse the flow velocity was reduced to about one third. Three BTCs were produced from column VI under different flow velocities. Column VII was conducted to evaluate the influence of flow interruption on atrazine transport with incubation time of 16 d. Column VIII was used to study the effect of flow interruption on tritium BTC where 15 d of interruption period followed a tritium pulse application. Unexpectedly, few of the large pores appeared to empty during flow interruption and the soil was no longer considered water-saturated. Since a steady flow was well controlled by the pistol pump during tritium elution, an atrazine pulse application (2.94 p.v.) was thereafter introduced to the column in a similar manner to the saturated columns. An average $\theta$ was measured at the end of the transport experiment and was considerably lower (0.510 cm$^3$ cm$^{-3}$) than in all others (Table 4.1).

The effluents were analyzed on liquid scintillation counting (LSC). Selected breakthrough BTCs were analyzed using high pressure liquid chromatograph (HPLC)
Table 4.1. Listing of the experimental conditions of soil columns. L, column length; θ, soil water content; P.V., input pulse in pore volumes; $C_0$, input atrazine concentration; $v$, pore water velocity.

<table>
<thead>
<tr>
<th>Column</th>
<th>L (cm)</th>
<th>Aggregate size</th>
<th>θ (cm$^3$/cm$^3$)</th>
<th>Pulse no.</th>
<th>P.V. (µg/ml)</th>
<th>$C_0$ (µg/ml)</th>
<th>$v$ (cm/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>10</td>
<td>2-4</td>
<td>0.600</td>
<td>Pulse 1</td>
<td>9.03</td>
<td>10.47</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pulse 2</td>
<td>9.02</td>
<td>5.30</td>
<td>0.52</td>
</tr>
<tr>
<td>II</td>
<td>10</td>
<td>2-4</td>
<td>0.587</td>
<td></td>
<td>7.58</td>
<td>10.44</td>
<td>1.26</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>&lt;2</td>
<td>0.549</td>
<td></td>
<td>8.14</td>
<td>10.35</td>
<td>1.26</td>
</tr>
<tr>
<td>IV</td>
<td>15</td>
<td>2-4</td>
<td>0.609</td>
<td>Pulse 1</td>
<td>6.20</td>
<td>8.53</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pulse 2</td>
<td>6.06</td>
<td>8.53</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pulse 3</td>
<td>6.07</td>
<td>9.14</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pulse 4</td>
<td>7.51</td>
<td>9.14</td>
<td>0.66</td>
</tr>
<tr>
<td>V</td>
<td>15</td>
<td>2-4</td>
<td>0.591</td>
<td>Pulse 1</td>
<td>6.20</td>
<td>8.53</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pulse 2</td>
<td>6.06</td>
<td>8.53</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pulse 3</td>
<td>6.07</td>
<td>9.14</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pulse 4</td>
<td>7.51</td>
<td>9.14</td>
<td>0.66</td>
</tr>
<tr>
<td>VI</td>
<td>10</td>
<td>4-6</td>
<td>0.592</td>
<td>Pulse 1</td>
<td>7.58</td>
<td>11.33</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pulse 2</td>
<td>6.80</td>
<td>11.33</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pulse 3</td>
<td>5.17</td>
<td>11.33</td>
<td>1.30</td>
</tr>
<tr>
<td>VII</td>
<td>15</td>
<td>2-4</td>
<td>0.598</td>
<td>6.22</td>
<td>9.40</td>
<td>1.97</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>15</td>
<td>2-4</td>
<td>0.510</td>
<td>2.94</td>
<td>9.40</td>
<td>2.17</td>
<td></td>
</tr>
</tbody>
</table>
to test the accuracy of LSC measurement. Detailed information on atrazine measurements is provided elsewhere (Chapter 2). Tritiated water was used to evaluate the dispersion coefficient (D) and solute transport path (Ls) by curve fitting (see Chapter 5). A computer program using finite-difference was employed to solve the CDEs (Selim et al. 1990). The program was modified in order to simulate multipulses obtained under different velocities and input concentrations. Flow interruption was accounted for in our model by simply assuming \( v=0 \) and \( D=D_0 \) (molecular diffusion coefficient) during the incubation period. A \( D_0 \) value of \( 5.472 \times 10^{-4} \) cm\(^2\)/hr for atrazine was estimated from Lavy (1970).

4.3.2 Batch experiments

Two batch adsorption experiments were conducted to provide the necessary parameters for the two models used here. The first is a kinetic batch experiment where we quantified atrazine adsorption as functions of reaction time using standard methods (Amacher et al. 1986). Six atrazine concentrations (2.95, 5.91, 11.94, 17.73, 23.48 and 29.45 \( \mu \)g/ml) and seven reaction times (2, 8, 24, 96, 192, 288, and 504 h) were used. In addition, two soil:water ratios of 1:6 and 1:15 (g/ml\(^{-1}\)) were employed. The second batch experiment was to measure atrazine adsorption capacity \( (S_{max}) \) by repeated replacements of supernatant with atrazine (input) solutions. The experimental procedure was the same as above except for replacing the supernatant with their corresponding atrazine solutions after each sampling. Four atrazine concentrations (\( C_0 \) of 11.94, 17.73, 23.48 and 29.45 \( \mu \)g/ml) used in this study where
a soil:solution of 1:2 was maintained. Additional details of experimental protocol can be found in Chapter 3.

4.4 Results and Discussion

Figure 4.2 shows atrazine results from column effluent as measured using LSC and HPLC analysis. The BTCs measured by LSC and HPLC are in agreement. In fact close agreement can be observed for pulse 1 of column I (Fig. 4.2a) whereas slightly higher atrazine concentrations were measured by HPLC compared to LSC for the two pulses shown in Fig. 4.2b (pulses 3 and 4 of column V). This may partly be due to a decrease in count efficiency of LSC at higher $^{14}$C activity (van Genuchten and Wierenga 1977). This agreement in HPLC and LSC measurements is consistent with previous reports (Chapter 2) and suggests that no measured radioactivity in the soil solution is due to atrazine degradation products within the experimental error. Thus, it is valid to assume an irreversible reaction (4.4) in our model under present experimental conditions.

Figure 4.3 shows selected measured (closed circles) and simulated (solid curves) tritium results for selected columns. Tritium BTCs were successfully described using the CDE (eq.4.1) for nonreactive solutes. To obtain model calculations, D and $L_e$ were obtained by use of nonlinear optimization (fitting). Fitted D and $L_e$ were subsequently used as independent estimates for atrazine transport predictions. The D and $L_e$ values were influenced by both soil aggregate size and velocity (see Table 4.2). In tritium BTC analysis, we decided to obtain best-fit values for $L_e$ rather than $\nu$, since it is mathematically equivalent to fit $L_e$ or $\nu$. However,
Figure 4.2. Atrazine concentrations measured using HPLC and LSC; (A) column I, and (B) column V (pulses 3 and 4).
Figure 4.3  Tritium breakthrough curves (BTCs) fitted with diffusion coefficient D and solute transport length Ls; (A) tritium BTC of column I, and (B) tritium BTC of column IV.
fitting $L_e$ is more physically meaningful than that for $\nu$. One advantage of fitting $L_e$ is that we can define a tortuosity factor ($\tau$) from the fitted solute transport length $L_e$ and the column length $L$ such that $\tau = L / L_e$. In fact, $\tau$ has been widely used in solute diffusion where a tortuosity factor was incorporated into an effective diffusion coefficient ($D_e$) (see Porter et al. 1960, Van Schaik and Kemper 1966, Gillham et al. 1984, Sadeghi et al. 1989). Assuming $D_e$ as a function of $\tau$, Porter et al. (1960) estimated $\tau$ based on measured $D_e$. A similar approach was used by other investigators. For example, Van Schaik and Kemper (1966) estimated $\tau$ ranging from 0.70-0.74 depending on soil water content and flow pattern. Gillham et al. (1984) obtained $L / L_e$ of 0.77-0.92 from chloride diffusion and 0.57-0.84 from tritium diffusion in bentonite-sand mixtures. Sadeghi et al. (1989) calculated $\tau$ ($= L / L_e$) of 0.85 based on urea diffusion in seven soils. From Table 4.2, our results indicate that $\tau$ is less affected by $\nu$ and more affected by soil aggregate size. It ranged from 0.7 for 4-6 mm aggregates and close to 1.0 for aggregates < 2 mm. Best-fit $D$ was more variable than $\tau$, and was affected primarily by $\nu$. For the 2-4 mm aggregates, $D$ ranged from 1.232 cm$^2$ h$^{-1}$ at $\nu$ of 0.66 cm h$^{-1}$ and $D$ of 4.618 cm$^2$ h$^{-1}$ at $\nu$ of 1.69 cm h$^{-1}$. The goodness of fitting in terms of root mean squares (RMS) is also listed in Table 4.2. Moreover, when attempts were made to use $D$ and $\nu$ or $D$ and retardation factor (R) as the fitted parameters, no improvements in tritium predictions were obtained. In fact, we obtained comparable RMS values for all fitting strategies.

Atrazine batch data were used to obtain estimates for the parameters required by the SOTS and MRTM models. The atrazine capacity ($S_{max}$) for the second-order
Table 4.2. Best-fit dispersion coefficients (D) and solute transport lengths (L_e) based on tritium results. The goodness of fit was expressed as the root mean squares (RMS). The tortuosity factor \( \tau (=L/L_e) \), column length L, pore water velocity \( v \), and aggregate size d are also listed.

<table>
<thead>
<tr>
<th>Column</th>
<th>L</th>
<th>d</th>
<th>( v )</th>
<th>D</th>
<th>SE+</th>
<th>L_e</th>
<th>SE+</th>
<th>RMS</th>
<th>( \tau=L/L_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm)</td>
<td>(mm)</td>
<td>(cm/hr)</td>
<td>(cm(^2)/hr)</td>
<td>(cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>10</td>
<td>2-4</td>
<td>0.52</td>
<td>1.995</td>
<td>0.068</td>
<td>12.568</td>
<td>0.119</td>
<td>0.015225</td>
<td>0.780</td>
</tr>
<tr>
<td>II</td>
<td>10</td>
<td>2-4</td>
<td>1.26</td>
<td>3.787</td>
<td>0.265</td>
<td>10.560</td>
<td>0.171</td>
<td>0.026083</td>
<td>0.947</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>&lt;2</td>
<td>1.26</td>
<td>3.804</td>
<td>0.284</td>
<td>9.990</td>
<td>0.159</td>
<td>0.024475</td>
<td>1.001</td>
</tr>
<tr>
<td>IV</td>
<td>15</td>
<td>2-4</td>
<td>1.08</td>
<td>2.847</td>
<td>0.107</td>
<td>15.638</td>
<td>0.185</td>
<td>0.020572</td>
<td>0.959</td>
</tr>
<tr>
<td>V (Pulse 1)</td>
<td>15</td>
<td>2-4</td>
<td>1.69</td>
<td>4.618</td>
<td>0.269</td>
<td>15.761</td>
<td>0.131</td>
<td>0.023444</td>
<td>0.951</td>
</tr>
<tr>
<td>V (Pulse 4)</td>
<td>15</td>
<td>2-4</td>
<td>0.66</td>
<td>1.232</td>
<td>0.039</td>
<td>16.794</td>
<td>0.083</td>
<td>0.015433</td>
<td>0.893</td>
</tr>
<tr>
<td>VI (Pulse 1)</td>
<td>10</td>
<td>4-6</td>
<td>1.76</td>
<td>4.226</td>
<td>0.093</td>
<td>13.548</td>
<td>0.043</td>
<td>0.009356</td>
<td>0.738</td>
</tr>
<tr>
<td>VI (Pulse 2)</td>
<td>10</td>
<td>4-6</td>
<td>0.90</td>
<td>1.870</td>
<td>0.026</td>
<td>13.100</td>
<td>0.025</td>
<td>0.006167</td>
<td>0.763</td>
</tr>
</tbody>
</table>

+ Standard error of estimate.
model and the exponent \( n \) for the multireaction model were derived (independently) using the same adsorption isotherm (see Fig. 4.4). Here we chose the 192 h isotherm to approximate quasi equilibrium conditions. Moreover, we assumed that during such a time frame \( S_i \) is assumed negligible. We utilized the Langmuir equation (7) in a linearized form to obtain a best fit of \( S_{\text{max}} \) of 184.62 \( \mu \)g/g for SOTS (Chapter 3). In addition we utilized Freundlich from (4.15) to obtain, using nonlinear regression, a value for \( n \) of 0.7635 for the MRTM model. Figure 4.4 shows measured and fitted atrazine adsorption isotherms using Langmuir and Freundlich equations which indicate somewhat improved isotherm description using the Langmuir form equation.

In an effort to validate the models presented here, several attempts were made to estimate model parameters. Two sets of the parameters \( K_c, k_3, k_4, k_5 \) of SOTS were obtained using kinetic batch results. Parameter set I was obtained by fitting SOTS to atrazine adsorption results for soil:water ratio of 1:6 where the supernatants were monitored periodically without replacing the soil solution (See Materials and Methods). Measured and simulated adsorption kinetics are shown in Fig. 4.5a. Parameter set II was obtained by fitting SOTS to atrazine adsorption results for soil:water of 1:2 where the supernatant was replaced with atrazine solution after each sampling in an attempt to estimate the adsorption capacity (Chapter 3). Both sets of parameters and their standard errors are listed in Table 4.3 (see also Fig. 4.5a and 4.5b). The two kinetic batch data sets were also used to estimate \( \kappa_1, \kappa_3, \kappa_4, \) and \( \kappa_5 \) for MRTM. Best-fit parameter values are also given in Table 4.3 and simulations are
Figure 4.4  Atrazine adsorption isotherms fitted using a linearized Langmuir and a nonlinear Freundlich equation. The experimental data were from adsorption kinetic batch study at 192 h and soil:water ratios of 1:6 and 1:15.
Figure 4.5 Atrazine adsorption as functions of reaction time. Solid or dashed curves are fitted using the second-order model (SOTS); (A) adsorption kinetic experiments (without replacing the supernatant), fitted parameter set I; and (B) adsorption capacity experiment (with replacement of the supernatants), fitted parameter set II.
shown in Fig. 4.6a and 4.6b. Best-fit values for the irreversible rate coefficients for both models (k_5 and k_5) were not significantly different. This consistency suggested that the introduction of an irreversible reaction is valid. Although both models simulated the adsorption kinetic data well, the second-order model provided somewhat better description of the data (r^2). The consistency between quasi-equilibrium and kinetic parameters for both models was checked using equations (4.9) and (4.16). Best fit ω using Langmuir equation (4.7) was 0.0261 (μg^{-1} ml) based on the data of Fig. 4.4. This ω value is close to that from kinetic parameters of SOTS based on equation (4.9) (0.0263 for parameter set I and 0.0244 for set II). For MRTM, best-fit η using the Freundlich equation (4.15) was 6.427 (cm^3/g). This value (η of 6.840 cm^3/g) approximates well that obtained using equation (4.16) for the kinetic parameters set I. However, it is considerably different from that obtained from parameter set II (4.244 cm^3/g). Therefore, the η value obtained from soil:water ratio of 1:6 cannot explain the behavior of atrazine at soil:water ratio of 1:2. This inconsistency in MRTM could be responsible for its ill prediction of atrazine BTCs as discussed in later sections.

