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Retention and movement of reactive chemicals in soils

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RETENTION AND MOVEMENT OF REACTIVE CHEMICALS IN SOILS

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ABSTRACT

Adsorption-desorption and transport behavior of pesticides are important processes that influence the amount retained by the soil and that which is susceptible to runoff or movement within the soil profile. Kinetic batch experiments were used to study the adsorption-desorption behavior of metolachlor (a non-ionic herbicide) and deltamethrin (a pyrethroid insectcide) in soils, and atrazine (a triazine) in sugarcane mulch residue. Miscible displacement experiments under steady flow conditions were carried out to examine the mobility of these pesticides in soils.

Metolachlor adsorption and desorption by Sharkey clay soil(Very-fine, smectitic, thermic Chromic Epiaquerts) and Commerce silty loam soil (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Epiaquepts) soil were strongly kinetic. The K_d values of metolachlor adsorption for Sharkey were significantly higher than for Commerce. After six desorption steps, the average metolachlor desorbed was 30.5% and 43.9% for Sharkey and Commerce, respectively, and was dependent on the initial input concentration. Adsorption and desorption of atrazine by sugarcane mulch exhibited extensive kinetic behavior. Adsorption isotherms appeared linear for all reaction times. A linear multireaction model which accounted for reversible equilibrium and kinetic retention along with a consecutive irreversible reaction described both adsorption and desorption of atrazine retention results (r^2=0.99).

Deltamethrin retention by soils was strong, and positively related with cation-exchange capacity (CEC) and negatively related with soil pH. Deltamethrin recovery was dependent upon the initial input concentration, and did not exceed 10.2% of the total amount adsorbed for all the four soils (Sharkey clay, Mahan sand loam, Vacherie silty loam and Mhoon silt clay loam) representing a wide range of organic matter and

clay contents. Extremely low mobility and thus strong retention for deltamethrin in the soil columns were observed.

A new hysteresis coefficient based upon the difference in the area between adsorption and desorption isotherms was proposed. This coefficient was capable of quantifying hysteresis for both types of desorption isotherms: traditional desorption isotherms and time-dependent desorption isotherms. Results suggested that when an isotherm is measured based upon laboratory adsorption-desorption experiments or field measurements, equal reaction times should be maintained.

CHAPTER 1: INTRODUCTION

Using agricultural chemicals for pest and weed control has been an effective agricultural practice, while the fate of those chemicals in the soil environment continues to cause great concern. It was reported that, of the pesticides used in agriculture, only 0.1% actually reached the targeted pests, the rest (over 99%) is distributed into the ecosystem (Pimental and Levitan, 1986). The latter may cause serious environmental problems, such as groundwater contamination, food contamination, and air pollution (Pimental et al., 1991). Studies have documented the occurrence of agricultural chemicals in surface waters (Goolsby et al., 1991; Thurman et al., 1991; Keeney and DeLuca, 1993) and ground waters (US Environmental Protection Agency, 1992). Pesticides leached from agricultural fields, leaking storage tanks, or transport through the air during spraying or after volatilizing appear in ground-water samples, often years after application (Jury et al., 1987). These widely reported contamination problems led to increased public pressure to regulate the application of herbicides due to their potential adverse effects on human health. Therefore, studies of agricultural chemicals and their role in soils and the environment have been the focus of investigators in several scientific disciplines.

Numerous studies have been presented in the literature and scientific meetings related to the environment and agriculture (Garner et al., 1986; Cheng, 1990; Somasundaram and Coats, 1991). Efforts have also been made in modeling the fate of agricultural chemicals in the soil environment as influenced by soil physical, chemical and biological processes. Information regarding retention and release, and transport of agricultural chemicals on soils is an essential for mathematical modeling. The variation of soil properties, such as pH, cation exchange capacity (CEC), clay and organic matter

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content, soil moisture content, and electrolyte concentration, influence the adsorption and

desorption characteristics of agricultural chemicals to soils. Of equal importance are the

physical and chemical properties of the chemicals, such as concentration, pH,

dissociation constant (pKa), vapor pressure, and solubility. Moreover, the adsorption-

desorption processes for most herbicides from soils are kinetic rather than equilibrium.

Hysteretic characteristics of adsorption and desorption on soils were reported (Swanson

and Dutt, 1973; Ma et al., 1993; Xue and Selim, 1995). In order to predict the fate of

herbicides, it is necessary to acquire reaction information on the agricultural chemicals

frequently used in practice.

1.1 Statement of Problem

Atrazine, metolachlor and metribuzin are frequently used in Louisiana for soybean,

sugarcane, peanut and corn. Southwick et al. (1992) detected atrazine concentrations as

high as 403 µg/L in 1-m-depth tile-drain water samples 7-d post-application from a

Sharkey clay soil. In a similar study, Southwick at al. (1995) found high concentrations

of atrazine (81.1µg/L) and metribuzin (94.0µg/L) within 8-10 d after application. Smith

et al. (1990) observed atrazine at 350µg/L 12 d after application in a sandy soil.

Metolachlor in Pennsylvania ground-waters and Iowa were found in concentrations

ranging from 0.1 to 0.5µg/L. Deltamethrin is a synthetic pyrethroid that has been widely

used as a pesticide on tobacco, potatoes, broccoli and cabbage. Recently, efforts have

been made to investigate the fate of deltamethrin as a termiticide due to its high

insecticidal activity, low mammalian toxicity, and adequate stability. However,

information about the fate of deltamethrin in soil is limited. Understanding the reactivity

and mobility of such herbicides and pesticide provides necessary information for

regulating the application of these chemicals. As a result, a number of best management

practices (BMPs) such as no till systems have been proposed. Moreover, using a no till

system is accompanied by the presence of crop residue. Thus, the effect of residue mulch

on the fate of those chemicals becomes another interesting research focus.

1.2 Objectives

The objectives of this study are: 1) To study the adsorption-desorption

characteristics of metolachlor and deltamethrin in soils; 2) To quantify the hysteresis of

adsorption-desorption of selected agricultural chemicals in soil and mulch residue from

sugarcane; 3) To investigate the effect of soil properties on deltamethrin retention

characteristics and mobility in soils; 4) To study the effect of sugarcane residue mulch on

the fate of selected agricultural chemicals in the field; 5) To test the applicability of

kinetic multireaction models and second order transport models to predict the retention

reaction behaviors in soils and sugarcane mulch residue.

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CHAPTER 2: HYSTERETIC BEHAVIOR OF METOLACHLOR ADSORPTION-DESORPTION IN SOILS

2.1 Introduction

Retention reactions of applied agricultural chemicals that occur in the soil environment are important processes that influence their concentrations levels in the soil solution and their downward movement in the soil profile. Several models that describe the potential mobility of dissolved chemicals have been developed to infer the mechanisms governing their reactivity in soils. Linear, Freundlich, and Langmuir (equilibrium) approaches are commonly used to predict pesticide distribution or partitioning between the soil matrix and the solution phase. Recent approaches include models that are based upon soil heterogeneity and kinetics of adsorption-desorption reactions (Selim et al., 1976; Gamble and Khan, 1990; Ma and Selim, 1994a,b). Such models assume that the governing retention mechanisms include linear and/or nonlinear, kinetic and/or equilibrium reactions of the reversible and/or irreversible types. A multireacton approach was incorporated with transport models and was successfully used to describe adsorption and movement of atrazine in a Sharkey clay soil (Ma and Selim, 1994b), and adsorption-desorption of alachlor in a Gigger silt loam soil (Xue and Selim, 1995; Xue et al., 1997). Attempts to predict pesticide retention in soils based on general purpose multireaction approaches are sparse, however. Rigorous validation of general purpose models for a wide range of chemical species and for soils having different physical and chemical properties is a prerequisite prior to their adoption and implementation.

Metolachlor [2-chloro-N- (2-ethyl-6-methylphenyl) -N- (2-methoxy-1-methylethyl) acetamide] is a preemergence herbicide commonly used in corn, soybean, peanut and sorghum cultivation in Louisiana and other areas of the country. The chemical structure is shown in Figure 2.1. It has been frequently detected in surface and groundwaters (Ritter, 1990; Maas et al., 1995). It is a nonionic herbicide with a water solubility of 530 $\mu g \ mL^{-1}$, vapor pressure of 1.69×10^{-3} Pa at 20^0C, and molecular weight of 283.80 g mol^{-1} (Wauchope et al., 1992).

Information regarding the adsorption and desorption characteristics of metolachlor by soils is essential for predicting its fate within the soil environment. Johnson and Sims (1993) investigated the effect of selected soil properties on the sorption of five ^{14}C-labeled herbicides including metolachlor using the batch equilibrium technique. Their results indicated that metolachlor retention was best correlated with organic matter content and effective cation exchange capacity. Seybold and Mersie (1996) studied the adsorption and desorption of metolachlor in two soils from Virginia and found that differences in the composition of organic matter and/or the contribution of other components (e.g., clay) to adsorption plays a significant role in the sorption process.

Several efforts have been made to study the movement and dissipation of metolachlor as well as a number of control release formulations under field conditions (; Bowman, 1993; Weber and Swain, 1993; Wietersen et al., 1993a,b; Gaynor et al., 1995; Widmer and Spalding, 1995). Numerous studies indicated that values for metolachlor half-lives are highly dependent on experimental conditions; namely field or laboratory (for a review see Chesters et al., 1989). In fact, half-lives for metolachlor have been reported as low as 11 d and as high as 440.3 d. Examples of laboratory

experiments include Lavy et al. (1996) who reported half-lives of 109.8-440.3 days for two soils from two depths each. The half-life of metolachlor was also reported as 10.1 weeks by Bouchard et al. (1982). In a field experiment, Bouchard (1982) reported a half-life of 52 days for the summer and a half-life of 277 days for the winter. There was no leaching in the winter, thus, the dissipation was dependent only upon degradation. This significant increase in half-life of metolachlor during the summer was attributed to both degradation and leaching. In another field experiment, Braverman et al. (1986) found that metolachlor is mobile and leaching is an important mechanism for its dissipation within the soil. He reported half-lives as low as 11 to 14 days

Desorption or release characteristics of pesticides such as metolachlor influences their leaching and bioavailability in soils (Seybold and Mersie, 1996). Soils are generally more retentive of herbicides during desorption than adsorption, a phenomenon known as hysteresis. Consequently, desorption parameters can be substantially different from that for adsorption. Desorption coefficients for metolachlor have not been reported as much as adsorption coefficients (Graham and Conn, 1992). Seybold and Mersie (1996) found that the total amount of metolachlor desorbed after four desorption cycles was 40% of that applied. They also reported there was no significant differences between soils or between initial concentrations on the percentage of metolachlor desorbed (released).

Several investigations attempted to identify possible sources of observed hysteretic retention of a number of pesticides in soils. Graham and Conn (1992) concluded that degradation and inadequate equilibration were not likely explanations for metolachlor hysteresis. It has been reported that the most likely cause of metolachlor hysteresis was

irreversible or slowly reversible chemical sorption (Pignatello and Huang, 1991; Seybold and Mersie, 1996). This study examines the adsorption and desorption characteristics of metolachlor for two Louisiana soils: Sharkey clay and Commerce silt loam. Specifically, the objectives are: 1) to study the adsorption and desorption kinetic characteristics of metolachlor in soils; 2) to determine the capability of equilibrium and multireaction kinetic approaches in describing metolachlor adsorption and desorption; 3) to quantify metolachlor adsorption-desorption hysteresis using a simplified Freundlich approach; and 4) to compare two distinct types of desorption isotherms: the traditional (or consecutive) type and a time-dependent type.

2.2   Model Formulation

Two models, the Freundlich (nonlinear) equilibrium approach and a multireaction model, were used to describe metolachlor adsorption-desorption in Sharkey clay and Commerce silt loam soils.

2.2.1 Freundlich Approach

The Freundlich equation is empirical in nature and imposes no limits on adsorption and relates adsorbed and solution phase concentrations at equilibrium. It may be expressed as:

$$S = K_f\, C^{\,N} \qquad\qquad [2.1]$$

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_f is the distribution or partitioning coefficient ($cm^3\ g^{-1}$) and N is a dimensionless parameter commonly less than unity. It was reported that soil

adsorption of metolachlor was better described by Freundlich than Langmuir (Wood et al., 1987).

2.2.2 Multireaction model (MRM)

A widely used multireaction model is the two-site model proposed by Selim et al. (1976). This model was developed for the purpose of describing observed batch results, which showed a rapid initial retention reaction followed by a slower reaction. In a similar formulation to the hypothetical model of Gamble and Khan (1990), it is assumed that metolachlor in the soil is presented in four phases (Fig 2.2). Here C is the solute concentration in solution (μg mL^{-1}), S_e is assumed to represent the amount retained on the equilibrium sites (μg g^{-1}) and has a low binding energy, S_k is the amount retained on the kinetic sites (μg g^{-1}) through strong interactions with the soil matrix, S_i represents the amount retained irreversibly (μg g^{-1}), K_e is an equilibrium constant (dimensionless), k_1 and k_2 (h^{-1}) are the forward and backward reaction rate coefficients associated with the kinetic sites, respectively. The parameter k_3 (h^{-1}) is the irreversible rate coefficient associated with the kinetic sites. The multireaction model is based upon the assumption that the number of sorption sites is not limited. Therefore the retention reactions are only functions of solute concentrations such that (Selim et al., 1976):

$$S_e = k_e \left[\frac{\theta}{\rho} \right] C^n \qquad [2.2]$$

$$\frac{\partial S_k}{\partial t} = k_1 \left[\frac{\theta}{\rho} \right] C^m - [k_2 + k_3] S_k \qquad [2.3]$$

$$\frac{\partial S_i}{\partial t} = k_3 S_k \qquad [2.4]$$
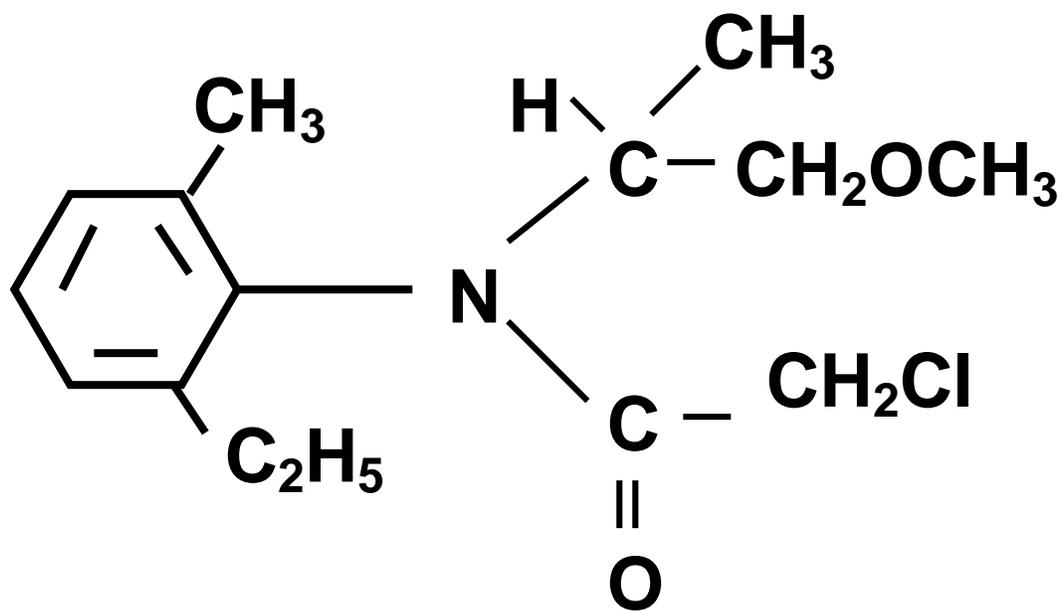
Figure 2.1 Chemical structure of metolachlor
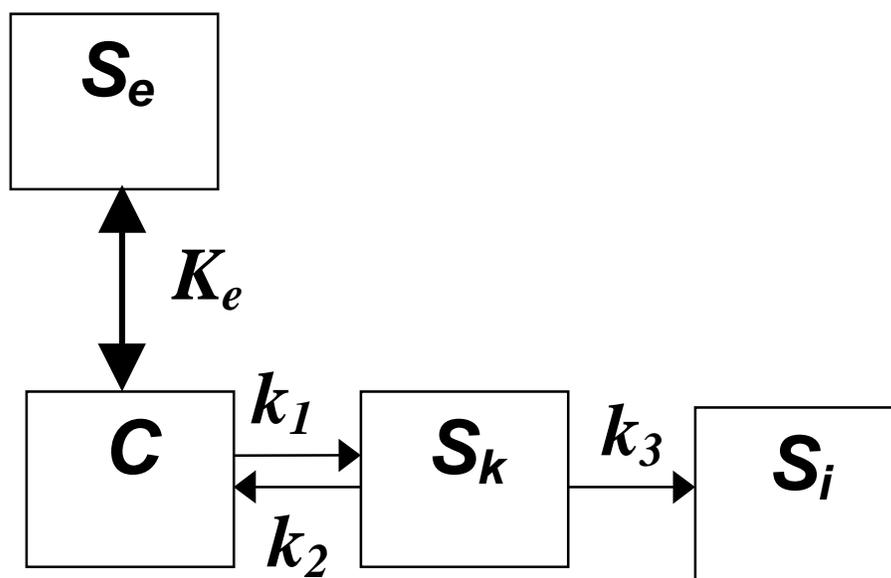
Figure 2.2 Schematic diagram of the multireaction model

where the parameters n and m are the reaction orders associated with S_e and S_k respectively, θ is the soil water content (cm^3 cm^{-3}), ρ is the soil bulk density (g cm^{-3}). m = n is assumed here. This assumption was made since there is no independent method available to determine the reaction orders of such retention mechanisms. This assumption was also adopted to study atrazine and alachlor retention in soils (Ma and Selim, 1994a; Xue and Selim, 1995). In this study, the values of n used were the average of Freundlich parameter N at all the reaction times during adsorption.

2.3   Materials and Methods

2.3.1 Adsorption - Desorption

Metolachlor adsorption was carried out using a batch equilibration technique. The soils used are Sharkey clay (Very-fine, smectitic, thermic Chromic Epiaquerts) and Commerce silt loam (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Epiaquerts) from Iberville Parish, Louisiana. The soils were taken from the Ap horizons and selected physical and chemical properties are presented in Table 2.1. Radioactive metolachlor (^{14}C-UL ring labeled) was used as a tracer to monitor the extent of retention. The labeled material was diluted to 0.43×10^5 Bq L^{-1} and used as the input solutions. Seven ^{14}C-metolachlor spiked metolachlor solutions having initial concentrations (C_i) of 5, 10, 20, 40, 60, 80 and 100 μg mL^{-1} in 0.005 M $CaCl_2$ were used. Three replicates were used for each initial concentration. Adsorption was initiated by mixing 15 g of air-dried soil with 30 mL of the various metolachlor solutions in 40-mL Teflon centrifuge tubes. The slurries were kept shaking and centrifuged at $5 \times g$ for 10 minutes after each reaction (or sampling) time. A 0.5-mL aliquot was sampled from

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Table 2.1: Selected physical and chemical properties of the Sharkey and Commerce soils

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Soil	Sand	Silt	Clay	pH	Organic Matter %	Cation Exchange Capacity meq/100g
	-----------%------------					

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Soil	Sand	Silt	Clay	pH	Organic Matter %	Cation Exchange Capacity meq/100g
Sharkey	3.0	36	61	6.48	1.41	39.4
Commerce	30	54	16	5.93	1.31	16.5

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the supernatant at reaction times of 2, 8, 24, 48, 96, 192, 288, and 504 hours. The slurries were vortex mixed and returned to the shaker after each sampling. The collected samples were analyzed using liquid scintillation counting (LSC).

Desorption commenced immediately after the last adsorption time step (504 hour). Each desorption step was conducted by replacing the supernatant with metolachlor free 0.005 M $CaCl_2$ solution and shaking for 24 hours. Six desorption steps were carried out for a total desorption time of 6 days. Metolachlor in solution following each desorption step was also analyzed with LSC.

2.3.2 Metolachlor Analysis

Liquid scintillation counting method was used in this study. A 0.5 mL of supernatant was mixed with 5 mL of scintillation cocktail and counted for 10 minutes on LSC. The radioactivity was recorded as counts per minute (CMP). Metolachlor concentration was calculated as relative to the initial input concentrations. The amount of metolachlor adsorbed by each soil was calculated as the difference in concentrations of supernatant and that of the initial solution.

2.3.3 Statistical Analysis

A two by seven factorial design was used with the soil types and seven initial (input) concentrations as the treatments. Repeated measures of metolachlor concentration in solution were carried out to examine time dependency. There were three replications for each treatment combination corresponding to the two soil types and seven initial concentrations. Treatment effects were evaluated with analysis of variance using the general linear model procedure of SAS. Multisource regression technique was used to check if separate intercepts and slopes were needed when the

Freundlich model was used. Means and 95% confidence intervals were computed for regression coefficients derived from the Freundlich equation. Desorption isotherm coefficients were also estimated using simple linear regression of the logarithmic form of the Freundlich equation. The kinetic retention of metolachlor was described using the multireaction model where model parameters were estimated based upon nonlinear least-square optimization.

2.4   Results and Discussion

For metolachlor in soils, chemical degradation is minor, and degradation of its side chain is the primary detoxication pathway for metolachlor. Microbial degradation products are chemically similar to metolachlor with slightly higher water solubility (Chesters et al, 1989). Since ring-labeled metolachlor was used, the measurements did not differentiate between metolachlor and its degradation products. In a similar laboratory experiment to our study, Johnson and Fuhrmann(1993) measured the relative abundance of metolachlor and its degradation products based upon methanol extracts following a 73-d laboratory incubation. They found that transformation of metolachlor to degradation products was only 3.8 to 4.6%. We should reiterate here that in our study, degradation of metolachlor was not explicitly considered and our results may be best viewed as the adsorption-desorption of ring-labeled metolachlor and its degraded analogies.

2.4.1 Adsorption

Metolachlor adsorption results were described using the Freundlich equilibrium model. Best-fit values of the parameters K_f and N for Sharkey and Commerce soils

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Table 2.2: Estimated adsorption parameters (with 95% confidence intervals) for metolachlor adsorption by soils at different reaction times.

Soil	Reaction time (hours)	Freundlich Model			Linear Model	
		K_f $(cm^3 g^{-1})$	N	r^2	K_d $(cm^3 g^{-1})$	r^2
Sharkey	2	4.027±0.0874	0.900±0.0312	0.995	2.794±0.124	0.991
	8	4.631±0.0641	0.912±0.0241	0.997	3.431±0.093	0.997
	24	5.331±0.0583	0.920±0.0229	0.997	4.090±0.123	0.996
	48	6.177±0.0569	0.910±0.0231	0.997	4.598±0.166	0.994
	96	5.770±0.0543	0.948±0.0222	0.998	4.914±0.110	0.998
	192	6.229±0.0282	0.926±0.0117	0.999	4.927±0.111	0.998
	288	7.713±0.0462	0.879±0.0196	0.998	5.303±0.168	0.995
	504	7.799±0.162	0.883±0.0706	0.977	5.708±0.185	0.995
Commerce	2	1.616±0.500	0.960±0.134	0.922	1.513±0.192	0.931
	8	2.384±0.0775	0.968±0.0269	0.997	2.180±0.0762	0.994
	24	3.069±0.0563	0.940±0.0198	0.998	2.521±0.0610	0.997
	48	3.345±0.0522	0.956±0.0189	0.998	2.926±0.0508	0.999
	96	3.638±0.0488	0.941±0.0178	0.998	3.003±0.0712	0.997
	192	3.658±0.0550	0.918±0.0198	0.998	2.774±0.0727	0.997
	288	3.885±0.0731	0.911±0.0263	0.996	2.906±0.100	0.995
	504	4.003±0.0876	0.899±0.0313	0.995	2.885±0.0832	0.996

were given in Table 2.2 for all reaction times during adsorption. The Freundlich

adsorption parameter K_f represents the extent or strength of adsorption, and N takes in

account nonlinearity in adsorption isotherm. When N=1, adsorption is linear and a

distribution coefficient (K_d) is the appropriate parameter. The N values ranged from

0.90 to 0.96 and were significantly less than one (P<0.0001) for all reaction times and

for both soils. Therefore, a Freundlich nonlinear isotherm is more appropriate than a

linear one. Moreover, based on r^2 values, metolachlor adsorption was well described by

the Freundlich equation. The larger K_f values for the Sharkey soil than the Commerce

soil suggests higher sorption capacity for Sharkey as a result of its higher clay content.

For both soils, the positive correlation of K_f values with the reaction time indicating the

nonequilibrium or kinetic of metolachlor adsorption by both soils with time.

Since the estimated N values for the Freundlich model were significantly different

for the two soils, comparison of K_f values is not appropriate. Therefore, estimated K_d

values were calculated assuming linear adsorption (see Table 2.2). Such K_d values are

clearly time dependent for both soils, especially for long reaction time. Moreover, these

K_d values are within the range of previously reported values in the literature. Peter and

Weber (1985) investigated metolachlor sorption on nine soils and obtained K_d values

ranging from 0.48 to 10.95 mL g^{-1} (organic matter content ranging from 0.5 to 8.7%).

Johnson and Sims (1993) reported metolachlor K_d values of 0.66 to 2.96 mL g^{-1} on six

Atlantic coastal plain surface soils, and Pignatello and Huang (1991) reported K_d values

of 0.77 to 2.96 mL g^{-1} for four soils from Connecticut. In this study, K_d value for

Sharkey soil (2.794 to 5.708 mL g^{-1}) is significantly higher than that for Commerce soil
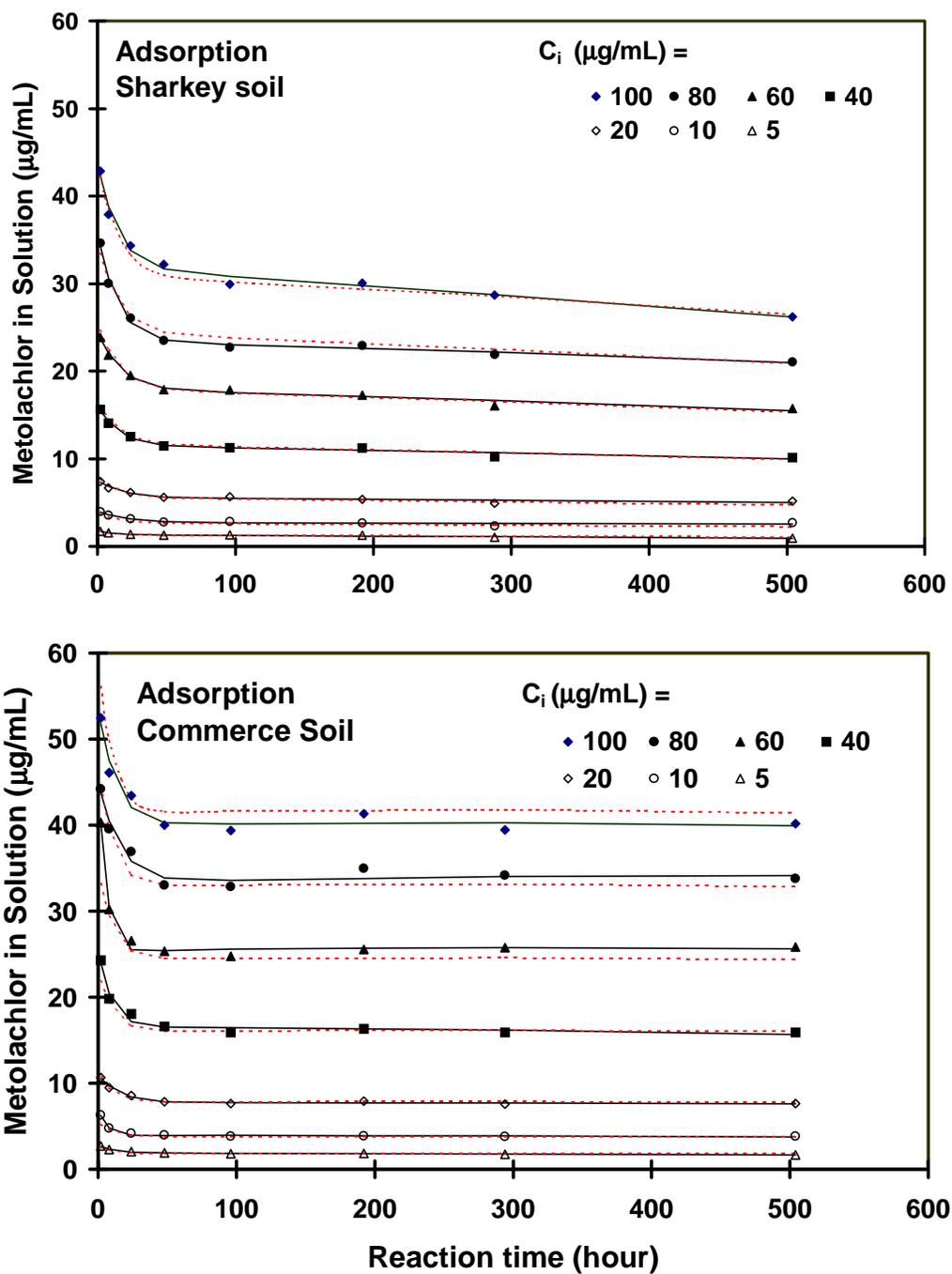
Figure 2.3 Metolachlor concentration in soil solution versus time during adsorption for Sharkey clay (top) and Commerce loam (bottom) and different initial concentrations (C_i's). Dashed and solid curves are multireaction model (MRM) predictions using an overall set and individually estimated sets of parameters, respectively

(1.513 to 2.885 mL g^{-1}). The smaller K_d values for Commerce indicate a greater potential mobility for metolachlor in this soil than in Sharkey soil. Soil organic matter and clay contents and clay type have been suggested as contributing significantly to metolachlor adsorption in soils (Peter and Weber, 1985). This is consistent with our findings since Sharkey soil contains much higher clay content than Commerce.

The Freundlich parameter estimates given in Table 2.2 indicate a time-dependent behavior of metolachlor adsorption for both soils. Therefore, the use of the multireaction model (MRM) to describe such time-dependent behavior for both soils is justified. Based on model simulation, the time-dependent behavior of metolachlor retention in Sharkey and Commerce soils were well described by the multireaction model (Table 2.3, 2.4 and Fig. 2.3). The adsorption pattern indicates an initial fast adsorption, which occurred within the first 48 hours. This was followed by a slow reaction, which appear to be the dominant processes. This assessment is consistent with increased K_d during adsorption. Multireaction model(MRM) parameter estimates given in Table 2.3 were obtained using nonlinear least square optimization for each initial concentration C_i (5, 10, . . , 100 μg mL^{-1}). Moreover, I obtained one set of parameters for the MRM model where the entire data set for all C_i's were used in the nonlinear least-square parameter estimation procedure. As a result, a set of model parameter estimates, hereafter referred to as the overall set of parameters, and parameters corresponding to each C_i were obtained (Table 2.3 and 2.4). The kinetics of metolachlor adsorption for the range of concentrations and time were well described by the MRM model. This is clearly shown by the solid curves they represent MRM predictions based

Table 2.3: Goodness of fit, model parameters values, and their standard error (SE) for metolachlor retention in Sharkey soil using the multireaction (MRM) model. Model parameters are given for adsorption data (ads) and adsorption-desorption data (ads-des) separately.

Data Set	C_i $\mu g/mL$	r^2	RMS	K_e	SE	k_1 h^{-1}	SE h^{-1}	k_2 h^{-1}	SE h^{-1}	k_3 h^{-1}	SE h^{-1}
Ads	5	0.9742	0.0544	1.8153	0.1305	0.07988	0.03447	0.0737	0.03135	0.003096	0.000738
	10	0.9233	0.193	1.6407	0.1407	0.04433	0.01858	0.03063	0.01499	0.00056	0.000727
	20	0.9498	0.2469	1.9407	0.1141	0.05692	0.0173	0.03788	0.01578	0.001086	0.000607
	40	0.9854	0.3055	1.855	0.07078	0.05877	0.01228	0.0436	0.009864	0.001213	0.00033
	60	0.9879	0.4138	1.8749	0.06299	0.0536	0.01057	0.04234	0.009091	0.001361	0.00032
	80	0.9937	0.493	1.6444	0.05122	0.07278	0.009194	0.04367	0.006	0.000854	0.000198
	100	0.9879	0.7886	1.7439	0.06899	0.05998	0.0126	0.0464	0.0105	0.001597	0.000344
	overall	0.9984	0.4753	1.7459	0.02785	0.06233	0.004959	0.04459	0.003836	0.001277	0.000127
Ads-des	5	0.9934	0.04647	1.8014	0.1223	0.08753	0.03767	0.08949	0.03609	0.004282	0.000662
	10	0.9623	0.2834	1.5754	0.2713	0.06732	0.0678	0.06991	0.06956	0.00394	0.001555
	20	0.9808	0.3632	1.8662	0.2222	0.07305	0.06163	0.08132	0.06402	0.003727	0.00116
	40	0.9869	0.624	1.808	0.1732	0.07705	0.04399	0.07185	0.03924	0.003188	0.000723
	60	0.9892	0.8441	1.8497	0.1464	0.06334	0.03284	0.0611	0.03154	0.003166	0.000679
	80	0.9896	1.1921	1.5975	0.1414	0.09017	0.03394	0.0646	0.02376	0.002347	0.000425
	100	0.9943	1.0538	1.7101	0.102	0.07156	0.02331	0.06235	0.01995	0.002719	0.00039
	overall	0.9958	0.6923	1.7062	0.04609	0.07663	0.01086	0.06434	0.008903	0.002702	0.000168

Table 2.4: Goodness of fit, model parameters values, and their standard error (SE) for metolachlor retention in Commerce soil using the multireaction (MRM) model. Model parameters are given for adsorption data (ads) and adsorption-desorption data (ads-des) separately.

Date set	C_i µg/mL	r^2	RMS	K_e	SE	k_1 h^{-1}	SE h^{-1}	k_2 h^{-1}	SE h^{-1}	k_3 h^{-1}	SE h^{-1}
Ads	5	0.9892	0.04761	0.7729	0.04505	0.05784	0.01049	0.06122	0.01113	0.001174	0.000244
	10	0.9866	0.1326	0.4399	0.05709	0.107	0.01755	0.0865	0.0133	0.000445	0.000197
	20	0.9817	0.1997	0.9223	0.04552	0.03832	0.007625	0.0424	0.008915	0.000397	0.000267
	40	0.9702	0.6728	0.6459	0.07547	0.06935	0.01862	0.06611	0.01733	0.00055	0.000322
	60	0.9901	0.6879	0.3633	0.0502	0.121	0.01626	0.09318	0.01173	0.000162	0.000147
	80	0.9532	1.128	0.09304	0.06622	0.03764	0.01149	0.04563	0.01416	0.000143	0.000357
	100	0.9515	1.324	1.0549	0.0748	0.04575	0.01502	0.05401	0.0175	0.000353	0.000361
	Overall	0.991	1.531	0.852	0.0534	0.05859	0.01232	0.06247	0.01266	0.000299	0.000224
Ads-des	5	0.9898	0.09354	0.7479	0.09792	0.0684	0.0276	0.08173	0.03033	0.002271	0.000427
	10	0.9798	0.3099	0.3899	0.1637	0.1336	0.06418	0.1232	0.04995	0.001571	0.000407
	20	0.9793	0.5822	0.8835	0.1655	0.05309	0.004435	0.07832	0.05983	0.002537	0.00089
	40	0.9818	1.1502	0.5807	0.157	0.09802	0.05461	0.1072	0.05163	0.001813	0.000501
	60	0.9808	1.9369	0.3114	0.1804	0.1492	0.07469	0.1296	0.05437	0.001186	0.00035
	80	0.9802	2.4234	0.9088	0.1707	0.04629	0.04349	0.07489	0.064	0.002215	0.000915
	100	0.9846	2.4898	0.9744	0.1906	0.07959	0.06665	0.1148	0.07966	0.002107	0.000753
	Overall	0.9858	1.7236	0.779	0.07705	0.09096	0.02737	0.1154	0.02881	0.001833	0.000255

upon individual parameters for each C_i data set, and the dashed curves which were

obtained based on the overall set of model parameters (see Fig. 2.3).