For all column transport experiments (Table 4.1), predictions were independently obtained using the SOTS and MRTM models. For each model, two predictions were obtained which were based on parameter sets I and II. Therefore, as illustrated in Figs. 4.7 - 4.12, experimental results along with four BTC model predictions are shown. Based on these BTC predictions for columns having different velocities, column lengths, soil aggregated sizes and input concentrations, the SOTS
Table 4.3. Best-fit model parameters for the second-order (SOTS) and multireaction (MRTM) models as estimated from batch experiments. Data set I refers to parameters derived from the kinetic batch data set, whereas data set II refers to parameters derived from the adsorption capacity data set.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Parameter Estimate</th>
<th>SE⁺</th>
<th>Parameter Estimate</th>
<th>SE⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Data Set I</strong></td>
<td></td>
<td></td>
<td><strong>Data Set II</strong></td>
<td></td>
</tr>
<tr>
<td><strong>SOTS Model</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_{\text{max}}$ (µg/g)</td>
<td>184.62</td>
<td>6.18</td>
<td>184.62</td>
<td>6.18</td>
</tr>
<tr>
<td>$K_e$ (µg/ml)$^{-1}$</td>
<td>0.016040</td>
<td>0.000307</td>
<td>0.017928</td>
<td>0.000366</td>
</tr>
<tr>
<td>$k_3$ (µg/ml)$^{-1}$ hr$^{-1}$</td>
<td>0.000107</td>
<td>0.000019</td>
<td>0.000324</td>
<td>0.000048</td>
</tr>
<tr>
<td>$k_4$ (hr$^{-1}$)</td>
<td>0.009465</td>
<td>0.003175</td>
<td>0.029945</td>
<td>0.004404</td>
</tr>
<tr>
<td>$k_5$ (hr$^{-1}$)</td>
<td>0.001628</td>
<td>0.000486</td>
<td>0.001804</td>
<td>0.000208</td>
</tr>
<tr>
<td><strong>MRTM Model</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>0.7635</td>
<td>0.02722</td>
<td>0.7635</td>
<td>0.02722</td>
</tr>
<tr>
<td>$K_f$</td>
<td>0.697266</td>
<td>0.013359</td>
<td>1.710511</td>
<td>0.050855</td>
</tr>
<tr>
<td>$\kappa_3$ (hr$^{-1}$)</td>
<td>0.003935</td>
<td>0.000815</td>
<td>0.008526</td>
<td>0.004419</td>
</tr>
<tr>
<td>$\kappa_4$ (hr$^{-1}$)</td>
<td>0.008551</td>
<td>0.003425</td>
<td>0.013292</td>
<td>0.009208</td>
</tr>
<tr>
<td>$\kappa_5$ (hr$^{-1}$)</td>
<td>0.001806</td>
<td>0.000817</td>
<td>0.002241</td>
<td>0.000890</td>
</tr>
</tbody>
</table>

⁺ Standard error of estimate.
Figure 4.6  Atrazine adsorption as functions of reaction time. Solid or dashed curves are fitted using the multireaction model (MRTM); (A) adsorption kinetic experiments (without replacing the supernatant), fitted parameter set I; and (B) adsorption capacity experiment (with replacement of the supernatants), fitted parameter set II.
model provided better overall predictions than MRTM. Moreover, improved predictions were obtained when parameter set I rather than set II was used. Use of parameter set II resulted in a BTC shift to the right and lower peak concentrations. Therefore, parameter set II overpredicted the extent of tailing and underpredicted the steepness of BTC fronts. Best BTC prediction based on parameter set I was obtained in Fig. 4.9 where the aggregate size was similar to that used in our batch experiment (<2mm). In contrast, MRTM failed to provide adequate predictions for most column transport results.

Model predictions by the second-order model further prove the validity of the model and its assumption. Along with the successful application in batch experiments (Chapter 3), the second-order model provided a good description of atrazine behavior in our soil. Although the multireaction model gave equivalent goodness of fit of atrazine adsorption of batch experiments (Fig. 4.6), its prediction capability of atrazine BTCs of Figs. 4.7-4.12 was not acceptable. The lack of predictability implies that the multireaction model is inadequate in describing atrazine transport in Sharkey soil in spite of its good mathematical fitting of batch results. Thus, a model validity can only be judged by its prediction for several data sets of different conditions but not by its goodness of fit for one experimental condition. Better SOTS predictions using parameter set I suggest that atrazine adsorption-desorption behavior in column experiments is similar to that in batch experiments where the supernatants were not displaced repeatedly with atrazine solutions. Therefore, the concentration change in
Figure 4.7  Predicted atrazine BTCs from Column I using SOTS and MRTM with parameter sets I and II.
Figure 4.8 Predicted atrazine BTC from Column II using SOTS and MRTM with parameter sets I and II.
Figure 4.9  Predicted atrazine BTC from Column III using SOTS and MRTM with parameter sets I and II.
Figure 4.10  Predicted atrazine BTC from Column IV using SOTS and MRTM with parameter sets I and II.
Figure 4.11 Predicted atrazine BTCs from Column V using SOTS and MRTM with parameter sets I and II.
Figure 4.12 Predicted atrazine BTCs from Column VI using SOTS and MRTM with parameter sets I and II.
soil solution during column miscible experiments was not as drastic as that in experiments for atrazine capacity measurement $S_{max}$ (Chapter 3).

Predictions of the SOTS model of atrazine movement in our soil columns clearly (Figs. 4.7 - 4.12) depict the capability of the model based on an independently determined set of model parameters (from batch experiments). Specifically, parameter set I provided consistently good BTC predictions over those using parameter set II or the multireaction model. An example of almost a perfect BTC prediction is that shown in Fig. 4.9 (column III) using SOTS parameter set I. In addition, adequate SOTS predictions of all other BTCs were obtained regardless of input atrazine concentrations $C_0$ (see Fig. 4.7), column length $L$ (see Figs. 4.8 and 4.11) and pore velocities $\nu$ (Figs. 4.11 and 4.12). We are not aware of other studies in the literature where a conceptual model achieved such a wide prediction capability.

The above predictions strongly suggest that the second-order model successfully described the effects of experimental conditions on atrazine transport. Thus, if environmental and epadatic conditions (rainfall pattern, water infiltration rates, solute diffusion coefficient, and solute transport length) were known at any given period of time, the SOTS model could be employed to field conditions. However, the prediction deteriorated as the soil aggregate size increased from <2 to 2-4 to 4-6 mm (Fig. 4.8, 4.9 and 4.12). This implies that our model failed to explain the difference caused by the aggregate size. In an effort to explain this lack of prediction, we attempted to improve model predictions based on fitted rather than independently measured parameters. The adsorption capacity ($S_{max}$) was chosen as
the fitting parameter based on our assumption that it is conceivable that $S_{\text{max}}$ is influenced by the aggregate size. Our hypothesis was that it is possible that as aggregate size increases the accessibility of atrazine in solution to sorption sites becomes more limited which results in a decrease in $S_{\text{max}}$. Therefore, $S_{\text{max}}$ was fitted to predict BTCs shown Fig. 4.13 and 4.14 where the remaining parameters were those from parameter set I. A best fit $S_{\text{max}}$ which resulted in the improved predictions shown in Figs 4.13 and 4.14 results in smaller values for $S_{\text{max}}$ (118.31 and 130.34 $\mu g/g$) than that based on batch data (184.62 $\mu g/g$). However, as is shown in Fig. 4.14, the fitted BTC could not explain all observed deviation. Therefore, factors other than $S_{\text{max}}$, e.g., physical nonequilibrium in large soil aggregates, are probably responsible for the deviation in BTC predictions.

The second-order model was further tested for its capability to predict transport of atrazine when the soil is water-unsaturated and when the flow into the soil column was interrupted. As indicated in Fig. 4.15, the SOTS successfully predicted the BTCs (column VIII of Table 4.1) for unsaturated water content. In this case, flow interruptions (or incubation) occurred for a period of 4 d following pulse application. The BTC under unsaturated water flow was well predicted using SOTS model. As expected, the fitted D value ($D = 17.25 \text{ cm}^2/\text{h}$) from the unsaturated tritium BTC was larger than for saturated columns (see Table 4.2). On the other hand, fitted $L_e$ was close to $L$ with $\tau$ value of 1.06. Moreover, the SOTS model well described the sharp decrease (dip) in effluent concentration following 4 d of flow interruption. This sharp decrease in effluent concentration was also observed in other (saturated
Figure 4.13  Predicted atrazine BTCs in Column I by SOTS and parameter set I with fitted $S_{\text{max}}$. 

\begin{figure}[h]
\centering
\includegraphics{column_i_predict.png}
\caption{Predicted atrazine BTCs in Column I by SOTS and parameter set I with fitted $S_{\text{max}}$.}
\end{figure}
Figure 4.14  Predicted atrazine BTCs in Column VI using SOTS and parameter set 1 with fitted $S_{\text{max}}$. 
Figure 4.15  Breakthrough curves of atrazine from column VIII (unsaturated soil) with 4 d flow interruption.
columns) as shown in Figs. 4.16 and 4.17 for 8 and 16 d of flow interruption, respectively. This dip in atrazine solution concentration is a strong evidence that the retention (adsorption-desorption) mechanism is kinetic in nature. However, this phenomenon was not observed in the tritium breakthrough results with 15 d flow interruption (Fig. 4.18). The tritium results further suggest that there was no obvious evidence of chemical or physical nonequilibrium governing tritium transport in Sharkey soil. Therefore, the assumption of chemical heterogeneity in describing atrazine adsorption kinetics in the above models is considered valid. In our models, the kinetic characteristic was reflected by both reversible and irreversible kinetic reactions. This kinetic behavior is perhaps responsible for the tailing of BTCs and observed hysteresis in batch experiments (Chapter 3). It may be also responsible for multi-peaks of atrazine concentrations in field and laboratory transport studies (Kladivko et al. 1991, Smith et al. 1992, Johnson, et al. 1992). Furthermore, flow interruption caused a decrease in the amount of atrazine recovery from the effluents due to increased irreversible and irreversible retention. For example, 78% of applied atrazine was recovered in the effluent solution from column V (8 d interruption) in comparison to some 90% recovery when the atrazine pulse was not interrupted.
Figure 4.16 Breakthrough curves of atrazine from column V, pulse 3 (8 d flow interruption).
Figure 4.17 Breakthrough curves of atrazine from column VII (16 d flow interruption).
Figure 4.18 Tritium breakthrough curves from column VIII with 15 d flow interruption.
CHAPTER 5

TORTUOSITY, MEAN RESIDENCE TIME AND DEFORMATION OF TRITIUM BREAKTHROUGHS FROM UNIFORM SOIL COLUMNS

5.1 Introduction

Solute transport in soils is often studied by examining measured breakthrough curves (BTCs) or effluent concentrations from miscible displacement experiments. One approach is the moment method, in which BTCs are characterized by mean residence time (\( t_m \)), variance, skewness, and kurtosis. These parameters are represented by the first, second, third, and fourth time moment of effluent concentration, respectively (Leij and Dane 1991, Sardin et al. 1991). Although the time to peak flow may also provide useful information on solute transport and retention (Hamlen and Kochanowski 1992, Kookana et al. 1992), the mean residence time is the most commonly used BTC parameter which may be expressed as (Leij and Dane 1991):

\[
 t_m = \frac{\int_0^\infty tC(t)dt}{\int_0^\infty C(t)dt}
\]  

(5-1)

where \( t_m \) is the first-order time moment or the mean breakthrough time for a solute and \( C(t) \) is solute concentration in the effluent as a function of time \( t \).

Another approach to BTC analysis is based on the traditional convection-dispersion equation (CDE). The CDE equation is characterized by an average pore
water velocity $\nu$ (convection) and hydrodynamic dispersion coefficient $D$. For a nonreactive tracer ($^{2}$H$_{2}$O or $^{36}$Cl), the CDE can be written as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x}$$

(5.2)

where $C(x,t)$ represents tracer concentration ($\mu$g ml$^{-1}$), $D$ is the hydrodynamic dispersion coefficient (cm$^2$ h$^{-1}$), $\nu$ is the average pore-water velocity (cm h$^{-1}$), $t$ is time (h), and $x$ is the spatial coordinate (cm). The following boundary (third-type) and initial conditions are commonly applied with the above CDE:

$$C=C_i \quad t = 0, \quad 0 < x < L_e$$

(5.3)

$$\nu C_o = -\theta D \frac{\partial C}{\partial x} + \nu C \quad x=0, \quad t<t_p$$

(5.4)

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

(5.5)

$$\frac{\partial C}{\partial x} = 0 \quad x=L_e, \quad t>0$$

(5.6)

where $L_e$ is solute transport length (cm); $\theta$ is the volumetric water content (cm$^3$ cm$^{-3}$); $t_p$ is the duration of solute pulse input (h); $C_i$ is initial solute concentration in the soil column, and $C_o$ is solute concentration in the applied pulse ($\mu$g ml$^{-1}$).

In a number of miscible displacement studies, the main purpose of a tracer application is to estimate the hydrodynamic dispersion coefficient, $D$. A commonly used technique for estimating $D$ is through curve-fitting of a tracer BTC where
tritium, chloride-36, bromide, or other tracers are used. Traditionally, we assume $L_c = L$ (column length) and attribute all variations to the parameter $D$. However, the goodness of fit of tracer BTCs are usually unacceptable when $D$ is the only fitting parameter. Thus, two parameters are fitted ($D$ along with the flow velocity $v$) in order to improve the goodness-of-fit of tracer BTCs (Jaynes et al. 1988, Andreini and Steenhuis 1990, Gamerdinger et al. 1990, 1991). Other commonly fitted parameters include pulse duration $t_p$ and a retardation factor $R$ for solute retention (van Genuchten 1981). However, since $v$ can be experimentally measured under steady-state flow, it may not be appropriate to fit $v$ to achieve improved fitting of BTCs. In addition, the best-fit velocity $v$ is often different from that experimentally measured.

One can also derive the CDE parameters based on the method of moments (Leij and Dane 1989, 1991). Hamlen and Kachanoski (1992) calculated average velocity ($v$) based on mean residence time ($t_m$) from the method of moments, that is $v = L/t_m$. Based on calculated $v$ and measured Darcy's flux $q$, they calculated an effective moisture content $\theta_T (=q/v)$. Their calculated $\theta_T$ was greater than that measured using time domain reflectometry (TDR). However, when $\theta_T$ was calculated using the time to peak flow, the differences between $\theta_T$ and $\theta_v$ was considerably decreased. On the other hand, Elrick et al. (1992) derived mean residence time ($t_m$) from the CDE fitted parameter $v$ and the column length $L$ such that $t_m = L/v$. They found that calculated $t_m$ based on three different methods (CDE fitting, moment analysis, and convective lognormal transfer function (CLT)) were close to one another. Based on these studies, if we use $t_m$ from eq. (5.1) and measured $v$ from
controlled water flux, we can obtain an "equivalent column length" \( L_e (= \nu_t) \). Such a parameter \( L_e \) is a measure of the effective solute transport length.

By defining a set of dimensionless parameters, eq. (5.2) can be rewritten as:

\[
\frac{\partial C}{\partial T} = \frac{1}{P} \frac{\partial^2 C}{\partial z^2} + \frac{\partial C}{\partial z} \tag{5.7}
\]

where

\[
T = \frac{\nu t}{L_e} \tag{5.8}
\]

\[
P = \frac{\nu L_e}{D} \tag{5.9}
\]

\[
z = \frac{x}{L_e} \tag{5.10}
\]

The solution to eq. (5.7) with initial and boundary conditions shown in eqs. (3.6) can be expressed as (Brenner 1962, van Genuchten and Alves 1982):

\[
C(z,t) = \begin{cases} 
C_i + (C_o - C_i) A(z,t) & 0 < t < t_p \\
C_i + (C_o - C_i) A(z,t) - C_o A(z,t-t_p) & t > t_p 
\end{cases} \tag{5.11}
\]

where

\[
A(z,t) = 1 - \sum_{m=1}^{\infty} \frac{2P \beta_m [\beta_m \cos(\beta_m z) + \frac{P}{2} \sin(\beta_m z)] \exp[\frac{zP}{2} - \frac{PT}{4} - \frac{\beta_m^2 T}{P}]}{[\beta_m^2 + \frac{P^2}{4} + P][\beta_m^2 + \frac{P^2}{4}]} \tag{5.12}
\]
where the eigenvalue $\beta_m$ are the positive roots of

$$\beta_m \cot(\beta_m) - \frac{\beta_m^2}{P} + \frac{P}{4} = 0$$

(5.13)

For $z=1$, we have the effluent concentration $C(t)$

$$C(t) = \begin{cases} 
C_i + (C_o - C_i)A(1,t) & 0 < t < t_p \\
C_i + (C_o - C_i)A(1,t) - C_oA(1, t-p) & t > t_p 
\end{cases}$$

(5.14)

where

$$A(1,t) = 1 - \sum_{m=1}^{\infty} \frac{2P\beta_m[\beta_m \cos(\beta_m) + \frac{P}{2} \sin(\beta_m)] \exp\left[\frac{P}{2} - \frac{PT}{4} - \frac{\beta_m^2T}{P}\right]}{[\beta_m^2 + \frac{P^2}{4} + P][\beta_m^2 + \frac{P^2}{4}]}$$

(5.15)

Therefore, $C$ is a function of $P$ and $T$, which, in turn, are functions of $\nu$, $D$, and $L_e$. As a result, one can obtain best-fit estimation of BTCs using either $L_e$ or $\nu$, since it is mathematically equivalent to fit $L_e$ and $\nu$. However, fitting $L_e$ is more physically meaningful than fitting $\nu$, because $\nu$ can be estimated experimentally under steady-state water flux. One advantage of fitting $L_e$ is that we can define a tortuosity factor ($\tau$) from the fitted solute transport length $L_e$ and the column length $L$ such that $\tau = L/L_e$. The other advantage is that $L_e$ can be verified experimentally from measured mean residence time ($t_m$). In fact, $\tau$ has been widely used in the solute diffusion equation, where the tortuosity factor ($\tau$) is incorporated into an effective diffusion coefficient ($D_e$) (Porter et al. 1960, Olsen and Kemper 1968, van Schaik and Kemper 1966, Gillham et al. 1984, Robin et al. 1987, Sadeghi et al. 1989). Assuming $D_e$ as a
function of $\tau$, Porter et al. (1960) estimated $\tau$ based on measured $D_e$. A similar approach was used by other investigators. For example, Gillham et al. (1984) and Robin et al. (1987) estimated $\tau$ from $D_e$ in bentonite-sand mixtures for chloride diffusion that was subsequently used to predict strontium diffusion. van Schaik and Kemper (1966) estimated $\tau$ ranging from 0.70-0.74 depending on soil water content and flow pattern. Gillham et al. (1984) calculated $\tau$ of 0.77-0.92 from chloride diffusion and 0.57-0.84 from tritium diffusion in bentonite-sand mixtures. They also found that $\tau$ is higher in pure media than that in mixed media. Porter et al. (1960) estimated $\tau$ of 0.39 for a silty clay loam soil under tension of 1 atm. Sadeghi et al. (1989) calculated a value of 0.85 for $\tau$ based on urea diffusion in seven soils. However, based on the above investigations and a literature search, we find that application of the tortuosity concept to modeling of solute transport in the soil profile is sparse.

Preferential flow is another phenomenon which can be examined based on BTC analysis. In a field study with three Swedish soils, Bergstrom (1990) claimed evidence for preferential flow path in his study when he detected chlorsulfuron and metsulfuron methyl after 70 mm of accumulated drainage which was considerably smaller than one pore volume for the soil profile. Omoti and Wild (1979) determined preferential flow path by analyzing the cross section of dyed soils. Singh and Kanwar (1991) suspected the existence of rapid flow through macropores if the pore volume to achieve 0.5 relative solute concentration ($C/C_0$) in the effluent was well before one pore volume. McMahon and Thomas (1974) quantified the by-passing flow of water
and chloride by the pore volume at which the first significant amount of solute was detected in the effluent. Andreini and Steenhuis (1990) examined preferential flow in a bromide study where BTCs from individual collecting cells at the bottom of a grid lysimeter were measured. A total of 52 cells were examined, with only 16 cells under-no-till and 21 cells under tilled treatment where water flow was detected. They also confirmed the presence of preferential flow by examining the flow paths of a dye after dissecting soil in the grid.

Preferential flow has been considered by many scientists as a major flow process under both soil water-saturated and unsaturated conditions (Singh and Kanwar, 1991; Andreini and Steenhuis 1990, Seyfried and Rao 1987, Jury et al. 1986). Although preferential flow was attributed mostly to swelling and shrinking cracks, worm holes and channels in structured soils (Czapar et al. 1992, Singh and Kanwar 1991, Beven and Germann 1982, Shipitalo et al. 1990, Starr and Glotfelty 1990, Kluitenberg and Horton 1990, Beven 1991), it was also observed in relatively homogeneous soils where the presence of macropores was not apparent (Ghodrati and Jury 1990, Butters et al. 1989, Hendrickx and Dekker 1991, Kladivko et al. 1991, Beven 1991, Pendexter and Furbish 1991, Jury et al. 1986). Therefore, preferential flow could be caused by macropores or a region with higher than average hydraulic conductivity (Andreini and Steenhuis 1990, Ghodrati and Jury 1990), or the instability of a wetting front (Hendrickx and Dekker 1991, Pendexter and Furbish 1991). An extensive review of preferential flow is available from Helling and Gish (1991). In soils demonstrating preferential flow pattern, flow occurs down macropores
representing only a small fraction of the soil structure (Andreini and Steenhuis 1990, Hendrickx and Dekker 1991, Bouma et al. 1977, Shipitalo et al. 1990, Watson and Luxmoore 1986). It is also commonly accepted that preferential flow can only be triggered under certain conditions, such as higher than average hydraulic conductivity, high water application rate, and low initial water contents (Ghodrati and Jury 1990, Czapar et al. 1992, Jaynes et al. 1988, Beven and Germann 1982, Shipitalo et al. 1990, Kluitenberg and Horton 1990). BTCs under these conditions showed consistently early breakthrough of solutes with bimodal concentration peaks in some cases (Butters et al. 1989, Villermaux 1974, Hornberger et al. 1990, Ligon et al. 1977, Jury et al. 1986).

In an attempt to describe the phenomena of preferential flow in soils, several models have been presented in the literature. van Genuchten and Wierenga (1976) proposed a mobile-immobile (two-region) approach to explain the excessive tailing and early breakthrough under preferential flow. Villermaux (1974) showed that bimodal peaks could be the result of two adsorption sites with different affinities for solutes to solid matrix surfaces. Skopp et al. (1981) proposed a two-domain transport model to explain early breakthrough and bimodal peaks in solute transport. Utermann et al. (1990) successfully predicted double peaks using bimodal probability density function (pdf).

In this study, miscible displacement methods were used to obtain tritium breakthrough curves (BTCs) for several soils and materials in uniformly packed columns under water-saturated and steady upward flow conditions. Since a literature
search revealed that preferential flow was primarily observed in soils in which solute was driven by gravity, one objective of this work was to demonstrate preferential flow and bimodal peaks of a tracer solute (tritium) in uniformly packed soils under upward flow condition. The second objective was to estimate the tortuosity soil parameter $\tau$ from breakthrough results of applied tritium pulses. The third objective was to test the applicability of $\tau$ and the transport path length $L_e$ in describing tracer transport in soils.

5.2. Materials and Methods

A tritiated 0.01 N Ca(NO$_3$)$_2$ solution was used throughout all experiments. Five soils (Sharkey, Cecil, Eustis, Dothan, and Mahan) and two uniform materials (glass beads and acid washed sand) were used. Their characteristics and soil classification are listed in Table 5.1. The miscible displacement technique as described by Selim et al. (1992) was followed. Each soil was uniformly packed into a 10 cm or 15 cm column and purged with CO$_2$ to achieve better water saturation. Soil columns were saturated upward with 0.01 N Ca(NO$_3$)$_2$ solution. Several pore volumes were introduced and the desired water flux was achieved prior to the introduction of tritium pulses. Steady-state water flux was controlled by a piston pump, and the effluent was collected using a fraction collector and analyzed using liquid scintillation counting (LSC).

Two types of tritium breakthrough curves (BTCs) were generated in order to achieve the goals of this study. The first type is referred to as a short pulse BTC (or impulse) and was used to measure the solute transport path length ($L_e$). This impulse
Table 5.1. Taxonomic classification and selected properties of soils in this study.

<table>
<thead>
<tr>
<th>Soils</th>
<th>Classifications</th>
<th>pH</th>
<th>% O.M.</th>
<th>Clay</th>
<th>Silt</th>
<th>Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sharkey Ap</td>
<td>very-fine, Montmorillonitic, nonacid</td>
<td>6.5</td>
<td>1.7</td>
<td>61</td>
<td>36</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Vertic Haplaquept.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cecil Bt</td>
<td>Clayey, Kaolinitic, thermic,</td>
<td>5.4</td>
<td>0.26</td>
<td>51</td>
<td>19</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Typic Hapludult</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eustis Ap</td>
<td>Psammentic Paleudult</td>
<td>4.9</td>
<td>0.71</td>
<td>4</td>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td>Mahan B</td>
<td>Clayey, Kaolinitic Typic Hapludult</td>
<td>5.6</td>
<td>0.5</td>
<td>40</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Dothan Ap</td>
<td>Fine-loamy, Siliceous, Thermic,</td>
<td>6.4</td>
<td>0.8</td>
<td>11</td>
<td>13</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>Plintic Paleudults</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dothan Bt</td>
<td>Fine-loamy, Siliceous, Thermic,</td>
<td>6.8</td>
<td>0.2</td>
<td>40</td>
<td>7</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Plintic Paleudults</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
was generated by introducing an extremely small tritium pulse into the soil column (≈ 0.03 pore volume). The applied tritium pulse was recovered by four pore volumes of tritium-free 0.01 Ca(NO₃)₂ solution following pulse application. The breakthrough results were used to determine the mean residence time \( t_m \) based on the first time-moment using eq. (5.1). Since the impulse was small and lasted for only a few minutes, we assumed that the calculated \( t_m \) approximates the time for a particle to travel through a soil column of length \( L \). The solute transport path length (\( L_c \)) was then obtained from the measured \( t_m \) and the average pore-water velocity (\( v \)) according to \( L_c = t_m \cdot v \). The second type of tritium BTCs was generated in the same way as the first (impulse) type except that the input tritium pulse was larger (about 1 pore volume). This type of BTCs was used to obtain the parameters \( D \) and \( L_c \) using the CDE (eq. 5.2) through curve-fitting. A numerical finite-difference method was applied in solving the CDE (Selim et al. 1990), and a nonlinear least-square optimization scheme was used to obtain best-fit estimates for \( D \) and \( L_c \) (van Genuchten 1981).