2.4.2 Desorption or Release

Results of metolachlor desorption versus time following adsorption (for 504 h)

are shown in Fig.2.4 As expected, a solution concentration decrease after each

successive desorption time step (of 1 day) was observed. The capability of MRM model

to describe these metolachlor desorption versus time results was also tested. To achieve

model predictions shown by the solid curves in Fig.2.4, I utilized MRM as a predictive

mode where all parameters were independently derived from our adsorption results. As

a result, we relied solely on adsorption data sets to *predict* the behavior of metolachlor

release or desorption versus time in the two soils. Although such desorption predictions

may be at best considered adequate, the overall trend resulted in overprediction of

concentrations versus time.

To further test the capability of multireaction model to describe metolachlor

desorption, I utilized MRM in a descriptive or simulation mode where the necessary

parameters were based upon both adsorption and desorption results, i.e. the entire

batch data sets. The resulting parameter estimates for different C_i's are given in Tables

2.3 and 2.4 for Sharkey and Commerce soils. As indicated by the dashed curves in Fig.

2.4, improved description of desorption results were achieved when adsorption and

desorption parameters were used. Similar trends were observed for Sharkey soil when a

second-order two-site model (SOTS) was used (Selim et al.,1999).

Based upon six consecutive desorption steps, the total amount of metolachlor

desorbed were $30.5 \pm 1.2\%$ and $43.9 \pm 0.8\%$ of total adsorbed for Sharkey clay
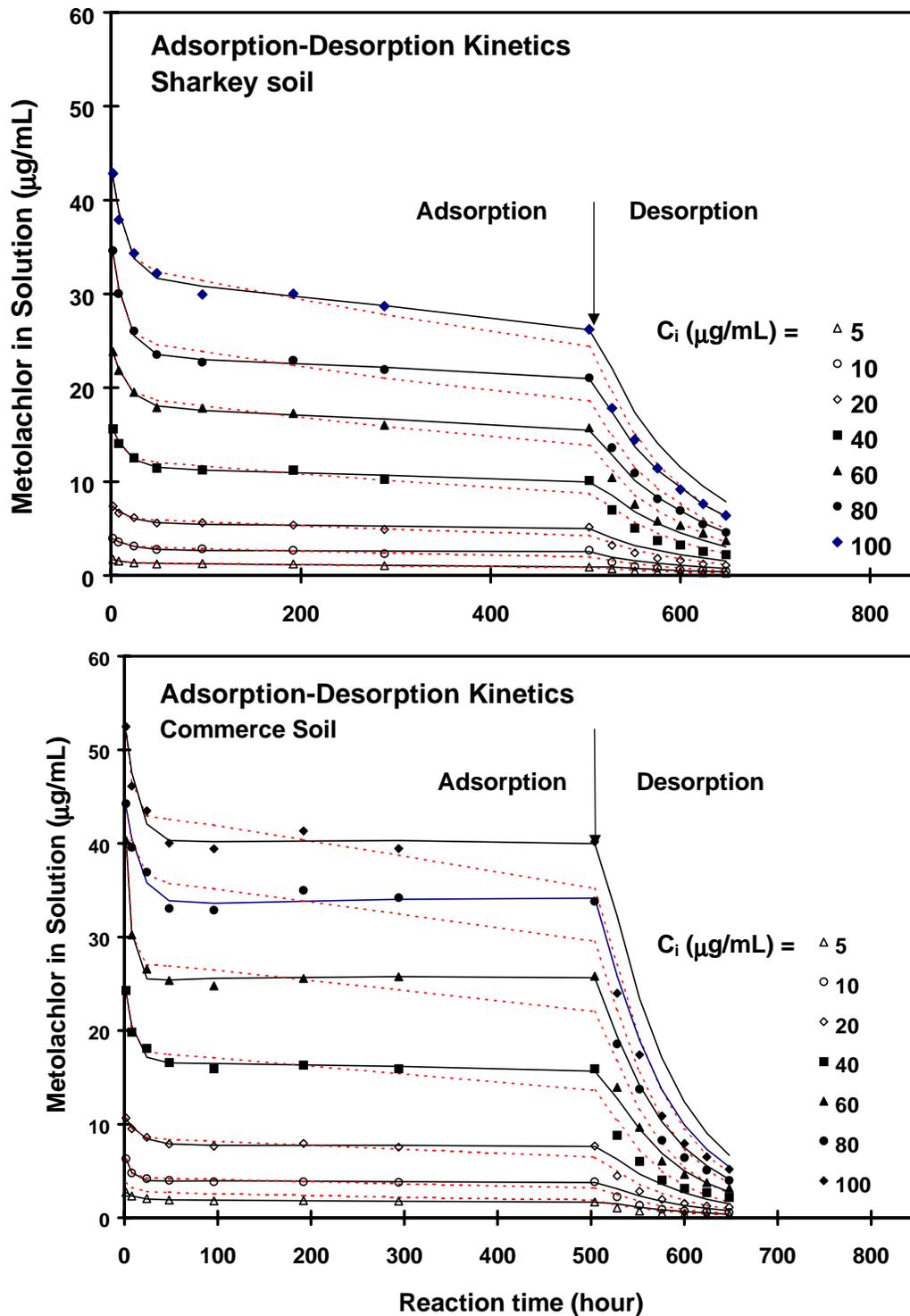
Figure 2.4 Metolachlor concentration in soil solution versus time during adsorption and desorption for Sharkey clay (top) and Commerce loam (bottom). Solid curves are MRM model predictions based on adsorption data. Dashed curves are MRM simulations based on adsorption as well as desorption data sets

Commerce silt loam, respectively. These represent metolachlor that was desorbed

during the course of the six successive desorption steps. Thus the amount desorbed

represents the sum of water soluble and readily desorbable or weakly retained

metolachlor fractions. Such desorbed amounts indicate strong retention of metolachlor

by these soils and the existence of a significant component of the adsorbed metolachlor

that is difficult to desorb. Significant differences of the amount desorbed between

different concentrations and between the two soils were observed with p-values less

than 0.0001. As the initial input metolachlor C_i increased from 5 to 100 $\mu g \ mL^{-1}$, the

desorbed amount, as the percentage of total adsorbed, increased from 26% to 37% for

Sharkey soil and from 42% to 48% for Commerce. The higher release for Commerce

soil than for Sharkey, is likely due to difference in clay content. In a desorption study of

two soils (Cullen and Emporia), Seybold and Mersie (1996) found that the amount of

metolachlor desorbed following four desorption steps (averaged across soils and initial

concentrations) was $40 \pm 3\%$. In their study, a similar background solution ($CaCl_2$) was

used except that adsorption was limited to 24 h.

2.4.3 Hysteresis

In Fig. 2.5, desorption results are presented in the traditional manner along with

the adsorption isotherm for the last (504 hours) retention time, i.e. prior to

commencement of desorption (solid curves). Here, the results from successive

desorption steps are presented for each initial (input) concentration (C_i). The obvious

discrepancies of this family of desorption isotherms from the adsorption isotherm (solid

curve), i.e., for all concentrations, are indicatives of hysteresis. Such observed
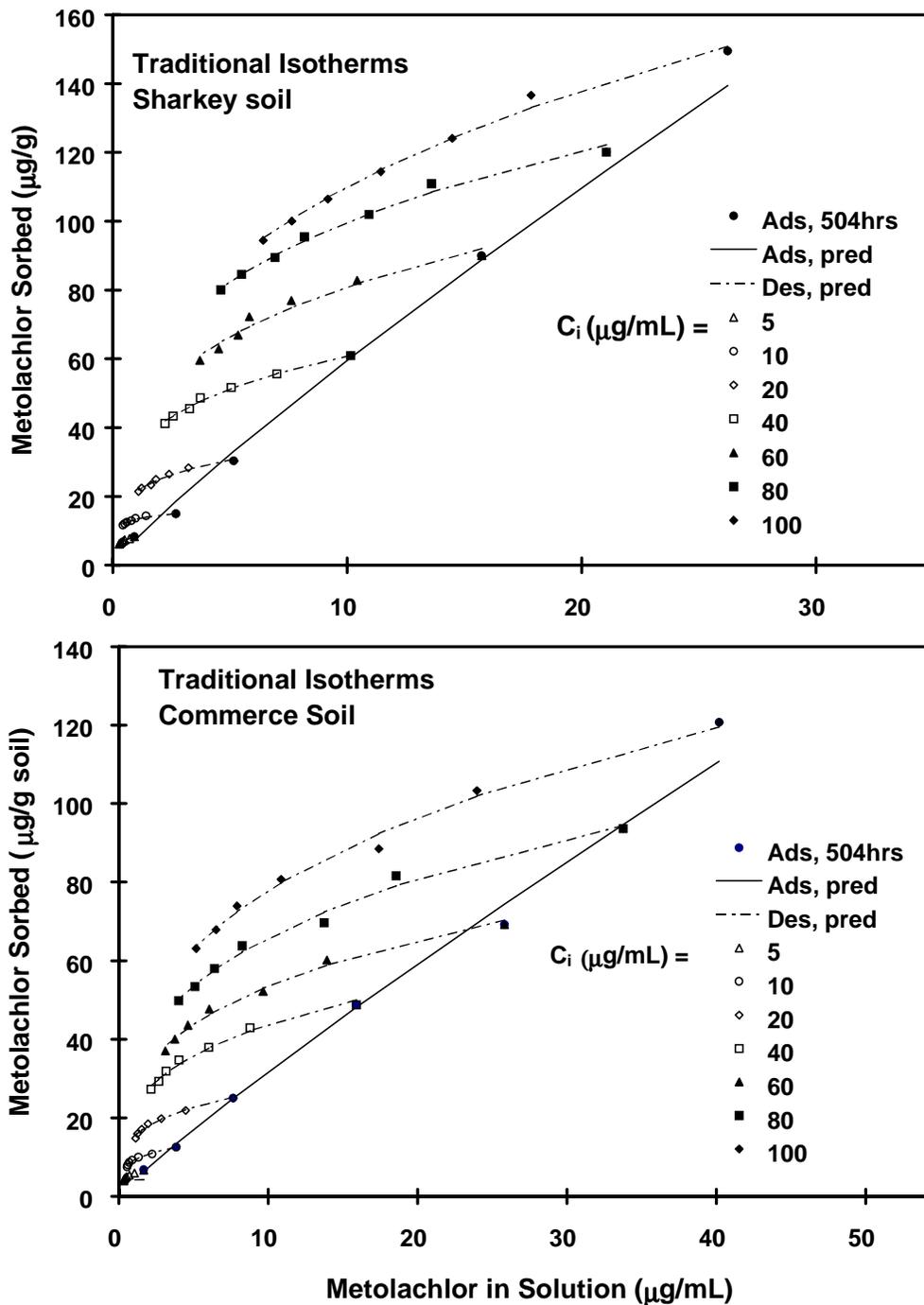
Figure 2.5 Traditional desorption isotherms for metolachlor in Sharkey (top) and Commerce loam (bottom) based on successive desorptions for different C_i's. Solid and dashed curves are predicted isotherms based on the Freundlich model
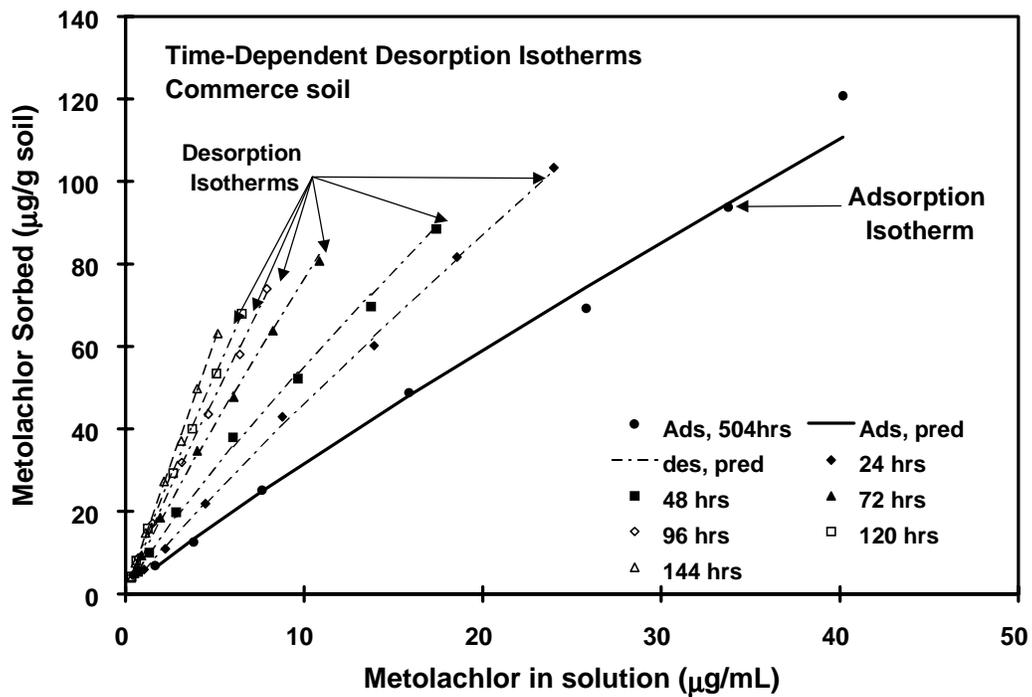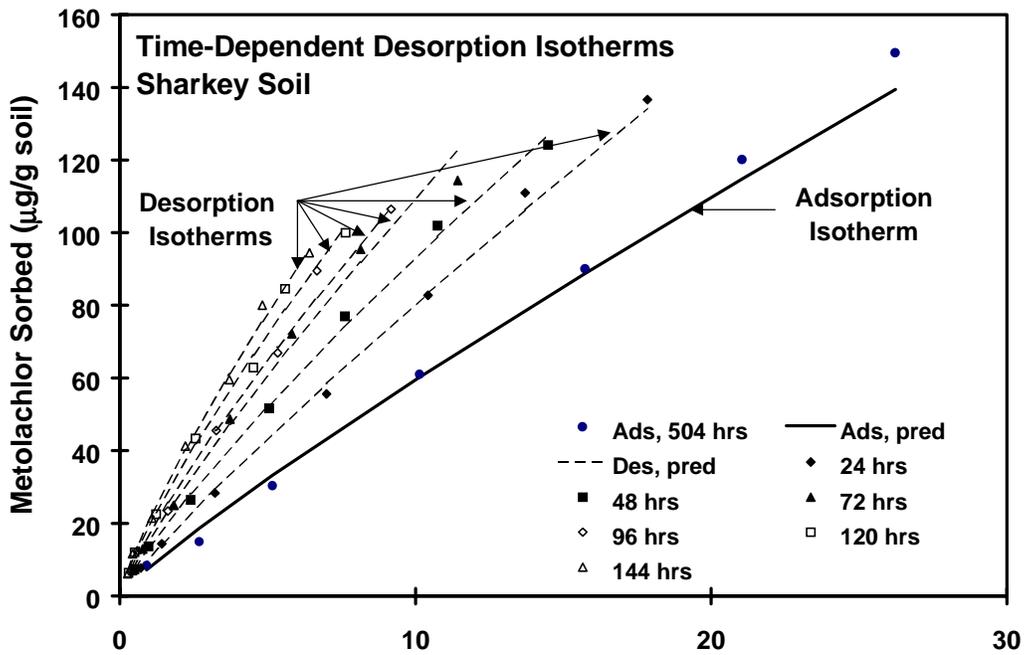
Figure 2.6 Time-dependent desorption isotherms for metolachlor in Sharkey (top) and Commerce loam (bottom) for different times of desorption. Solid and dashed curves are predicted isotherms based on the Freundlich model

hysteresis is absent only if the adsorption (solid curve) and desorption isotherms (dashed curves) were indistinguishable.

A new method for representing isotherms based upon desorption results was proposed here. In the new proposed method, desorption isotherms are defined as the relationship between the amount sorbed S and the corresponding concentration C for a given time of reaction t, and at constant temperature. For desorption, the time of reaction represents that of the desorption time plus time of adsorption prior to commencement of desorption. In Fig.2.6, our desorption results for the Sharkey and Commerce soils are now presented for each time of reaction (adsorption and desorption). As result, I present a family of desorption isotherms that are similar to those for adsorption. That is, in the new proposed method, I maintained the overall isotherm definition of C versus S for a given reaction time of adsorption or adsorption and desorption. Therefore, this family of desorption isotherms are shown for each desorption time (or step), and can be referred to as time-dependent desorption isotherms. Once again, if hysteresis is absent, the adsorption and desorption results should coalesce, and the dashed and solid curves should be indistinguishable. One can also regard such a family of curves as of the kinetic type since each curve represents desorption (release) at a given desorption time following adsorption.

It is recognized that the traditional method of isotherm presentation for desorption has been examined using a number of approaches (van Genuchten et al., 1974; Clay and Koskinen, 1990; Ma et al., 1993). Therefore, an attempt was made to describe the desorption data based on the traditional isotherm approach (Fig.2.5) and those based on the time-dependent isotherms (Fig.2.6) using the Freundlich equation [2.1]. As a result

Table 2.5: Freundlich parameters for metolachlor desorption based on the traditional and time dependent isortherms for Sharkey and Commerce soils

| | Parameters from Traditional Isotherms | | | | | | | Parameters from Time-Dependent Isotherms | | | | | |
Soil	Initial conc. $\mu g/mL$	$(K_f)_a$ $cm^3\,g^{-1}$	N_d	r^2	ω	H	λ	Desorption time (h)	$(K_f)_d$ $cm^3\,g^{-1}$	N_d	r^2	H	λ
Sharkey	5	8.26	0.194	0.742	354	21.4	60.0	24	10.4	0.888	0.997	97.6	30.2
	10	13.4	0.122	0.724	622	13.4	70.2	48	13.5	0.837	0.996	92.0	69.0
	20	21.4	0.223	0.945	296	24.5	56.2	72	15.5	0.850	0.991	93.4	94.0
	40	34.3	0.248	0.957	255	27.3	53.0	96	17.3	0.82	0.982	90.1	116.5
	60	42.0	0.285	0.937	210	31.3	48.7	120	19.6	0.811	0.979	89.1	145.3
	80	53.0	0.274	0.974	222	30.1	50.0	144	21.1	0.810	0.975	89.0	164.1
	100	51.6	0.329	0.950	169	36.1	43.8						
Commerce	5	5.88	0.302	0.940	198	32.1	49.1	24	5.56	0.918	0.997	97.7	39.0
	10	9.17	0.235	0.890	283	25.0	57.1	48	7.68	0.857	0.997	91.2	92.0
	20	15.0	0.256	0.958	251	27.2	54.5	72	9.81	0.891	0.997	94.8	145.3
	40	22.5	0.289	0.978	210	30.8	50.5	96	11.2	0.905	0.996	96.3	180.0
	60	27.5	0.289	0.970	211	30.7	50.5	120	12.2	0.912	0.995	97.0	205.0
	80	33.2	0.297	0.986	202	31.6	49.6	144	12.7	0.980	0.994	104.3	217.5
	100	38.3	0.308	0.986	191	32.8	48.3						

two sets of values for best estimates of K_f and N were obtained and are given in Table 2.5. It is clear that the Freundlich approach is adequate in describing both families of desorption isotherms. Higher r^2 values indicates that the Freundlich approach provided better overall description of the time-dependent desorption isotherms over the traditional ones.

Based upon the K_f and N estimates for desorption given in Table 2.5, a number of observations can be made. For the traditional desorption isotherms (see Fig. 2.5), K_f values were consistently higher than those associated with adsorption isotherms. The opposite trend was observed for the nonlinear parameter N. Moreover, K_f for desorption was significantly dependent on initial metolachlor concentration C_i as depicted in Fig.2.7 for both soils. Such dependency on C_i was more pronounced for Sharkey than Commerce. Similar findings for atrazine were previously reported (Clay and Koskinen, 1990; Ma et al., 1993). The dependence of N for successive desorption isotherms on C_i is only significant for Sharkey soil (p=0.0077) but not for Commerce (p=0.15). These results imply that the Freundlich model is an oversimplification of metolachlor desorption based on the traditional manner for both soils. Moreover, this comparison is further complicated since exceedingly small N values for desorption were estimated (0.19 to 0.33).

For the time-dependent isotherms proposed here (see Fig.2.6), estimated N values were similar to that for adsorption (Table 2.5) with no significant differences for both Sharkey (p=0.205) and Commerce soil (P=0.803). This is an important finding since a meaningful comparison can be made between K_f values for adsorption and for the different desorption isotherms, i.e., K_f associated with different desorption history.
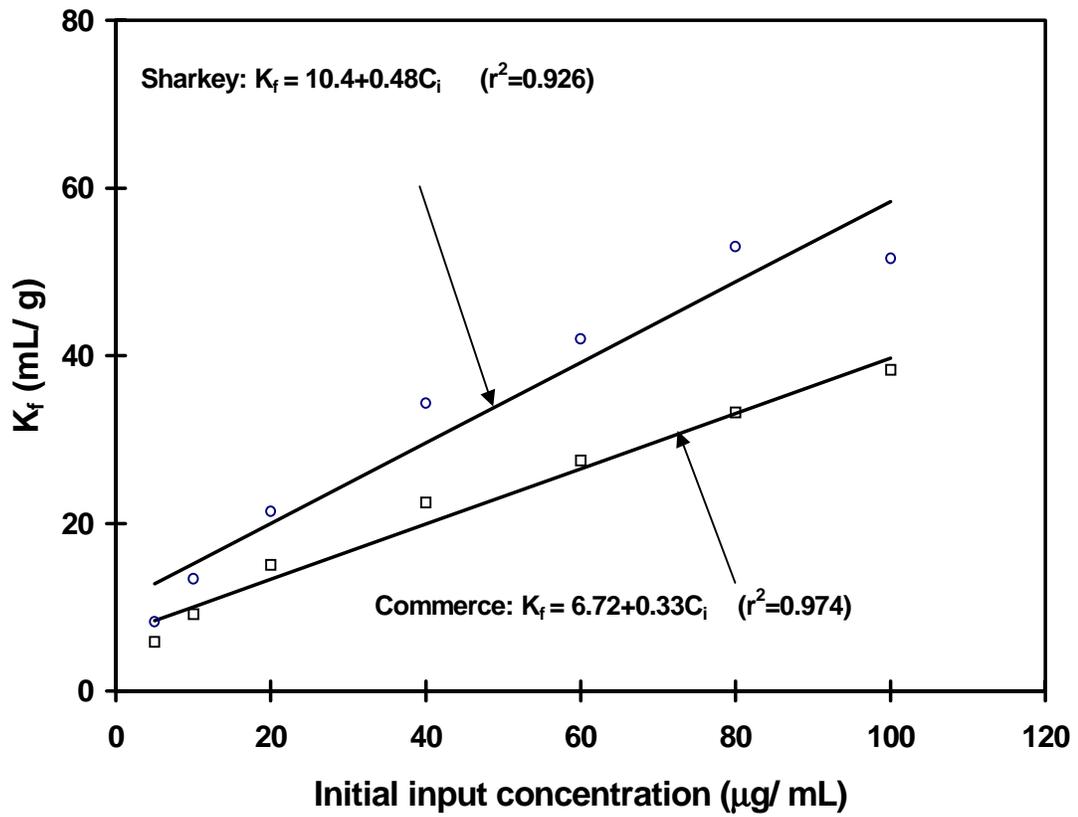
Figure 2.7 Freundlich K_f for successive desorption isotherms versus initial input concentration C_i's for Sharkey and Commerce soils. The solid lines are based on linear regression.
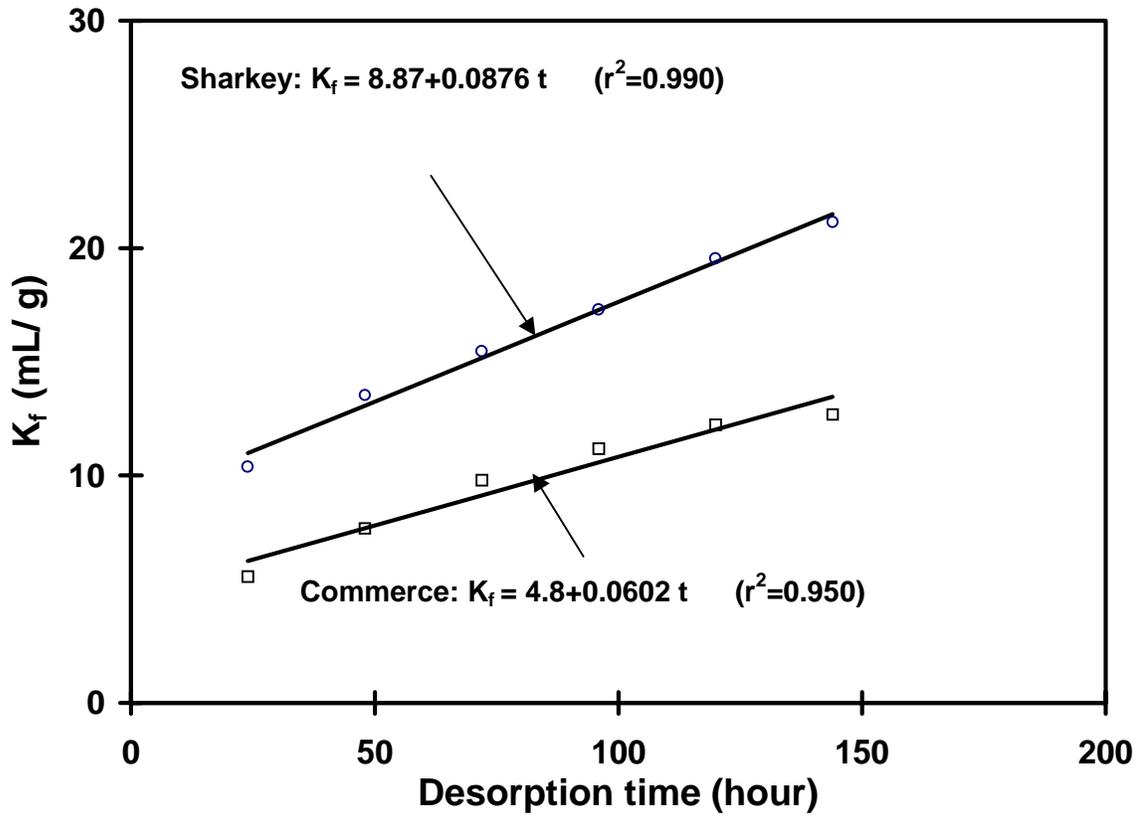
Figure 2.8 Freundlich K_f for time-dependent desorption isotherms versus time for desorption for Sharkey and Commerce soils. The solid lines are the based linear regression.

Fig.2.8 presents a relationship between K_f and desorption time which indicates an

increase of K_f as desorption time increases. Such an increase in K_f was more

pronounced in Sharkey than Commerce soil, indicated by a larger value of the slope of

the regression line.

Pignatello and Huang (1991) determined an apparent sorption constant (K_{app}) by

measuring sorbed and solution concentrations following suspension of field soil sample

in water for 24 h. They also determined K_d values in the traditional manner based on 24

h sorption isotherm of freshly added herbicide. They found that K_{app}/K_d ratio varied

from 2.3 to 42 and was directly related to the "age" of the residue (i.e., time between

sampling and application). This finding is consistent with the time-dependent

desorption isotherms results where K_f increased as desorption time increased (see

Fig.2.8). I recognized that it is customary to utilize short-term equilibration periods

(24h) for determining herbicide adsorption distribution K_d.. Based on results, such

measured K_d may not be representative in describing residues concentrations under field

conditions. Thus, parameters based on time-dependent desorption isotherms rather than

24h K_d values are more appropriate to predict herbicide residue in the field, and thus

more meaningful for environmental assessment.

2.4.4 Hysteresis Coefficient λ

Several efforts have been made to quantify hysteresis based on adsorption and

desorption parameters. For example, Ma et al. (1993) defined hysteresis as the

difference between adsorption and desorption isotherms. They quantified hysteresis

based on the maximum difference between an adsorption and a desorption isotherm as,

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$$\omega = \left[\frac{N_a}{N_d} - 1 \right] \times 100 \qquad [2.5]$$

where N_a and N_d are Freundlich N for adsorption and desorption, respectively. Cox et al. (1997) proposed a desorption hysteresis coefficient H, based on the ratio of desorption and adsorption isotherm parameters as,

$$H = \frac{N_d}{N_a} \times 100 \qquad [2.6]$$

The coefficient H is a simple one and easy to use. In contrast, ω is only applicable for the traditional type isotherms of successive desorptions (shown in Fig. 2.5). For time-dependent desorption isotherms (shown in Fig. 2.6), ω is not defined and thus cannot be calculated. This is because the point which corresponds to the maximum difference between an adsorption and desorption isotherm does not exist within the range of concentration. In this paper, I present a new hysteresis coefficient λ with the distinct advantage that it is applicable for both types of desorption isotherms, i.e., the traditional and time-dependent type.

If A_a represents the area under an adsorption isotherm curve for concentration from 0 to some solution concentration C, and A_d represents the area under a desorption isotherm at the same concentration range, we define the parameter λ as,

$$\lambda = \left[\frac{A_d - A_a}{A_a} \right] \times 100 \qquad [2.7]$$

where A_a and A_d can be calculated from the area under each curve as,

$$A_a = \int_0^C (K_f)_a \, C^{N_a} dc \qquad [2.8]$$

$$A_d = \int_0^C (K_f)_d \, C^{N_d} dc \qquad [2.9]$$

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substitution of eqs. [2.8] and [2.9] into eq. [2.7] we obtain,

$$\lambda = \left\{ \frac{(K_f)_d (N_a +1)}{(K_f)_a (N_d +1)} C^{N_d - N_a} -1 \right\} \times 100 \qquad [2.10]$$

As a result, λ as given by eq. [2.10] is valid for both types of desorption isotherms. The

extent of λ dependency on C is determined by the difference in N_d and N_a. For the

traditional desorption type isotherms, it is reasonable to select C when adsorption and

desorption isotherms join, where $C = [(K_f)_a / (K_f)_d]^{1/(N_d - N_a)}$. Upon substitution into

eq. [2.10], eq. [2.10] was simplified:

$$\lambda = \left[\frac{N_a +1}{N_d +1} -1 \right] \times 100 \qquad [2.11]$$

On the other hand, for time-dependent desorption isotherms, no significant differences

in N values for adsorption and desorption were observed (see Table 2.5) as discussed

above. Thus it is reasonable to make the approximation $N_d = N_a$. In this case, the

expression of λ can be simplified,

$$\lambda = \left[\frac{(K_f)_d}{(K_f)_a} -1 \right] \times 100 \qquad [2.12]$$

If N_d is significantly different from N_a, eq. [2.10] rather than [2.12] should be used.

Based on the above formulations, we obtained values for λ as well as ω and H, which

are given in Table 2.5. Values for λ decreased as C_i increased for Sharkey soil, but no

such relationship was observed for Commerce. Similar trends were observed for

ω, whereas the opposite was observed for H value. Ma et al. (1993) calculated ω for

atrazine on Sharkey soil and indicated that ω increased linearly with incubation time,

which is the time interval between the end of adsorption and the beginning of the

desorption process. However, they did not observe an effect of C_i on ω. Seybold and

Mersie (1996) calculated ω for metolachlor in two soils and found that ω is C_i

dependent for Cullen soil which contained 31% clay and 1.3% of organic carbon, but

this phenomena was not apparent in Emporia soil which contains less clay and less

organic carbon. This dependence of desorption on C_i has been reported for other

herbicides, e.g., Bowman and San, 1985; Graham and Conn, 1992, among others.

For the time-dependent desorption isotherms shown in Fig. 2.5, values for λ

increased as desorption time increased for both soils which is indicative of the

dependency on desorption history. Similar trends were also observed for ω (see Table

2.5). The p-values for linear regression with desorption time are less than 0.001,

indicating that as desorption step increased, it is difficult to desorb metolachlor from

soils. Our explanation for this behavior is the existence of irreversible reactions which

caused a decrease of desorbed herbicide amounts as desorption time increased.

2.5 Conclusions

Families of desorption isotherms were presented in two different ways; namely

the traditional type of successive desorptions, and the other is based on time-dependent

desorptions. This resulted in two different sets of model parameter estimates for

desorption. The main advantage of the time-dependent type isotherms is that, for

metolachlor in Sharkey and Commerce soils, no significant difference of N for

adsorption and desorption were observed. Thus K_f becomes the only significant

parameter when simulation of adsorption and desorption processes are sought. On the

other hand, parameters from successive isotherms provide an understanding of the

distribution of a herbicide between soil and solution for a given initial (input)

concentration (Bowman and Sans, 1985). Another advantage of the time-dependent

desorption isotherm is that the isotherm definition remains unaltered, and when an

isotherm is measured based on laboratory adsorption-desorption experiments or based

on field measurements equal reaction times should be maintained. Data sets based on

the traditional or successive desorption isotherms no longer satisfies the requirement of

an isotherm, instead time-dependent or kinetic desorption results are often presented.

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CHAPTER 3 ADSORPTION-DESORPTION OF DELTAMETHRIN IN DIFFERENT SOILS

3.1 Introduction

Deltamethrin [(S) - α - cyano - 3 - phenoxybenzyl - (1R,3R) - cis - 2,2 - dimethyl-3-(2,2-dibromovinyl) cyclopropanecarboxylate], $C_{22}H_{19}Br_2NO_3$, also commonly known as decamethrin, was first reported as an insecticide by Elliott et al. (1974) and subsequently developed commercially in France by Roussel Uclaf (Lhoste, 1982). It is perhaps the first pyrethroid composed of a single isomer of eight possible stereoisomers (Table 3.1). Parent deltamethrin isomer is designated 1 and the only other isomer toxic to insects, although to lesser extent in each case, is designated 3. The cis 1R, 3R configuration about the cyclopropane ring and the S configuration for the cyano group at the benzylic carbon atom are essential for its high toxicity. As a member of the pyrethroid family, deltamethrin is a colorless crystalline powder with a molecular weight of 505.2 g/mole. It is characterized by a melting point of 98.0 to101^{o}C, a vapor pressure of 0.002 MPa and a solubility in water of less than 0.2 μg/mL at 20^{0}C. Due to this low solubility and associated higher affinity to soil, deltamethrin is perhaps less susceptible to downward movement and to leaching losses in the soil and water runoff compared to other herbicides.

Deltamethrin is active against a wide range of insects that attack crops and animals. It has been recommended for foliar applications on various vegetable and field crops (FAO/WHO, 1981). Recently, efforts were made to investigate the fate of deltamethrin as a termiticide due to its high insecticidal activity, low mammalian toxicity, and low stability. Su et al., (1991) examined the efficacy of eleven soil

Table 3.1: Structural designations of isomers of deltamethrin

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Isomer	Configuration	Isomer	Configuration
1	α-S, 1R cis	3	α-S, 1R trans
1'	α-R, 1S cis	3'	α-R, 1S trans
2	α-R, 1R cis	4	α-R, 1R trans
2'	α-S, 1S cis	4'	α-S, 1S trans

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termiticides and found that deltamethrin was the most toxic. Extensive research on the fate of deltamethrin in aquatic systems has been carried out by Mulla et al., (1978), Zitko et al, (1979), Bocquet and L'Hotellier (1985), among others. Because of the high toxicity of deltamethrin to aquatic organisms, contamination of streams and ponds near sprayed fields is of major concern. For this reason, filter strips or buffer zones of 15 and 100 m in width are commonly used between the sprayed areas and water bodies when deltamethrin is sprayed from the ground or air, respectively. Despite these measures, some of the applied deltamethrin may be susceptible to drift and thereby contaminating water bodies. As a result, numerous efforts have been made to characterize the aquatic persistence and fate of this highly toxic insecticide in the environment (Maguire et al., 1989; Maguire, 1990 and 1991). Equally significant is the knowledge of the processes governing the fate of deltamethrin following spray application, specifically processes that dominate the reactivity and mobility of deltamethrin in the soil environment.

An important consideration in the choice of an insecticide for crop production is the length of time for which toxic residues persist on plants as well as the soil system. Half-lives for deltamethrin ranging from one week to several months have been reported by Hill (1983) and Zhang et al., (1984). This indicates that deltamethrin is degradable in the soil environment. The rate of degradation is dependent upon a number of factors such as soil properties, aerobic or anaerobic conditions, incubation time, method of application and temperature. Degradation of deltamethrin occurs via two principal pathways: hydrolysis of the ester linkage, which yields Br_2CA and 3-phenoxybenzoic acid (PBacid); and hydrolysis of a cyano group to yield first an amide and subsequently carboxylic acid. Thus the main metabolites are Br_2CA and PBacid

(Zhang et al., 1984). These two metabolites along with PBald appear to have no tendency to accumulate in soils. The compounds thus produced undergo further degradation, resulting in the formation of oxidative products, such as HO-Pbacid and HO-Pbalc. The later was found in only trace amounts as reported by Zhang et al., (1984).

Identification of metabolites present in extractable phases confirmed the metabolic pathways described above. For example, according to a report by WHO (1990), an unpublished study by Kaufman and Kayser (1980) was cited where they examined deltamethrin degradation under anaerobic conditions using ^{14}C labeled material. They found that CO_2 evolution was dependent upon the flooding duration. Generally, flooding reduced or initially inhibited the rate of CO_2 dissipation. Khan et al., (1988) reported that the total radioactivity recovered in the soil following a 40-month incubation amounted to 35.8% of deltamethrin initially applied. By increasing the incubation time from 6 months to 40 months, deltamethrin in bound residue forms decreased from 19.2% to 16.3%, and the extractable amount decreased from 59.0% to 19.6% (Khan et al., 1988). In a long-term study, Khan et al., (1993) found that, following an incubation period of nine years, the soil contained 32.2% of ^{14}C initially applied.

Degradation and persistence of deltamethrin, under aerobic conditions, may be considered rapid according to the unpublished work of Kaufman and Kayser (1979) as cited in WHO (1990). They found that deltamethrin degradation in Dubbs fine sandy loam and Memphis silt loam soils, over a 128-day incubation period, occurred rapidly in both soils with CO_2 evolution of 62-77% and 52-60%, respectively. The half-life of

deltamethrin varied from 11 to 19 days in the two soils. When deltamethrin was applied to a sandy clay loam soil, Hill (1983) reported half-lives of 4.9 and 6.9 weeks under indoor and field conditions, respectively. The difference in the rate of disappearance of deltamethrin was attributed to climatic effects. Degradation of deltamethrin was also investigated by Zhang et al. (1984) in an organic soil over a 180-day incubation period. Only 0.25-1.5% of ^{14}C in deltamethrin was evolved as CO_2, thereby indicating negligible mineralization. As a result, a half-life of 72 d was obtained, which indicate that deltamethrin is likely to be less susceptible to degradation in organic soils compared to mineral soils.

Losses or disappearance of applied deltamethrin to the soil surface has been reported as predominately via photo decomposition. Maguire (1990) argued that, since at 25°C the vapor pressure for deltamethrin is 0.002 MPa , it is difficult to attribute its surface losses to volatility. Ruzo et al. (1977) documented the photo-labile nature of deltamethrin in solution as well as the solid phases on glass and silica gel. Although the importance of deltamethrin photolysis on the soil surface is not well understood, it has been observed for other synthetic pyrethroids (permethrin, fenvalerate) where sunlight significantly accelerates the degradation process. Thus, photodegradation may be responsible for "fast" surface losses. Once this process is completed, losses due to slower degradation processes become dominant. This may be the reason for the extensive variability of the half-life reported. According to Hill (1983), in the absence of sunlight, a half-life for deltamethrin could be as long as several months, whereas when sprayed on the soil surface, under field conditions, its half-life was in the one- to two-week range.

The increased agricultural use of deltamethrin requires periodic assessment of the behavior of its residues as well as their fate and movement in the soil. Thus far, most research efforts focused on the photochemistry and metabolism of deltamethrin in plants and animals (Cole et al., 1982; Raha et al., 1993; Westcott and Reichle 1993; Hill et al., 1992). Specifically, limited information is available regarding deltamethrin interaction in the soil system. Moreover, to our knowledge, no kinetic adsorption-desorption information on the reactivity of deltamethrin within the soil environment is available. Perhaps this is due to its extremely low solubility in water, thus limiting the concentration range for which deltamethrin adsorption isotherms can be quantified.

The present study was initiated due to concerns caused by damage from Formosan termites in the French Quarter of New Orleans, Louisiana (Henderson et al., 2000). A recent report (McClain, 2001) raised concerns due to increased incidents of Formosan termites in Baton Rouge and the surrounding areas. To this end, the success of a termiticide such as deltamethrin in stopping termites from entering structures is an essential part of termite control strategies. Application of a termiticide usually includes mixing the chemical with water, then applying the mixture several centimeters below the soil surface. As a result, the applied chemical is not highly susceptible to photodegradation. In this study, deltamethrin adsorption and subsequent desorption in several soils having different organic matter and clay contents were investigated. Specifically our objectives were: (1) to determine the adsorption-desorption behavior of deltamethrin in soils; (2) to correlate the reactivity of deltamethrin in soils with soil properties; and (3) to investigate the effect of soil properties on the hysteretic characteristics of deltamethrin reactivity in soils.

3.2   Materials and Methods

3.2.1 Soils

Four soils having different characteristics were used in this study. Selected

chemical and physical as well as soil classification information of the soils are given in

Table 3.2. The soils were taken from the Ap horizons, air-dried, mixed, and passed

through a 2-mm screen before use. Acid washed sand was also used as a reference

matrix where no clay and organic matter are present. Selim et al. (1998) previously

used this sand material as a reference matrix in metribuzin transport (column)

experiment.

3.2.2 Chemicals

Benzyl-^{14}C-labeled radioactive deltamethrin (International Isotope Munchen,

Bayer, Germany) was used in our study as a tracer to monitor the extent of deltamethrin

retention by the different soils. ^{14}C-labeled deltamethrin stock solution was prepared by

dissolving a portion of the material with 10 mL methanol to yield a concentration of

228.86 µg mL^{-1} (15.61 µC$_i$). A stock solution containing 1014.3 µg mL^{-1} unlabeled

deltamethrin (AgrEvo USA Company, Montvale, NJ) was also prepared in methanol.

Seven ^{14}C-deltamethrin spiked deltamethrin solutions having initial concentrations (C$_i$)

of 0.0915, 0.183, 1.01, 4.97, 9.84, 21.1, and 48.69 µg mL^{-1} in 0.005 M CaCl$_2$ aqueous

solution were used. The input deltamethrin solution having the first two low initial

concentrations (within deltamethrin solubility in water) were prepared by directly

diluting the ^{14}C-labeled deltamethrin stock solution with 0.005 M CaCl$_2$ solution. Input

solutions having C$_i$ of 1.01 to 48.69 µg mL^{-1} were prepared by mixing ^{14}C-labeled and

unlabeled deltamethrin stock solutions in CaCl$_2$ solution. Here, methanol was used as a

Table 3.2: Selected chemical and physical properties of soils

Soils	Taxonomic Class	pH	CEC Meq/100g	O.M.	Sand	Silt	Clay	DOC µg/mL
				----------------%---------------				
Mhoon	Fine-silty, mixed, nonacid, thermic Typic Fluvaquents	6.4	43.3	4.15	10	55	35	537.6
Mahan	Clayey, kaolinitic, thermic Typic Hapludults	6.1	7.00	0.96	49	20	31	153.0
Sharkey	Very-fine, montmorillonitic, nonacid, thermic, Vertic Haplaquept	5.9	39.4	1.41	3	36	61	80.95
Vacherie	Coarse-silt over clayey, mixed, nonacid, thermic Aeric Fluvaquents	7.6	16.2	2.51	50	48	2	261.3
Sand	-----------	6.27	0	0	81	19	0	-

cosolvent as a precaution against precipitation. Cosolvent is essential for studying deltamethrin

behavior in aqueous systems due to its extremely low solubility. Maguire (1990) used

acetonitrile as a co-solvent in a deltamethrin isomerization study.

3.2.3 Adsorption

The deltamethrin adsorption experiment was carried out using the kinetic batch technique

as outlined by Selim et al. (1999). Adsorption was initiated by mixing certain amount of air-dried

soil with 30 mL of the various deltamethrin concentration solutions in a 40-mL Teflon centrifuge

tube. The amount of air-dried soil used was 1 g when the initial concentrations were 0.0915 and

0.183 μg mL^{-1}, and 5 g when the initial input concentrations were above deltamethrin solubility.

For those solutions having initial concentrations higher than solubility, the solutions were used

immediately following preparation to ensure uniformity. Three replicates were used for each

initial concentration. The slurries were kept shaking and after each specific reaction (sampling)

time, they were centrifuged at 500×g for 10 minutes. A 1-mL aliquot was sampled from the

supernatant at reaction times of 2, 8, 24, 48, 72, 120, and 360 hours. The slurries were then

vortex mixed and returned to the shaker after each sampling. The collected samples were mixed

with 5 mL scintillation cocktail (Parkard Ultima Gold) and analyzed by using liquid scintillation

counting (LSC).

3.2.4 Desorption

Desorption was initiated immediately following the last adsorption time step (360 h of

reaction time) as described above. Desorption was carried out over six consecutive steps (6

days). Each desorption step was conducted by replacing the supernatant with deltamethrin-free

0.005 M CaCl$_2$ solution and shaking for 24 hours. Thus the total desorption time was 6 days.

After the sixth desorption step the soil residue in the centrifuge tube was extracted with pure

methanol for another 24 hours. 1 mL samples were taken at each step and deltamethrin in

solution was analyzed using LSC. The amount of deltamethrin transferred from solution to solid

for adsorption or from solid to solution for desorption at each step was calculated based on the

change of deltamethrin concentration in the solution phase.

3.2.5 Data Analysis

Adsorption and desorption isotherms were used to estimate the distribution coefficients and

Freundlich parameters (eqs. 3.1 and 3.2) by employing SAS statement PROC NLIN. SAS

procedure PROC REG with 'rsquare' selection was also used to assess the significance of soil

properties in affecting the retention distribution coefficients.

3.3 Results and Discussions

3.3.1 Adsorption

The concentrations of deltamethrin in solution versus time of retention reaction (h) in all

soils and the acid-washed sand are presented in Figs.3.1 through 3.5. The results that illustrate

the removal of deltamethrin from solution by the solid matrix are presented for the range of

initial (or input) concentration (C_i). Adsorption was carried out during the first 360 h of reaction

time. These figures also illustrate the behavior of deltamethrin during desorption, based on

successive dilutions, which commenced following adsorption (times greater than 360 h).

Rapid decrease in deltamethrin concentration in solution was observed within the first 2 h

of adsorption. This observation was found for all initial concentrations used. The extent of

deltamethrin retention is indicated by the decrease in solution concentration from the input

concentration. The results clearly indicate a significant portion of deltamethrin was retained by

soils in a relatively short time. For example, within six hours of retention, and for C_i of 0.183

µg/mL, the concentration in the soil solutions decreased below 0.03 µg/mL for Mahan and
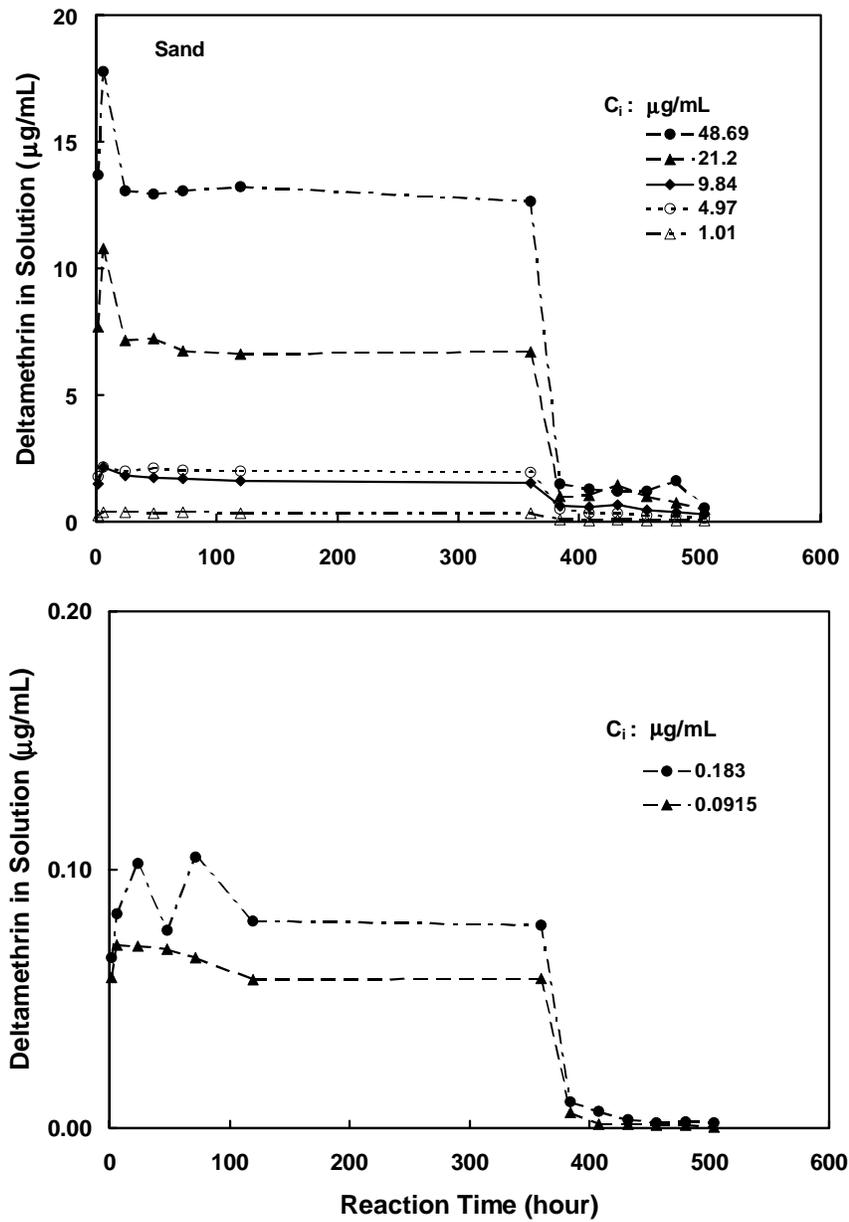
Figure 3.1 Deltamethrin concentration in soil solution versus time during adsorption for acid washed sand with different initial concentrations (C_i's).
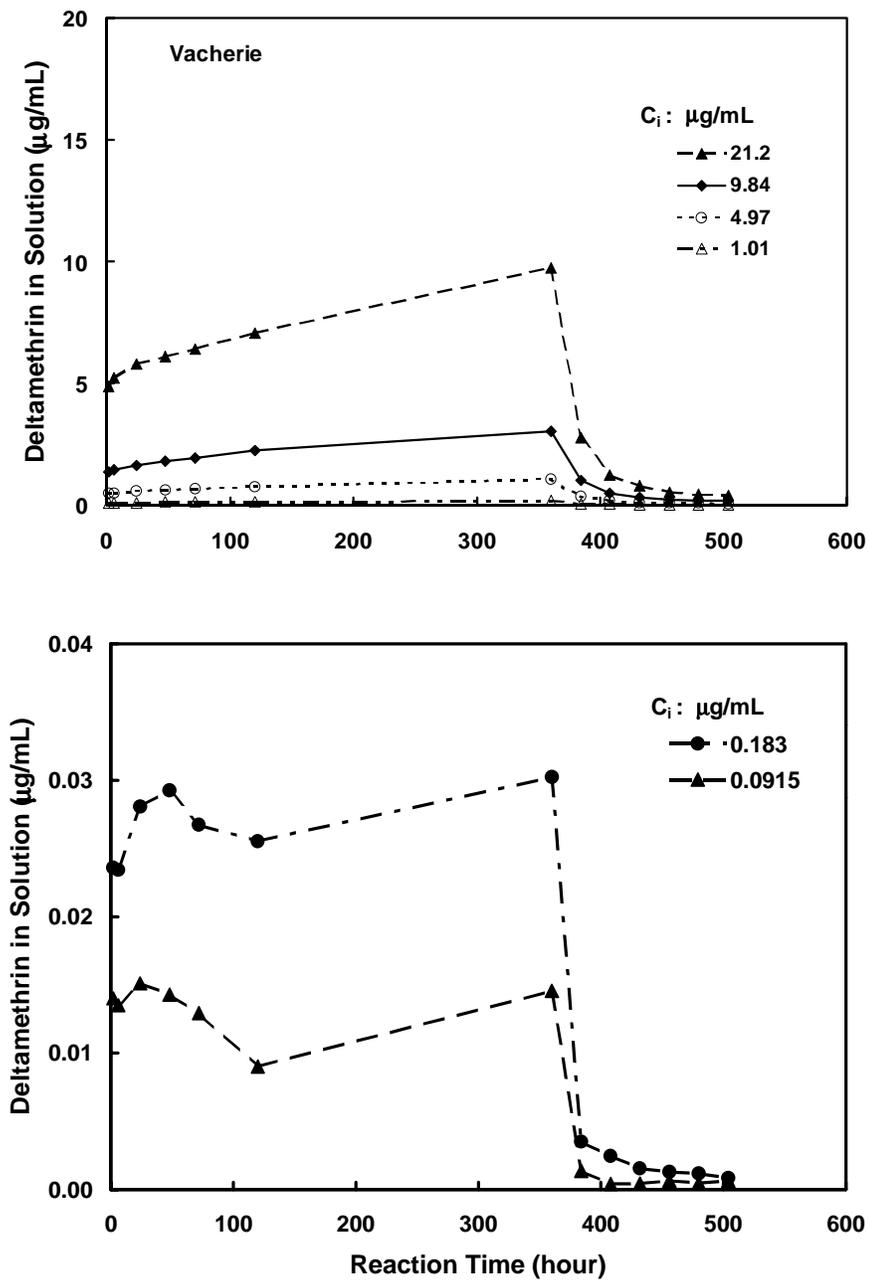
Figure 3.2 Deltamethrin concentration in soil solution versus time during adsorption for Vacherie soil with different initial concentrations (C_i's).
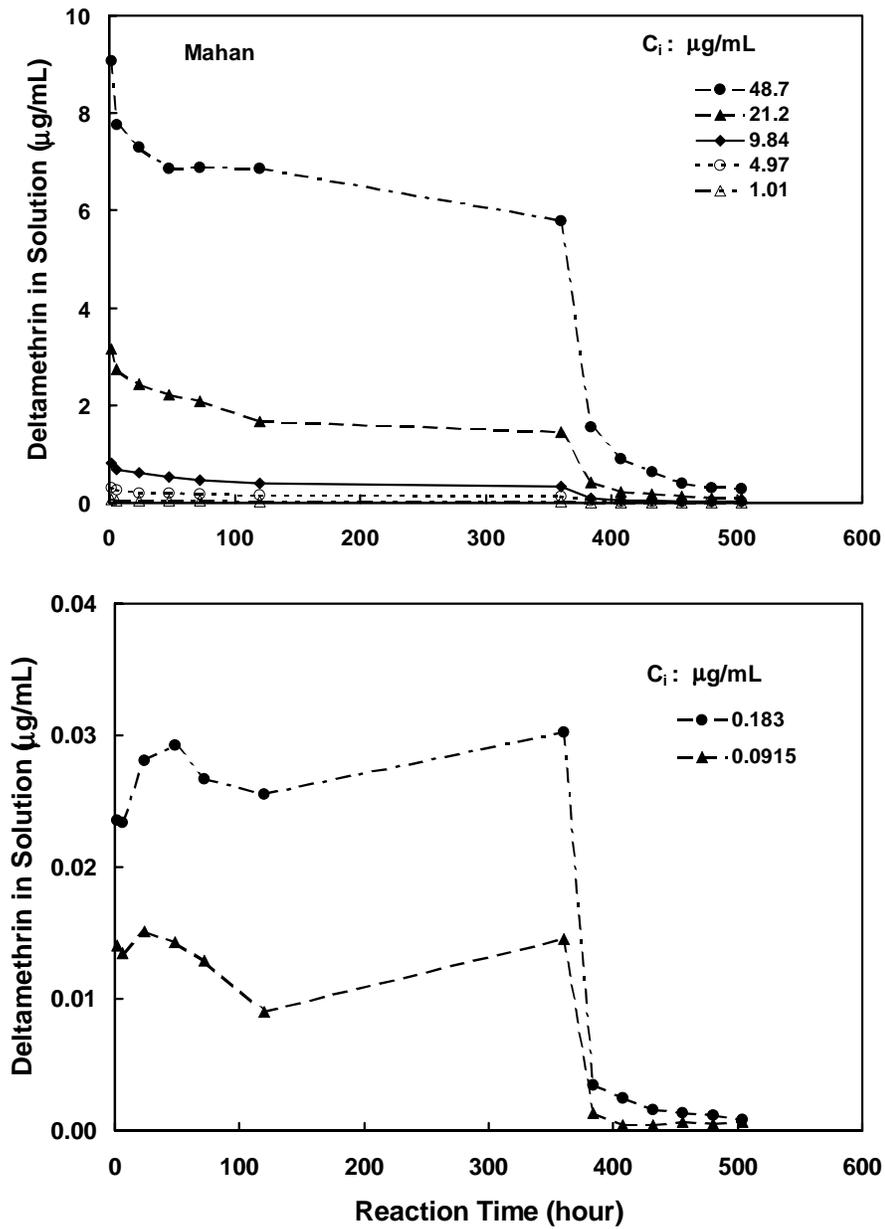
Figure 3.3 Deltamethrin concentration in soil solution versus time during adsorption for Mahan soil with different initial concentrations (C_i's).
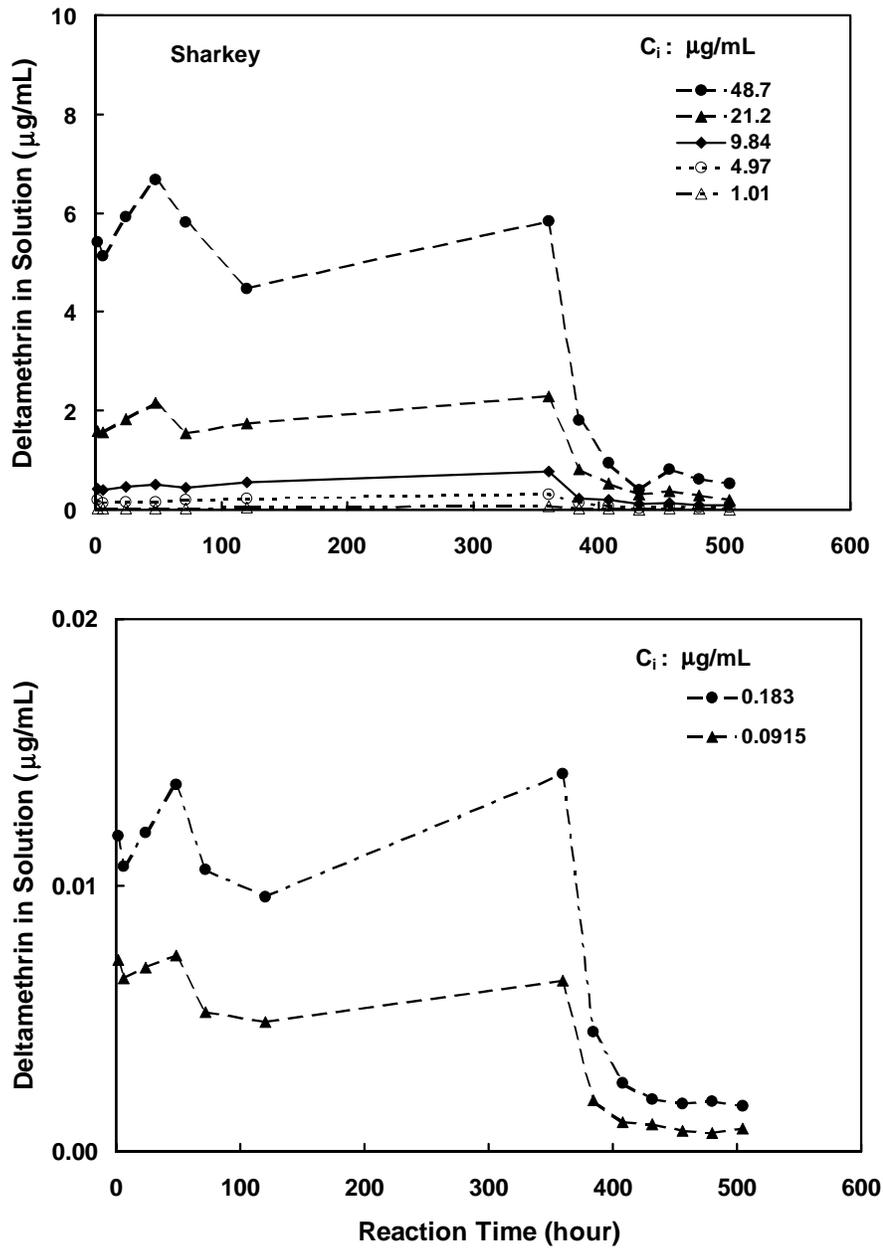
Figure 3.4 Deltamethrin concentration in soil solution versus time during adsorption for Sharkey soil with different initial concentrations (C_i's).
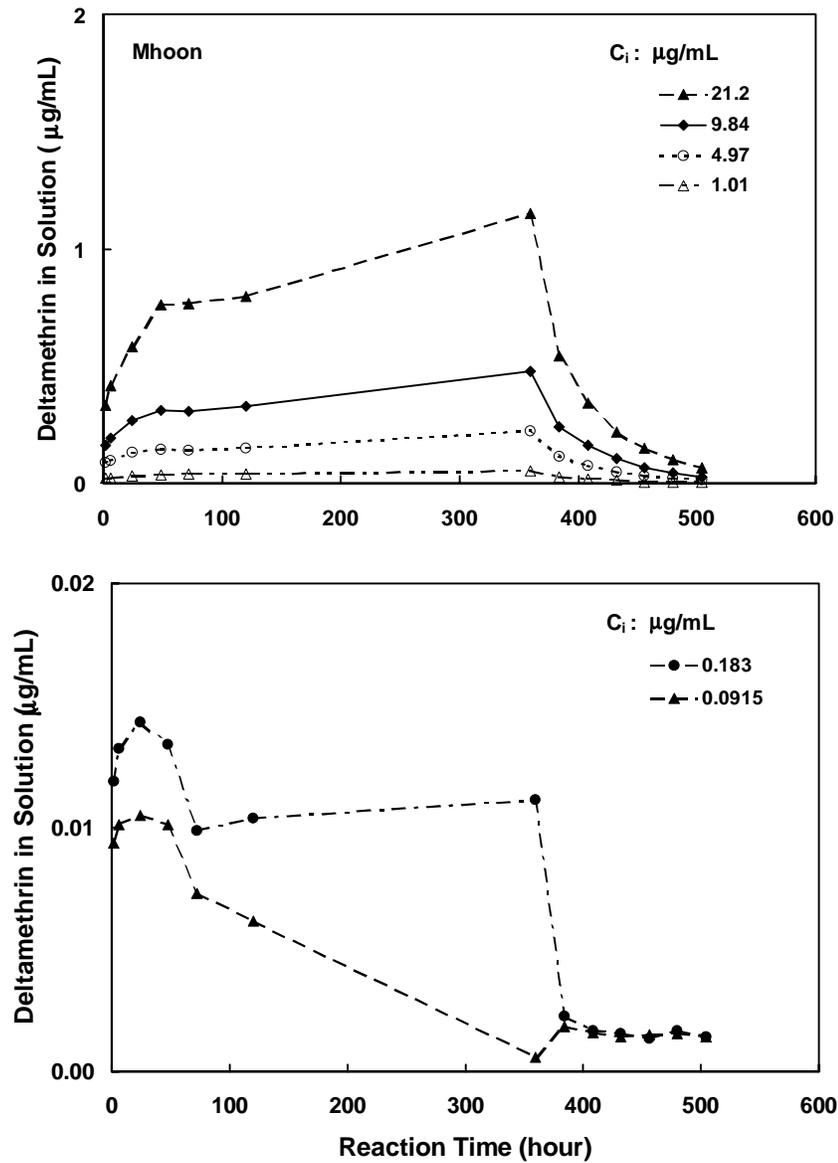
Figure 3.5 Deltamethrin concentration in soil solution versus time during adsorption for Mhoon soil with different initial concentrations (C_i's).

Vacherie, and 0.02 µg/mL for Sharkey and Mhoon soils. For the acid-washed sand, which is devoid of clay or organic matter, the decrease in deltamethrin concentration was signficantly less than all other soils. Based on the decrease in concentrations, our calculation indicated that, for C_i = 0.183 µg/mL, 64.0%, 87.1%, 87.0%, 93.5% and 93.5% of deltamethrin were retained by the acid-washed sand, Vacherie, Mahan, Sharkey and Mhoon soils, respectively.

The extent of retention by these soils as illustrated in Figs. 3.1-3.5 is indicative of the high affinity and strong adsorption behavior for deltamethrin and thus it becomes less susceptible to leaching losses from the zone of application. The extent of retention by the acid-washed sand was not surprising in spite the fact that this material was selected as a reference matrix. As such it was assumed that little if any reactivity with solutes in the soil solution will take place. Evidence of adsorption of organics by sand material has been reported by Goltz and Roberts (1986) for a field experiment in an uncontaminated unconfined glaciofluvial sand aquifer of the borden. A retardation factor of 1.8 for bromoform and carbon tetrachloride, and 3 for tetrachloroethylene is an indication of adsorption of those chemicals by the sand aquifer. In another study, Shahalam, et al. (1997) used Ottawa sand as a reference material together with river sand, sea sand and mountain sand to investigate their adsorption behavior of benzene, toluene, and xylene. They reported considerable adsorption of benzene, toluene and xylene by the reference sand with 44, 127 and 167 µg/g as the amounts adsorbed, respectively. Recently, Clausen, et al. (2001) quantified the contributions from different mineral surfaces and their characteristics for pesticide adsorption. For quartz, Freundlich distribution coefficients (K_f) for atrazine and 2,4-D were 0.020 and 0.022 L/µmol, respectively. Kaolinite was found the most absorptive compared to quartz, calcite, and α-alumina. Although it is not possible to identify reaction mechanisms responsible for the observed decrease in solution concentration of

deltamethrin, we postulate that precipitation and surface adsorption by weak electrostatic forces are responsible for the retention in our acid-washed sand. The lack of continued decrease, of deltamethrin concentration during adsorption indicates that little retention occurred during times greater than 6 h of retention for the initial concentrations used. Such behavior is indicative of fast reaction during sorption with equilibrium conditions attained in a relatively short time for all soil materials used.

The change of concentration of deltamethrin with time during adsorption was not consistent among all soils. Specifically, for the Vacherie and Mhoon soils there was a gradual increase of deltamethrin concentration over time of reaction. Such an increase was gradual and followed the initial decrease of early retention time (less than 6 h). These results indicate the release of deltamethrin retained by the soil matrix or dissolution of deltamethrin in precipitated forms into the solution phase. This phenomena was more pronounced for the high initial (input) concentration (C_i's). The result is an indication that deltamethrin retained by the organic matter fraction of these two soils is of relatively low affinity and is thus easy to release. This behavior may also suggest that deltamethrin transfer from the solution to the solid phase may not only follow a simple mechanism. Dissolved organic carbon (DOC) may act as a co-solvent in dissolution of deltamethrin which was in precipitated forms during the first six hours of reaction. Deltamethrin might be adsorbed subsequently by other mechanisms such as hydropholic, hydrophobic and electrostatic. Some of the adsorbed molecules may be weakly bound to the solid surface (organic matter in this case) and can be relatively easy desorbed, while other molecules may be strongly bound to other soil fractions of the adsorbent (clay in this case) and cannot be easily removed. In order to obtain definitive mechanisms for deltamethrin adsorption-

desorption on organo-clays, molecular data need to be gathered and a spectrocopic technique is needed (Zhang and Sparks, 1993).

3.3.2 Effect of Soil Properties

Adsorption isotherms are commonly used to quantify the affinity of sorption behavior of solute by a porous media. Such behavior is often described by either Freundlich- or Langmuir-type models. In this study, adsorption results were described based on the Freundlich approach:

$$S = K_f C^N \qquad\qquad [3.1]$$

where S is the amount of solute sorbed per gram soil (μg/g), C is concentration in the liquid phase (μg/mL), K_f is the partitioning coefficient (mL/g), and N is a dimensionless parameter commonly less than unity. For cases where N = 1, it is the linear form of adsorption isotherms:

$$S = K_d C \qquad\qquad [3.2]$$

where the parameter K_d (mL/g) is the solute distribution coefficient which is commonly reported in the literature. Values of the distribution coefficient K_d for an extensive list of agricultural chemicals is given in Wauchop et al. (1992). Reported values often represent a 24 h equilibration time of the solute solution with the soil. A literature search revealed that K_d or K_f values for deltamethrin isotherms are not available. In our study, the Freundlich equation adequately described the retention behavior of deltamethrin by the four soils and reference sand and for each reaction time during adsorption. Best fit parameters (K_f and N) which were obtained using nonlinear least-square optimization are given in Table 3.3 along with their coefficient of determination (r^2). An example of the adsorption isotherm results for the four soils is presented in Fig. 3.6. The reaction time was 24 hours. Although the Freundlich model provided a good description of our retention results with time, we obtained estimates for the commonly cited distribution coefficient K_d of the linear model (Table 3.3). Parameter estimatesd for K_f and K_d

values decrease as follows: Mhoon >Sharkey >Mahan >Vacherie >Sand. The extremely high K_d

for deltamethrin, as much as 100 mL/g, is indicative of the strong retention by the soil matrix. A

primary consequence of strong retention of deltamethrin is its limited mobility in the soil profile

and thus low risk of ground water contamination.