5.3 Results and Discussion

5.3.1 Deformation of tritium BTCs

Deformation of tritium BTCs was observed for all soils and for both short and long input pulses. The deformation includes early breakthrough of tritium pulses with considerable tailing of the desorption side of BTCs (Figs. 5.1-5.9). Such behavior was more obvious for BTCs resulting from short pulses than long pulses. However, deformation was not obvious for the two artificial materials (acid washed sand and glass beads) or their mixture (Fig. 5.1). Among the soils studied, the sandy textured
Eustis showed least deformation with BTC similar in shape to the acid washed sand (Fig. 5.2). However, the deformation was aggravated in the sequence of Sharkey (Fig. 5.3), Dothan subsoil (Bt) (Fig. 5.4), Dothan topsoil (Ap) (Fig. 5.5), Mahan (Figs. 5.6 and 5.7), and Cecil (Figs. 5.8 and 5.9). Bimodal peaks of short pulse BTCs were also observed in Dothan topsoil (Fig. 5.5), Mahan (Fig. 5.6), and Cecil soils (Fig. 5.8). The double peaks from Mahan and Dothan top soil columns were not as obvious as that from the Cecil soil columns. Furthermore, the double peaks were more distinct with increasing water velocity (Figs. 5.6 and 5.8) and less obvious in the corresponding BTCs from long tritium pulses (Figs. 5.7 and 5.9). Early breakthrough of tritium was detected in most BTCs. Appreciable amount of tritium was detected in the effluent at 0.5 pore volume for Cecil, Mahan and Dothan soils in comparison to 0.7-0.8 pore volume in acid washed sand and Eustis soil.

Several investigators attributed the early arrival of BTCs and bimodal peaks to flow heterogeneities in soils (Skopp et al. 1981, Hornberger et al. 1990, Hamlen and Kachanoski 1992). Although soil heterogeneity is often attributed to the pore size distribution, soil structure alone cannot determine the flow field in soils. Other experimental conditions such as the flow velocity, can also affect the relative size of different flow regions (Nkedi-Kizza et al. 1983, Hornberger et al. 1990). In this paper, we compared different soils based on soil aggregate size distributions. Using standard aggregate size distribution (dry sieving) methods, each soil with aggregate size less than 2 mm was sieved into five aggregate sizes; <0.05, 0.05-0.25, 0.25-0.50, 0.50-1.0, and 1.0-2.0 mm. Aggregate size results are given in Table 5.2 and
Figure 5.1 Tritium BTCs for acid washed sand. A: short pulse and B: long pulse.
Figure 5.2  Tritium BTCs for Eustis soil. A: short pulse and B: long pulse.
Figure 5.3  Tritium BTCs for Sharkey soil; A: short pulse and B: long pulse.
Figure 5.4 Tritium BTCs for Dothan (Bt) soil. A: short pulse and B: long pulse.
Figure 5.5  Tritium BTCs for Dathan (Ap) soil. A: short pulse and B: long pulse.
Figure 5.6 Tritium BTCs for Mahan soil (short pulses) for three pore water velocities ($v$). A: 2.02 cm/h; B: 3.82 cm/h; and C: 5.29 cm/h.
Figure 5.7  Tritium BTCs for Mahan soil (long pulses) for three pore water velocities (v). A: 2.02 cm/h; B: 3.82 cm/h; and C: 5.29 cm/h.
Figure 5.8  Breakthrough curves from short tritium pulses in Cecil soil at different pore water velocities ($v$); A: 1.07 cm/h; B: 2.23 cm/h; and C: 5.21 cm/h.
Figure 5.9  Breakthrough curves from long tritium pulses in Cecil soil at different pore water velocities ($v$); A: 1.07 cm/h; B: 2.23 cm/h; and C: 5.21 cm/h.
show extensive variations among soils and materials used in this study. Glass beads, acid washed sand and Eustis soil represent mostly uniform aggregate (particle) size distributions and hence exhibit little deformation of tritium BTCs (Figs. 5.1 and 5.2). In contrast, Cecil, Dothan and Mahan soils which exhibited nonuniform aggregate size distributions, produced extensive deformation of BTCs as shown in Figs. 5.4-5.9. Whereas, the BTCs from a Sharkey clay with aggregate size of 4-6mm exhibited little deformation (see Fig. 5.3). To further assess the relationship between the shape of BTCs and aggregate size distribution, two aggregate size ranges of Cecil soil (0.25-0.50mm and 0.50-1.0mm) were used to generate additional tritium BTCs for several flow velocities. These results are given in Figs. 5.10 through 5.12 and show distinct deformation of BTCs for the two aggregate sizes. The double peaks associated with the short tritium pulse for the 0.25-0.50 mm aggregate size (Fig. 5.10A) were not observed for the 0.50-1.0mm aggregate size (Fig. 5.11A). These results suggest that Cecil perhaps exhibits greater uniformity in the 0.50-1.0 mm compared to the 0.25-0.5 mm aggregate size range. Therefore, the aggregate size distribution analysis may not provide valuable information on soil heterogeneity. The BTCs shown in Figs. 5.10 and 5.11 also indicate that for the short pulses, the double peaks became more distinct with increased flow velocity. This observation is inconsistent with the field monitoring results of Br⁻ as reported by Hornberger et al. (1990). In contrast, for the long tritium pulse, the double peaks were masked (Fig. 5.12) and consistent with observed BTCs for other soils (see Figs. 5.5, 5.7 and 5.9).
Table 5.2. Measured aggregate size distributions of selected soils used.

<table>
<thead>
<tr>
<th>Soil</th>
<th>0-0.05</th>
<th>0.05-0.25</th>
<th>0.25-0.50</th>
<th>0.50-1.0</th>
<th>1.0-2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dothan Ap</td>
<td>2.24</td>
<td>27.43</td>
<td>43.82</td>
<td>21.96</td>
<td>4.18</td>
</tr>
<tr>
<td>Dothan Bt</td>
<td>1.87</td>
<td>19.95</td>
<td>24.76</td>
<td>31.8</td>
<td>21.37</td>
</tr>
<tr>
<td>Mahan B</td>
<td>1.26</td>
<td>30.74</td>
<td>33.03</td>
<td>18.33</td>
<td>16.51</td>
</tr>
<tr>
<td>Cecil Bt</td>
<td>1.98</td>
<td>16.48</td>
<td>50.63</td>
<td>23.66</td>
<td>7.16</td>
</tr>
<tr>
<td>Eustis Ap</td>
<td>0.00</td>
<td>5.96</td>
<td>60.43</td>
<td>33.61</td>
<td>0.00</td>
</tr>
<tr>
<td>Glass beads</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>97.23</td>
<td>2.13</td>
</tr>
<tr>
<td>Acid washed sand</td>
<td>0.00</td>
<td>0.77</td>
<td>79.96</td>
<td>19.23</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Figure 5.10  Tritium BTCs (short pulses) for Cecil soil (0.25-0.50mm aggregate size) for two pore water velocities (2.26 and 3.81 cm/h).
Figure 5.11  Tritium BTCs (short pulses) for Cecil soil (0.50-1.0 mm aggregate size) for two pore water velocities (2.05 and 4.15 cm/h).
Figure 5.12 Tritium BTCs (long pulses) for Cecil soil for two aggregate sizes ((0.25-0.50 and 0.5-1.0 mm) for two pore water velocities (2.26 and 2.05 cm/h).
Observed double peaks of BTCs may be attributed to the presence of multiple flow domains in soils (Skopp et al. 1981, Hornberger et al. 1990, Hamlen and Kachanoski 1992). In soils with two distinct pore size ranges, there may be two separate or distinct breakthrough curves. In such a case two BTCs are responsible for double peaks of observed BTCs. In a bromide study, Andreini and Steenhuis (1990) found that BTCs from individual collecting cells at the bottom of a grid lysimeter were of differing velocities and peak concentrations. These variations in BTCs from individual cells contributed to the asymmetry and tailing of an overall BTCs. Skopp et al. (1981) found that the behavior of heterogeneous or structured soils may decrease the efficiency of transport between regions which differ in their dispersion, porosity and flow velocity. This decrease in interaction may be a cause of early breakthrough, or observed double peaks for nonreactive solutes. In a field study, Hornberger et al. (1990) observed double peaks for Br\textsuperscript{-1} associated with several water application rates. The double peaks were distinct and their peak heights decreased as the application rate increased from 2.5 to 10 cm h\textsuperscript{-1}. They also observed early breakthrough and extensive tailing of Br\textsuperscript{-1} BTC associated with high application rate.

5.3.2 Superposition

To explain the observed BTC results from the short and long tritium pulse inputs, the question was whether one can predict the long pulse BTCs from their corresponding observed short pulse BTCs using the principle of superposition. We attempted to utilize BTC results having double peaks associated with short tritium pulses to generate other BTC results for the same soil. It is important to recognize that
the tritium BTCs from both types of pulses were generated under similar experimental conditions, except for pulse duration \(t_p\) and total amount of tritium introduced. Based on the solution given by eq. (5.14) for the CDE (eq. 5.7), we can easily show that effluent concentration \(C\) for a pulse having a duration \(t_p\) is identical to that derived for a system composed of a series of smaller (successive) input pulses under the same conditions; i.e., the same \(D, \theta, \rho, \nu, \) etc. In other words, the total sum of the solutions given by eq. (5.14) for \(n\) successive CDEs having input pulses of different durations; \(0 < t < t_1, t_1 < t < t_2, t_2 < t < t_3, \ldots, t_{n-1} < t < t_n\) is identical to that of one single long input pulse of duration \(t_p\) provided that \(t_p = t_n\). This is true for linear equations such as the CDE given in eq. (5.14). Therefore, one concludes that the linear CDE eq. (5.7) can describe the soil system if the superposition of a number of short pulses yields a BTC identical to that from a long pulse with the same \(t_p\). The predicted long pulse BTCs from short pulse BTCs using superposition are shown in Figs. 5.1-5.5, 5.7, 5.9 and 5.12, along with the experimentally measured ones. It can be seen that the superimposed BTCs are in consistent agreement with the measured BTCs \((r^2 > 0.99)\). This agreement suggests that the soil system behaves in accordance to the CDE (eq. 5.7). This finding also proves that the observed bimodal peaks from the short pulses were not due to experimental artifacts. It is also shown that the observed double peaks in the short pulse BTCs were masked or alleviated after the process of superposition. Our findings are consistent with observed multiple peaks of solute BTCs from field studies when tracers were applied for a very short duration as an impulse to the soil surface (Hornberger et al. 1990).
5.3.3 Tortuosity and transport path length

Tritium BTCs for the long pulses were also described using the CDE (eq. 5.7) where the parameters $D$ and $L_e$ were obtained using nonlinear (optimization) curve-fitting methods. The fitted curves along with BTCs obtained using superimposed short pulses are shown in Figs. 5.1-5.5, 5.7, 5.9 and 5.12. Values of parameter estimates for $D$ and $L_e$ along with their root mean squares (RMSs) are given in Table 5.3. Unlike fitted $L_e$ values, wide variations for the fitted $D$ parameter were obtained. According to Elrick and French (1966), large $D$ value indicates increased soil physical heterogeneity and preferential flow. Best-fitted BTCs using the CDE were considered adequate for most observed BTCs. However, the CDE predictions (fittings) failed to adequately describe the deformations of observed BTCs for Cecil and Mahan soils and for high pore water velocities (Figs. 5.7, 5.9 and 5.12). The humps in the tailing (desorption) side of BTCs were not described by the fitted BTCs. However, they were successfully predicted from the short pulse BTCs using the principle of superposition. Using chloride as a tracer, Leij and Dane (1989) observed a hump in the tailing side of the BTC for Dothan top (Ap) which is consistent with our results for tritium (see Fig. 5.5B). However, no humps were observed for Dothan subsoil, Bt (Fig. 5.4B). The failure of the CDE in describing tritium BTCs for a number of columns (see Figs. 5.5, 5.7, 5.9 and 5.12) may be attributed to other factors not addressed in this study. Such factors may include nonequilibrium between different flow domains. It is perhaps conceivable to describe such BTCs based on a multi-domain flow approach (Skopp et al. 1981, Hornberger et al. 1990).
Table 5.3. Selected parameters form long tritium pulses with their measured mean residence time ($t_m$), fitted dispersion coefficient ($D$), fitted transport path length ($L_c$), and calculated tortuosity ($\tau$)