With the exception of the acid washed sand, the behavior of adsorption was clearly

nonlinear. This is based on the best-fit estimated parameter N significantly different from 1. In

fact, for Vacherie and Sharkey soils, N ranged from 0.56-0.69. For Mahan and Mhoon soils,

higher estimated N values were obtained with a range from 0.70-0.95. Nonlinear isotherm

behavior is a measure of the extent of heterogeneity of retention reactions and/or the presence of

sites having variable affinities for sorption of deltamethrin by the matrix surfaces. Based on the

estimated N values, we anticipate strong retention for our soils at low deltamethrin

concentrations.

The correlation of K_d with selected soil properties had been reported for several

pesticides (Mallawatantri et al., 1996; Pusino, et al., 1994). For a given hemical, the contribution

of organic matter to the adsorption capacity can be quantified by the associated K_{oc} values

representing the distribution coefficient K_d to the unit weight organic carbon ($K_{oc}= K_d/F_{oc}$)

(Pusino, et al., 1994). Here F_{oc} represents the weight fraction of organic carbon present in the

soil (dimensionless). For the four soils used, high values for deltamethrin adsorption were

obtained. For example, we obtained K_{oc} values of 119 and 505 mL/g for Mhoon and Mahan

soils, respectively. Perhaps due to its low solubility, K_d or K_{oc} values for deltamethrin are not

available in the literature. For other pyrethroids, extremely high K_{oc} values of 5,300 and 100,000

mL/g were reported for fenvalerate and permethrin, respectively (Wauchope et al., 1992).
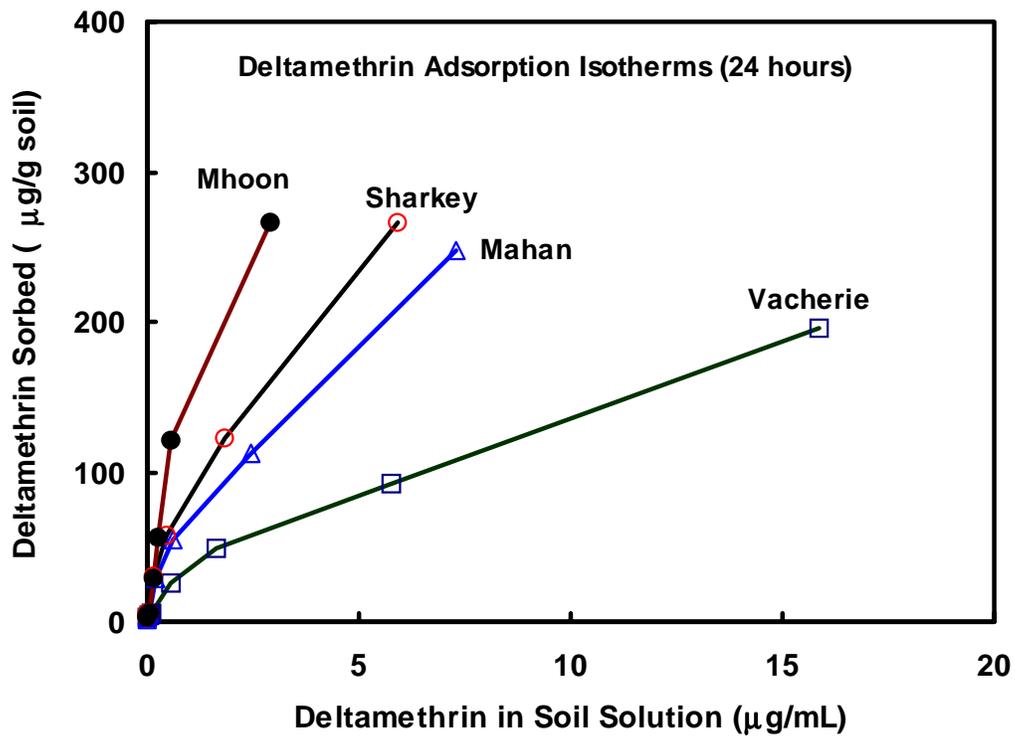
Figure 3.6 Adsorption isotherms for deltamethrin by four soils for 24 h reaction time.

Table 3.3: Estimated Freundlich and linear model parameters (with 95% confidence interval) for deltamethrin adsorption by soils at different reaction time

Soil	Time (hr)	Freundlich Model K_f (mL/g)	N	r^2	Linear Model K_d (mL/g)	r^2
Sand	6	11.88 (10.50-13.45)	0.87 (0.81-0.93)	0.92	9.09 ± 0.60	0.92
	24	13.83 (12.56-15.24)	1.01 (0.96-1.06)	0.95	15.00 ± 0.56	0.97
	48	15.15 (13.37-17.17)	0.94 (0.87-1.00)	0.92	15.00 ± 0.64	0.97
	72	14.50 (13.20-15.93)	1.00 (0.95-1.05)	0.95	15.27 ± 0.57	0.97
	120	16.64 (15.00-18.47)	0.91 (0.86-0.96)	0.94	15.19 ± 0.51	0.98
	360	17.03 (15.30-18.95)	0.91 (0.86-0.97)	0.94	15.85 ± 0.58	0.97
Vacherie	6	36.75 (35.03-38.55)	0.63 (0.61-0.65)	0.99	15.07 ± 0.59	0.97
	24	33.22 (31.76-34.74)	0.63 (0.61-0.65)	0.99	12.93 ± 0.53	0.97
	48	31.72 (30.23-33.28)	0.62 (0.61-0.64)	0.98	12.28 ± 0.49	0.97
	72	31.53 (29.92-33.23)	0.61 (0.59-0.63)	0.98	12.88 ± 0.43	0.98
	120	29.90 (28.06-31.87)	0.57 (0.55-0.60)	0.97	11.20 ± 0.37	0.98
	360	23.17 (21.70-24.74)	0.56 (0.54-0.54)	0.97	7.65 ± 0.24	0.98
Mahan	6	60.28 (57.83-62.83)	0.72 (0.70-0.73)	0.99	32.65 ± 1.22	0.97
	24	65.96 (61.87-70.32)	0.73 (0.71-0.75)	0.98	35.54 ± 1.43	0.97
	48	69.90 (63.64-76.76)	0.74 (0.70-0.77)	0.96	38.43 ± 1.65	0.96
	72	76.33 (71.91-81.01)	0.69 (0.67-0.71)	0.98	38.61 ± 1.83	0.96
	120	82.35 (77.18-87.86)	0.67 (0.65-0.69)	0.98	39.19 ± 2.31	0.93
	360	92.30 (84.86-100.38)	0.64 (0.61-0.66)	0.97	47.53 ± 2.71	0.94
Sharkey	6	97.51 (92.74-102.53)	0.68 (0.67-0.67)	0.99	55.41 ± 2.47	0.96
	24	87.18 (83.20-91.35)	0.68 (0.66-0.69)	0.99	47.34 ± 2.11	0.96
	48	80.00 (76.19-84.00)	0.67 (0.65-0.69)	0.99	40.93 ± 2.07	0.95
	72	89.39 (85.40-93.57)	0.66 (0.65-0.68)	0.99	49.07 ± 2.52	0.95
	120	87.97 (82.50-93.80)	0.67 (0.65-0.69)	0.98	63.41 ± 2.17	0.98
	360	68.38 (63.25-73.91)	0.67 (0.65-0.70)	0.97	47.58 ± 1.73	0.97
Mhoon	6	206.65 (187.88-227.28)	0.91 (0.88-0.98)	0.98	142.05 ± 7.88	0.94
	24	146.94 (135.33-159.54)	0.86 (0.83-0.83)	0.98	97.80 ± 5.62	0.94
	48	120.06(110.75-130.15)	0.82 (0.79-0.84)	0.98	76.19 ± 4.42	0.94
	72	112.17 (102.14-123.19)	0.75 (0.72-0.78)	0.97	65.63 ± 4.32	0.92
	120	109.18 (100.45-118.66)	0.74 (0.72-0.77)	0.98	65.78 ± 4.16	0.93
	360	74.14 (63.43-86.66)	0.53 (0.49-0.58)	0.89	54.12 ± 2.91	0.95

It was also suggested that soil CEC has the greatest influence on the adsorption mechanism of chemical retention by soils (Kozak, et al., 1992; Mallawatantri, et al., 1996). Our observed trend is of decreasing K_d and K_f is in accordance with the order of CEC of the different soils (except for Mahan soil). CEC provided the highest correlation coefficient with K_f among all other variables (OM, clay content and pH). This is because the that CEC is a reflection of both OM and clay contents of soils.

The pH of a soil suspension influences the adsorption mechanism of chemicals by soils (de Jonge, et al., 2000; Kozak, et al., 1992; Mallawatantri, et al., 1996). The correlation between K_f or K_d and pH was analyzed in this study. Deltamethrin adsorption increased as the pH of soil suspensions decreased. The ester and cyano groups of deltamethrin are the two protonation sites. Physical forces, hydrogen bonding or cationic binding between the protonated ester and cyano groups of deltamethrin and organic functional groups and the clay surface of soil, perhaps can account for most of the adsorption by the matrix surfaces. Increasing soil pH results in less protons and subsequent decrease of deltamethrin retention by the soil. It is thus reasonable to assume that a combination of higher pH and lower CEC values may be responsible for the lower K_f and K_d values of Vacherie soil in comparison to those for the other soils. In contrast, high retention of deltamethrin (large K_f and K_d values) for Mahan soil, with predominantly kaolinite-type clays and low organic matter maybe related with iron oxide content in this soil.

The effect of soil properties on Freundlich parameters was investigated using multiple linear regression. The use of multiple rather than simple linear regression is often recommended to explain the effect of soil properties due to the interactions among soil properties on adsorption parameters (de Jonge, et al., 2000; Kozak, et al., 1992; Mallawatantri et al., 1996; Pusino, et al., 1994). Here I focused on soil organic matter content, clay content, cation exchange capacity

(CEC) and pH in regression analysis. Our regression results indicated that Freundlich K_f and N

values can not be explained by a single variable (soil property), rather a combination of pH and

CEC, clay or OM was necessary to explain the variability of deltamethrin retention by the

various soils. Specifically, for Freundlich parameter K_f, the CEC was the most important variable

(explaining some 75.8% of the variance). In contrast, for the parameter N, soil pH explained

most of the variance.

3.3.3 Desorption or Recovery

Results of deltamethrin desorption versus time following adsorption are also shown in

Figs 3.1-3.5. As expected, a drop of concentration in solution after each successive desorption

time step (of 1 day) was observed for all soils. The amount of deltamethrin desorbed at the end

of six consecutive desorption steps and the amount of deltamethrin released subsequently using

methanol as the final extraction step were quantified, respectively. These results along with the

amount retained after 360 h of adsorption are given in Table 3.4. In Fig. 3.7, we expressed these

results in terms of percent recovery from the successive extractions using the background

solution (0.005 M CaCl$_2$) and subsequent methanol extraction. In all our soils we found

extremely low proportion of retained deltamethrin was extractable with the background solution.

This is due probably to deltamethrin's low aqueous solubility and strong sorption or affinity to

the retention sites.

As expected, the total desorbed deltamethrin following six steps of desorption using

0.005M CaCl$_2$ solution as percent of adsorbed was the highest for the acid-washed sand. For the

different input concentrations (C_i's), actual amounts of recovery ranged from 18.8% to 53.6% of

that adsorbed by the acid-washed sand material (see Table 3.4). This suggests that nearly half of

the amount adsorbed was retained by the acid-washed sand regardless of input concentration.

The silt fraction, which accounts for 19% of acid-washed sand, may be responsible for the lack of complete recovery of the amount sorbed. The lowest measured recovery of the amount desorbed deltamethrin was observed for Mahan soil. For Sharkey and Mhoon soils, the desorbed proportions were much lower than that of Vacherie soil. This may be a direct result of the high clay content in both soils. Kaufman et al. (1981) found that deltamethrin and its degradation products were least mobile in an acidic loamy sand soil compared to a nonacidic silty clay loam soil (with pH of 7.6). This finding was obtained despite the higher organic matter content (2.26%) in the nonacidic soil compared to the acidic soil (0.98%). As a result, Kaufman, et al. (1981) suggested that pH is the primary factor affecting mobility of deltamethrin in such soils.

Based on our desorption experiments, the proportion of the amount of deltamethrin desorbed or recovered was, for the most part, unaffected by the initial or input for the different soils (Fig. 3.7). In fact, for both Sharkey and Mhoon soils, the percent recoveries of deltamethrin, by either the $CaCl_2$ background solution or methanol, were somewhat similar for all input concentrations (C_i). However, Vacherie soil, which is characterized by highest pH and high organic matter content, exhibited increased proportion of recovery or desorption with increasing input concentration (C_i). Soil organic matter may play a dual role; i.e. , adsorbing deltamethrin as well as enhancing its solubility. A number of studies showed that DOC was responsible for the enhanced solubility of pesticides in the soil solution (Chiou et al., 1986; 1987; Gao et al., 1998; Stevenson, 1972). Such enhancement effects were effectively explained in terms of a partition like interaction of solutes with dissolved high molecular weight humic materials on the basis of the properties of the solutes and humic materials (Chiou, et al.,1986). Recently, Gao et al. (1998) observed a decrease in K_d for atrazine and bifenox in soil pore water than in pure.

Table 3.4: Mass balance of applied deltamethrin following 360 h adsorption, six desorptions and methanol extraction

Soil	Input Concen-tration (C_i)	Total amount adsorbed[1]	Total amount desorbed[2]	Total amount desorbed (percent of adsorbed	Total amount retained (percent of Input)	Amount of Methanol extractable[3]	Amount of residual (percent of input)
	(μg/mL)	(μg/g soil)	(μg/g soil)	(%)	(%)	(μg/g soil)	(%)
Sand		0.92	0.312	34.1	22.0	0.173	17.4
Vacherie	0.0915	2.31	0.104	4.51	80.4	0.077	77.6
Mahan		2.50	0.005	0.20	90.8	0.003	90.7
Sharkey		2.64	0.189	7.15	89.5	0.136	84.5
Mhoon		2.49	0.221	8.86	86.6	0.168	76.5
Sand		17.7	9.58	53.6	27.2	7.03	3.68
Vacherie	4.98	24.5	4.48	18.5	66.1	2.77	56.9
Mahan		28.9	0.10	0.35	96.5	0.08	57.6
Sharkey		29.3	2.12	7.25	90.8	1.55	85.6
Mhoon		28.2	1.34	4.76	89.8	0.81	87.1
Sand		48.8	16.8	34.5	54.2	13.6	31.1
Vacherie	9.84	43.3	12.5	28.8	52.2	7.70	39.2
Mahan		57.1	0.154	0.27	96.5	0.111	96.3
Sharkey		57.0	4.91	8.61	88.2	4.00	81.4
Mhoon		55.1	2.79	5.06	88.6	1.68	85.7
Sand		211.1	39.6	18.8	58.7	34.4	4.70
Vacherie	48.7	172.7	56.9	32.9	39.5	36.1	24.2
Mahan		260.6	2.41	0.92	88.4	1.58	87.8
Sharkey		274.0	28.0	10.2	84.2	20.8	77.1
Mhoon		252.2	24.6	9.76	77.9	15.1	72.7

[1] Following 360 h of reaction time.
[2] Following six desorption steps using 0.005M CaCl$_2$
[3] The amount extracted using methanol following six CaCl$_2$ desorption steps
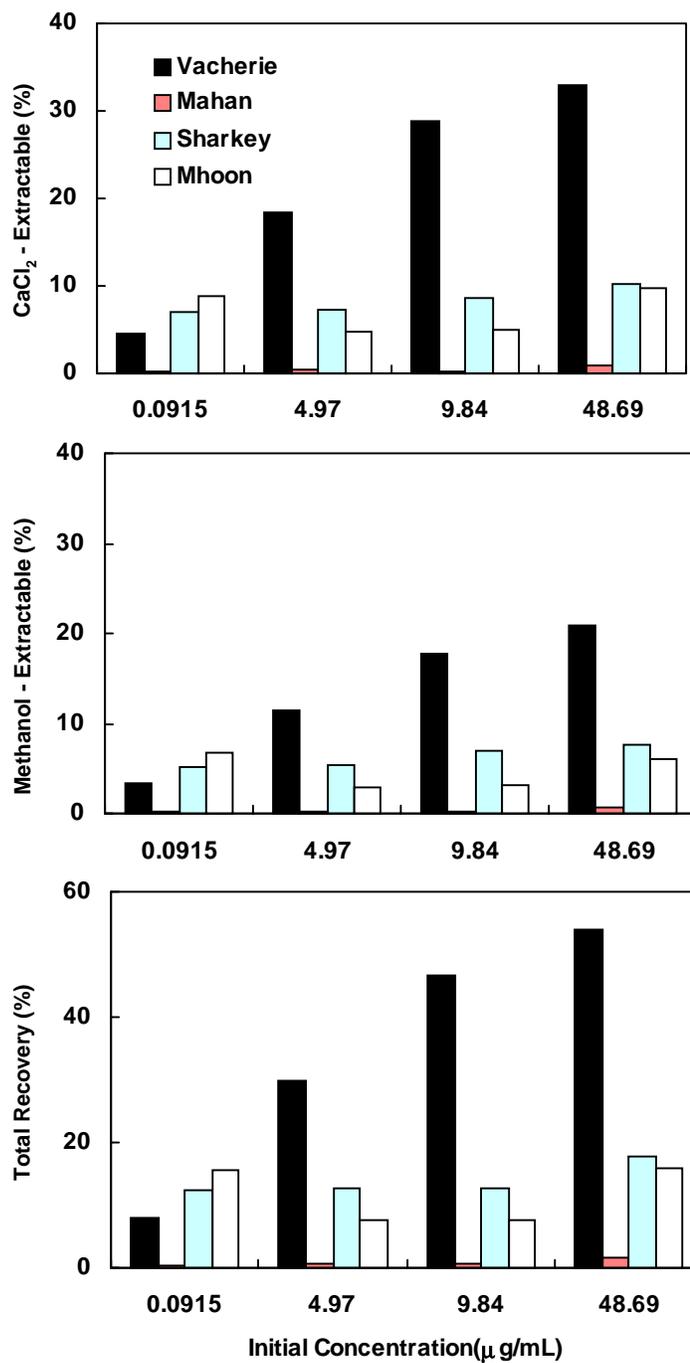
Figure 3.7 The percentage of 0.01 N CaCl$_2$ solution, methanol and total extractable deltamethrin as from the total amount adsorbed by soils after 360 h of reaction

water, which was explained by DOC solubilization effect in the soil solution. Since deltamethrin is of extremely low solubility in water, this "DOC solubilization effect" could be significant with consequent on enhanced potential mobility in the soil system

As illustrated In Table 3.4, the total amount of deltamethrin retained, following desorption, ranged from 78 to 97% of total input for all soils. The only exception was for the nonacidic Vacherie soil, which showed the lowest amount retained (39.5% of input). Such strong retention for deltamethrin following desorption is further exhibited by the high amounts of deltamethrin in the residual phase. The residual amounts of deltamethrin, after extraction with methanol in the final step of our adsorption-desorption experiment, are also given in Table 3.4. These residual amounts as expressed in terms of total input and clearly exhibit the strong retention characteristics of deltamethrin in soils.

3.3.4 Hyteresis

Adsorption-desorption results are presented as isotherms in the traditional manner in Figs. 3.8 to 3.11. These isotherms clearly indicate considerable hysteresis in all soils. This hysteretic behavior resulting from discrepancy between adsorption and desorption isotherms was not surprising in view of the strong retention behavior of deltamethrin in our soils. Selim et al. (1976), and Xue and Selim (1995) showed that observed hysteresis from batch experiments is indicative of irreversible adsorption of solutes by the soil matrix. They showed that lack of equilibrium conditions may be responsible for observed desorption hysteresis. The isotherms of Figs. 3.8 to 3.11 indicate that the amount of irreversible or nondesorbable phase did not decrease appreciably during desorption as clearly illustrated from the traditional type isotherms shown. Furthermore, deltamethrin

may be retained by heterogeneous type sites having a wide range of binding energies. At

trace concentrations (below solubility in water), binding may be irreversible. The amount

of nondesorbable pesticide almost always increased with time (Wauchope and Myers,

1992). It was reported that hysteresis may be due to hydrophobic bonding of the

chemical to organic matter of soil for compounds very poorly soluble in water (Pusino

et al., 1994). In terms of its energy status in soils, methanol-extractable pendamethrin

exhibited stronger interaction with soil organic matter and clay than did water-extractable

fractions (Pusino et al., 1994). Methanol-nonextractable forms exhibit the strongest bonds

in soil and are referred to as soil bound residues. Furthermore, lack of complete recovery

has been reported by many others (e.g., Bowman and Sans, 1985; Pignatello and Huang,

1991).

3.4   Conclusions

Deltamethrin exhibited strong retention over time for all soils studies. Adsorption was

positively correlated with increasing cation-exchange capacity (CEC) and decreasing

soil pH. After 1 d of reaction, more than 90% of applied deltamethrin was adsorbed by

Mahan and Sharkey clay soils. In contrast, lowest retention was observed for the

nonacidic Vacherie soil (pH of 7.6 and clay content of 2%). Deltamethrin adsorption by

the different soils was quantified by the distribution parameters (K_d) and the Freundlich

coefficients (K_f) as derived from the adsorption isotherms. The K_d values after 1 day

sorption were as much as 98 mL/g soil. Moreover, our results indicate that, with the

exception of the reference sand material, adsorption was not time-dependent. The extent

of recovery or desorption of deltamethrin adsorbed varied among soils and input
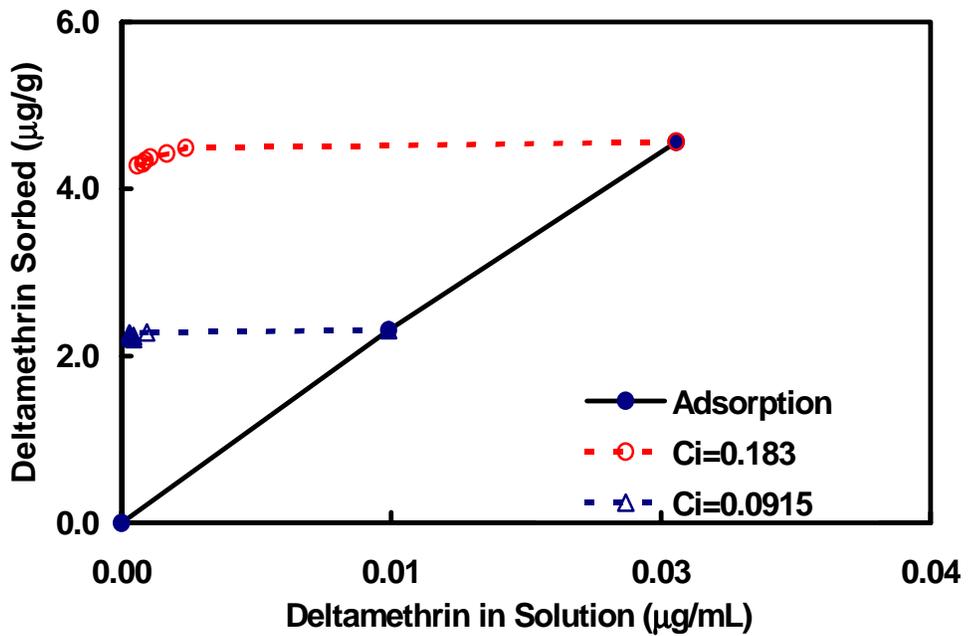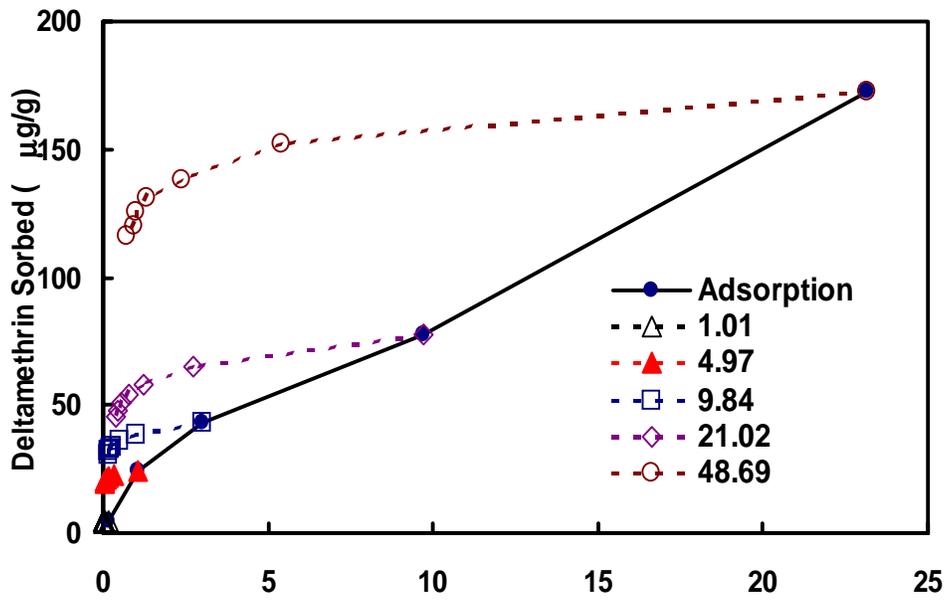
Figure 3.8 Desorption isotherms for deltamethrin in Vacherie soil based on successive dilutions for different C_i's.
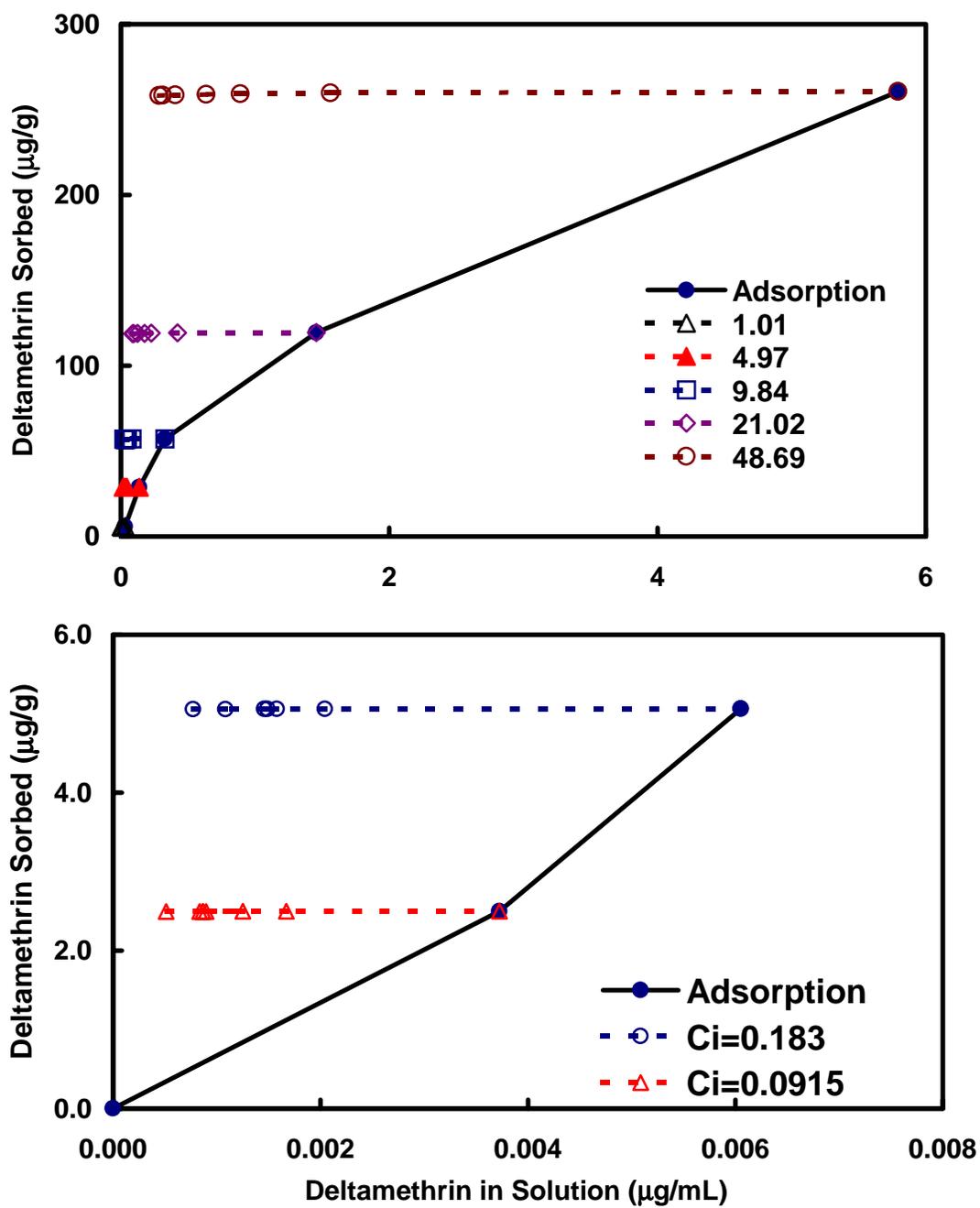
Figure 3.9 Desorption isotherms for deltamethrin in Mahan soil based on successive dilutions for different C_i's.
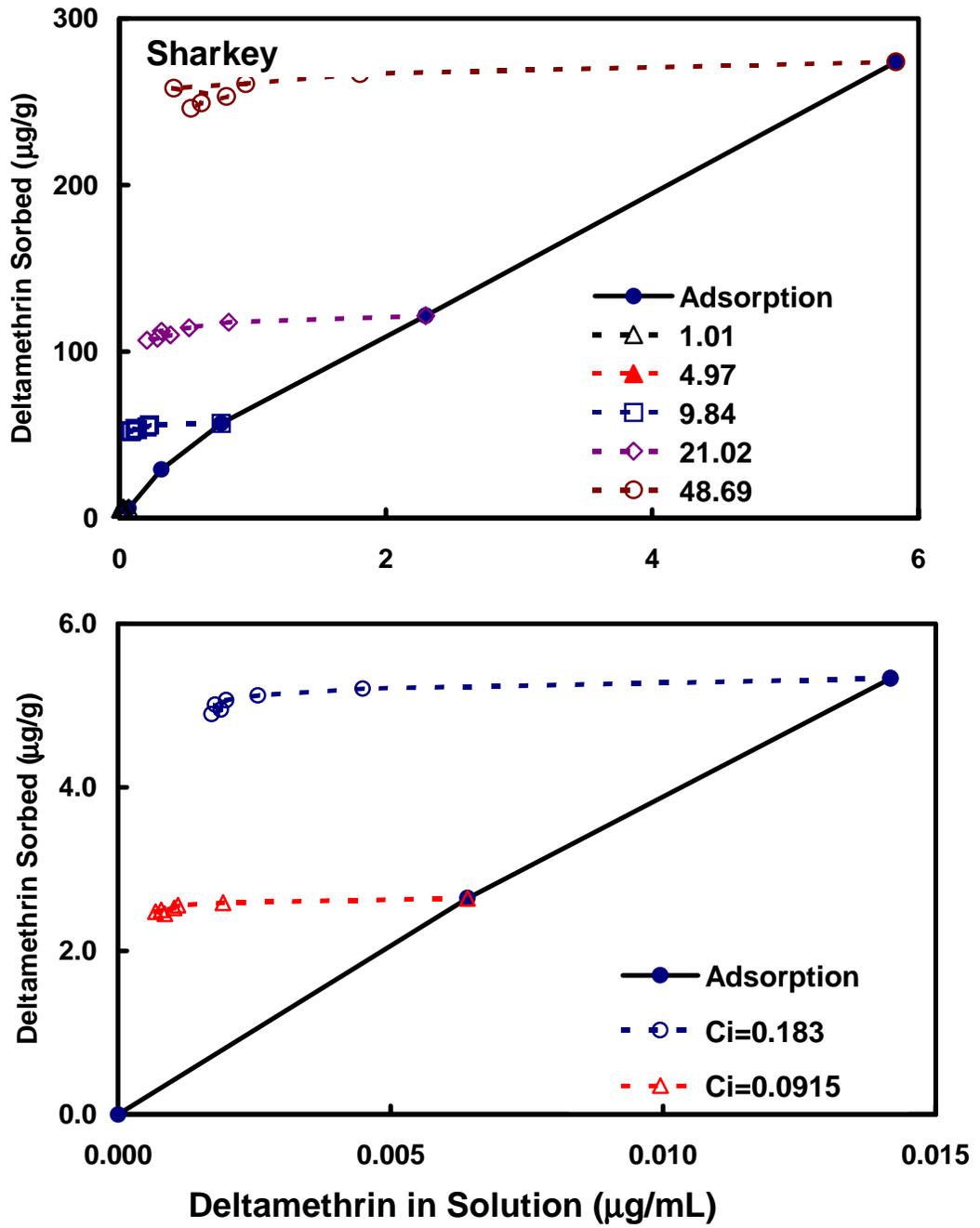
Figure 3.10 Desorption isotherms for deltamethrin in Sharkey soil based on successive dilutions for different C_i's.
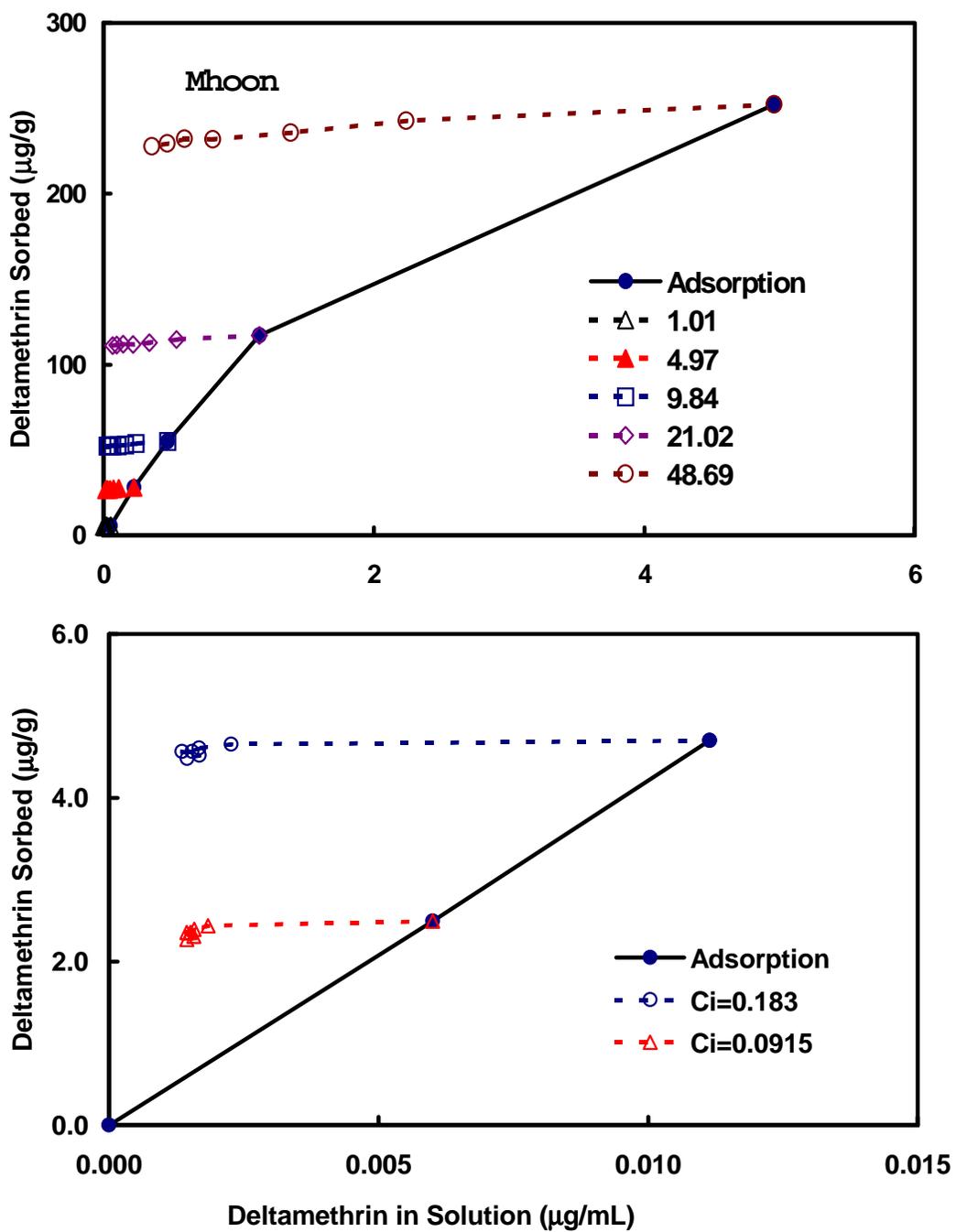
Figure 3.11 Desorption isotherms for deltamethrin in Mhoon soil based on successive dilutions for different C_i's.

concentrations.The total desorbed deltamethrin (resulted from six successive dilution steps) as percent of amount adsorbed ranged from 0.20% for Mahan to 32.9% for Vacherie soil. Nevertheless, for all soils, the total amount retained, following desorption, ranged from 78 to 97% of total input. The only exception was for Vacherie soil, which showed highest recovery and the lowest amount retained (39.5% of input). This high recovery for Vacherie soil may be due to solubilization effect of dissolved carbon (DOC), as well as the decrease of pH-dependent charge at high pH. Strong hysteresis behavior of deltamethrin adsorption-desorption was observed for all soils as illustrated by the discrepancy between the adsorption and desorption isotherms. Due to strong adsorption and low recovery, we conclude that deltamethrin is not highly susceptible to leaching losses from the zone of application.

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CHAPTER 4:   TRANSPORT OF DELTAMETHRIN IN SOIL COLUMNS

4.1   Introduction

Deltamethrin [(S) - α - cyano - 3 - phenoxybenzyl - (1R,3R) - cis - 2,2 - dimethyl-3-(2,2-dibromovinyl) cyclopropanecarboxylate] is active against a wide range of insects that attack crops and animals, and has been recommended for foliar applications on various vegetable and field crops (FAO, 1981). It has also been recommended as a termiticide by Su et al. (1991), Gatti and Henderson (1996), among others. Su et al. (1991) found that among eleven soil termiticides investigated, deltamethrin was the most toxic. Because deltamethrin is especially toxic to aquatic organisms (Mulla et al., 1978; Zitko et al., 1978; Bocquet and L'Hotellier, 1985), numerous studies focused on characterizing the persistence and fate of deltamethrin in aquatic systems.

The rate of dissipation of field applied deltamethrin from the soil surface is affected by several processes including volatilization, photo-decomposition, and degradation. In addition, deltamethrin is subject to leaching losses due to runoff as well as infiltration and subsequent movement to lower depths in the soil profile. The rate of dissipation also depends on the method of application of the chemical, e.g., whether incorporated into the soil or surface applied. Hill (1983) reported that when deltamethrin was applied via ground and serial boom sprayers, a two-compartment or bi-phasic model was necessary to describe the dissipation rate over time. A two-compartment approach suggests that the overall rate of dissipation depends on the relative contribution of two competing processes: a "fast" surface loss from a deposited residue compartment versus a "slower" degradation loss from a retained residue

compartment. The biphasic dissipation for other synthetic pyrethroids on soils was also reported by Chapman and Harris (1981). They suggested that the dissipation of fenvalerate on the surface of a mineral soil was faster than when incorporated.

Application of deltamethrin as a termiticide usually includes mixing the chemical with water where most applied is placed several centimeters below the soil surface. As a result, the applied chemical is not highly susceptible to photodegradation. It was also reported that when deltamethrin was used as a termitecide (Deltagard TC), no significant dissipation after a six month period (p=0.1675, 0.6598) was observed in two residences in New Orleans, Louisiana (G. Henderson, 2000, unpublished data). In the previous chapter, the adsorption-desorption behavior of deltamethrin in several soils was investigated and the reactivity of deltamethrin was correlated with major soil properties. The approach utilized was that of a kinetic batch method for adsorption followed by successive dilutions for desorption. It was found that adsorption was not kinetic or time-dependent with the exception of a reference sand material. Deltamethrin adsorption was positively correlated with increasing cation-exchange capacity (CEC) and decreasing soil pH. The extent of desorption or recovery of applied deltamethrin varied among soils and input concentrations. Strong hysteretic behavior of deltamethrin adsorption-desorption was observed for all soils as illustrated by the discrepancy between the adsorption and desorption isotherms where the amount desorbed ranged from 1% to 53% of the amount adsorbed.

Investigations regarding the transport and potential mobility of deltamethrin in soils are limited. Available published work reveal that deltamethrin is best characterized by its limited mobility in most mineral soils. The work of Kaufman et al. (1981) is one

of the few investigations that studied deltamethrin mobility in soils. They found that based on soil column experiments, deltamethrin was essentially immobile in three different soils (silty clay, silty clay loam, and loamy sand). As a result, it was classified as a low-mobility to immobile compound in soils. Kaufman et al. (1981) also found that deltamethrin and its degradation products were least mobile in a loamy sand soil with lowest organic matter content (0.98%), and most mobile in a silty clay loam soil with an intermediate organic matter content (2.26%). However, this silty clay loam soil was of higher pH than other soils investigated (pH =7.5). As a result, Kaufman, et al. (1981) suggested that for nonacidic soils, the pH is perhaps a primary factor affecting mobility of deltamethrin in such soils.

Investigations on deltamethrin published by WHO in 1990, reported on the immobile nature of deltamethrin based on soil column transport experiments. According to an unpublished study by Hascoet (1977), as cited by WHO (1990), a Fontainebleau sand column was leached continuously with water equivalent to 1030 mm of rain. The results indicated that approximately 97% of the applied ^{14}C-deltamethrin remained in the upper 0-2.5 cm layer and only 2% was found in the leachate. The report concluded that deltamethrin was unlikely to leach in cultivated soils having higher sorption properties than that for the sand material (with organic matter of 0.03%). Low sorption properties was assumed for this sand material. Based on another study cited by WHO (1990), the leaching of deltamethrin in three different German soils with organic matter contents ranging from 0.8 to 2.6% was investigated by Their and Schmidt (1976, unpublished report). Their study was carried out using the commercial product Decis EC 25 at a rate equivalent rate of 1 liter/ha (or 25 g

deltamethrin per ha). Each column was leached with an equivalent of 200 mm rainfall over a 2 d period. Under these conditions, the amount of active ingredient detected in effluent water was less than 1 μg mL^{-1} for all soils. This amounted to less than 2% of the original amount applied. These findings, as reported by WHO (1990), are consisted with those reported earlier by Kaufman, et al. (1981).

Based on the above, there is ample information in the literature regarding deltamethrin photochemistry and metabolism in plants and animals, whereas little is known regarding its movement in the soil and the influence of soil properties on its fate in the soil system. Information regarding the mobility of applied deltamethrin in soils is essential for environmental assessment. The focus of this study was to investigate the transport and leaching potential or release of deltamethrin in soils having different soil properties. The approach utilized was that of a modified miscible displacement or transport approach where soil columns under constant flux and soil-water saturated conditions were maintained. The extent of leaching losses of deltamethrin as measured in the effluent solution was quantified. In addition, the distribution of the amount of deltamethrin retained by the soil was measured with depth in the soil columns.

4.2   Materials and Methods

4.2.1   Soils

Four soils having different characteristics were used in this study. Selected chemical and physical as well as soil classification information of the soils are given in Table 3.1. The soils were taken from the Ap horizons, air-dried, mixed, and passed through a 2-mm screen before use. Acid washed sand was also used as a reference

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matrix where no clay and organic matter are present. Ma and Selim (1995) previously

used this sand (reference) matrix in tracer transport (column) experiments.

4.2.2 Chemicals

Benzyl-^{14}C-deltamethrin (International Isotope München, Bayer, Germany)

33.29 mg with purity greater than 98% and 0.21 mCi radioactivity, was used as a tracer

to monitor the movement of deltamethrin through the soil columns. ^{14}C-labeled

deltamethrin stock solution was prepared by dissolving the material with 100 mL

methanol to reach a concentration of 306.2 μg mL^{-1}. Non-labeled technical deltamethrin

(AgrEvo USA Company, Montvale, NJ) was used to prepare deltamethrin stock

solution containing 1014.3 μg mL^{-1}. 15 mL of ^{14}C-labeled and 8 mL of unlabeled

deltamethrin stock solutions was mixed in a 25 mL volumetric flask, additional

methanol was added to bring the volume to 25 mL. This deltamethrin methanol solution

was later used as the input solution for the miscible displacement experiment.

Deltamethrin concentration in this solution was measured by GC with electron capture

detector, and the radioactivity of the solution was measured by mixing 0.5 mL solution

in 5 mL LSC (liquid scintillation counter) Cocktail. The concentration measured was

501.3 μg mL^{-1} with 1.14×10^6 counts per minute. A pulse volume of deltamethrin

solution was used to obtain deltamethrin breakthrough curve through an acid-washed

sand column, and the solution was prepared by diluting ^{14}C-labeled stock solution in

0.005 M CaCl$_2$ background solution to give a concentration of 0.2 μg mL^{-1}.

4.2.3 Transport Experiment

A modified miscible displacement technique was employed to obtain

deltamethrin breakthrough curves (BTCs) for the various soils. The aim was to apply

deltamethrin at some depth below the soil surface in a manner depicting that for termite application. To achieve this, plexiglass columns (10 cm long $\times$ 6.4 cm i.d.) were uniformly packed with air-dried soils (<2mm). Water saturation in each column was achieved by slowly introducing 0.005 M $CaCl_2$ solution where upward flow was maintained and a constant flux was controlled by a piston pump. After saturation, each column received approximately one pore volume of a tritium (^3H_2O) pulse in 0.005 M $CaCl_2$ as a tracer solution and was subsequently leached for several pore volumes with the background solution (0.005 M $CaCl_2$). Tritium samples in the effluent were analyzed using liquid scintillation counter. The examples of tritium breakthrough curves for Vacherie and reference sand are exhibited in Figure 4.1. Application of a tracer solution is used commonly in miscible displacement experiments in order to characterize the flow behavior (dispersivity and retardation of breakthrough results) in packed soils subject to different soil structure or different flow velocities (Ma and Selim, 1994). Based on the tritium Breakthrough curves, dispersion coefficient (D) was estimated using CDE and was used to model the transport behavior of deltamethrin in the reference sand column.

Following the completion of the tritium breakthrough experiment, the piston pump was stopped and the flow in the soil column was thus interrupted. Subsequently, the top (inflow) end of the column was taken apart and the top 5 mm soil was carefully removed. An 8 mL volume of the prepared labeled deltamethrin solution (9.32 μg/g soil, total radioactivity was 10μCi), which is equivalent to the rate used for termite control in the residences in New Orleans, Louisiana (G. Henderson, 2000, unpublished data), was evenly applied to the new soil surface, which was allowed to evaporate for 2

80
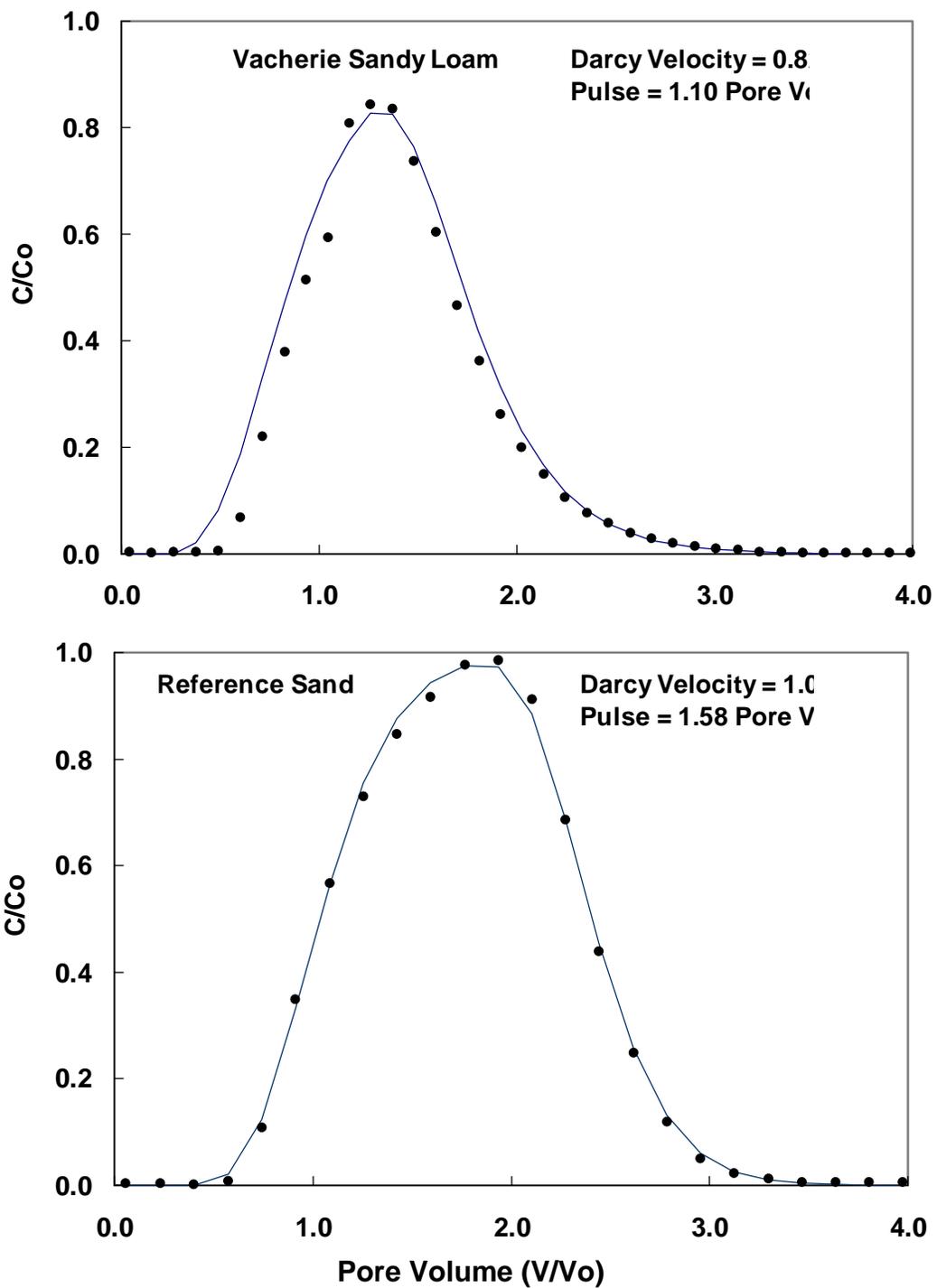
Figure 4.1 Tritium breakthrough curves for reference sand and Vacherie soil columns. Column length = 10 cm.

h. An equivalent amount of air-dry soil to that removed was then added to the soil column and the top-end of the column was replaced and all parts retightened. Using the 0.005M CaCl$_2$ background solution, slow flow was then initiated until the newly added (top dry) soil was fully-saturated. In order to maintain full-saturation, the soil column was then inverted and upward flow maintained. To monitor the mobility of deltamethrin through the soil column, the effluent was collected using a fraction collector. A four-day flow interruption was employed for each column experiment after 18 days (approximately 35 pore volumes) of continuous leaching. Following the 4-d flow interruption period, nine-day of leaching was implemented. Thus the applied volume was equivalent to a 500 mm rainfall for the leaching process.

Unlike the transport experiments discussed above, an additional column packed with reference sand was used to examine the deltamethrin transport behavior using the traditional miscible displacement techniques. Here a pulse of ^{14}C-labeled deltamethrin solution (21.8 pore volumes) having a concentration of 0.204 µg mL^{-1} was introduced to the sand column, which was subsequently followed by leaching with the 0.005M CaCl$_2$ background solution. Such low concentration (0.204 µg mL^{-1}) was used because of the limitation caused by deltamethrin solubility. The total leaching volume was approximately 63 pore volumes. During leaching, a period of 4-day flow interruption was implemented after 9.62 pore volumes of the background solution leached through the column. Flow interruption is often used to understand physical and chemical nonequilibrium behavior of reactive solutes in soils (Ma and Selim, 1998). Physical nonequilibrium results from the existence of regions with the porous medium in which there is minimal advective flow, and chemical nonequalibrium results from rate-limited

interactions between the solute and specific sorption sites of the sorbent. Flow interruption provides experimental condition to understand the nonequilibrium phenomena. The time of the leaching process including the 4-day flow interruption was 31 d. Effluent samples collected were analyzed using Liquid Scintillation Counter by mixing 1 mL sample with 5 mL LSC cocktail. The concentration was determined by back calculating the specific activity to a standard with known concentration of deltamethrin. A total of six column studies were performed, and the physical properties for each soil column are listed in Table 4.1.

Following the transport experiments, each soil was sectioned into approximately 2-cm increments. The amount of deltamethrin retained by the soil matrix within each 2-cm section was determined by sequential extraction of the soil using pure methanol. Attempts to section Mhoon soil column failed due to extensive swelling of this soil. Extraction steps included mixing approximately 15 g of soil from each section of the column with 30 mL methanol in 40 mL Teflon tubes, shaking for 24 hours, centrifuging for 10 minutes at 500 x g, and decanting the supernatant. This process was repeated three times and the extracts were combined and brought to a volume of 100 mL. Meanwhile, soil moisture content was measured for each section using the oven-dry method to determine deltamethrin concentration on the dry weight bases. A 1 mL aliquot was then taken for the analysis of ^{14}C specific activity. The amount of deltamethrin extracted from each column was calculated based on concentration of the extractants. Percentage recovery of deltamethrin (eluted and extracted) was determined based on the total input amount for each column.

Table 4.1: Experimental conditions of the miscible displacement experiments for the different soils

Soil	Input Deltamethrin	Bulk Density (ρ_b)	Water Content (θ)	Pore Volume (p.v.)	Darcy Velocity (v)	θ at 0.33 bar	Dispersion Coefficient (D)
		g/cm^3	cm^3/cm^3	cm^3	cm/h	cm^3/cm^3	cm^2/h
Mahan Sand Loam	Methanol solution	1.34	0.513	165	0.788	0.118	0.172
Sharkey Clay	Methanol solution	1.27	0.439	141	0.918	0.342	3.438
Vacherie Silty Loam	Methanol solution	1.24	0.479	154	0.804	0.351	0.832
Reference Sand	Methanol solution	1.79	0.342	110	1.272	0.131	0.348
Mhoon Silty Clay Loam	Methanol solution	1.08	0.585	188	0.631	0.460	0.531
Reference Sand	water solution	1.66	0.339	109	0.953	0.128	1.99

4.2.4   Data Analysis

   The experimental data were analyzed by using SAS Version 8.0 (SAS Instutite

Inc., 1999) to investigate the relationships between soil properties and deltamethrin

release from the soil column. SAS statement PROC PrinComp was used to detect any

structure in the relationship between observed soil properties and deltamethrin mobility

for the principal component analysis. Principal components analysis constructs a set of

p normalized orthogonal linear combinations of the data selected in such a way that the

first linear combination has variance as large as any possible single linear combination

can have for the data. The first two linear combinations have a total variance (sum of

variances) as large as any possible two orthogonal linear combinations can have for the

data. This continuous for up to p linear combinations. So, for the first k linear

combinations, the proportion of the total sample variance explained by the k linear

combinations is as large as is possible. Each principal component consists of

coefficients from a linear combination of the observed variables. The sign and

magnitude of the coefficients contained in a principal component reflect the

relationships between observed variables.

   Soil properties, column parameters and deltamethrin movement and retention

characteristics included in the principal component analysis were: soil organic matter

content (OM), clay content (Clay), bulk density of soil column (BK), soil pH (PH), soil

moisture content at 0.33 bar (theta033), final effluent deltamethrin concentration

(FianlC), the amount of deltamethrin recovered after thirty pore volumes of leaching

(pv30), mean breakthrough time in hours for tritium BTC (Tmhr), peak positon of

deltamethrin release curve in pore volumes (peakPV) and deltamethrin concentration at

peak (peakC) of breakthrough curves.

4.3   Results and Discussion

4.3.1   Deltamethrin Breakthrough Curves

Transport results of deltamethrin in the various soil columns are given by the breakthrough curves (BTCs) shown in Figures 4.2 through 4.5. The BTCs are presented as concentration (ppm) versus relative pore volume (V/V_o) where V_o is the pore volume of the column (cm^3). The concentrations presented here are based on LSC measurements of the radioactive carbon (^{14}C) in the column effluent solution and thus did not differentiate between the applied compound (^{14}C -labeled deltamethrin) and its degradation products. Furthermore, for easy comparison, all columns were maintained under somewhat similar flow velocities (Table 4.1).

All measured BTCs exhibited extensive asymmetry as illustrated by the differences in shape of the effluent and desorption sides of the measured BTCs (Figs. 4.2 through 4.4). In addition to these asymmetries, a sharp front of the BTC for Vacherie soil was observed which is in contrast with more gradual change of effluent concentrations for the Mhoon and Mahan soils. The time (or pore volumes) of the arrival of the BTC peak or the concentration maximum varied among the different soil columns. The time of arrival (or number of pore volumes) of the BTC is indicative of the extent of mobility of deltamethrin in each soil column. The early arrival of the BTC peak for Vacherie soil (≈ 4 pore volumes) is indicative of lower retardation and thus relatively higher deltamethrin mobility among the different soils. In contrast, for Mahan and Mhoon soil columns, stronger deltamethrin retention and less mobility with observed BTC peaks after 7 and 9 pore volumes, respectively. Such differences in

Figure 4.2 Deltamethrin breakthrough curve through Vacherie soil column with flow interruption. Column length = 10 cm. Deltamethrin was sprayed on the surface of soil before leaching with 0.005 M CaCl$_2$ solution.

Figure 4.3 Deltamethrin breakthrough curve through Mahan soil column with flow interruption. Column length = 10 cm. Deltamethrin was sprayed on the surface of soil before leaching with 0.005 M CaCl$_2$ solution.

Figure 4.4 Deltamethrin breakthrough curve through Mhoon soil column with flow interruption. Column length = 10 cm. Deltamethrin was sprayed on the surface of soil before leaching with 0.005 M CaCl$_2$ solution.

mobility are consistent with the adsorption characteristics based on the 24 h isotherm results shown in Fig. 3.6. It is obvious that the nonacidic Vacherie soil exhibited least capacity of deltamethrin retention whereas maximum retention was observed for Mhoon soil.

Results shown in Figures 4.2 – 4.4 indicate that despite the differences in the shape of BTCs, measured maximum deltamethrin concentration of the effluent peaks were similar (at 0.05 ppm) for three soils; Mahan, Mhoon and Vacherie. Such concentration maximum in column effluent is considerably below deltamethrin solubility in water. The desorption (right) side of the BTCs showed continued but slow release of deltamethrin in the effluent from the soil columns. As a result, the BTCs exhibited excessive tailing as illustrated by the continued release of deltamethrin over time. For Mahan soil, the desorption side was gradual which is indicative of slow release of the kinetic type (Ma and Selim, 1998). After some 30 pore volumes, a somewhat constant concentration of deltamethrin in the effluent was observed ($\cong 0.011$ ppm). For Mhoon and Vacherie soils, a consistent trend was not observed. Rather a slight increase in concentration was observed indicating accelerated release over time. Such accelerated release is possibly due to the effect of facilitated transport of deltamethrin by dissolved organic carbon (DOC). It is conceivable that deltamethrin retained by the organic matter fraction in these two soils is of relatively low affinity and is thus easy to release. This behavior may also suggest that deltamethrin transfer from the solid phase to the solution be affected by DOC which may act as a co-solvent in dissolution of deltamethrin in precipitated forms. Besides, some of the adsorbed deltamethrin may be weakly bound to the solid surface (organic matter in this case) and

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can be relatively easy released to the solution phase. While other molecules may be strongly bound to other soil fractions of the adsorbent (clay in this case) and cannot be easily removed. In order to obtain definitive mechanisms for deltamethrin adsorption-desorption on organo-clays, molecular data need to be gathered and spectrocopic technique is needed (Zhang and Sparks, 1993).

The influence of a 4 day no-flow or flow-interruption on the shape of BTC for deltamethrin was well illustrated in Vacherie and Mhoon soils and was less pronounced in the Mahan soil. As discussed by Brusseau et al. (1989), and Ma and Selim (1998), flow interruption may provide an understanding of the nonequilibrium behavior of solutes in soils. For Mahan soil, the lack of noticeable change of concentration of deltamethrin following flow-interruption is indicative of the lack of nonequilibrium conditions where chemical and/or physical reactions for deltamethrin behavior is dominant. In contrast, for Vacherie and Mhoon soils, an increase in concentration (about 0.01 ppb in magnitude) due to flow-interruption was observed. Such an increase in concentration was gradual with peaks some 5-6 pore volumes following interruption. This increase in concentration indicates that kinetic type reactions or nonequilibrium behavior of deltamethrin are the governing mechanisms for the release of deltamethrin during flow in soils. A jump in concentration due to flow-interruption was observed for other chemicals where both adsorption-desorption and mobile-immobile (physical) mechanims of the time-dependent type were dominant (Brusseau et al., 1989, and Ma and Selim, 1998).

Contrary to the deltamethrin BTCs shown in Figures 4.2 - 4.4, the BTC for Sharkey soil exhibited no distinct peaks or concentration maxima (see Fig. 4.5). Rather

the concentration in the effluent exhibited a gradual increase with no apparent decrease with time or pore volume. In fact, after some 20 pore volumes, the concentration remained about 0.02 ppm. It is not clear whether such retardation of deltamethrin mobility in this montmorillinitic soil, is due to strong retention reaction and/or a measure of the slow release of that retained in reversible phases. It is important to point out that, in the Sharkey soil column, the influence of flow interruption was less noticeable compared to that observed for Vacherie and Mhoon soils. This is clearly indicative of slow release reactions of deltamethrin for the Sharkey soil column.

The transport of applied deltamethrin in the reference sand column is shown in Fig. 4.6. Here the early arrival and high concentration in the effluent solution is indication of rapid mobility in our reference material in comparison to the four soil columns. Furthermore, the BTC shows a narrow peak with sharp adsorption (right) and release (left) fronts of the BTCs. The continued slow deltamethrin release in the out coming solution is clearly illustrated by the decrease in concentration from 0.01 ppm after 10 pore volumes to less than 0.005 ppm after more than 60 pore volumes. These concentrations are lower than those observed for the soil columns (Figs. 4.2 – 4.5). In addition, an increase in concentration resulting form flow-interruption was observed for our reference material. Such an increase in concentration was not gradual with a distinct peak some 5 pore volumes following flow-interruption and illustrates the nonequilibrium release mechanism of deltamethrin during water flow in the reference material.
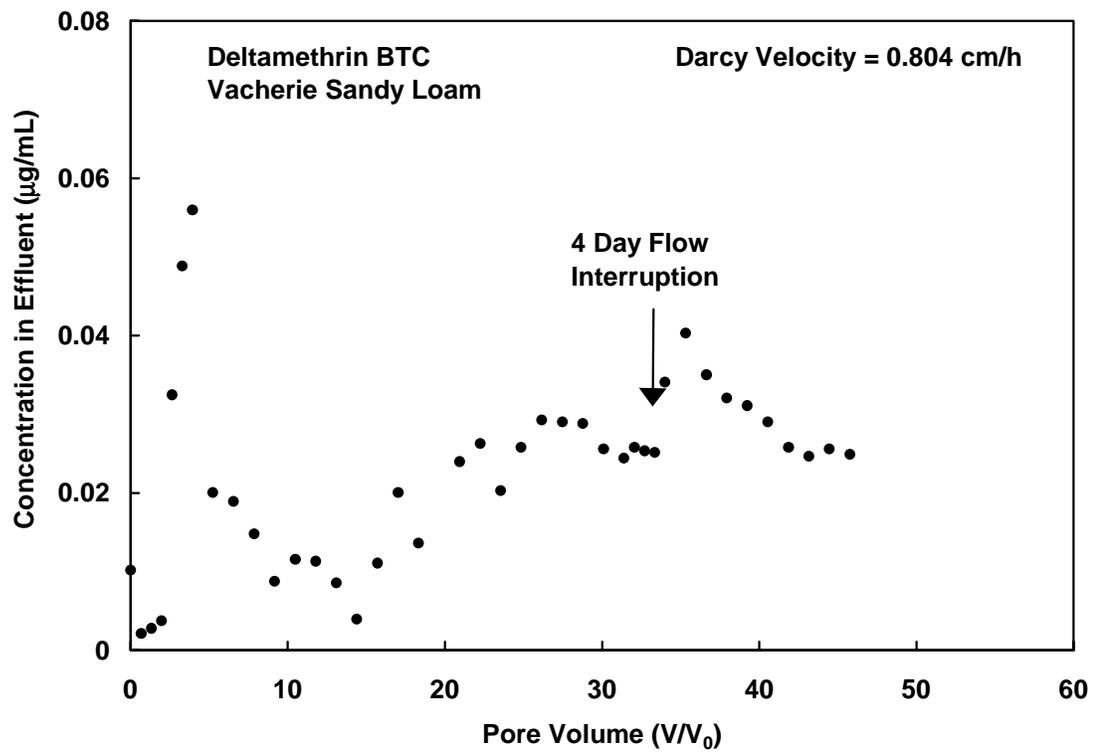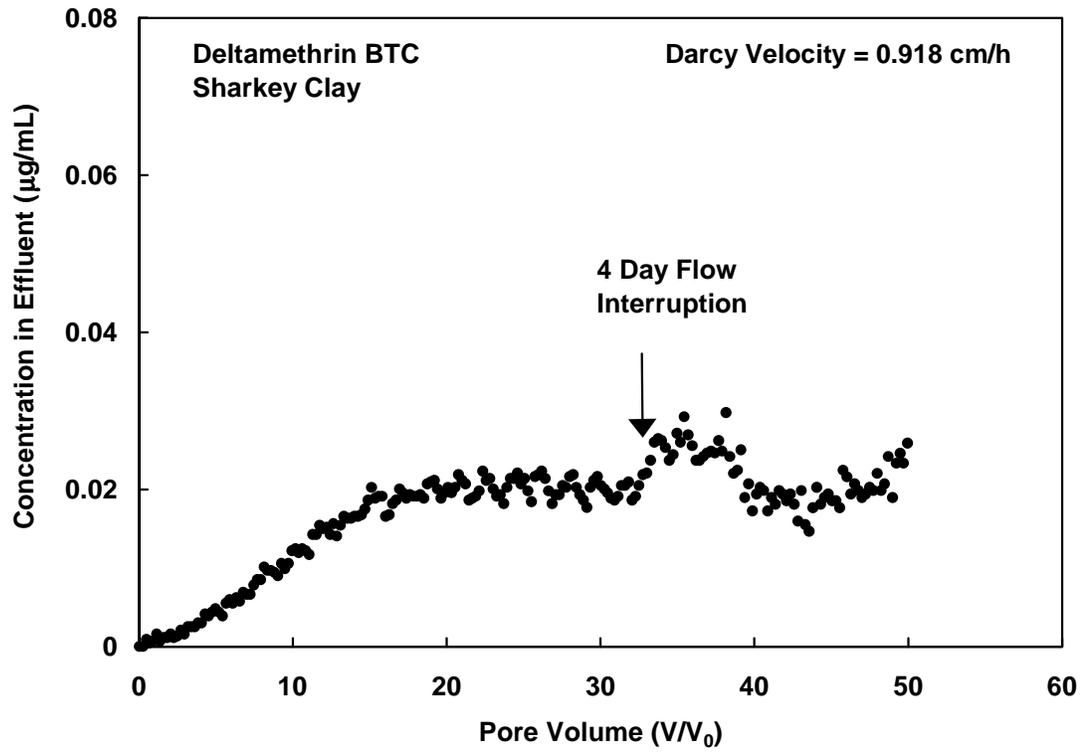
Figure 4.5 Deltamethrin breakthrough curve through Sharkey soil column with flow interruption. Column length = 10 cm. Deltamethrin was sprayed on the surface of soil before leaching with 0.005 M $CaCl_2$ solution.
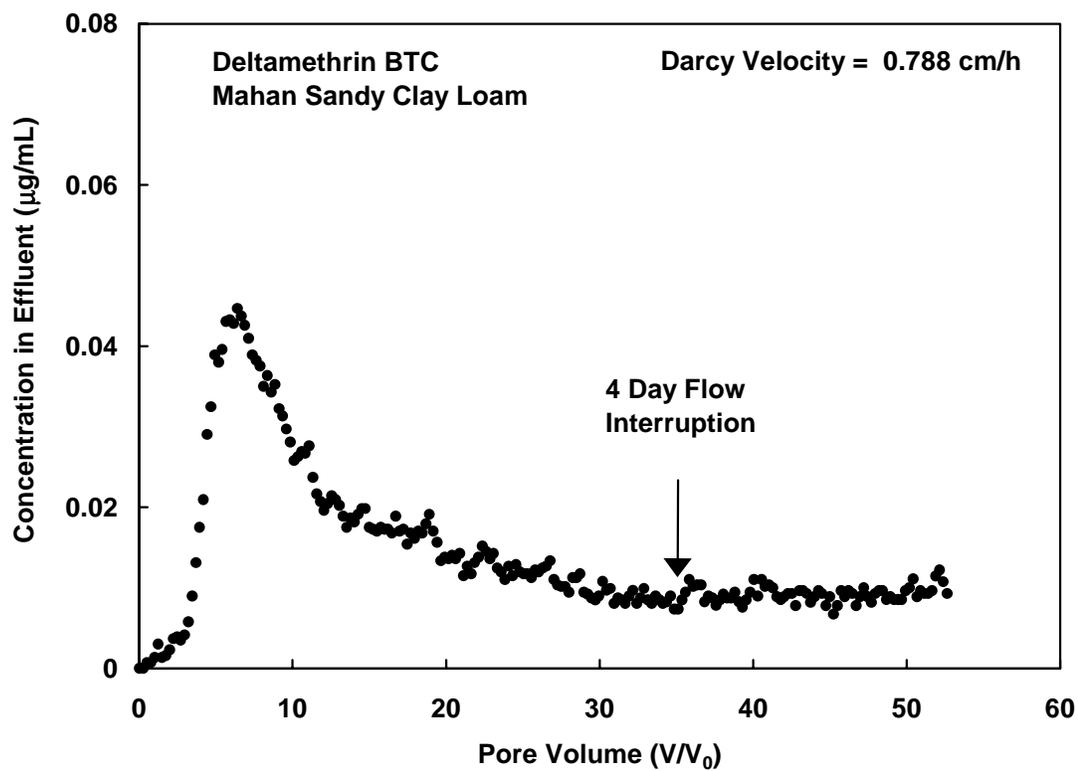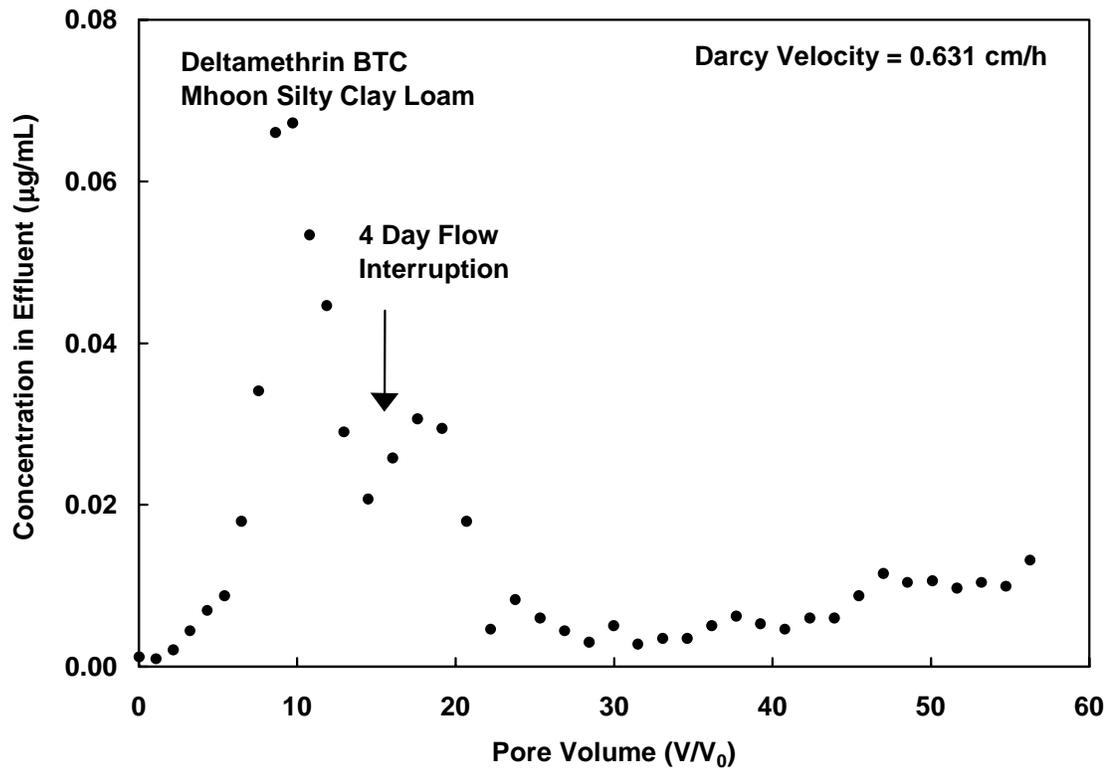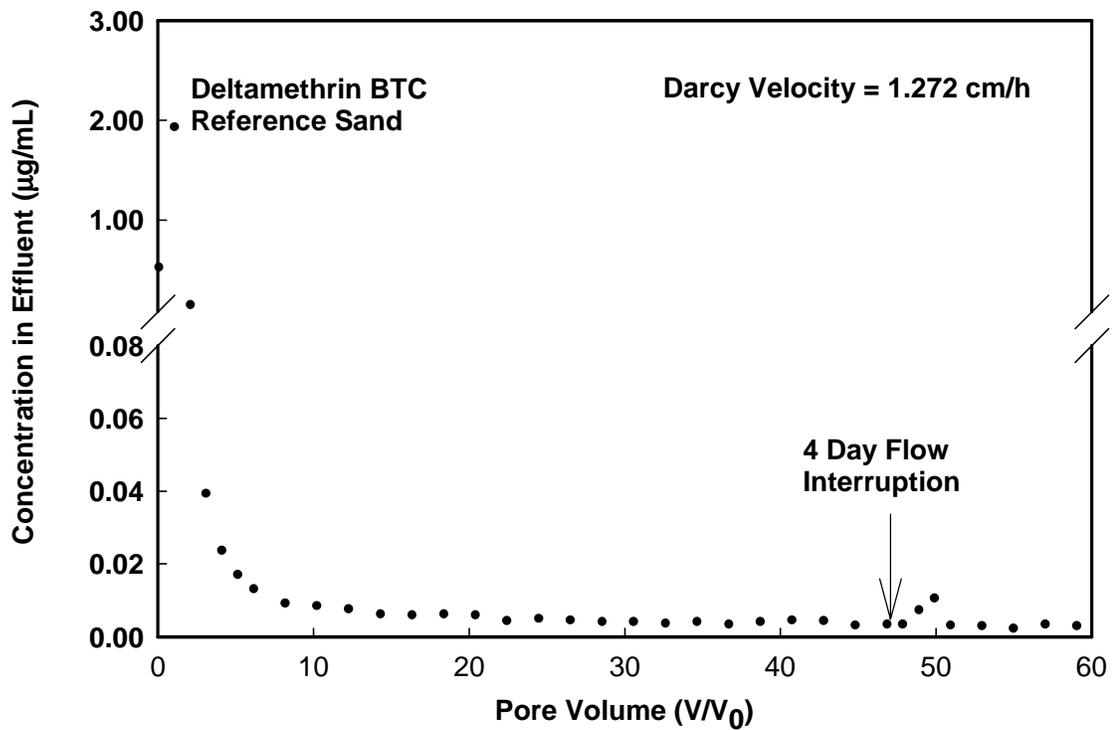
Figure 4.6 Deltamethrin breakthrough curve through reference sand column with flow interruption. Column length = 10 cm. Deltamethrin was sprayed on the surface of soil before leaching with 0.005 M CaCl$_2$ solution.