<table>
<thead>
<tr>
<th>Soils</th>
<th>Column Velocity ($u$) (cm)</th>
<th>$t_m$ (hr)</th>
<th>D - Fitted (cm$^2$/hr)</th>
<th>$L_c$ - Fitted (cm)</th>
<th>RMS$^\dagger$</th>
<th>$L_c \ast \ast$ (cm)</th>
<th>$\tau$-Fitted</th>
<th>($\tau$)$\ast \ast$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sharkey 4-6mm</td>
<td>10</td>
<td>1.75</td>
<td>6.97</td>
<td>9.02(±0.436)</td>
<td>12.18(±0.141)</td>
<td>0.009421</td>
<td>11.67</td>
<td>0.821</td>
</tr>
<tr>
<td>Sharkey 4-6mm</td>
<td>15</td>
<td>1.85</td>
<td>9.83</td>
<td>7.66(±0.408)</td>
<td>18.39(±0.244)</td>
<td>0.011126</td>
<td>18.22</td>
<td>0.816</td>
</tr>
<tr>
<td>Eustis &lt;2mm</td>
<td>15</td>
<td>2.66</td>
<td>6.51</td>
<td>2.02(±0.213)</td>
<td>18.31(±0.268)</td>
<td>0.020686</td>
<td>17.30</td>
<td>0.819</td>
</tr>
<tr>
<td>Cecil &lt;2mm</td>
<td>15</td>
<td>1.07</td>
<td>15.93</td>
<td>2.39(±0.246)</td>
<td>18.86(±0.422)</td>
<td>0.021363</td>
<td>17.09</td>
<td>0.796</td>
</tr>
<tr>
<td>Cecil &lt;2mm</td>
<td>15</td>
<td>2.23</td>
<td>8.44</td>
<td>8.32(±1.505)</td>
<td>19.34(±1.023)</td>
<td>0.030477</td>
<td>18.81</td>
<td>0.776</td>
</tr>
<tr>
<td>Cecil &lt;2mm</td>
<td>15</td>
<td>5.21</td>
<td>3.97</td>
<td>20.82(±3.059)</td>
<td>19.18(±0.443)</td>
<td>0.029820</td>
<td>20.73</td>
<td>0.782</td>
</tr>
<tr>
<td>Cecil 0.5-1.0mm</td>
<td>15</td>
<td>2.05</td>
<td>7.25</td>
<td>3.71(±0.674)</td>
<td>16.19(±0.612)</td>
<td>0.037441</td>
<td>17.25</td>
<td>0.927</td>
</tr>
<tr>
<td>Mahan &lt;2mm</td>
<td>15</td>
<td>2.02</td>
<td>9.00</td>
<td>9.79(±1.529)</td>
<td>19.37(±0.845)</td>
<td>0.024375</td>
<td>18.16</td>
<td>0.775</td>
</tr>
<tr>
<td>Mahan &lt;2mm</td>
<td>15</td>
<td>3.82</td>
<td>4.60</td>
<td>15.86(±3.376)</td>
<td>18.21(±1.126)</td>
<td>0.029679</td>
<td>17.55</td>
<td>0.824</td>
</tr>
<tr>
<td>Mahan &lt;2mm</td>
<td>15</td>
<td>5.29</td>
<td>3.48</td>
<td>23.05(±5.291)</td>
<td>18.07(±1.169)</td>
<td>0.033855</td>
<td>18.43</td>
<td>0.830</td>
</tr>
<tr>
<td>Dothan Ap &lt;2mm</td>
<td>15</td>
<td>2.74</td>
<td>6.28</td>
<td>11.03(±2.063)</td>
<td>18.24(±0.369)</td>
<td>0.024622</td>
<td>17.20</td>
<td>0.822</td>
</tr>
<tr>
<td>Dothan Bt &lt;2mm</td>
<td>15</td>
<td>2.32</td>
<td>6.76</td>
<td>11.07(±2.353)</td>
<td>16.61(±0.879)</td>
<td>0.032858</td>
<td>15.69</td>
<td>0.903</td>
</tr>
<tr>
<td>Acid wash sand</td>
<td>15</td>
<td>2.92</td>
<td>6.06</td>
<td>1.10(±0.080)</td>
<td>17.39(±0.108)</td>
<td>0.010670</td>
<td>17.71</td>
<td>0.863</td>
</tr>
<tr>
<td>Glass + sand *</td>
<td>15</td>
<td>3.08</td>
<td>5.32</td>
<td>0.73(±0.089)</td>
<td>16.62(±0.144)</td>
<td>0.016836</td>
<td>16.35</td>
<td>0.903</td>
</tr>
</tbody>
</table>

* 50% glass and 50% sand by weight.
# values in parentheses are 95 % confidence interval.
$^\dagger$ Root Mean Squares
$^\ast \ast$ L$_c$ = $u t_m$, $\tau$ = L/L$_c$.
Fitted average transport length $L_e$ from the long pulses were used to calculate the tortuosity factor $\tau$. These fitted $\tau$ values from the CDE were then compared with the estimated $\tau$ values from the short tritium pulses. The latter were not obtained by curve fitting, rather they were calculated from the average transport length ($L_e$) through measured mean residence times ($t_m$), as discussed earlier. Fitted $L_e$ values, based on the long tritium pulses, and calculated (measured) $L_e$ from the short pulses, are given in Table 5.3. The $L_e$ values based on the two types of pulses were in agreement. However, for most cases, fitted $L_e$ values were greater than the calculated (or measured) $L_e$'s. The reason for this trend is not known. For some BTCs, incomplete recovery of applied tritium short pulses may be responsible for such low measured $L_e$ values. Incomplete recovery was a result of extensive tailing and/or early termination of column experiments. A linear regression of calculated values, $(L_e)_c$, versus fitted values, $(L_e)_f$, provided a good linear fit with $r^2$ of 0.997. The regression equation is $(L_e)_c = 0.98 \times (L_e)_f$ and the slope was not significantly different from one ($p=0.173$). Therefore, we conclude that it is appropriate to use $L_e$ as a fitting parameters in describing tracer BTCs using the CDE.

Calculated tortuosity $\tau$ from the short pulses and those obtained by curve fitting of the long tritium pulses are given in Table 5.3. A linear regression of calculated $\tau$ (or $\tau_c$) versus fitted $\tau$ (or $\tau_f$) provided good fit with $\tau_m = 1.02 \times \tau_f$, $r^2$ of 0.998 and the slope was not significantly different from one ($p=0.111$) (Fig. 5.13). These $\tau$ values are in close agreement with that suggested by Gillham et al. (1984) of 0.82. Moreover, fitted and calculated $\tau$ values from a 10 cm and 15 cm column for
Figure 5.13  Fitted tortuosity ($\tau$) from long pulses versus measured tortuosity ($\tau$) from short tritium pulses for all soils and materials (see Table 5.1).
Sharkey soil were similar. However, the difference between $\tau_c$ and $\tau_f$ may be a result of experimental errors as well as curve fitting errors. As pointed out by Brusseau et al. (1989a), the nonlinear least-square optimization used in this paper gives more weight to $C/C_0$ range of 0.2-0.8. In addition, the fitted parameters may not be unique to the data set (Brusseau et al. 1989a). Since bimodal peaks were observed for a number of BTCs with long pulse inputs, the use of the CDE for these BTCs may not be strictly applicable.

In conclusion, this research demonstrated the presence of bimodal peaks of tritium BTCs in uniformly packed soil columns with upward steady flow in the laboratory. Therefore, preferential flow is a phenomenon not restricted to gravity driven flow systems and field conditions. We also tested the validity of fitting solute transport length ($L_e$) or tortuosity ($\tau$) using the CDE. We conclude that $L_e$ (or $\tau$) is another parameter in the fitting of tracer BTCs in addition to the dispersion coefficient ($D$). Due to the fact that $\tau$ increases with water content $\theta$ (Porter et al. 1960, van Schaik and Kemper 1966), adjustments of $\tau$ with respect to $\theta$ could improve the predictability of solute transport models for water-unsaturated conditions.
CHAPTER 6

EVALUATION OF CHEMICAL AND PHYSICAL NONEQUILIBRIUM
IN ATRAZINE TRANSPORT IN A SHARKEY SOIL

6.1 Introduction

The retention mechanisms of reactive solutes with the soil matrix have been investigated through numerous laboratory studies, such as batch equilibrium and column transport experiments. The deduction of reaction processes based on experimental observations is usually presented in the form of mathematical models. The earliest models were the equilibrium ones, such as the Freundlich and Langmuir isotherms. However, equilibrium models are often inadequate in describing experimental data for many solutes. An improvement of the equilibrium model was made by introducing different model parameters for adsorption and desorption processes (Swanson and Dutt 1973, van Genuchten et al. 1974). Later, a kinetic approach was proposed to account for the increased solute adsorption with reaction time, which improved description of experimental data. A further improvement of the kinetic model by dividing retention into adsorption and desorption processes was discussed by van Genuchten et al. (1974). Recent development on reaction mechanisms was based on soil heterogeneity. Selim et al. (1976) proposed a two reaction site model, in which two types of sites were assumed to have different affinities to solutes. The two types of sites were assumed to be independent. That is, each type reacted independently with the solute in soil solution. One approach to the
two-site model is the equilibrium-kinetic model (Cameron and Klute 1977, Rao et al. 1979, Wauchop and Mayer 1985, Jardine et al. 1992). The other approach is a fully kinetic model (Jardine et al. 1992, van Genuchten and Wagenet 1989). Recent modifications on the two-site model are the incorporation of nonlinear reversible kinetics and/or first order degradation (van Genuchten and Wagenet 1989, Selim 1989, Selim et al. 1992). The two-site approach was further developed to a multireaction model (Amacher et al. 1988, Selim et al. 1992) and a second order two-site model (Selim and Amacher 1988).

A mobile-immobile (two-region) model was also developed based on soil physical heterogeneity (Skopp and Warrick 1974). Physical nonequilibrium models assume one of the three approaches: diffusion models, mass transfer models, and effective dispersion models (van Genuchten and Dalton 1986, Brusseau and Rao 1989). Spherical particle size is usually assumed in physical diffusion models (Rao et al. 1980a, 1982). However, other particle shape models were also found in the literature and could be transformed into an equivalent spherical shape model by a form factor (Rao et al. 1982, van Genuchten and Dalton 1986, Rasmuson 1985). However, due to the uncertainty surrounding soil particle shape and pore geometry, diffusion models may be simplified by use of a physical mass transfer model, where mass transfer between the mobile and immobile phases was described by a simple kinetic first-order mass transfer equation (Rao et al. 1980b, van Genuchten and Dalton 1986, Brusseau and Rao 1989). Thus, assumption about the porous medium’s structure is no longer required. This approach has been widely used in mobile-immobile models.

Although the models proposed by different authors were able to describe their experimental data to some degree, the reliability of these models remained questionable. The main obstacle is the difficulty in directly measuring model parameters. A complicated model with more parameters usually yields better description of experimental data, but it increases the difficulty of estimating model parameters. On the other hand, an oversimplified model with few model parameters usually gives poor description of experimental results. The commonly used method of deriving model parameters is through curve-fitting. The disadvantage of curve-fitting is that different model formulations give similar description to experimental data. Moreover, when a model having a large number of parameters often yield similar goodness of fit with different model parameters; i.e. the criteria for uniqueness of parameter values is not satisfied.
Efforts have been made to evaluate different models and to single out models with as fewer parameters as possible without significantly decreasing their descriptivity. van Genuchten et al. (1974) compared two kinetic models and one equilibrium model on picloram movement. They found that there was not much different between the kinetic and equilibrium models at low pore water velocities. However, neither models provided good description of the picloram breakthrough curves (BTCs) at high pore water velocities. They attributed the failure to less reaction time between picloram and soil matrix at high pore water velocities. Rao et al. (1979) compared a two-site model with a two-region model in a transport study for 2,4-D and atrazine. They found that the two-site model provided better predictions than the two-region model. Selim and Amacher (1988) developed a second-order two-site model (SOTS) and a second-order mobile-immobile model (SOMIM) in order to study Cr (VI) transport in three soils. They found that SOTS provided better description of Cr (VI) than SOMIM. In a transport study with exchangeable cations (Ca, Mg, Na) in an aggregated soil, Gaston and Selim (1990) found that a two-region model offered no improvement in prediction over the classic convective-dispersive (one-region) model. However, Selim et al. (1987) obtained better predictions of Mg and Ca with a two-region model in an aggregated Swiss soil. Jardine et al. (1992) evaluated three conceptual two-site models on dissolved organic carbon (DOC). They found that a one-site model was more appropriate for low DOC concentrations while a two-site model for high DOC concentrations. In Chapter 4, we found that a second-order model provided better predictions for atrazine BTCs in an aggregated soil than a first-
order two-site model. However, a judgement among these models is difficult to address. Most model comparisons were based on goodness of fit. Few attempts were made to evaluate models based on their predictability. A best-fit model may not reflect the true or actual adsorption mechanisms in the soil (Chapter 3 and 4, Rao et al. 1980b, Brusseau et al. 1989b).

The objective of this paper was to test physical versus chemical nonequilibrium models for their prediction capability of atrazine transport under varied experimental conditions. For this purpose, we developed a mobile-immobile model (or two-region) where retention is based on a modified second order formulation. This model was also used to verify the validity of certain difficult-to-measure model parameters, such as the volume fraction of mobile water phase ($F$), mass fraction of the dynamic soil region ($f$), and average soil aggregate size ($a$) or mass transfer coefficient ($\alpha$). Since all the model parameters were estimated independent of atrazine transport studies, the proposed model was examined based on solute predictions rather than curve-fitting of transport results.

6.2 Model Formulation

Atrazine adsorption can be divided into three steps: a fast adsorption which is too fast to monitor; a slow adsorption; and an extremely slow adsorption process (Gamble and Ismaily 1992). In previous chapters (Chapter 3 and 4), we found that a second-order two-site model (SOTS) with a first order degradation term could successfully explain this phenomenon. We also noticed that model predictions of BTCs were deteriorated as soil aggregate size increased from $< 2$ mm to 2-4 mm to 4-6 mm
(Chapter 4). This deterioration could be due to physical nonequilibrium within the aggregated soil. Therefore, there could be a coexistence of chemical and physical nonequilibrium in an aggregated soil such as Sharkey clay. Brusseau et al. (1989b) proposed a model where both chemical and physical nonequilibrium were assumed. Chemical nonequilibrium was described based on heterogeneity of adsorption sites of the soil matrix (Selim et al. 1976), while physical nonequilibrium may be caused by the nonuniform distribution of flow field. The simplest approach to physical nonequilibrium is to partition the liquid phase into "mobile" and "immobile" water phases (Skopp and Warrick 1974, van Genuchten and Wierenga 1976). The convective-diffusive transport was assumed to be confined in the mobile water phase. The rate of solute transfer between the two water phases was assumed proportional to the concentration gradient. The mechanisms of mass transfer between the two water phases could be diffusion according to Fick's law or displacement of the immobile water by incoming mobile water.