4.3.2 Deltamethrin Versus Soil Depth and Mass Balance

Movement of deltamethrin in the soil columns is presented in terms of concentration versus soil depth in Fig. 4.7. Here the amount deltamethrin are presented as a percent of the total radioactive carbon recovered by extraction from each 2-cm soil segment after termination of the flow experiment. Based on the results illustrated in Fig. 4.7 and Table 4.2, there is little movement of deltamethrin through Sharkey and Mahan soil columns after more than 50 pore volumes of leaching with 0.005 M $CaCl_2$. This 50 pore volumes of effluent which leached through each column is equivalent to more than 2500 mm rainfall. In fact, between 92 to 93% of applied ^{14}C activity remained within the 0-2 cm layer for both Sharkey and Mahan soils. Only 0.5% of ^{14}C activity was present in the subsequent two segments (2-4 cm and 4-6 cm layers) and another 0.1% within the 6-10 cm depth. Moreover, for both soil columns, the portion of deltamethrin which leached out from the 10-cm column was only 3.56% and 2.99% of the total amount applied for Sharkey and Mahan, respectively. In a similar experiment carried out by Kaufman et al. (1981), only one pore volume of water was used to leach out applied ^{14}C-deltamethrin. Their results indicated that some 96-97% of ^{14}C activity remained in the zone of application in the soil column. No radioactivity was detected in the collected leachate from the soil columns. This extremely low mobility of deltamethrin in soils can be regarded as environmentally safe since it is not susceptible to leaching from the soil.

Less deltamethrin was extracted from the Vacherie and reference sand columns than other columns (see Figure 4.7). This maybe that the higher amounts of deltamethrin were leached out; 4.5 and 8.7% for the Vacherie soil and the reference

% of Deltamethrin Leached to Depth Indicated
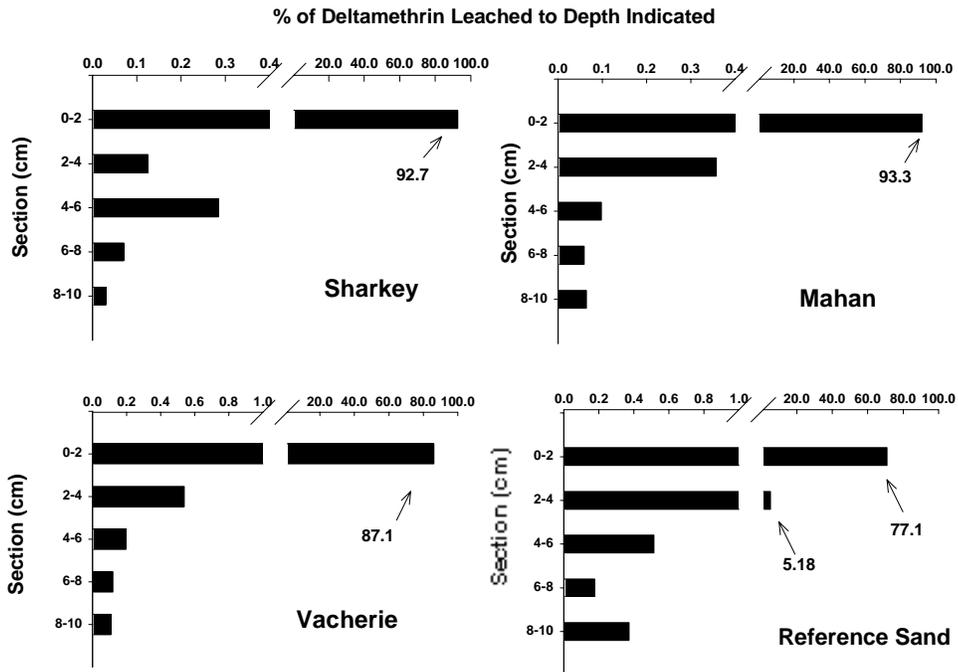
Figure 4.7: The percentage of deltamethrin extracted as against to the total input from different depth of soil column using three steps of methanol extraction

Table 4.2: Deltamethrin release and movement in soil columns

Soil	Mahan Sand Loam	Sharkey Clay	Vacherie Silty Loam	Reference Sand
Total applied (μg)	4010	4010	4010	4010
Cumulative leached (μg)	119.8	142.9	180.5	351.2
% Leached	2.99	3.56	4.50	8.76
Amount Extracted (μg) Depth:				
0 - 2 cm	3719	3694	3455	2842
2 - 4 cm	5.00	14.36	21.55	207.7
4 - 6 cm	11.38	3.93	7.85	20.64
6 - 8 cm	2.82	2.37	4.76	7.06
8 - 10 cm	1.21	2.57	4.33	14.94
Total Extracted	3739	3717	3493	3092
% Extracted	93.25	92.69	87.11	77.11
% Recovery	96.24	96.23	91.61	85.88

sand material, respectively. Specifically, for the Vacherie column, 86% of radioactivity was extracted from the 0-2 cm soil layer, with only some 1% extracted from all other layers. For the reference material (acid-washed sand), 71% of radioactivity was extracted from the 0-2 cm layer, 5% from 2-4 cm layer and 2% from all the other layers. The apparent mobility of deltamethrin in Vacherie soil is possibly due to the effect of facilitated transport by dissolved organic carbon (DOC), and high pH value for this soil. Several studies suggested that DOC was responsible for the enhanced solubility of pesticides in the soil solution (Chiou et al., 1986; 1987; Gao et al., 1998; Stevenson, 1972). It was recently reported by Huang and Lee (2001) that due to the strong affinity of dissolved organic matter (DOM), sorption of chlorpyrifos (Dursban) by soils was reduced and thus potential mobility was enhanced. Chlorpyrifos is a widely used insecticide. The relatively high mobility of deltamethrin in the sand column is due to the low retention capacity of this reference material as well as its high permeability.

Since measured radioactivity in the effluent and that extracted from soil segment versus depth represents the sum of the parent deltamethrin and its metabolites, deltamethrin degradation during our experiments was perhaps extremely low. This finding is based on the immobile nature of deltamethrin in our soil columns. The study of Kaufman et al. (1981) reported that deltamethrin degradation products were more mobile in soils than the parent deltamethrin. We should also point out that deltamethrin was not fully recovered from all the columns after three extraction steps with pure methanol. Nevertheless, mass balance or recovery of deltamethrin ranged between 86% to 96% of that applied.

4.3.3 Miscible Displacement - Sand Column

In Figure 4.8, we present a BTC for deltamethrin based on the traditional miscible displacement methods where a pulse of ^{14}C -labeled deltamethrin (in solution) was applied to the acid-washed sand column. The BTC results exhibited a sharp sorption front (left hand side) around 2 pore volumes with a peak concentration or a plateau after 5 pore volumes. This plateau appears to be closely associated with the size of the input pulse (21.8 pore volumes) of the applied deltamethrin. Average peak concentrations ranged from 0.045 to 0.052 µg/mL or a relative concentration (C/C$_o$) of 0.25 where C$_o$ is the concentration in the pulse solution (0.204 µg/mL).

The release or desorption front (right hand side) of the deltamethrin BTC of Figure 4.8 was more gradual than that for the adsorption side. This gradual desorption front was followed by a continued slow release as indicated by the excessive tailing during leaching for several pore volumes. In fact, deltamethrin concentration in the effluent was almost constant during 50 pore volumes of continuous leaching. This excessive tailing is indicative of slow (or kinetically-controlled) release of the applied deltamethrin. During this slow release, deltamethrin concentration in the effluent was approximately 0.005 µg mL^{-1}, representing a relative concentration (C/C$_o$) between 0.02 to 0.03 of that applied. The extent of retention of deltamethrin by the sand column is exemplified by a mean breakthrough time (t$_m$) of 234.4 h compared with that for a tritium pulse of 16.61 h (not shown). Furthermore, the magnitude of the second central moment of (σ^2) 38691 h^2 is indicative of a pronounced spreading of the deltamethrin BTC.

The retardation of the BTC is indicative of strong retention reaction of deltamethrin by the reference sand. These our column transport experiments results are consistent with adsorption results from batch experiments for this reference material (Chapter 3). A K_d value of 15 mL/g for adsorption of the reference sand was observed. The reference sand contained 19% silt-size material, which may be responsible for the observed retention. The extent of retention by the reference sand was not surprising, however. Evidence of adsorption for several chemicals (e.g., carbon tetrachloride, tetrachloroethylene, benzene, toluene, xylene, atrazine and 2,4-D) by sand material and different mineral surfaces has been reported by Goltz and Roberts (1986), Shahalam et al. (1997), and Clausen et al. (2001).

4.3.4   Multireaction and Transport Model (MRTM)

The simulation data represented by the solid curve shown in Fig. 4.8, is our attempt to describe the BTC from the sand column where a deltamethrin input pulse solution was introduced.   The model used was the multireaction and transport model (MRTM) which is described in detail by Ma and Selim (1998). This multipurpose model accounts for several concurrent and consecutive type retention reactions as well as transport of reactive solutes in soils. These reactions include equilibrium and kinetic mechanisms of the reversible and irreversible types. The model version chosen in this analysis was presented by equations 2.2 – 2.4, where:

$$S = S_e + S_k + S_i \qquad\qquad [4.1]$$

Incorporation into the convection-dispersion transport equation yields,

$$\Theta \, \frac{\partial C}{\partial t} \; + \; \rho \, \frac{\partial S}{\partial t} \;\; = \;\; \theta D \, \frac{\partial^2 C}{\partial z^2} \; - \; v \, \frac{\partial C}{\partial z} \qquad\qquad [4.2]$$

where D is the dispersion coefficient (cm^2/h), ν (=q/θ) is the average pore-water velocity (cm/h), where q is Darcy's flux density (cm/h). A value for D of 1.99 cm^2 h^{-1}, which was obtained from our tritium pulse data (not shown), was used in our simulation. In this study, we used n = 0.92 which was independently derived from the average Freundlich parameter (N) values for different reaction times from batch adsorption (Table 3.3).

To obtain the simulation shown in Figure 4.8, we utilized the multireaction model along with a nonlinear least-squares optimization scheme which provided best-fit of the model to the experimental data. We assumed that if the model is incapable of describing measured results BTCs, the model is an inaccurate representation of the retention mechanisms. For the curve shown in Figure 4.8, the goodness of fit as measured by r^2 was 0.979. Parameter estimates which provided the best-fit of the BTC were 0.158, 0.000762 and 0.00068 h^{-1} for k_1, k_2, and k_i, respectively. The standard errors for k_1, k_2, and k_i were 0.0028, 0.00013 and 0.00038 h^{-1}, respectively. Estimate for the equilibrium rate coefficient K_e was 0.659, with a standard error of 0.013 (dimensionless). According to our simulated curve in Figure 4.8, the total amount of deltamethrin leached in the effluent solution from the soil column was 40.4% of that applied. This amount leached in the effluent compares well with our experimental measurements as obtained from the area under the BTC curve (31.3%).

Based on model calculations, after 80 pore volumes, the amounts of deltamethrin retained by the soil in the S_k and S_i forms were approximately equal. Moreover, the sum of S_k and S_i represent in excess of 97% of the total deltamethrin retained with less than 3% in the equilibrium form (S_e). Both S_k and S_i forms may be regarded as strongly retained
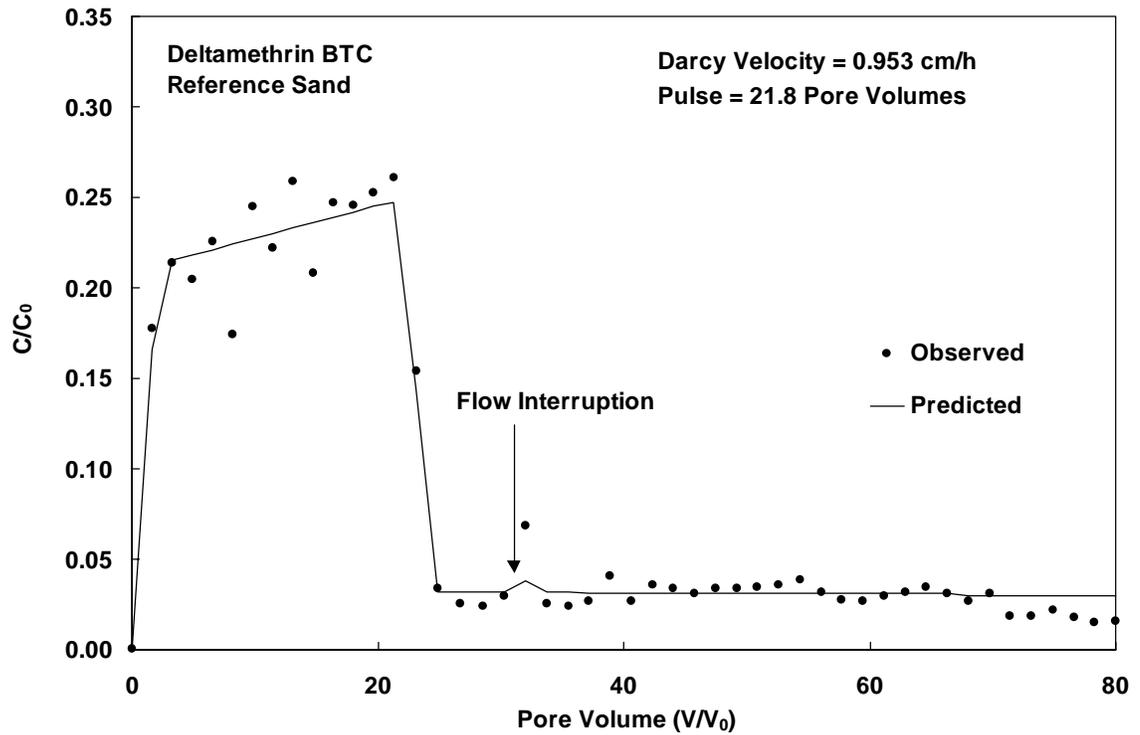
Figure 4.8 Deltamethrin breakthrough curve through reference sand column with flow interruption. Column length = 10 cm. Deltamethrin was introduced with 21.8 pore volumes of deltamethrin solution with concentration of 0.204 µg/mL. The curve was predicted using a Multireaction and transport model (MRTM).

where S_i is assumed to be fully irreversible and S_k is slowly reversible. In order for the

kinetic phase S_k to be considered as a slowly reversible or strongly held, it is a

prerequisite that the associated forward rate coefficient k_1 must be much greater than the

backward rate k_2, as was the case. As a result, it can be assumed that the S_k and S_i forms

are best regarded as strongly retained which is consistent with our measurements. Based

on these calculations, kinetic behavior of the irreversible and/or slowly reversible are the

dominant mechanisms for the retention of deltamethrin in our reference sand.

4.3.5   Principal Component Analysis on Variables

The principal component analysis technique has been widely used in soil

classification (Okuda, et al., 1995; Lin, et al., 1999), soil quality assessment (Wander

and Bollero, 1999), and water and chemical transport (Granovsky, et al., 1993).

Comparing difference of deltamethrin release among soils is important to ascertain the

effect of soil properties on deltamethrin release from soils. In this study, principal

component analysis technique was used to examine the variance structure of

deltamethrin mobility data consisted with 10 variables. The eigenvectors that relate the

PCs to the original variables, along with the proportion of total variance accounted for

by each of the PCs are given in Table 4.3. Principal component scores for each soil are

listed in Table 4.4, and the effect of soils with different properties on the first and

second principal components of the data set are presented in Figure 4.9. The

eigenvalues indicate that there were four significant PCs that together explained 100%

of the variance, implying that the original set of variables contain redundant

information. The first, second, third and fourth PCs explained 55.8%, 25.1%, 14.9% and

5% of the total variance, respectively. Since all the variance can be explained by the

first four principal components, interpretation of the remained PCs is not useful, thus are not listed in Table 4.3.

The coefficients of the first principal component show a positive relationship of final deltamethrin concentration in effluent (FinalC) and pore volumes corresponding to the deltamethrin peak concentration (peakPV) with those variables that are related to soil structure, including organic matter content, clay content, and moisture content of soil column at 0.33 bar suction, mean breakthrough time of tritium BTC, and negatively related with the deltamethrin recovery after 30 pore volumes of leaching (pv30) and deltamethrin concentration at peak (peakC). Because of the negative correlation between those soil structure variables with soil bulk density, the relationship of FinalC, peakPV, pv30 and peakC with bulk density is just the opposite. pH does not seem to be an important factor for principal component one. A high value of FinalC and a delay of the peak concentration of the release curve can be considered as the high potential of long term deltamethrin release from soils. The coefficient of PC1 provides the information that those soils with high organic matter and clay content, and high content of relatively immobile water (theta033) have high potential of long term deltamethrin release. On the other hand, a high peak concentration and a high recovery in the early stage of leaching representing a high potential of short term leaching of deltamethrin from soils. The coefficient of PC1 indicates that sandy soil with low organic matter content and with low relatively immobile water content has high potential for short term deltamethrin release.

Principal component 2 is more dominated by soil pH and organic matter content. A high soil pH is also an indication of high potential of long term deltamethrin release,
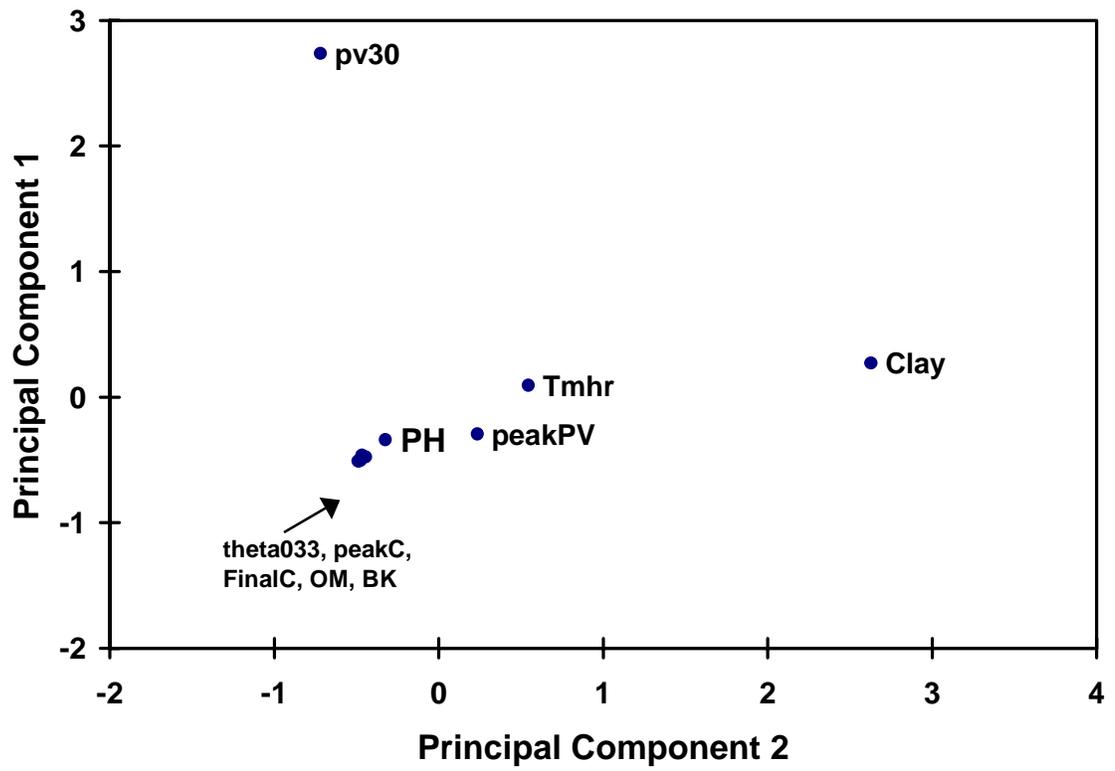
Figure 4.9: The first and second principal component scores for each of soil properties

Table 4.3: Coefficient for the principal components (PCs) of the ten variables

Variable	Principal component (% variance explained)			
	PC1 (55.8%)	PC2 (25.1%)	PC3 (14.9%)	PC4 (5%)
OM	0.285	0.302	0.458	-.217
Clay	0.326	-.400	0.00076	0.103
BK	-.390	-.173	-.117	0.337
PH	-.025	0.623	-.118	0.070
Theta033	0.312	0.249	0.396	0.403
FinalC	0.278	0.303	-.389	0.500
Pv30	-.274	-.008	0.636	0.160
Tmhr	0.372	-.281	0.110	-.147
PeakPV	0.348	-.298	0.038	0.443
PeakC	-.388	-.095	0.193	0.410

Table 4.4: Principal component scores for each soil

Soil	Prin1	Prin2	Prin3	Prin4
Mahan	-0.0761	-0.589	-0.788	-1.492
Mhoon	0.668	0.195	1.594	-0.417
Sharkey	0.936	-0.922	-0.491	1.111
Vacherie	0.104	1.633	-0.681	0.246
Reference Sand	-1.631	-0.317	0.365	0.552

but this relationship is dependent on organic matter content. This may be that the ability of organic matter to retain deltamethrin is pH dependent. PC2 is also a negative function of clay, mean breakthrough time of tritium BTC and pore volumes of peaks at release curve. The coefficient of PC2 indicates that PC2 is more related to soil chemical properties rather than to physical properties of soil column. The result is also presented by the principal component scores for each soil (Figure 4.9). Principal components 3 and 4 seem to indicate the relationship of soil column physical properties with deltamethrin release, and the effect of organic matter content on this relationship. However, this interpretation is not obvious. Since only a small portion of variance was explained by PC3 and PC4, the information provided by the coefficient is not as meaningful as those provided by PC1 and PC2.

4.3.6   Principal Component Analysis on Soils

In order to examine the relationship among variables, principal component analysis using soil as factors was performed. Only two principal components were significant, and 99.7% of variance were explained by PC1 and PC2. Almost equal importance of each individual soil for principal component 1 was reflected by the similar values of the coefficients (Table 4.5). PC2 is positively and greatly contributed by Sharkey soil, and negatively contributed by Vacherie and sand, indicating the importance of clay content and soil pH to PC2. The principal component scores for each of the variables were listed in Table 4.6, and the scores of PC1 versus PC2 are potted in Figure 4.10. The closer the distance between the two variables in Figure 4.10, the more similar the soils are. The results showed that if soils have similar organic matter content, pH, bulk density and relatively immobile water content, they would have similar peak
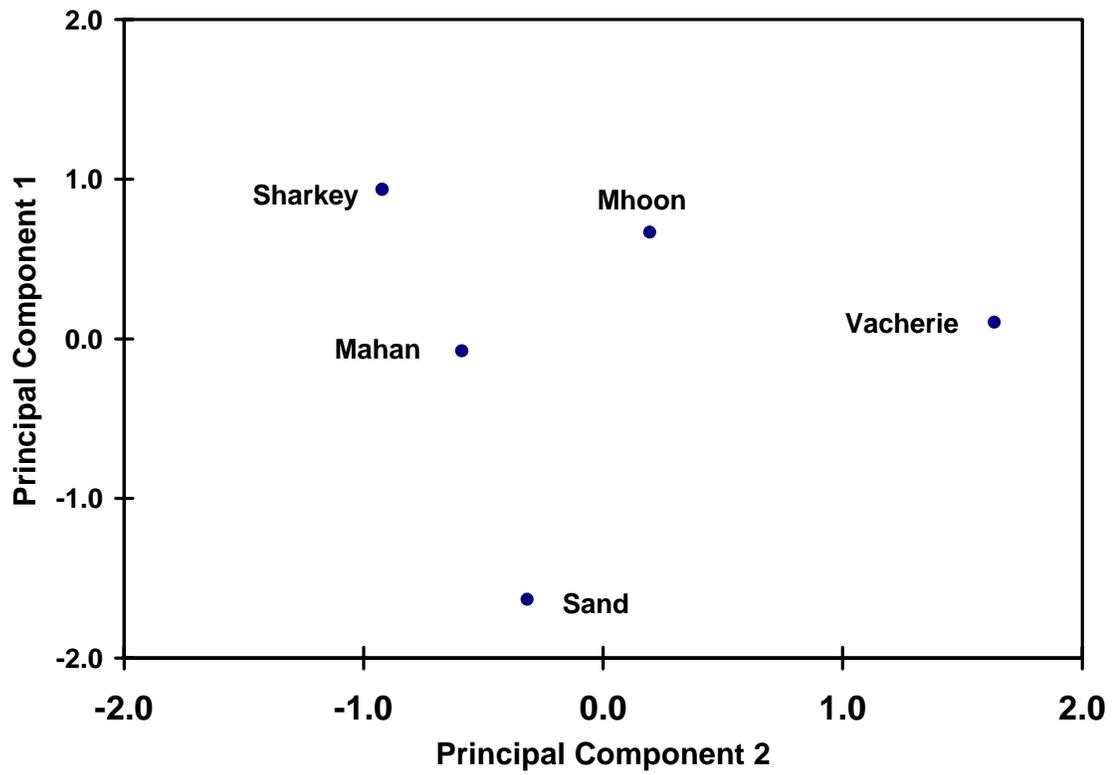
Figure 4.10: The first and second principal component scores for each soil

Table 4.5: Coefficient for the principal components (PCs) of soils

Soil	Principal component (% variance explained)	
	PC1 (91.7%)	PC2 (8.0%)
Mahan	0.463	0.194
Sharkey	0.401	0.812
Vacherie	0.455	-0.342
Sand	0.452	-0.393
Mhoon	0.463	-0.178

Table 4.6: Principal component scores for each variable

Variable	Prin1	prin2
OM	-0.465	-0.465
Clay	0.271	2.628
Bk	-0.477	-0.445
PH	-0.340	-0.325
theta033	-0.504	-0.476
Finalc	-0.511	-0.485
pv30	2.738	-0.719
Tmhr	0.0918	0.545
peakPV	-0.295	0.234
peakC	-0.508	-0.491

deltamethrin concentration, final concentration of the release curve and close pore volumes for the peaks to appear. Mean breakthrough times of tritium BTCs are also closely related with those variables, and clay content is equally important as well. However, deltamethrin recovered after 30 pore volumes of leaching and soil clay content are much more independent with those variables based on our result.

4.4   Conclusions

The results of this investigation indicated that the synthetic pyrethroid insecticide deltamethrin has extremely low mobility and strong retention in the soil columns. After leaching 50 pore volumes of 0.005 M CaCl$_2$ solution, which is equivalent to approximately 2500 mm rainfall, the amount of deltamethrin leached out from each soil column was small and ranged only from 3 to 8% of the total amount applied, and the amount varied among soils. For clay soil and loamy soil, over 90% of deltamethrin remained where it was applied. The mobility of deltamethrin can be facilitated in soils with high organic matter due to the enhanced solubility of deltamethrin by dissolved organic carbon. DOC may act as co-solvent in dissolution of deltamethrin in precipitated forms. The mobility of deltamethrin was observed for a nonacid sandy soil with pH of 7.6 and clay content of 2% (Vacherie). The use of a multireaction and transport model (MRTM) proved successful in describing the BTC from the sand column and in close agreement with measured deltamethrin results. Based on its extreme low mobility in soils, deltamethrin may be considered not susceptible to leaching from the soil profile, and thus low risk of ground water contamination.

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CHAPTER 5: FATE OF ATRAZINE IN SOIL AS AFFECTED BY SUGARCANE RESIDUE

5.1 Introduction

A recent shift of sugarcane harvesting technology from burning leaves to leaving leaves on the soil surface caused concern regarding its effect on the fate of herbicides in the soil environment. The conservation tillage system is characterized by the presence of residue cover ranged from a minimum of 30% to as high as 90% which is quite possible with no-till system (Andraski et al., 1985). The presence of a residue mulch left on the soil surface protects it from water and wind erosion and conserves soil water for crop production (Unger and Wiese, 1979). Crop residue in conservation tillage systems plays an important role in the environmental dispersion of agricultural chemicals applied in the field. Recycled crop residues can be a temporary storage medium for herbicides, altering patterns of chemical dispersion in conservation tillage when compared to conventional practices (Dao, 1991). The effect of surface crop residues on interception, subsequent wash-off, and movement of herbicides through soil are major concerns associated with no-tillage practice.