6.2.1 Model I

In the mobile-immobile approach, water is divided into mobile water phase ($\theta^m$, cm$^3$/cm$^3$), and immobile water phase ($\theta^{im}$, cm$^3$/cm$^3$). Moreover, the soil matrix was divided into a dynamic region and a stagnant region as shown in Figs. 6.1 and 6.2 (van Genuchten and Wierenga 1976). A parameter $f$ is also introduced to quantitatively differentiate the dynamic and stagnant regions. This $f$ value can be interpreted as that fraction of retention sites that are in direct contact with the mobile water. The total mass of solute in a control volume ($M$, $\mu$g/cm$^3$) can be written as:
Figure 6.1. A conceptual model of the mobile-immobile model.
Figure 6.2 A schematic of atrazine retention in the mobile-immobile model.
where \( C^m \) and \( C^{im} \) are the solute concentration in the mobile and immobile water phases, (\( \mu g/cm^3 \)); and \( S^m \) and \( S^{im} \) are the solute adsorbed in the dynamic and stagnant soil regions, respectively (\( \mu g/g \)). A general formulation of the convective-dispersive equation of reactive solutes transport in mobile-immobile two-regions can be written as

\[
M = \theta^m C^m + \theta^{im} C^{im} + f \rho S^m + (1-f) \rho S^{im}
\] (6.1)

where \( D \) is the dispersion coefficient (\( cm^2/hr \)), \( v^m (=q/\theta^m) \) the average pore water flux of the mobile phase (\( cm/h \)), \( \rho \) the soil bulk density (\( g/ml \)), \( X \) the spatial coordinate (\( cm \)), and \( t \) time (\( h \)). The mass transfer between the mobile and immobile water phases can be expressed as:

\[
\theta^m \frac{\partial C^m}{\partial t} + f \rho \frac{\partial S^m}{\partial t} = \theta^m D \frac{\partial^2 C^m}{\partial X^2} - \nu^m \theta^m \frac{\partial C^m}{\partial X} - \alpha(C^m - C^{im})
\] (6.2)

where \( \alpha \) is the mass transfer coefficient (\( h^{-1} \)) and can be estimated from physical parameters (Rao et al. 1980a):

\[
\alpha = \frac{D_0 \tau^2 \theta^{im}}{a^2 \alpha^*}
\] (6.4)

where \( D_0 \) is the molecular diffusion coefficient (\( cm^2/hr \)), \( a \) the radius of spherical aggregates (\( cm \)), \( \tau^2 \) the tortuosity factor. \( \alpha^* \) can be estimated from the following equations:
\[ \alpha^* = \frac{Fq_1^2}{1-b} \left( \frac{0.1}{T^*} \right)^b \quad \text{for} \quad 10^{-4} \leq T^* \leq 0.1 \]  \[ (6.5) \]

\[ \alpha^* = Fq_1^2 \left( 1 + \frac{0.1b}{(1-b)T^*} \right) \quad \text{for} \quad T^* > 0.1 \]  \[ (6.6) \]

where

\[ b = \frac{1.04472 \ln \left( \frac{\text{167}}{Fq_1^2} \right)}{Fq_1^2} \]  \[ (6.7) \]

and

\[ T^* = \frac{D_0 r^2 T}{a^2} \]  \[ (6.8) \]

where \( F \) is the mobile water phase fraction \( [F = \theta^m/(\theta^m + \theta^s)] \). \( q_1 \) depends on \( F \) and is listed in Table 1 of Rao et al. (1980a). \( T \) is the time over which \( \alpha \) average is taken. As suggested by Rao et al. (1980b), the mean residence time \( T (=L/v^m) \) gave good estimation of \( \alpha \). The tortuosity factor \( r^2 = (L/L_c)^2 \) was estimated from tritium BTCs (Chapter 4). Since our soil is closer to cubic shape, an equivalent radius \( a \) was calculated based on equal volume bases (Rao et al. 1982):

\[ a = 0.6203I \]  \[ (6.9) \]

where \( l \) in cm is the side of the cubic. If we further use the diagonal of the cubic \( (d) \) to represent the aggregate size, we have:
Chemically controlled (adsorption-desorption) reactions between solute in soil solution and matrix surfaces were assumed to take place in the mobile and immobile water phases. We also assumed that a second-order two-site retention approach governed the retention mechanisms (see Fig. 6.2). Furthermore, similar reaction rate coefficients \( (k_j \text{ to } k_5) \) associated with the dynamic and stagnant regions were chosen. Such an assumption that the mechanisms are equally valid for the two regions of the porous media was also introduced by Selim and Amacher (1988) for a chemically controlled two-site model. A similar assumption was made by van Genuchten and Wierenga [1976] for equilibrium linear and Freundlich sorption and by Selim et al. [1987] and Gaston and Selim (1990) for cation selectivity coefficients of ion-exchange reactions.

As illustrated in Fig. 6.2, the second-order approach accounts for two reversible kinetic retention mechanisms and one irreversible mechanism. Specifically, \( S_c \) and \( S_k \) are associated with reversible and \( S_i \) with irreversible reactions. This approach has been successful in describing atrazine adsorption and desorption kinetics (Chapter 2). According to second order formulation, the rate of reaction is not only a function of solute concentration in solution but also on the amount of available retention sites on matrix surfaces. As the sites become filled or occupied by the retained solute, the amount of vacant or unfilled sites which we denote as \( \phi \) (\( \mu g/g \) soil) approaches zero. In the mean time, the amount of solutes retained by the soil
matrix (S) approaches the total capacity or maximum sorption sites $S_{\text{max}}$. We further assume that $S_{\text{max}}$ is an intrinsic property of an individual soil and is thus assumed constant.

Extending the second-order concept to the mobile-immobile approach, we now describe the retention mechanisms associated with the dynamic soil region as,

\[
\frac{\partial S^m_e}{\partial t} = k_1 \theta^m C^m \phi^m - k_2 S^m_e
\]  \hspace{1cm} (6.11)

\[
\frac{\partial S^m_k}{\partial t} = k_3 \theta^m C^m \phi^m - (k_4 + k_5)S^m_k
\]  \hspace{1cm} (6.12)

\[
\frac{\partial S^m_i}{\partial t} = k_5 S^m_k
\]  \hspace{1cm} (6.13)

and the respective mechanisms for the stagnant region are:

\[
\frac{\partial S^{\text{im}}_e}{\partial t} = k_1 \theta^{\text{im}} C^{\text{im}} \phi^{\text{im}} - k_2 S^{\text{im}}_e
\]  \hspace{1cm} (6.14)

\[
\frac{\partial S^{\text{im}}_k}{\partial t} = k_3 \theta^{\text{im}} C^{\text{im}} \phi^{\text{im}} - (k_4 + k_5)S^{\text{im}}_k
\]  \hspace{1cm} (6.15)

\[
\frac{\partial S^{\text{im}}_i}{\partial t} = k_5 S^{\text{im}}_k
\]  \hspace{1cm} (6.16)

Equations (6.11)-(6.16) account for fully kinetic reversible and irreversible mechanisms where $S^m_e$, $S^m_k$ and $S^m_i$ are the amounts of solutes associated with the dynamic region whereas $S^{\text{im}}_i$, and $S^{\text{im}}_i$ and $S^{\text{im}}_i$ are associated with the stagnant region, respectively ($\mu g/g$ soil). Here $k_1$ and $k_3$ ($cm^3 \mu g^{-1} h^{-1}$) are the forward rate
coefficients, $k_2$ and $k_4$ (h$^{-1}$) are the backward coefficients, and $k_5$ (h$^{-1}$) is the rate coefficient for irreversible retention. Moreover, $\phi^m$ and $\phi^{im}$ (µg/g) represent the amount of vacant or unoccupied sites in the dynamic and stagnant regions, respectively;

$$\phi^m = S^m_{\text{max}} - (S^m_e + S^m_k) = fS^m_{\text{max}} - (S^m_e + S^m_k) \quad (6.17)$$

$$\phi^{im} = S^{im}_{\text{max}} - (S^{im}_e + S^{im}_k) = (1-f)S^m_{\text{max}} - (S^{im}_e + S^{im}_k) \quad (6.18)$$

where $S^m_{\text{max}}$ and $S^{im}_{\text{max}}$ are the total amount of sites in the dynamic and stagnant regions and are related by;

$$S^m_{\text{max}} = S^m_{\text{max}} + S^{im}_{\text{max}} = fS^m_{\text{max}} + (1-f)S^m_{\text{max}} \quad (6.19)$$

where we assumed that the sites are divided by the partitioning factor $f$ representing the fraction of dynamic sites ($S^m_{\text{max}}$) to maximum sorption capacity or total sites in the soil ($S^m_{\text{max}}$).

In the above formulation (eq. 6.11 and 6.14), if $k_1$ and $k_2$ associated with $S_e$ are extremely large, rapid rate of retention between $C$ and $S_e$ results and quasi equilibrium can be attained in a relatively short time frame. Therefore, one can rewrite eq. (6.11) and (6.14) as
where $K_e (= k_1/k_2)$ is now an equilibrium constant (cm$^3$ μg$^{-1}$) associated with $S_e$. Therefore, the above model two-region represents an "equilibrium-kinetic" approach which also accounts for irreversible retention reaction.

If irreversible retention is not included in our model or $k_5$ is close to zero, quasi-equilibrium may be reached at large times where $\partial C/\partial t$ approaches zero. Consequently, after rearrangements of the above equations, the amounts retained by the dynamic soil region at $t \to \infty$ are,

$$S_e^m = \frac{k_1}{k_2} \theta^m C^m \phi^m = K_e \theta^m C^m \phi^m \quad (6.20)$$

$$S_e^{im} = \frac{k_1}{k_2} \theta^{im} C^{im} \phi^{im} = K_e \theta^{im} C^{im} \phi^{im} \quad (6.21)$$

where $K_k (= k_3/k_4)$ is the equilibrium constant associated with $S_k$ (cm$^3$ μg$^{-1}$). Similarly, the corresponding equations for $S_e^{im}$ and $S_k^{im}$ for the stagnant soil region are
\[ S_{e}^{im} = \frac{K_{e} \theta^{im} C^{im}}{1 + (K_{e} + K_{k}) \theta^{im} C^{im}} \left(1 - f\right) S_{\max} \quad (6.24) \]

\[ S_{k}^{im} = \frac{K_{k} \theta^{im} C^{im}}{1 + (K_{e} + K_{k}) \theta^{im} C^{im}} \left(1 - f\right) S_{\max} \quad (6.25) \]

Summation of eq (6.22) to (6.25) to obtain the total amount sorbed (S) in the soil, upon further arrangements, yields the following generalized isotherm

\[ \frac{S}{S_{\max}} = \left[ \frac{\omega \theta^{m} C^{m}}{1 + \omega \theta^{m} C^{m}} \right] f + \left[ \frac{\omega \theta^{im} C^{im}}{1 + \omega \theta^{im} C^{im}} \right] \left(1 - f\right) \quad (6.26) \]

Equation (6.26) is analogous to the two-site Langmuir formulation where the amount sorbed in each region clearly identified. The langmuir parameter \( \omega \) represents the sum of equilibrium constants for \( S_{e} \) and \( S_{k} \) (\( \omega = K_{e} + K_{k} \)). Langmuir formulations are commonly used to obtain an independent estimate of sorption maxima \( S_{\max} \) and the affinity constant \( \omega \) (Sposito, 1984).

A major drawback of this model is the difficulty in arriving at a method to quantify the parameters \( \theta^{m} \) or \( F \) and \( f \). van Genuchten and Wierenga (1977) estimated \( \theta^{m} \) by curve-fitting of breakthrough curves (BTCs). Nkedi-Kizza et al. (1982) experimentally measured a \( \theta^{m} \) value by draining the soil column under 80 cm of water suction. Selim et al. (1987) estimated \( \theta^{m} \) from the amount of water drained under 20 cm suction. The estimation of \( f \) is more difficult, however. In fact, there is no known experimental method for the measurement of \( f \). Since a direct method to
obtain $f$ is not available, three ways to evaluate $f$ were carried out in this study. First, we assumed $f=1$, that is, the soil consists of only one (dynamic) region and $\theta^\text{im}$ does not exist. In such a case, Model I is reduced to the original second-order two-site model where only chemical nonequilibrium governs atrazine retention in soils. Therefore, adsorption-desorption reactions in the mobile water phase is purely based on chemical reaction. Second, we considered the case where $f=0$. Thus, chemical adsorption-desorption was assumed to take place only in the immobile phase. Thus adsorption-desorption in the mobile water phase is governed purely on physical diffusion (Nkedi-Kizza et al. 1983). One can argue that in aggregated media, the mobile phase may be in contact with matrix surfaces primarily through the immobile phase as illustrated schematically in Fig. 6.1. In fact, the soil surface in direct contact with the mobile water and thus the dynamic zone can be very small. In contrast, the third method was based on the assumption that $f=F$. This assumption has been used as a first approximation by several authors (Selim et al. 1987, Selim and Amacher 1988, Nkedi-Kizza et al. 1983, 1984, Gaston and Selim 1990). Under this assumption, the adsorption-desorption of solute in the mobile phase is both chemical and physical.

6.2.2 Model II

Due to the uncertainty about $f$, we reexamined the assumptions made by van Genuchten and Wierenga (1976). As shown in Fig. 6.1, a soil particle is surrounded by both mobile and immobile water phases, thus, chemical reactions take place from both sides of the particle simultaneously until all soil matrix surfaces approach an equilibrium. The dynamic and stagnant soil regions are connected to each other, and
there is no delineation between them. In fact, the ratio of the two regions depends highly on experimental conditions, such as particle size, water flux, solute concentration, and solute species (van Genuchten and Wierenga 1977, Nkedi-Kizza et al. 1983). Ideally, all vacant sites on the soil matrix should be accessible to solute in both the mobile and immobile water phases, otherwise equilibrium within the aggregates cannot be attained. Therefore, the potential reaction sites of the dynamic soil region is the total adsorption capacity ($S_{max}$) of the particle instead of a fraction of it ($fS_{max}$). Likewise, the potential reaction sites in the stagnant soil region is $S_{max}$ rather than $(1-f)S_{max}$. However, the total adsorption will not exceed adsorption capacity ($S_{max}$).

If the adsorption from the mobile water phase increases, the available adsorption sites for solutes in the immobile water phase will decrease, and vice versa. Therefore, there are two simultaneous adsorption processes in a soil particle. One is the adsorption from the mobile water phase, which penetrates towards the stagnant soil region. The other is the adsorption from the immobile phase, which expands to the dynamic soil region. These two simultaneous adsorption processes finally reach an equilibrium point. The importance of the two adsorption processes depends on pore water velocity, mass transfer between mobile and immobile water phases, and soil particle size. Thus, this conceptual model is different from the original SOTS only in one aspect, that is, it partitions the soil solution into two phases (mobile-immobile) based on their residence time in soil columns.
Based on the foregoing discussion, the adsorption-desorption reactions in both soil regions will still take the formulation of equation 6.11-6.16, except for 
\[ \phi^m = \phi^{im} = \phi, \]
where \( \phi \) is the total vacant adsorption site (\( \mu g/g \)), and takes the following form:

\[ S_{\text{max}} = \phi + S_e^m + S_k^m + S_e^{im} + S_k^{im} \quad (6.27) \]

and mass transfer between the mobile and immobile water phases are also modified as:

\[ \theta^{im} \frac{\partial C_i^{im}}{\partial t} + \rho \frac{\partial S_i^{im}}{\partial t} = \alpha (C^m - C^{im}) \quad (6.28) \]

The remaining model parameters are similar to those of Model I. Both models were subject to initial and boundary (of the third type) conditions. Model parameters were determined independent of column experiments; \( S_{\text{max}} \) was estimated from a batch adsorption isotherm, and \( K_e, k_3, k_4 \) and \( k_5 \) were calculated from another batch kinetic adsorption data set (Chapter 3 and 4). The diffusion coefficient \( (D) \) and solute path length \( (L_g) \) were obtained from tritium BTCs (Chapter 4). \( v^m, \theta \) and \( \rho \) were measured experimentally. The CDE was solved by the implicit-explicit Crank-Nicholson method (Selim et al. 1990).

6.3 Results and Discussion

6.3.1 Model parameter estimations

All model parameters were derived independent of the atrazine breakthrough curves (BTCs). The parameters \( v^m, \rho, \) and \( \theta \) were experimentally measured, and \( F \)
(\(=\theta^m/\theta\)) was estimated using 20 cm suction as proposed by Selim et al. (1987) and are listed in Table 6.1. A molecular diffusion coefficient \(D_o\) of \(5.472 \times 10^{-4} \text{ cm}^3/\text{hr}\) was estimated from Lavy (1970). \(D\) and \(L_e\) were obtained from tritium BTCs. Soil adsorption capacity \(S_{\text{max}}\) of 184.62 \(\mu\text{g/g}\) was estimated by fitting a linearized Langmuir equation to atrazine batch isotherms (Chapter 3). Rate coefficients \(K_e, k_3, k_4,\) and \(k_5\) were obtained from batch adsorption kinetic experiments (Chapter 3) and are listed in Table 6.2. Mass transfer coefficient \(\alpha\) was estimated by the method of Rao et al. (1980a,b). The average diagonal of cubic aggregates \((d)\) was taken as the midpoints of aggregate size ranges, specifically, \(d=0.1\) cm for <2 mm aggregates; \(d=0.3\) cm for 2-4 mm aggregates; and \(d=0.5\) cm for 4-6 mm aggregates. Thus, all input parameters required to derive the models were specified, and the models could be used solely in a prediction mode.

6.3.2 Model predictions

Selected atrazine breakthrough curves (BTCs) from Chapter 4 were used to evaluate the aforementioned models and assumptions. These BTCs were obtained under a wide range of experimental conditions and are listed in Table 6.1. Column I was conducted for 2-4 mm aggregates under pore water flux of 0.52 cm/hr and column length of 10 cm. Column II was under the same experimental conditions as Column I except for the pore water flux of 1.26 cm/hr. Column III was for <2 mm aggregates under pore water velocity of 1.26 cm/hr. Column IV was the same as Column II except for 15 cm soil column. Column V was obtained under the same conditions as Column IV except for higher pore water velocity (1.69 cm/hr). Column
Table 6.1. Listing of experimentally measured model parameters. L, soil column length; $L_e$, solute transport length; $d$, diagonal of soil aggregate; $\theta$, total water content; $\theta^m$, mobile water phase; $\rho$, soil bulk density; $v(=q/\theta)$, pore water velocity.

<table>
<thead>
<tr>
<th>Column ID</th>
<th>L (cm)</th>
<th>$L_e$ (cm)</th>
<th>$d$ (cm)</th>
<th>$\theta$ (cm$^3$/cm$^3$)</th>
<th>$\theta^m$ (cm$^3$/cm$^3$)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$v$ (cm/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>10</td>
<td>12.568</td>
<td>0.3</td>
<td>0.600</td>
<td>0.203</td>
<td>1.06</td>
<td>0.52</td>
</tr>
<tr>
<td>II</td>
<td>10</td>
<td>10.560</td>
<td>0.3</td>
<td>0.587</td>
<td>0.198</td>
<td>1.10</td>
<td>1.26</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>9.990</td>
<td>0.1</td>
<td>0.549</td>
<td>0.107</td>
<td>1.19</td>
<td>1.26</td>
</tr>
<tr>
<td>IV</td>
<td>15</td>
<td>15.638</td>
<td>0.3</td>
<td>0.609</td>
<td>0.206</td>
<td>1.04</td>
<td>1.08</td>
</tr>
<tr>
<td>V</td>
<td>15</td>
<td>15.761</td>
<td>0.3</td>
<td>0.591</td>
<td>0.200</td>
<td>1.09</td>
<td>1.69</td>
</tr>
<tr>
<td>VI</td>
<td>10</td>
<td>13.548</td>
<td>0.5</td>
<td>0.592</td>
<td>0.220</td>
<td>1.08</td>
<td>1.76</td>
</tr>
<tr>
<td>VII</td>
<td>15</td>
<td>15.760</td>
<td>0.3</td>
<td>0.598</td>
<td>0.202</td>
<td>1.06</td>
<td>1.97</td>
</tr>
<tr>
<td>VIII</td>
<td>15</td>
<td>17.246</td>
<td>0.3</td>
<td>0.510</td>
<td>0.172</td>
<td>1.06</td>
<td>2.17</td>
</tr>
</tbody>
</table>
Table 6.2. Listing of equilibrium and kinetic parameters from batch experiments. $S_{\text{max}}$, adsorption capacity; $K_e$ is the equilibrium constant; $k_3$, $k_4$ and $k_5$ are rate coefficients in the second-order models.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Estimates</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_e$ cm³ μg⁻¹</td>
<td>0.016040</td>
<td>0.000307</td>
</tr>
<tr>
<td>$k_3$ cm³ μg⁻¹ hr⁻¹</td>
<td>0.000107</td>
<td>0.000019</td>
</tr>
<tr>
<td>$k_4$ hr⁻¹</td>
<td>0.009465</td>
<td>0.003175</td>
</tr>
<tr>
<td>$k_5$ hr⁻¹</td>
<td>0.001628</td>
<td>0.000486</td>
</tr>
<tr>
<td>$S_{\text{max}}$ μg/g</td>
<td>184.62</td>
<td>6.18</td>
</tr>
</tbody>
</table>
VI was under experimental conditions of 4-6 mm aggregates, 10 cm column length and 1.76 cm/hr pore water velocity. Columns VII and VIII were obtained under similar conditions as Column V except that Column VII had 16 days and Column VIII had 4 days of flow interruption after pulse introduction.

Fig. 6.3 to 6.10 show predicted BTCs using the two model formulations under different \( f \) assumptions. Table 6.3 provides a list of the goodness of fit for BTC predictions in terms of root mean square (RMS). Generally, Model II provided best BTC predictions except for Column I and III. Model I with assumption of \( f = F \) yielded the worst predictions for all the cases. However, predictions using Model I with \( f = 1 \) and \( f = 0 \) varied depending on soil aggregate size and pore water velocity. We found that \( f = 0 \) provided best predictions of Column I (Fig. 6.3), whereas prediction of Column III was best when \( f = 1 \) was assumed. However, predicted BTCs with \( f = 1 \) were always shifted to the left in comparison with BTCs with \( f = 0 \). This shift was expected since we assumed that only a fraction of solute in the immobile water phase reacted with soil matrix (stagnant) under the assumption of \( f = 0 \). That is, solute in mobile water did not react with the soil, rather it passed through the column to the effluent directly. This phenomenon is often referred to as preferential flow and has been discussed by van Genuchten and Wierenga (1976).

The two assumptions (\( f = 1 \) and \( f = 0 \)) could also be used to test the significance of physical versus chemical nonequilibrium. The improved prediction of Column I with \( f = 0 \) may suggest that physical nonequilibrium play an important role in atrazine transport under our experimental conditions (2-4 mm aggregate size and \( \nu = 0.52 \))
Figure 6.3  Predicted atrazine BTCs of Column I. The experimental conditions are; 2-4 mm aggregates, $v=0.52$ cm/hr and 10 cm column length. Atrazine input solution are 10 ppm for pulse 1 and 5 ppm for pulse 2.
Figure 6.4  Predicted atrazine BTC of Column II. The experimental conditions are: 2-4 mm aggregates, 10 cm soil column, $v=1.26$ cm/hr, and 10 ppm atrazine input concentration.
Figure 6.5  Predicted atrazine BTC of Column III. The experimental conditions are: <2 mm aggregates, 10 cm soil column, \( u=1.26 \) cm/hr, and 10 ppm atrazine input concentration.
Figure 6.6  Predicted atrazine BTC of Column IV. The experimental conditions are: 2-4 mm aggregates, 15 cm soil column, $u=1.08$ cm/hr, and 10 ppm atrazine input concentration.
Figure 6.7 Predicted atrazine BTC of Column V. The experimental conditions are: 2-4 mm aggregates, 15 cm soil column, $u=1.69$ cm/hr, and 10 ppm atrazine input concentration.
Figure 6.8 Predicted atrazine BTC of Column VI. The experimental conditions are: 4-6 mm aggregates, 10 cm soil column, $v=1.76$ cm/hr, and 10 ppm atrazine input concentration.
Figure 6.9  Predicted atrazine BTC of Column VII. The experimental conditions are: 2-4 mm aggregates, 15 cm soil column, $v=1.97$ cm/hr, 10 ppm atrazine input concentration, and 16 days of flow interruption after pulse introduction.
Figure 6.10  Predicted atrazine BTC of Column VIII. The experimental conditions are: 2-4 mm aggregates, 15 cm soil column, \( \nu = 2.17 \) cm/hr, 10 ppm atrazine input concentration, and 4 days of flow interruption after pulse introduction. The soil water content is less than saturation.
Table 6.3. Goodness of prediction of atrazine BTCs in terms of root mean square (RMS)

<table>
<thead>
<tr>
<th>Column ID</th>
<th>RMS</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model I</td>
<td>Model II</td>
<td>Model II</td>
<td>Model II</td>
</tr>
<tr>
<td></td>
<td>$f=1$</td>
<td>$f=0$</td>
<td>$f=F$</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>0.087455</td>
<td>0.050653</td>
<td>0.141505</td>
<td>0.096257</td>
</tr>
<tr>
<td>II</td>
<td>0.085115</td>
<td>0.079063</td>
<td>0.164777</td>
<td>0.057376</td>
</tr>
<tr>
<td>III</td>
<td>0.030739</td>
<td>0.063882</td>
<td>0.170526</td>
<td>0.066261</td>
</tr>
<tr>
<td>IV</td>
<td>0.052363</td>
<td>0.151204</td>
<td>0.267964</td>
<td>0.049797</td>
</tr>
<tr>
<td>V</td>
<td>0.093798</td>
<td>0.095130</td>
<td>0.197592</td>
<td>0.044377</td>
</tr>
<tr>
<td>VI</td>
<td>0.170591</td>
<td>0.095941</td>
<td>0.134282</td>
<td>0.064288</td>
</tr>
<tr>
<td>VII</td>
<td>0.067674</td>
<td>0.162800</td>
<td>0.259636</td>
<td>0.066760</td>
</tr>
<tr>
<td>VIII</td>
<td>0.071108</td>
<td>0.093695</td>
<td>0.154681</td>
<td>0.051642</td>
</tr>
</tbody>
</table>
Improved predictions of Column III with $f=1$ rather than $f=0$, on the other hand, may infer that physical nonequilibrium is absent under experimental conditions of $<2$ mm aggregate size and $\nu=1.26$ cm/hr. As pointed out by Selim and Amacher (1988), a two-region model may decrease model predictability when chemical nonequilibrium is dominant. A similar result was reported by Gaston and Selim (1990) in a cation transport study with the Sharkey soil used in this study. Predictions using Model I with $f$ of 1 and 0 also were not consistent among different experimental conditions within the same aggregate size range. For example, among BTCs from 2-4 mm aggregates, $f=0$ improved predictions of Column I where $\nu=0.52$ cm/hr (Fig. 6.3). However, BTC predictions for $f=0$ are inferior for $f=1$ for Column IV, V, VII and VIII with $\nu$ ranging from 1.08 to 2.17 cm/hr (Figs. 6.6, 6.7, 6.9, and 6.10). Thus, the assumption of $f=0$ may overemphasizes the physical nonequilibrium in most cases.

Although $f=F$ has been used extensively in the literature, the use of $f=F$ in model I provided worst BTC predictions. This may be due to the fact that $\theta^m$ increased with increased size of soil aggregates (Table 6.1), but the outer surface area of soil decreases with soil aggregate size. Thus, as soil aggregate size increases, matrix surface area which is in direct contact with mobile phase decreases. Therefore, the fraction of dynamic soil region (related to soil surface area) decreases with increase in mobile water phase (due to increase in soil aggregate size). The assumption of $f=F$ could partially be responsible for the unsatisfactory predictability of the SOMIM model developed by Selim and Amacher (1988).
Improved BTC predictions using Model II strongly suggest the validity of our proposed model formulation (Figs. 6.4, and 6.6-6.10). Model II is perhaps similar to Model I with $f$ somewhere between 0 and 1. The assumption of $f=1$ usually underestimated the steepness of the front and overpredicted the tailing of BTCs. On the other hand, $f=0$ overpredicted the steepness of the front and underestimated the tailing of BTCs. Nkedi-Kizza et al. (1983) suggested that $\theta^n$ is a function of $\nu$, thus, the mobile and immobile water phases may be interchangeable. That is, some of the mobile phase can become immobile, and vice versa, dependent on experimental conditions. It may be reasonable to assume that adsorption sites are potentially accessible to all reactions rather than an "arbitrarily" fixed fraction of the total sites. Actual solute adsorption from either water phases is not easily understood, however, and is perhaps controlled by the probability of solute and adsorption site contact.