Few studies quantifying of pesticide concentration on the crop residues have been made as it often was assumed that all the chemical eventually would leach and be recovered in the soil. However, a previous year's crop residues may intercept chemical spray and thus reduce the efficacy of soil - applied herbicide (Banks and Robinson, 1982; Ghadiri et al., 1984; Crutchfield et al., 1985). Results regarding the effect of crop residues on herbicide fate in fields are varied from different crop residues and different experiments (Boyd, et al, 1990; Dao, 1991; Isensee and Sadeghi, 1994). In laboratory and field studies, wheat straw exhibited a strong affinity for metribuzin and its S-ethyl

analog. The retention capacity was associated with the lignin fraction of the residues

(Dao, 1991). It was reported that addition of straw matter to the soil elevated organic C

concentration in the near-surface zone of no-till soils, which resulted in a two- to five-

fold increase in metribuzin retention (Dao, 1995). Gaston et al. (2001) observed a

higher sorption of fluometuron by soils with no-till and crop cover than soils with

conventional till, which was consistent with the higher organic C content in no-till soils.

In a Michigan study, corn (*Zea mays L.*) residues showed a sorptive capacity for

benzene, ethylbenzene, and 1,2,3-trichlorobenezene that was 35 to 60 times greater than

that of the surface soil (Boyd, et al, 1990). The sorptive capabilities of corn residues and

soil organic matter for nonionic organic compounds were nearly identical as indicated

by the similarity of the corresponding K_{oc} values which are the K_d values normalized by

percentage of organic carbon content (Boyd et al., 1990). Thus, they concluded that it

may be unnecessary to distinguish the organic carbon in crop residue from humus

carbon in soil when predicting nonionic organic compound sorption coefficients.

However, crop residues were ground in this experiment which resulted in a great

difference of the residue specific surface area compared with the status of residues in

the field.

The effect of crop residue on the transport behavior of herbicides was also

reported. A column study conducted by Dao (1991) indicated small differences in the

affinity of ground wheat straw for metribuzin in contrast to batch sorption due to the

chemical nonequilibrium conditions in the sorption-desorption processes that existed in

leaching column experiments. The strong affinity of wheat straw residue for the

herbicides also resulted in asymmetrical BTCs for all combinations of straw ages

(straws collected at different time after harvesting) and chemicals (metribuzin or its S-ethyl analog). The asymmetry was also apparent at a lower pore-water velocity of 9.5 cm h^{-1}. Green et al.(1995) studied the effect of corn residue, placed on the surface of undisturbed soil columns, on the transport of atrazine and Cl^{-} at different saturated hydraulic conductivity (K$_{sat}$). They observed that atrazine recoveries from columns are affected by the hydraulic conductivity (K$_{sat}$). For high and medium K$_{sat}$, more atrazine was recovered from the columns with 100% residue cover than with the zero-residue columns, but this was not apparent for the low K$_{sat}$ columns, indicating that the existence of mulch on the soil surface facilitated the atrazine mobility when the K$_{sat}$ was high.

The weed control efficacy of herbicides can also be affected by the presence of residue mulch material and is dependent upon the mechanism of action of the herbicides (i.e., soil-activated, foliarly absorbed systemic, or contact). Preemergence and postemergence herbicides that are strictly soil-activated, must reach the soil surface or move into a shallow soil layer in order to inhibit germinated weed seeds or be taken up by actively growing weed seedlings. A change in application method may be necessary to penetrate the mulch and reach the soil surface to overcome the interference by the crop residue mulch . On the other hand, foliar sprays of contact or systemic postemergence herbicides will retain their chemical efficacy regardless of the presence of the residue mulch (Dao, 1987). The mulch intercepts excess surface chemical spray which would otherwise be sorbed and dispersed in the soil upon application. In addition, there is an added benefit of continued slow-release and increased efficiency of these herbicides leading to a potential reduction in postemergence chemical inputs as

gradual desorption from the straw mulch may provide extended control of second flushes of weed emergence and growth (Dao, 1991). Dao (1991) also reported that the retention capacity of the near surface zone could be managed to attenuate metribuzin in the field to achieve optimal herbicidal functions and dissipation.

Atrazine is a triazine family herbicide used worldwide since 1952 to control annual weeds in corn and sugarcane, and it is the most heavily used in all herbicides. Subsequently to this extensive use, reports on groundwater and river contamination have been documented (Gish et al., 1991; Southwick et al., 1992). Atrazine is a valuable and necessary component for weed control programs in Louisiana sugarcane production (Gianessi and Puffer, 1991). It is estimated that of the acres planted to sugarcane and corn, more than half receive atrazine as part of the annual crop cycle. Such application practices combined with the high annual rainfall of southern Louisiana could result in significant amounts of herbicides reaching non-target sites in the environment (Ma and Selim, 1996).

Abundant data have been published concerning the adsorption of atrazine on humic acids (Kalouskava, 1987, 1989; Piccolo et al., 1992; Senesi et al., 1995), clays (Laird et al., 1992) and oxyhydroxides (Laired et al., 1994). However, atrazine adsorption data for crop residues are sparse. In addition, the desorption of atrazine from these components is poorly documented (Piccolo et al., 1992; Laired et al., 1994; Moreau and Mouvet, 1998), in spite of the fact that desorption and adsorption are of equal importance in determining the fate of pesticides in soils and aquifers (Moreau and Mouvet, 1997 and 1998). Human-induced changes in soil characteristics, such as increasing in pH, total organic C content, and dissolved organic C, have been related to

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agricultural practices, which may result in the change of the behavior of herbicides in soils.

Studies of best management practices have shown advantages of no-tillage systems in soil and water conservation. However, a research of literature reveals that no studies have been carried out regarding the adsorption-desorption kinetics of herbicides by sugarcane residue. In fact, this information is essential for the understanding and the implementation of corrective actions needed to reduce herbicide off-target movement from sugarcane fields and for predicting the fate of herbicides applied in field (Ma and Selim, 1996). The objectives of this study were: 1) To study and describe the adsorption-desorption characteristic of atrazine by sugarcane mulch residue; 2) To quantify the hysteretic behavior of atrazine adsorption-desorption by sugarcane mulch residue; 3) To investigate the effect of the presence of sugarcane mulch residue on the transport of atrazine in soil columns; 4) To test the applicability of the multireaction and transport model (MRTM) on predicting atrazine transport through soil columns with mulch on the top of soils.

5.2 Materials and Methods

5.2.1 Sugarcane Residue Preparation

A bulk sample of sugarcane residue from first stubble (sugarcane variety: LCP85-384) was collected from a private farm south of Baton Rouge on April 16, 1999 prior to application of herbicides. The amount of mulch residue cover in the field was approximately 4.5 ton/acre and 5 cm thick after harvesting. The site was chosen to evaluate several best management practices (BMPs) including mulch management practices to determine their effect on herbicide retention and runoff losses. The residue

was left in the field as mulch material before it was collected, which represented the condition at the time of herbicide being applied. The residue was dried at 55^OC for 24 hours and then cut into one cm sections (in length) and stored in a closed container at 5^OC prior to the experiments.

5.2.2 Adsorption Capacity

Atrazine adsorption capacity of sugarcane mulch residue was quantified using the batch technique by repeatedly replacing the supernatants with atrazine solutions having initial input concentration(C_i) values of 12.02 and 29.30 µg/mL. All applied solutions were spiked with ^{14}C-labeled atrazine. One gram of dried sugarcane residue and 30 mL of atrazine solution were mixed in a 40-mL Teflon tube. Five replications were used for each atrazine concentration. After two hours of shaking, the mixtures were centrifuged and the solutions were replaced by 30 mL of their corresponding initial input solutions. The replacements were conducted at the reaction time of 8, 24, 48, 96, 192, 288 and 504 hours. Another set of experiments was conducted in a similar way except without replacement of the supernatants for comparison purposes.

5.2.3 Adsorption-Desorption:

Atrazine adsorption-desorption by sugarcane mulch residue was carried out using a batch equilibration technique (Ma and Selim, 1994a). Radioactive atrazine was used as a tracer to monitor the extent of retention. Six ^{14}C-atrazine spiked solutions having initial concentrations (C_i) of 3.37, 6.36, 12.34, 18.22, 24.30 and 30.16 µg mL^{-1} in 0.005 M $CaCl_2$ solution were used. Three replicates were used for each initial concentration. Adsorption was initiated by mixing 1 g of dried and cut sugarcane residue with 30 mL of the various atrazine concentration solutions in a 40-mL Teflon

centrifuge tube. The mixtures were kept shaking and centrifuged at $500 \times g$ for 10 minutes for each specific reaction times before sampling. A 0.5-mL aliquot was sampled from the supernatant at reaction times of 2, 8, 24, 48, 96, 192, 288 and 504 hours. The mixtures were returned to the shaker after each sampling. The collected samples were analyzed using Liquid Scintillation Analyzer (Packard Instrument Company, model TRI-CARB 2100TR) by mixing the 0.5-mL aliquot with 5 mL Ultima-Gold-LS cocktail. The amounts of atrazine that were adsorbed by sugarcane residue were calculated from the change of atrazine concentration in solutions. Desorption commenced immediately after the last adsorption time step (504 hour). Each desorption step was conducted by replacing the supernatant with atrazine free 0.005 M $CaCl_2$ solution and shaking for 24 hours. Six desorption steps were carried out with a total desorption time of six days. Following the sixth step, one further extraction using pure methanol was carried out. Atrazine in the supernatant solution during desorption was also analyzed using liquid scintillation (LS) and the amount of atrazine desorbed from each step was calculated based on the change of atrazine concentration in solution (before and after desorption).

5.2.4 Transport Experiment

Three column experiments were performed out using miscible displacement technique to obtain atrazine breakthrough curves (BTCs). Plexiglass columns (15 cm in length and 6.4 cm i.d.) were uniformly packed with different combinations of mulch layer and soil layer. The two surface soils used in this experiment were: Commerce silt loam (fine-silty, mixed, nonacid, thermic Aeric Fluvaquent) and Sharkey clay (very

Table-5.1: Soil properties and experimental conditions of individual columns of the miscible displacement experiments

Column ID	Experiment Matrix	Bulk Density (ρ)	Water Content (θ)	Pore Volume (V/Vo)	Darcy Velocity (q)	Dispersion Coefficient (D)
		g/cm^3	cm^3/cm^3	cm^3	cm/h	cm^2/h
I	Mixture[1]	1.57	0.419	201.8	0.366	0.448
II	5 cm Mixture	1.57	0.419	67.3	0.402	65.45
	10 cm Sharkey	1.375	0.481	154.7		
III	5 cm Mixture	1.57	0.419	67.3	0.412	0.443
	10 cm Commerce	1.387	0.477	153.2		

[1]: Mixture of reference sand and sugarcane mulch residue, the amount and thickness are equivalent to field, sand is used to support the mulch in order to achieve steady flow during transport experiment.

fine, montmorillonitic nonacid, thermic Vertic Haplaquept), from Iberville Parish,

Louisiana. Selected physical and chemical properties for the Commerce and Sharkey

are presented in Table 2.1. Experimental and transport parameters for each of the

columns are listed in Table 5.1. The amount of sugarcane mulch residue used for the

columns II-III was 2 g spread over an area of 32.15 cm^2, which is approximate to the

field amount of 4.5 ton/acre and 5 cm in thickness. The 2g sugarcane mulch residue was

uniformly mixed with 250g reference sand to form a depth of 5-cm, which is called the

mixture layer in Table 5.1. The mixture layer was prepared in such a way that the

amount and thickness of sugarcane mulch residue is equivalent to those in the field,

while reference sand was used to mix with residue material to assure the uniformity of

the transport process. The 5-cm mixture layer was placed on top of 10 cm layer soils:

Sharkey for column II and Commerce for column III.

Water saturation in each column was achieved by slowly introducing 0.005 M

$CaCl_2$ solution where upward flow was maintained and a constant flux was controlled

by a piston pump (FMI lab pump, Model QG 6, Fluid Metering Inc., Oyster Bay, NY).

After saturation, a tritium breakthrough curve was obtained by introducing

approximately one pore volume of ^{3}H-labeled 0.005 M $CaCl_2$ background solution and

then leached with about three pore volumes of tritium free 0.005 M $CaCl_2$ solution. The

effluent samples were collected using an ISCO fraction collector. Tritium BTCs were

used to determine the hydrodynamic dispersion coefficient (D). Following the tritium

BTCs, a pulse of atrazine solution, approximately 5 pore volumes for column I and 10

pore volumes for all the other columns, was introduced and then leached with 0.005 M

$CaCl_2$ background solution. A flow interruption was carried out during leaching at

about 20 pore volumes. The effluent samples were analyzed using Liquid Scintillation (LS) by mixing 0.5 mL sample with 5 mL cocktail. The concentration was determined by back calculating to a standard with known concentration of atrazine.

5.2.5   Data Analysis:

The isotherms of atrazine adsorption and desorption by sugarcane mulch residue were used to estimate Freundlich parameters, i.e., distribution coefficient K_f and nonlinear dimensionless parameter N. PROC NLIN in SAS version 8 (SAS Institute Inc., 1999) was used to carry out the nonlinear regression of the Freundlich equation. Means and 95% confidence intervals were computed for regression coefficients derived from the Freundlich equation. Desorption isotherm coefficients were also estimated using nonlinear regression. The kinetic retention of atrazine was described using a kinetic multireaction model where the system of equations (2)-(4) was solved by the finite difference (explicit-implicit) iteration method (Selim, et al., 1990), and model parameters were estimated based on nonlinear least-square optimization (van Genuchten, 1981). Atrazine breakthrough curves for each of the columns were described using multireaction and transport model. In addition, parameters of Freundlich and multireaction reaction model derived from batch kinetic experiment were used to simulate the miscible displacement experiments.

5.3   Results and Discussions

5.3.1   Adsorption Isotherm

The K_d value is a partition coefficient or distribution coefficient that represents the extent of strength of adsorption by solid materials (Ma et al., 1993; Seybold and Mersie, 1996). A quantitative comparison of the sorption of atrazine by Sharkey clay
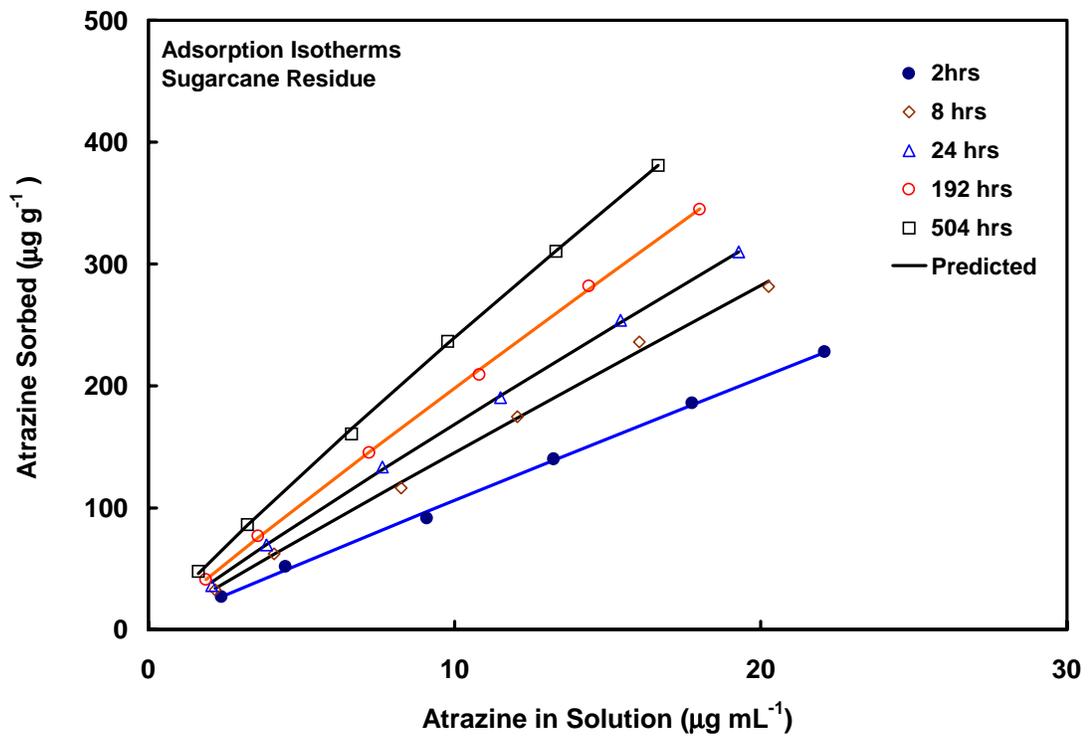
Fig.5.1: Adsorption isotherms of atrazine by sugarcane mulch residue at different reaction times. Solid lines are predictions using linear model.

Table 5.2: Estimated parameters with one standard deviation for atrazine adsorption by sugarcane mulch residue at different reaction time

Reaction Time (hour)	Freundlich Model			Linear Model	
	K_f (mL/g)	N	r^2	K_d (mL/g)	r^2
2	11.62 ± 1.42	0.961 ± 0.0429	0.996	10.40 ± 0.162	0.996
8	15.97 ± 1.126	0.959 ± 0.0255	0.999	14.27 ± 0.140	0.998
24	19.90 ± 1.078	0.928 ± 0.0200	0.999	16.40 ± 0.160	0.998
48	20.30 ± 1.04	0.939 ± 0.019	0.999	17.22 ± 0.151	0.999
96	20.75 ± 1.047	0.938 ± 0.0188	0.999	17.58 ± 0.154	0.999
192	22.66 ± 1.436	0.942 ± 0.0239	0.999	19.43 ± 0.195	0.998
288	22.34 ± 1.428	0.967 ± 0.0244	0.999	20.37 ± 0.184	0.999
504	29.48 ± 1.273	0.910 ± 0.0168	0.999	23.40 ± 0.239	0.998

and Commerce silt loam soils and sugarcane mulch residue can be made from the K_d

values estimated with the linear model ($S = K_d C$) for atrazine adsorption isotherms at

different reaction times (Fig. 5.1). The best-fit values for the distribution coefficient

(K_d) are listed in Table 5.2. The K_d values increased as the reaction time increased

(from 10.4 to 23.40 mL/g after 2 and 504 h, respectively) which is indicative of strong

kinetic behavior of atrazine adsorption by sugarcane mulch residue (Fig. 5.2). Such

values were an order of magnitude higher than that found for the Commerce silt loam

soil. This was expected since organic matter is the principal soil component affecting

the adsorption of many herbicides in the soil environment (Peter and Weber, 1985;

Pignatello and Huang, 1991). Specifically, the K_d values ranged for Commerce silty

loam from 2.095 to 2.352 cm^3/g after 24 and 384 h of reaction time, respectively

(Personal communication with Dr. Selim, unpublished data). Moreover, the K_d values

for the Commerce silty loam exhibited limited kinetic behavior of atrazine in

comparison to the sugarcane mulch residue (data not shown). The Freundlich model

(Eq. 2.1) provided an equally good description for the atrazine adsorption results by

sugarcane mulch residue (Table 5.2). However, K_d is more meaningful for comparison

purposes since K_d is unique for a specific isotherm, while the K_f values in the

Freundlich model may not be unique if N values are different for different reaction

times.

For a given organic chemical, the contribution of organic matter to the

adsorption could be measured by the distribution coefficient K_d normalized to the unit

weight of organic carbon (K_{oc}) (Pusino et al., 1994). Reported K_{oc} values for atrazine

differed based on the different soil properties, such as soil organic matter content and
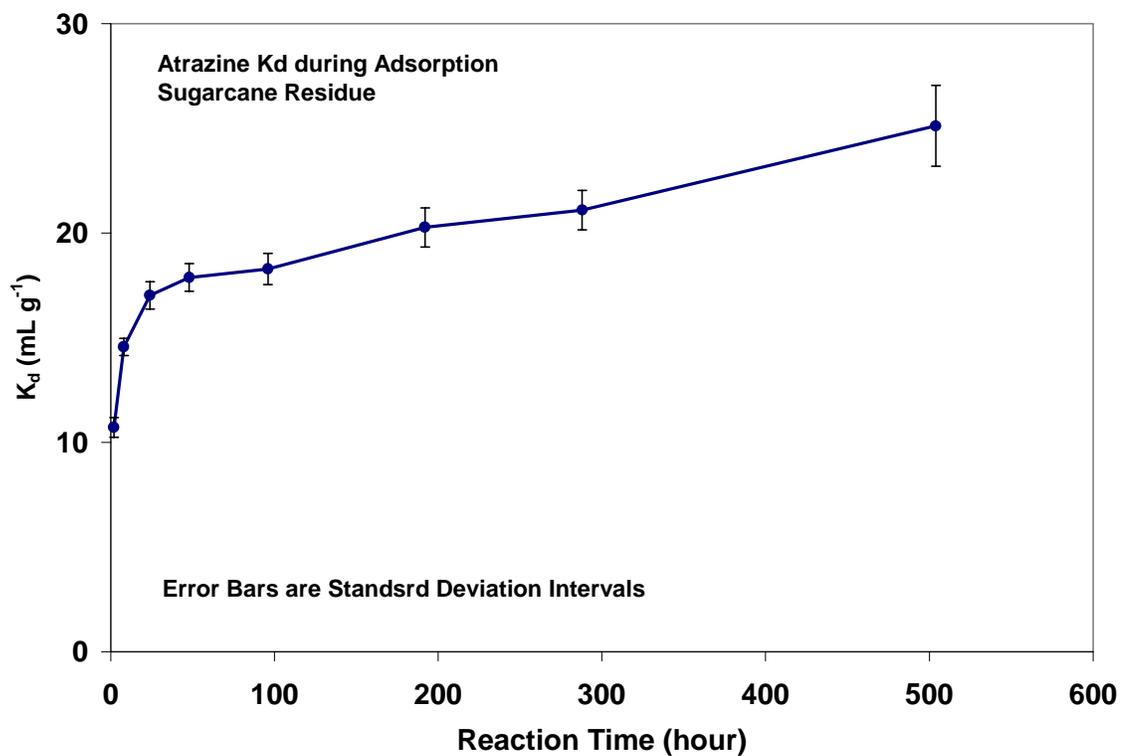
Fig.5.2: Measured atrazine distribution coefficient (K_d) versus adsorption reaction time for sugarcane mulch residue. Error bars represent one standard deviation.

components, and clay content and clay type. Guo et al. (1997) conducted a batch experiment to test the linear relationship between K_d and the application rate of organic matter, and a range of the K_{oc} values from 51.25 to 89.77 mL/g was reported. They observed an excellent linear correlation between the overall K_d values and the organic matter application rate, i.e. OM:Soil ratio. Comparing herbicide sorption by fresh plant organic matter and that by the humified organic matter of four soils, the study of Dao, 1991, indicated apparent differences between the two organic sources, at least in short-term equilibration period. Lignin fraction was thought to be the primary source of the sorptive capacity of intact winter wheat straw (Dao, 1991). The alcoholic and acidic functional groups were postulated to provide interaction sites with organic chemicals (Dao, 1987). Ahmad et al. (2001) recently studied the effect of the nature of soil organic matter on sorption of pesticides and found that the variations in K_{oc} values of the pesticides observed for the soils could be explained when variations in the aromatic components of soil organic matter were taken into consideration. The highly significant positive correlation of aromaticity of soil organic matter and K_{oc} values of carbaryl and phosalone revealed that the aromatic component of soil organic matter is a good predictor of a soil's ability to bind such nonionic pesticides (Ahmad et al., 2001). However, Boyd et al. (1990) observed that the K_{om} values of benzene, ethylbenzene, and 1,2,3-TCB were nearly identical to the soil K_{om} values, thus they concluded that the sorptive capability of whole corn residues and soil organic matter for nonionic organic compounds are very similar. In another study, for the Commerce silty loam which contains 1.31% organic matter, a K_{om} value of 160 mL/g at 24 hours reaction was obtained (personal communication with Dr. Selim, data not published). This is one
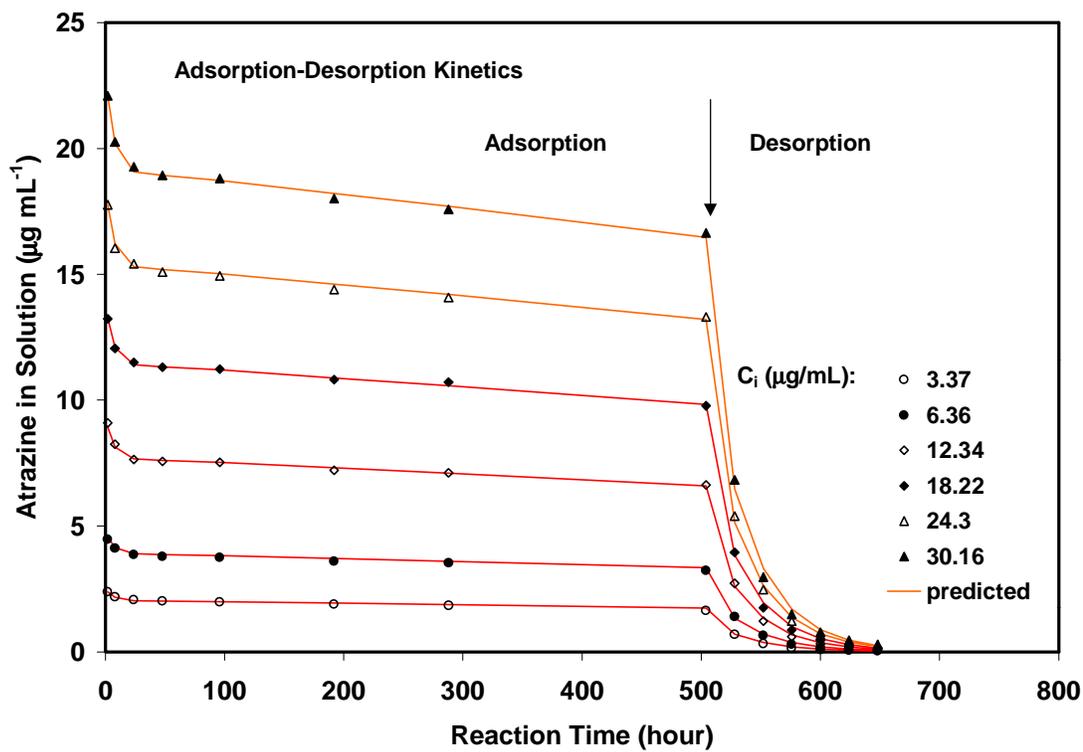
Fig.5.3: Atrazine concentration in solution during adsorption and desorption versus reaction time. Desorption was initiated after 504 hrs (see arrow). Results are from the batch kinetic experiment having a mulch to solution ratio of 1:30 and for several C_i. The solid curves are MRM predictions.
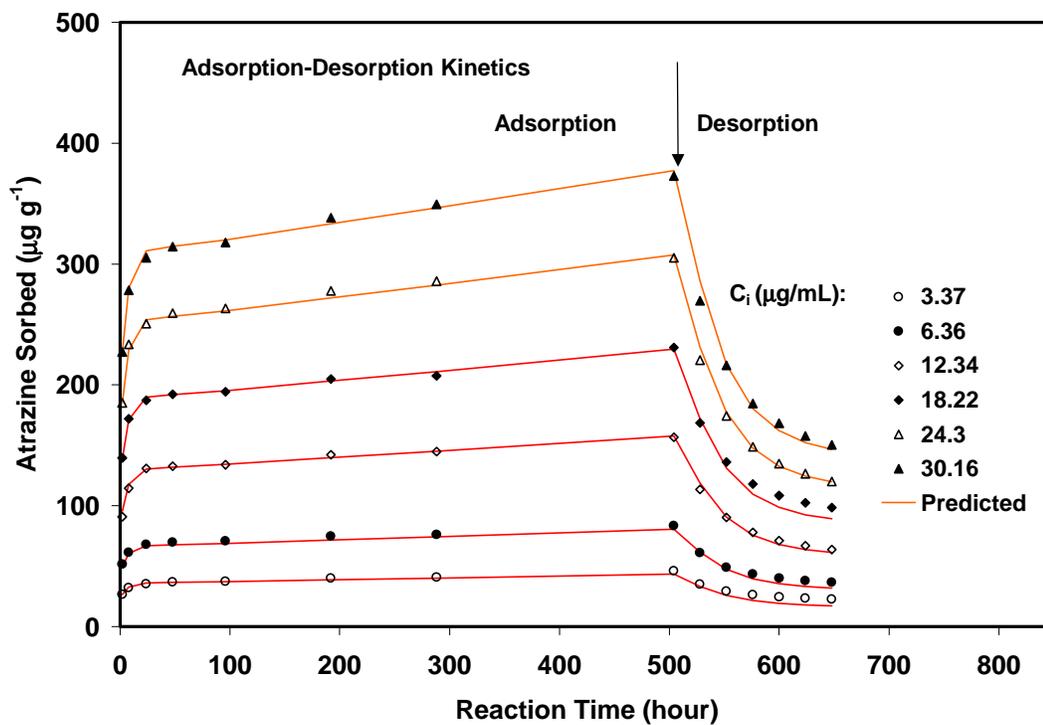
Fig.5.4: Amount of atrazine sorbed by sugarcane mulch residue versus reaction time. Desorption was initiated after 504 hrs (see arrow). Results are from the batch kinetic experiment having a mulch to solution ratio of 1:30 and for several Ci. The solid curves are MRM predictions.

order of magnitude higher than the K_d value observed from the sugarcane mulch residue for atrazine.

5.3.2 Adsorption-Desorption Kinetics

The atrazine concentration in solution and the amount of atrazine adsorbed by sugarcane residue (both adsorption and desorption) versus reaction time are illustrated in Figs. 5.3 and 5.4, respectively. Examination of these two figures suggests that the adsorption of atrazine by sugarcane residue was initially rapid, and slowed after 24 hours. Continuous adsorption of atrazine by the sugarcane residue was observed as the reaction time increased to 504 hours. Results of atrazine desorption versus time following adsorption (for 504 h) are also shown in Figs. 5.3 and 5.4. As expected, a drop in concentration in solution after each successive desorption time step (of 1 day) was observed. To describe the kinetic behavior of atrazine adsorption by sugarcane mulch residue, we used a multireaction kinetic model (Selim et al., 1976), which accounts for several concurrent and consecutive type retention reactions. These reactions include equilibrium(S_e) and kinetic (S_k) mechanisms of the reversible and irreversible (S_i) types. m = n was assumed. In this study, the values of n used were the average of Freundlich parameter N at all the reaction times during adsorption.

The best-fit estimates of reaction coefficients correspond to each specific reaction type along with the standard error were obtained using nonlinear optimization of MRM (Table 5.3). MRM model parameter estimates given in Table 5.3 were obtained for each initial input concentration C_i. Moreover, I obtained one set of parameters for the MRM model where the entire data set for all C_i's were used in the nonlinear least-square

Table 5.3: Goodness of fit, model parameters values, and their standard error (SE) for atrazine retention in sugarcane mulch residue using the multireaction (MRM) model. Model parameters are given for adsorption data (ads) and adsorption-desorption data (ads-des) separately.

Date set	C_i µg/mL	r^2	RMS	K_e	SE	k_1 h^{-1}	SE h^{-1}	k_2 h^{-1}	SE h^{-1}	k_3 h^{-1}	SE h^{-1}
Ads	3.37	0.953	0.05216	0.3840	0.03071	0.03461	0.009932	0.1058	0.02688	0.002796	0.000397
	6.36	0.989	0.04109	0.4214	0.01366	0.03528	0.004366	0.1006	0.01086	0.002190	0.000142
	12.34	0.986	0.09249	0.3599	0.01581	0.04300	0.005254	0.1056	0.01106	0.001681	0.000125
	18.22	0.969	0.1862	0.3931	0.02582	0.04827	0.01007	0.1327	0.02256	0.002056	0.000216
	24.30	0.996	0.2582	0.3881	0.02733	0.05252	0.01069	0.1331	0.02200	0.001841	0.000200
	30.16	0.937	0.4447	0.4120	0.03506	0.04137	0.01211	0.1122	0.02779	0.002006	0.000310
	Overall	0.9998	0.09864	0.3579	0.008279	0.04092	0.00300	0.1194	0.007303	0.001983	0.000076
Ads-des	3.37	0.998	0.04255	0.3795	0.02569	0.03670	0.008655	0.1115	0.02261	0.002741	0.000293
	6.36	0.999	0.05390	0.4155	0.01848	0.03806	0.006208	0.1081	0.01492	0.002161	0.000167
	12.34	0.999	0.09438	0.3558	0.01644	0.04501	0.005631	0.1109	0.01161	0.001704	0.000115
	18.22	0.999	0.1590	0.3894	0.002254	0.05027	0.009039	0.1384	0.01985	0.002073	0.000712
	24.30	0.999	0.2192	0.3850	0.02351	0.05414	0.009352	0.1366	0.01882	0.001813	0.000154
	30.16	0.998	0.3643	0.4074	0.02940	0.04362	0.01051	0.1180	0.02346	0.001993	0.00023
	Overall	0.9997	0.1114	0.3542	0.009546	0.04283	0.003564	0.1251	0.008489	0.001977	0.000079

parameter estimation procedure. As a result, a set of model parameter estimates, hereafter referred to as the overall set of parameters, and parameters corresponding to each C_i were obtained (Table 5.3). Both the individual fitting and overall fitting were carried out for the data sets with adsorption results only, and the datasets with both adsorption and desorption results. The kinetics of atrazine adsorption and desorption for the range of concentrations and time were well described by the MRM model. This is clearly shown by the solid curves which represent MRM predictions based on overall parameters for both adsorption and desorption dataset (See Figs. 5.3 and 5.4).

The multireaction model described the data adequately as indicated by the high r^2 value and low parameter standard error. All the parameters listed in Table 5.3 are not significantly different between estimates from individual fitting and from overall fitting (all of the P-values > 0.05), between estimates from the adsorption result only and from adsorption-desorption results (all of the P-values>0.05). Thus, one set of parameters is capable of describing the entire data set for all initial input concentrations, and for both adsorption and desorption kinetics (Table 5.3). An overall set of parameters is preferred due to the large degree of freedom and the resulting small standard errors. When MRM was used to model the atrazine kinetic reaction with a Sharkey clay soil, it was found that the use of overall estimated MRM parameters for desorption predictions resulted in overprediction of concentrations versus time during desorption for atrazine (Ma and Selim 1994a) and metolachlor (Chapter 2). In this study, the overall set of the parameters predicted the concentration during both adsorption and desorption adequately. The kinetic behavior of atrazine retention by sugarcane mulch residue is

consistent with continuous increase of the partition coefficient (K_d) (Fig.5.2, Table 5.2) and Freundlich distribution coefficient (K_f) (Table 5.2) with reaction time.

MRM parameters were estimated for atrazine reaction with a Sharkey soil (Ma and Selim, 1994a and 1994b). Comparison of the parameter values indicated that the K_e value for Sharkey clay (0.697±0.0134) was almost double of the K_e for sugarcane mulch residue (0.358±0.00828), and irreversible reaction coefficient (k_3) values are almost identical for the two matrices (Sharkey clay soil or sugarcane mulch residue). The k_1 and k_2 were more than one magnitude higher for sugarcane mulch residue than that for Sharkey clay. However, values for $K_k = k_1/k_2$ are close: they are 0.344 and 0.460 for mulch and Sharkey clay, respectively. Large rate coefficients for the kinetic reaction suggests that mulch residue affects mostly the extent of kinetic reaction (Ma and Selim, 1994a). Both S_k and S_i forms may be regarded as strongly retained where S_i is assumed to be fully irreversible and S_k is slowly reversible. In order for the kinetic phase S_k to be considered as slowly reversible or strongly held, it is a prerequisite that the associated forward rate coefficient k_1 must be much greater than the backward rate k_2. However, this is not the case for this study, which indicates that the large amount of atrazine sorbed on the kinetic site may not be strongly held. This suggests that the reversible reaction may be the dominant mechanism for the retention of atrazine by sugarcane mulch residue.