Compared to the chemical nonequilibrium model ($f=1$), improvement of Model II on BTC predictions is more significant for the desorption or tailing part of the BTCs. This is especially true for the large aggregates of 4-6mm (Fig. 6.8) and where flow interruption was carried out (Fig. 6.9 and 6.10). Thus, physical nonequilibrium is more significant during desorption of atrazine. This phenomenon can be more clearly demonstrated through flow interruption (Brusseau et al. 1989a). Since the dip in the BTCs was better predicted by the chemical nonequilibrium assumption ($f=1$) than by the physical nonequilibrium assumption ($f=0$) in the mobile water phase (Fig. 6.9 and 6.10), chemical nonequilibrium was assumed responsible for the dip of the BTCs (Chapter 4). On the other hand, Model II offered better prediction of the dip
and tailing than the pure chemical nonequilibrium ($f=1$). Therefore, there is a coexistence of chemical and physical nonequilibrium during atrazine transport, which together contributes to the adsorption-desorption of atrazine in the mobile phase. Jardine et al. (1990) fully discussed the role of small pores in physical nonequilibrium of Br$^-$ transport. These small pores have high Br$^-$ concentration during leaching and serve as a source for the increase in large pore Br$^-$ concentration.

6.3.3 Model sensitivity analysis

At the present time, there are three essential model parameters which are not easily measured or indirectly estimated. We have discussed the fraction of sites $f$. The two remaining parameters are the mobile water phase fraction ($F$), and the equivalent aggregate size radius ($a$). It is important to justify these parameters before we evaluate the two-region models. This justification was performed by sensitivity analysis using Column V as an example. Fig. 6.11 showed simulated results for different $F$ values, and Table 6.4 provided the corresponding RMS's. Generally, as $F$ increased, the BTC shifted to the right, indicating increased retardation. The simulation was best when $F=0.1$ for model assumptions of $f=0$ and $f=F$. However, our estimated $F$ value of 0.338 based on measured $\theta^m$ at 20 cm suction and $F=0.1$ provided equivalent simulation results with Model II. We can also see from Fig. 6.11 that Model II was less sensitive to changes in $F$. This resulted from the assumption that solutes in the mobile and immobile water phases had the same opportunity to react with adsorption sites except the mobile water phase has less contact time with
the soil matrix than the immobile water phase. This sensitivity analysis showed that estimated $F$ value was valid; at least, it was not underestimated.

The simulation results of Column V with different aggregate size radii $a$ are shown in Fig. 6.12, and their RMS listed in Table 6.4. The simulated BTCs were less symmetric as the aggregate size increases. As the soil aggregate size $a$ increased, the resulting BTCs showed steeper fronts and more tailing. The role of physical nonequilibrium increased as the aggregate size increased. However, the estimated $a$ (0.107 cm) yielded the best simulation in spite of the assumptions about $f$ regarding the fraction of sites. Therefore, the estimated aggregate radius $a$ is valid in our models for the Sharkey soil.

Since the $f$ value could not be determined experimentally, a sensitivity analysis of $f$ using Model I was also carried out. The $f$ value was allowed to change independent of $F$. Fig. 6.13 shows the simulation results with $f$ ranging from 0.1 to 0.7, and Table 6.4 lists their corresponding RMSs. Consistent with previous discussion, $f=0.1$ provided best simulation results. It is possible that the fraction of dynamic soil region is less than the volume fraction of mobile phase (i.e. $f \neq F$). This result may make Model I more difficult to use since there is no better way of estimating $f$. Model II, on the other hand, avoids this by not requiring a fixed partitioning of the two soil regions and is thus more promising for further applications.
Figure 6.11  Sensitivity analysis with model parameter $F$ (the mobile phase fraction) using Column V as an example. A: Model I with assumption $f=0$; B: Model I with assumption $f=F$; and C: Model II.
Figure 6.12 Sensitivity analysis with model parameter $a$ (equivalent aggregate radius) using Column V as an example. A: Model I with assumption $f=0$; B: Model I with assumption $f=F$; and C: Model II.
Figure 6.13  Sensitivity analysis with model parameter $f$ (the fraction of dynamic soil region) using Column V as an example. $F=0.338$ was used in this simulation.
Table 6.4. Goodness of prediction in sensitivity analysis in terms of root mean square (RMS)

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F = 0.1 )</td>
<td>0.041299</td>
</tr>
<tr>
<td>( F = 0.338 )</td>
<td>0.095130</td>
</tr>
<tr>
<td>( f = 0 )</td>
<td></td>
</tr>
<tr>
<td>( F = 0.5 )</td>
<td>0.143628</td>
</tr>
<tr>
<td>( F = 0.7 )</td>
<td>0.216050</td>
</tr>
<tr>
<td>( F = 0.1 )</td>
<td>0.067732</td>
</tr>
<tr>
<td>( F = 0.338 )</td>
<td>0.197592</td>
</tr>
<tr>
<td>( f = F )</td>
<td></td>
</tr>
<tr>
<td>( F = 0.5 )</td>
<td>0.237289</td>
</tr>
<tr>
<td>( F = 0.7 )</td>
<td>0.201426</td>
</tr>
<tr>
<td>( F = 0.1 )</td>
<td>0.042884</td>
</tr>
<tr>
<td>( F = 0.338 )</td>
<td>0.044377</td>
</tr>
<tr>
<td>( f = a )</td>
<td></td>
</tr>
<tr>
<td>( a = 0.107 )</td>
<td>0.197592</td>
</tr>
<tr>
<td>( a = 0.20 )</td>
<td>0.206424</td>
</tr>
<tr>
<td>( F = 0.5 )</td>
<td>0.057834</td>
</tr>
<tr>
<td>( F = 0.7 )</td>
<td>0.074007</td>
</tr>
<tr>
<td>( a = 0.107 )</td>
<td>0.044377</td>
</tr>
<tr>
<td>( a = 0.20 )</td>
<td>0.045515</td>
</tr>
<tr>
<td>( f = 0.1 )</td>
<td>0.101841</td>
</tr>
<tr>
<td>( a = 0.107 )</td>
<td>0.095130</td>
</tr>
<tr>
<td>( a = 0.20 )</td>
<td>0.150567</td>
</tr>
</tbody>
</table>

\( f \) sensitivity analysis

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F = 0.338 )</td>
<td>0.125615</td>
</tr>
<tr>
<td>( f = 0.338 )</td>
<td>0.197592</td>
</tr>
<tr>
<td>( (Model I) )</td>
<td></td>
</tr>
<tr>
<td>( F = 0.5 )</td>
<td>0.233661</td>
</tr>
<tr>
<td>( f = 0.7 )</td>
<td>0.252544</td>
</tr>
</tbody>
</table>
CHAPTER 7
SUMMARY AND CONCLUSION

The batch technique is the oldest approach in studying solute retention. Although it was at first developed to study adsorption equilibria, due to its simplicity, it has been increasingly used in adsorption kinetic studies. As a preliminary experiment, atrazine adsorption-desorption hysteresis was investigated (Chapter 2). Atrazine adsorption was assumed to reach equilibrium after 24 hours. Thus, adsorption isotherms were constructed and described using the Freundlich model \((S=K \, C^N)\). Following the 24 hour adsorption, six consecutive desorptions were conducted to generate a desorption isotherm which again was described by the Freundlich model. However, the desorption isotherm was considerably different from the adsorption isotherm, which is referred to as desorption hysteresis. The extent of hysteresis, quantified as the maximum difference between adsorption and desorption isotherms, increased with atrazine-soil reaction time (incubation time). An analysis of the Freundlich parameters from the desorption isotherms revealed that \(N\) decreased with incubation time, while the change of \(K\) with incubation time was dependent on initial atrazine input concentrations. \(K\) increased with incubation time at high initial atrazine concentrations (4.10 and 10.46 \(\mu g/ml\)), but it decreased with incubation time at low initial concentrations (0.54 and 1.05 \(\mu g/ml\)) during the first 4 day incubation period. The observation of hysteresis in batch equilibrium experiments suggested that atrazine adsorption in our soil was kinetic in nature.
Thus, a set of batch experiments was designed to study atrazine adsorption kinetics (Chapter 3). Instead of terminating the adsorption process at the end of 24 hours, this study monitored atrazine adsorption at different times (2, 8, 24, 96, 192, 288, and 504 hours). We also used six atrazine initial concentrations (2.95, 5.91, 11.94, 17.73, 23.48 μg/ml). The results showed that atrazine adsorption did not reach a quasi-equilibrium until 192 hours. An attempt was also made to measure atrazine adsorption capacity by maintaining a high atrazine concentration in soil solution. This attempt failed due to its low water solubility (29.45 μg/ml). Therefore, a linearized Langmuir equation was used to estimate atrazine adsorption capacity which was estimated at 184.62 μg/g. This estimated adsorption capacity was used throughout our modeling efforts.

A second-order two-site model (SOTS) was also developed at this point to model atrazine adsorption kinetics (Chapter 3). This model was based on three major assumptions: (1) There are two adsorption sites and one degradation reaction in soils. One of the adsorption sites is equilibrium, and the other is kinetic. A first-order degradation reaction is coupled with the kinetic adsorption site. (2) The adsorption sites on the soil matrix are limited. (3) All the adsorption sites are equally accessible to both kinetic and equilibrium adsorptions. The last assumption represents a major modification from the traditional second-order approach. Based on independently estimated model parameters, the SOTS yielded good predictions for atrazine adsorption kinetics regardless of initial atrazine concentration and soil:water ratio. It also successfully predicted atrazine desorption hysteresis.
Encouraged by good predictions of atrazine adsorption-desorption kinetics in batch experiments, we further validated the SOTS model in atrazine column transport studies (Chapter 4). Fourteen atrazine breakthrough curves (BTCs) were obtained under a wide range of experimental conditions, such as atrazine input concentration, flow velocity, column length, soil aggregate size, soil water content, and flow interruption. All model parameters were obtained either from batch experiments or from tritium BTCs, and the model was used solely in a prediction mode. Despite the wide range of experimental conditions, the proposed model provided good predictions for all atrazine BTCs, especially for smaller aggregates. Therefore, the SOTS is a reasonable approach in describing atrazine-soil reaction mechanisms.

Predictions using SOTS deteriorated as soil aggregate sizes increased from <2 mm to 2-4 mm and 4-6 mm. This deterioration with aggregate size may suggest physical nonequilibrium in this aggregated Sharkey soil. Thus, a coexistence of chemical and physical nonequilibrium was plausible. In an attempt to improve SOTS prediction, a second-order two-region approach was proposed (Chapter 6), in which both chemical and physical nonequilibrium were taken into account. Chemical nonequilibrium was described by using our proposed second-order approach, while the physical nonequilibrium was represented by a mobile-immobile (two-region) model. Based on mobile-immobile assumptions, a saturated soil system was divided into four regions, that is, a mobile water phase which is characterized by convection and dispersion; an immobile water phase with close to zero velocity; a dynamic soil region which is in direct contact with the mobile water phase; and a stagnant soil
region which is in direct contact with the immobile water phase. Since the fraction of
dynamic soil region \( (f) \) was not experimentally measurable, three assumptions about
\( f \) were evaluated. One was \( f=1 \) \( (\theta_{im}=0) \), which reduced to the original SOTS.
Another was \( f=0 \). Thereby, all adsorption was assumed to take place in the immobile
water phase. The third assumption was \( f=F \) (the volume fraction of mobile phase).
Again, the model parameters were estimated independent of atrazine BTCs. Among
the three \( f \) assumptions, \( f=F \) provided the worst predictions to BTCs. Thus, the
assumption of \( f=F \) may not be realistic and needs to be reconsidered. Although \( f=0 \)
improved BTC predictions, it overemphasized physical nonequilibrium in most of
cases. However, there was no better way to determine \( f \). Therefore, we proposed a
new approach where \( f \) was no longer a required parameter. To achieve this, we
assumed that all adsorption sites are equally accessible to solutes in both mobile and
immobile water phases. Thus, no "arbitrarily" fixed \( f \) ratio is needed. This modified
two-site two-region model provided improved BTC predictions for most data sets in
comparison to all other models investigated.

Another important feature of this study is the introduction of solute transport
length \( (L_c) \) in the transport models. The solute transport length \( (L_c) \) was estimated
from tritium BTCs by use of the hydrodynamic coefficient \( (D) \) and solute transport
length \( (L_c) \) as fitting parameters. The use of \( L_c \) not only makes better use of
information of tritium BTCs, but also provides a mean of estimating the tortuosity
factor \( (\tau) \) from solute transport length \( (L_c) \) and the column length \( (L) \). The validity of
the estimated tortuosity factor \( \tau \) was extensively evaluated in Chapter 5.
REFERENCES


to evaluate the environmental fate of atrazine (s-triazines). Agriculture, Ecosystems and Environment. 27:513-522.


VITA

Liwang Ma was born on April 13, 1965. He was raised in a countryside in Hubei Province, the People's Republic of China. He earned his B. S. and M. S. degrees in Biophysics at Beijing Agricultural University, Beijing, China, in 1984 and 1987, respectively. From 1987 to 1989, he was employed as a plant physiologist at Shanghai Institute of Plant Physiology, an institute of the Chinese Academy of Sciences. He came to U.S. to pursue his Ph.D degree in the Fall of 1989 and spent his first year in the Department of Agronomy and Soil Science at the University of Hawaii. He then transferred to Louisiana State University in the Fall of 1990. He has studied Soil Physics for the last three and half years and is a candidate for Ph. D. degree in soil science in the Department of Agronomy.
Candidate: Liwang Ma

Major Field: Agronomy

Title of Dissertation: Predicting the Movement and Retention of Pesticides in Soils: Physical and Chemical Nonequilibrium Modeling Approaches

Approved:

[Signature]
Major Professor and Chairman

[Signature]
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signature]

[Signature]

[Signature]

Date of Examination:

October 29, 1993