5.3.3 Hysteresis and Recovery

The amount of atrazine desorbed at the end of six consecutive desorption steps was quantified. In addition, I calculated the amount of atrazine released subsequently using methanol as the final extraction step. These results along with the amount retained

Table 5.4: Mass balance of applied atrazine following 504 h adsorption, six desorptions, and methanol extraction

Input Concentration (C_i)	Total amount adsorbed[1]	Total amount desorbed [2]	Total amount desorbed (percent of adsorbed	Total amount retained (percent of Input)	Amount of Methanol extractable [3]	Amount of residual (percent of input)
(μg/mL)	(μg/g mulch)	(μg/g mulch)	(%)	(%)	(μg/g mulch)	(%)
3.37	47.87	24.56	51.29	23.06	2.96	20.13
6.36	86.25	48.59	56.35	19.94	4.38	17.44
12.34	160.3	96.80	60.30	17.15	8.05	14.98
18.22	236.6	138.02	58.30	18.04	11.30	15.67
24.30	310.5	192.3	61.95	16.21	18.82	13.63
30.16	360.8	232.0	60.91	16.45	22.29	13.98

[1] Following 504 h of reaction time.
[2] Following six desorption steps using $0.005M$ $CaCl_2$
[3] The amount extracted using methanol following six $CaCl_2$ desorption steps

after 504 h of adsorption are given in Table 5.4. Based on six consecutive desorption steps, the total amount of atrazine desorbed, as a percentage of total adsorbed after 504 h retention, was $58.18 \pm 4.36\%$ over the range of atrazine initial input concentration. The recovery of atrazine for the lowest C_i (3.37 µg mL^{-1}) is significantly different from the recoveries for all other C_i's with a P-value of 0.00513. No significant difference in atrazine recovery was observed for all other C_i's when the lowest C_i was excluded (P-value=0.239). The amounts desorbed represent the sum of water soluble or readily desorbable atrazine fractions. As the initial input C_i increased from 3.37 to 30.16 µg/mL, the percentage of desorbed atrazine based on the total amount adsorbed increased from 51.29% to 60.91%. An average recovery of $43 \pm 3.2\%$ for atrazine after four desorption cycles, similar to our desorption steps (24 hours each step), was reported by Seybold and Mersie (1996) in sandy loam and clay soils, and no significant difference of atrazine recoveries were observed between the two soils. In their study, a similar background solution (CaCl$_2$) was used except that adsorption was limited to 24 h. The higher release of atrazine for mulch residue than soil is likely due to the higher amount of atrazine sorbed on kinetic reaction sites as described by MRM. The final extraction step using pure methanol recovered only $5.49 \pm 0.69\%$ of atrazine.

A major amount of atrazine was desorbed during the first two desorption steps, and less amount of atrazine was available for desorption as the desorption steps increased. The solute desorbed during the first step is likely to come from the most accessible sites and/or from the less-energy-consuming adsorption mechanisms, whereas the solutes adsorbed on the less accessible sites and the more strongly adsorbed solutes might only be desorbed in later steps. The availability of pesticide residues in

soils can be evaluated in relation to their extractability (Moreau and Mouvet, 1997 and 1998). For instance, all solvent extractable residues are potentially available and water extractable residues are the most readily available fraction. Atrazine extractable with methanol would be less readily available and could possibly be extractable with water if the extraction procedure was repeated enough times. The amount of nonextractable (i.e. strongly held) atrazine was related to the concentration initially bound to the solid and the energy level of the adsorption mechanisms (Moreau and Mouvet, 1998). The higher atrazine recovery from sugarcane mulch residue than that from soils is indicative of higher availability of atrazine adsorbed by the mulch residue.

In Fig. 5.5, desorption results are presented in the traditional manner along with the adsorption isotherm for the last (504 hours) retention time, i.e. prior to commencement of desorption (solid curves). In Fig. 5.6, our desorption results are presented for each time of reaction (adsorption and desorption) as a time-dependent manner. The discrepancies of both families of desorption isotherms (dashed curves) from the adsorption isotherm (solid curve) are indicative of hysteresis. The likely time-dependent nature of hysteresis of atrazine adsorption-desorption was reported (Ma et al., 1993; Moreau and Mouvet, 1998).

The Freundlich model (Eq. 2.1). was used to describe our desorption data based on the traditional isotherm approach (Fig. 5.5) and those based on our time-dependent isotherms (Fig. 5.6). As a result two sets of values for best estimates of K_f and N were obtained and are given in Table 5.5. For the traditional desorption isotherms (see Fig. 5.5), K_f values were consistently higher than those associated with adsorption isotherms (see Table 5.2). The opposite trend was observed for the nonlinear parameter N.

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Fig.5.5: Traditional desorption isotherms of atrazine by sugarcane mulch residue. The solid line is the adsorption isotherm after 504 hours reaction. The dashed curves are predictions using the multireaction model (top) and Freundlich model (bottom).
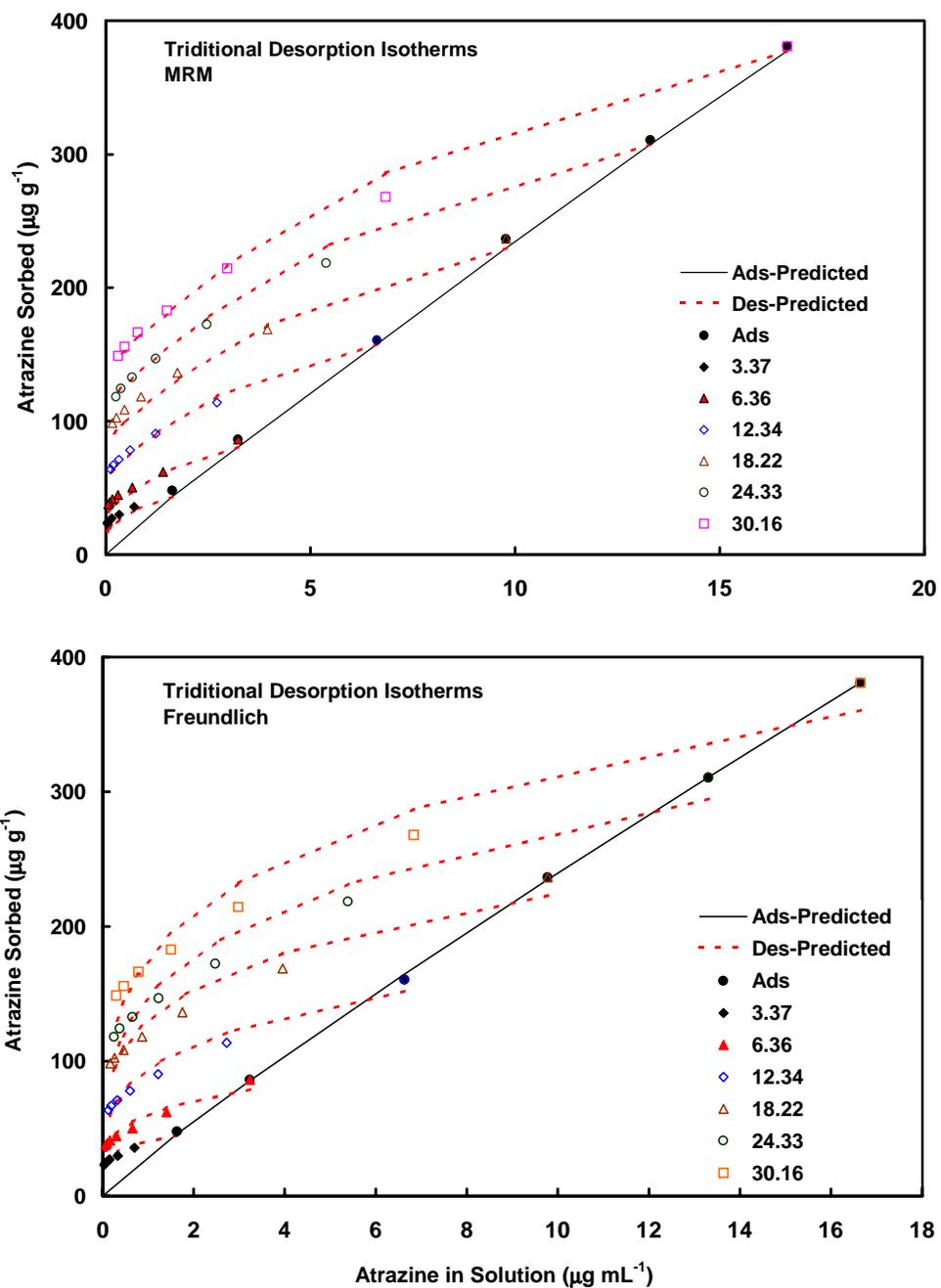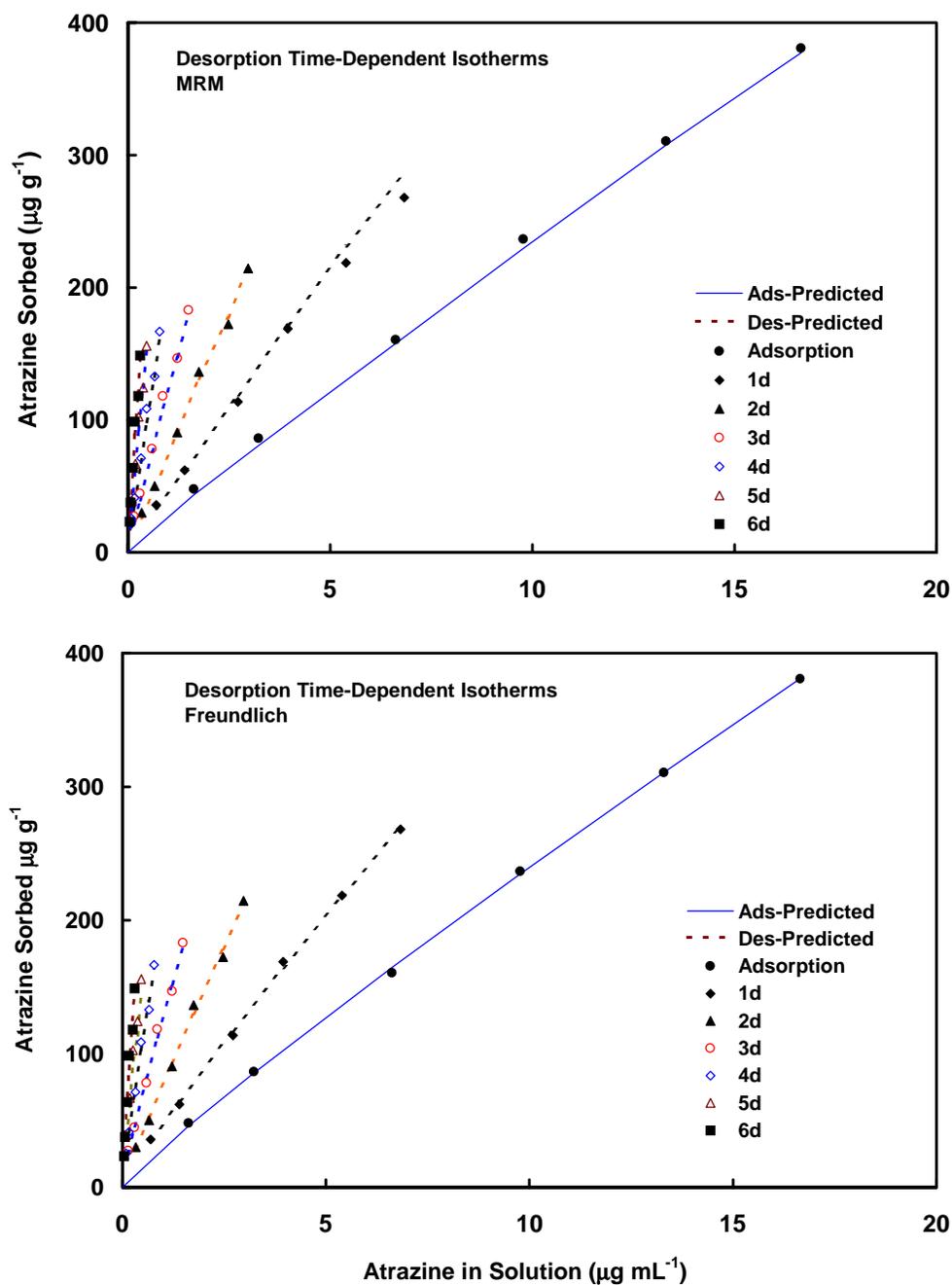
Fig.5.6: Time-dependent desorption isotherms of atrazine by sugarcane mulch residue. The solid line is the adsorption isotherm after 504 hours reaction. The dashed curves are predictions using the multireaction model (top) and Freundlich model (bottom).

Table 5.5 : Freundlich parameters and hysteresis coefficients for atrazine desorption based on the traditional and time-dependent isotherms for sugarcane mulch residue.

	Traditional desorption isotherms					
C_i (µg/mL)	K_f (mL/g)	N	r^2	ω	H	λ
3.37	40.91 ± 0.770	0.197 ± 0.0116	0.996	378.68	20.89	62.322
6.36	61.69 ± 1.257	0.227 ± 0.0157	0.992	315.42	24.07	58.354
12.34	94.24 ± 2.226	0.253 ± 0.0169	0.991	272.73	26.83	55.068
18.22	130.3 ± 2.774	0.236 ± 0.0134	0.994	299.58	25.03	57.201
24.30	147.7 ± 3.846	0.267 ± 0.0143	0.994	253.18	28.31	53.354
30.16	175.6 ± 4.528	0.256 ± 0.0130	0.995	268.36	27.15	54.697

	Time-dependent desorption isotherms					
Time (hour)	K_f (mL/g)	N	r^2	ω	H	λ
24	47.54 ± 1.779	0.903 ± 0.0223	0.999	---	95.758	61.26
48	77.71 ± 2.336	0.918 ± 0.0332	0.997	---	97.349	163.60
72	127.4 ± 2.021	0.855 ± 0.0377	0.996	---	90.668	332.16
96	201.1 ± 6.144	0.864 ± 0.0464	0.995	---	91.622	582.16
120	295.5 ± 17.07	0.849 ± 0.0505	0.993	---	90.032	902.37
144	405.3 ± 39.76	0.850 ± 0.0631	0.989	---	90.138	1274.9

Moreover, K_f for desorption was significantly dependent on initial atrazine concentration C_i. Similar findings for atrazine in soils were previously reported (Clay and Koskinen, 1990; Ma et al., 1993). Moreover, this comparison is further complicated since exceedingly small N values for desorption were estimated (0.197 to 0.267). For the time-dependent isotherms (see Fig. 5.6), the estimated N values were similar to that for adsorption (Tables 5.2 and 5.5) which is consistent with our results for metolachlor adsorption-desorption by a Sharkey clay soil (Chapter 2). The parameters estimated from time-dependent desorption isotherms rather than 24h K_d values are more appropriate to predict herbicide residue in the field, and thus more meaningful for environmental assessment.

The degree of hysteresis was quantified using hysteresis coefficients ω (Ma et al., 1993), H (Cox et al., 1997) and λ (Chapter 2). All those coefficients were defined based on the discrepancy between the adsorption isotherm and desorption isotherms, and calculated using Freundlich parameters estimated from adsorption and desorption isotherms. Values for λ (Eq. 2.11 and 2.12), ω (Eq. 2.5) and H (Eq.2.6) were obtained and are presented in Table 5.5. For traditional isotherms, values for λ and ω decreased as C_i increased, whereas the opposite was observed for H value. This is similar to the result of our study of metolachlor adsorption-desorption in Sharkey clay soil (see Chapter 2). Ma et al. (1993) calculated ω for atrazine on Sharkey clay soil and indicated that ω increased linearly with incubation time, which is the time interval between the end of adsorption and the beginning of the desorption process. However, they did not observe an effect of C_i on ω. Seybold and Mersie (1996) calculated ω for metolachlor in two soils and found that ω is C_i-dependent for Cullen soil which

contained 31% clay and 1.3% of organic carbon, but this phenomenon was not apparent

in Emporia soil which contains less clay and less organic carbon. Thus, the dependency

of ω on C_i in this study is inconsistent with the Seybold and Mersie (1996) results. For

the time-dependent desorption isotherms shown in Fig. 5.6, values for λ increased as

desorption time increased, indicative of the dependency on desorption history. This

behavior might be explained by the existence of irreversible reactions which caused a

decrease of desorbed herbicide amounts as desorption time increased.

5.3.4   Adsorption Capacity

Fig. 5.3 clearly indicates that atrazine adsorption capacity by sugarcane mulch

residue was not attained. In fact, amounts of atrazine adsorption continued to increase

with time for the two C_i's used. These adsorption results were directly measured using

our repeated replacement technique where we attempted to saturate the reaction sites on

matrix surfaces by maintaining high atrazine concentrations in solution (12.02 and

29.30 μg/mL). Obviously, an atrazine sorption capacity was not reached during the

reaction time for the concentrations used. Ma and Selim (1994a) did not observe an

atrazine adsorption capacity for a Sharkey clay soil. This may be limited by the low

solubility of atrazine in water, which makes it impossible to measure the adsorption

capacity by use of the batch saturation technique utilized here.

Despite the lack of an observed retention capacity, attempts were made to utilize

the adsorption data of Fig. 5.3 to arrive at an estimate or at least a first approximation.

The estimation was carried out using the method described by Sposito (1989) through

plotting S/C against S. A linear regression line (r^2=0.859) provided an estimated

adsorption capacity of 2430 μg/g, which is more than one magnitude higher than the
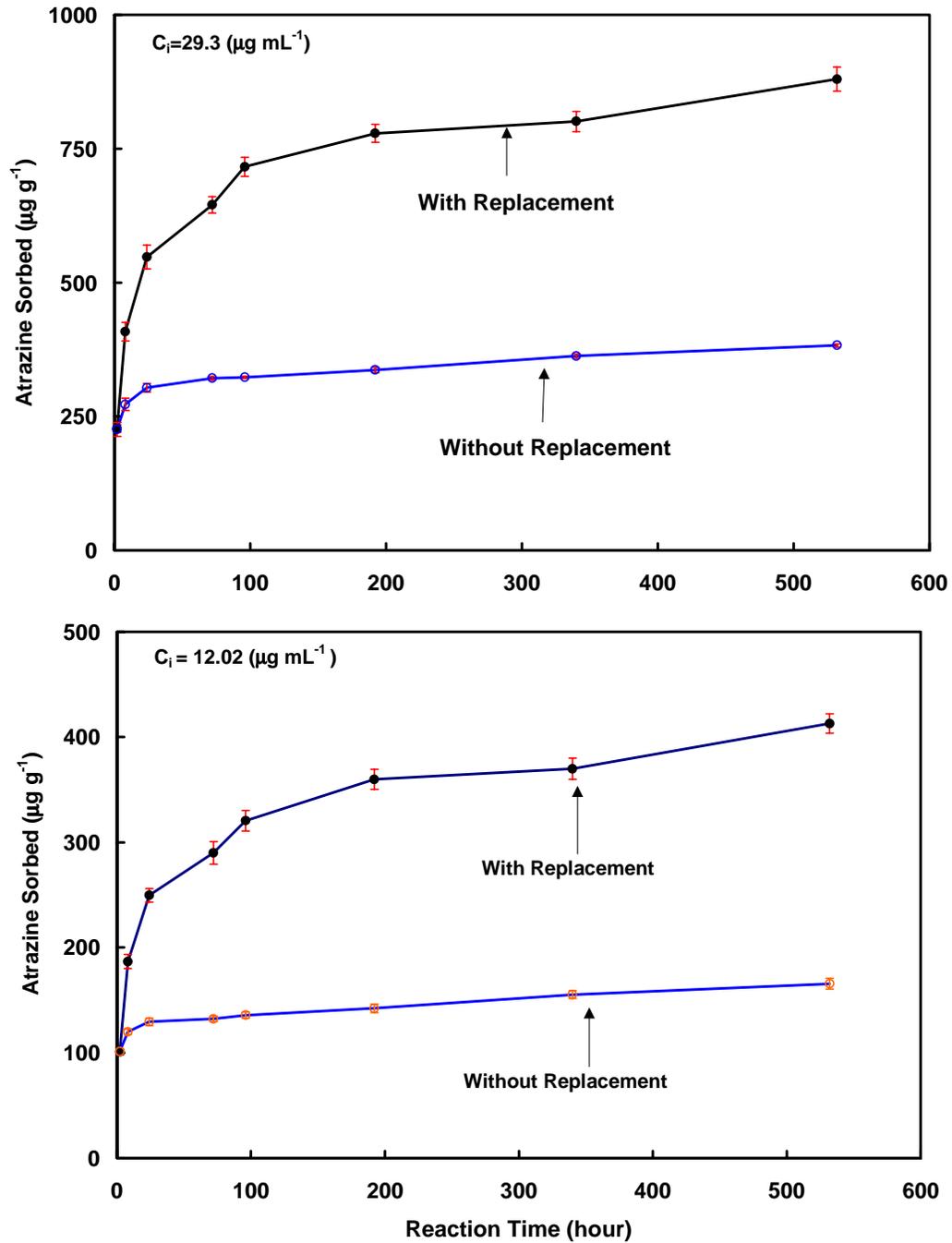
Fig.5.7: Atrazine adsorption versus time from batch adsorption capacity experiments with two initial concentration (C_i) of 12.02 and 29.30 $\mu g\ mL^{-1}$ with and without successive replacements of the supernatant.

value for atrazine adsorption by Sharkey soil (Ma and Selim, 1994a). For my

estimation, data at reaction time of 192 hours were used where the irreversible reactions

were assumed to be negligible. Similar assumption was made by Ma and Selim (1994a)

when this method was used to estimate atrazine adsorption capacity by a Sharkey clay

soil. Since the irreversible rate coefficients of MRM are very close for atrazine

adsorption for the Sharkey clay soil and by sugarcane mulch residue, it is considered

reasonable to make this assumption.

5.3.5   Transport

Fig. 5.8 – 5.10 are atrazine breakthrough curves through columns with the presence of

sugarcane mulch residue. We attempted to describe the BTCs using Freundlich and the

multireaction and transport model (MRTM) as detailed by Ma and Selim (1998). The

later multipurpose model accounts for several concurrent and consecutive type retention

reactions as well as transport of reactive solutes in soils. These reactions include

equilibrium and kinetic mechanisms of the reversible and irreversible types (Eq. 4.2).

Values of D for each column were obtained from our tritium breakthrough curves and

listed in Table 5.1. All the assumptions made in MRM are applied here. We utilized a

nonlinear least-squares optimization scheme which provided best-fit of the model to the

experimental data (van Genuchten, 1981). Best fitted MRTM and Freundlich model

parameters and their corresponding standard errors for each column are listed in Table

5.6. The multireaction model parameters (Table 5.3) which were independently derived

from batch adsorption experiments were also used to simulate atrazine BTCs obtained

from the column with reference sand and mulch residue mixture (Fig.5.8) and from the

column with 5 cm mixture and 10 cm Sharkey clay soil (Fig.5.9).

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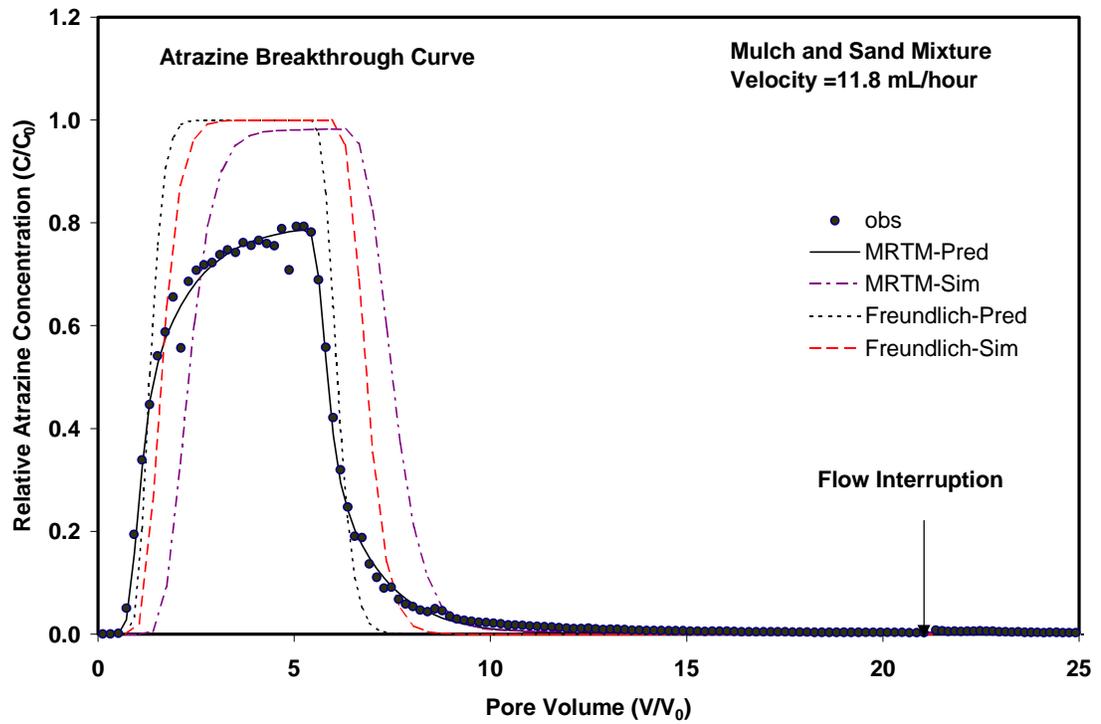
Fig.5.8: Measured and predicted atrazine BTCs for the column with sugarcane mulch residue mixed with sand as a reference material (column length = 15 cm) .

Fig.5.9: Measured and predicted atrazine BTCs from a 15 cm column consisting of 5 cm sugarcane mulch residue and reference sand above a 10 cm Sharkey clay soil layer.
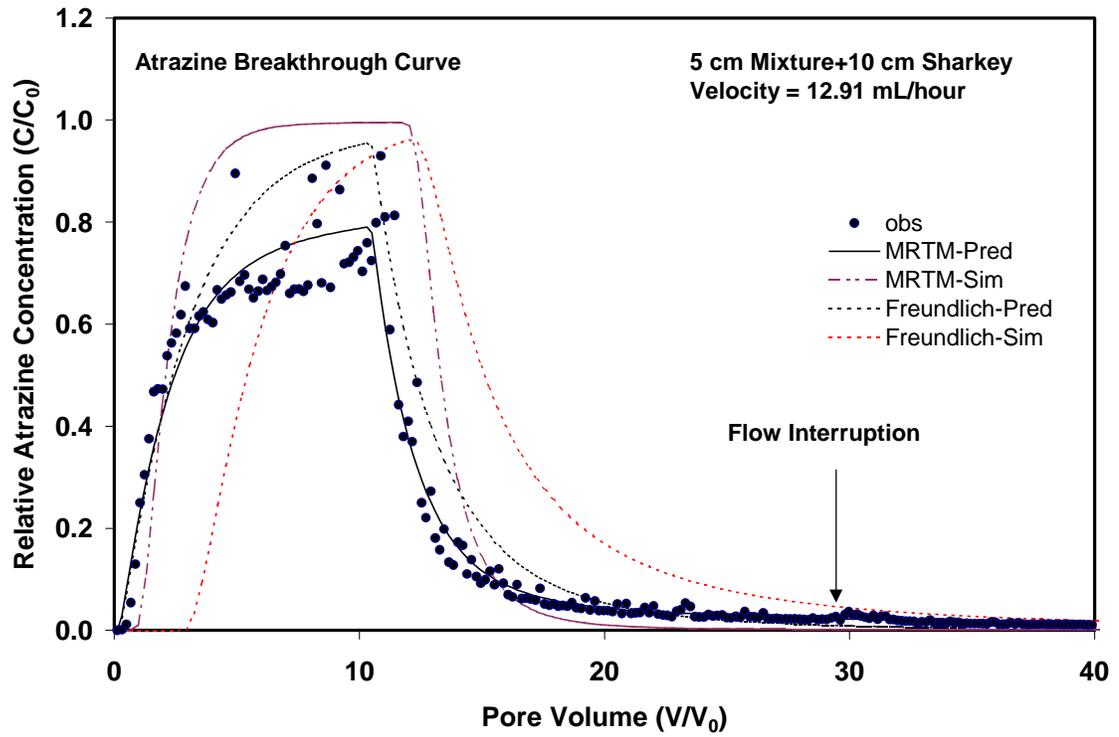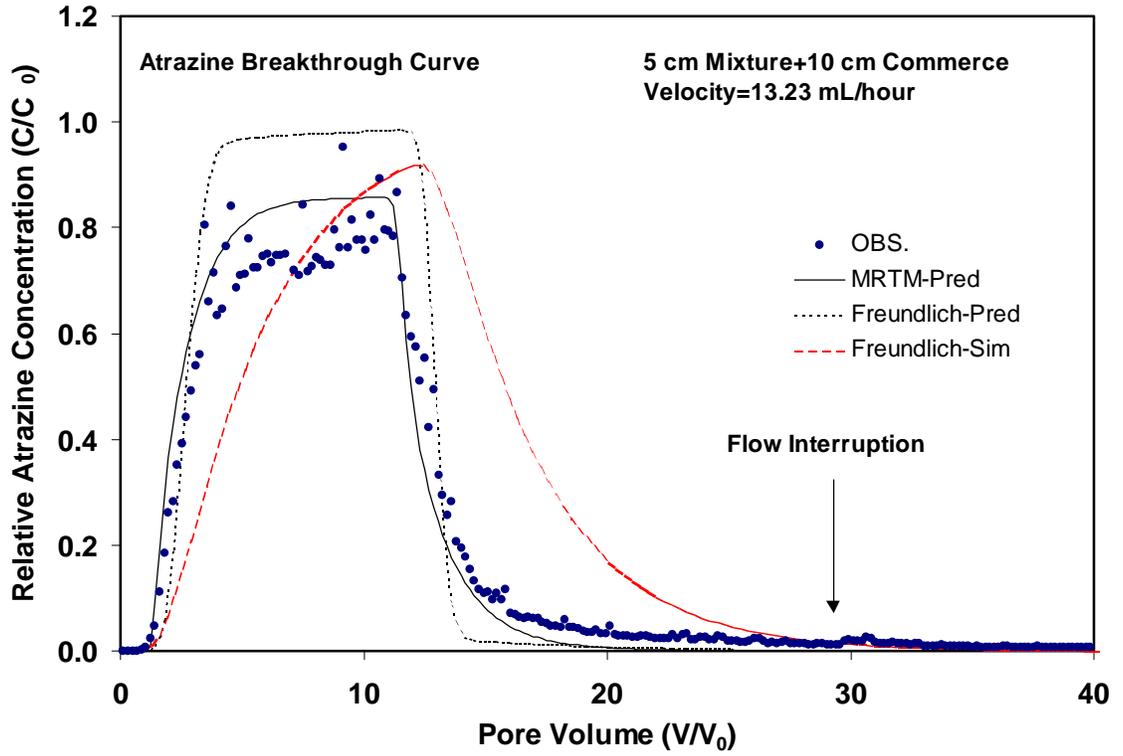
Fig.5.10: Measured and predicted atrazine BTCs from a 15 cm column consisting of 5 cm sugarcane mulch residue and reference sand above a 10 cm Commerce silty loam soil layer.

The transport breakthrough curves (BTC) of atrazine in the columns are exhibited in Figs. 5.8 - 5.10. The peak arrival times were similar for all the three BTCs. A slight lower atrazine peak concentration in the effluent solution and more extensive tailing of the BTC for the column with mulch residue and Sharkey clay soil was observed, indicating more atrazine adsorption by matrix and more kinetic behavior in this column. Furthermore, the relatively sharper adsorption (right) and release (left) fronts of BTCs were obtained for the BTCs of the other two columns. The continued slow atrazine release in the effluent solution is clearly illustrated and suggests nonequilibrium release mechanisms. In addition, an increase in concentration resulting from flow-interruption during desorption was observed. However, due to the late interruption of our experiment, the difference of the interruption effect on the different columns was not well depicted. Atrazine recovery was calculated by taking integral for the area under the BTCs, as a result, atrazine recoveries of 80.56, 80.52 and 85.19% were obtained for the mulch and reference sand mixture only, mixture and Sharkey clay, and mixture and Commmerce loam columns, respectively. The higher atrazine recovery for the mixture and Commerce loam column indicats a relatively higher mobility of atrazine.

Based on BTC shown in Figs. 5.8 – 5.10, MRTM provided better prediction of atrazine BTC for all the three columns. The Freundlich approach proved to be inadequate in describing our batch kinetics. Its prediction capability of atrazine BTCs was not acceptable either. This lack of prediction capability implies that the Freundlich model is

Table 5.6: Best fit parameters for multireaction and transport model and Freundlich model

| Column ID | MRTM | | | | | |
	Ke (g mL^{-1})	k_1 (h^{-1})	k_2 (h^{-1})	k_3 (h^{-1})	RMS	r^2
I	0.1285±0.01907 [1]	0.06289± 0.003467	0.05108±0.004497	0.01860±0.000948	0.01654	0.997
II	1.9723±0.1566	0.02576±0.002877	0.002459±0.001316	0.001678±0.001792	0.05534	0.965
III	0.6178±0.1147	0.1234±0.01854	0.05975±0.01318	0.007767±0.001206	0.06872	0.971

| | Freundlich | | | |
	K_f (g mL^{-1})	N	RMS	r^2
I	0.5266 ± 0.2166	0.8916 ± 0.1793	0.1052	0.979
II	2.2500 ± 0.5891	0.8072 ± 0.1063	0.09847	0.951
III	1.0936 ± 0.2880	1.1086 ± 0.1022	0.1444	0.968

[1]：one standard deviation of the estimated parameters

inadequate in describing atrazine transport in soil and mulch residue columns. As indicated by the smaller RMS values and higher r^2 values, MRTM provided better predictions than Freundlich prediction. This suggests that atrazine retention behavior in the column experiments was consistent with that in the batch experiments. Attempts to simulate BTCs with Freundlich parameters estimated from batch experiment was not successful for all three columns.

5.4   Conclusions

This study investigated the characteristics of sugarcane mulch residue for atrazine adsorption-desorption and transport in the soil environment. An adsorption kinetic-batch method was used to quantify retention of mulch for a wide range of atrazine concentrations and reaction times. Adsorption as well as desorption of atrazine by the mulch residue exhibited extensive kinetic behavior. Adsorption isotherms appeared linear for all retention times with K_d values increasing from 10.4 to 23.4 cm^3/g after 2 and 504 h, respectively. Use of an equilibrium-kinetic multireaction model was successful in describing adsorption results for the entire concentrations range. Desorption exhibited strong hyteresis for all input concentrations and was equally well-described by the multireaction model. Moreover, one set of model parameters estimated from the entire data set including both adsorption and desorption results for the entire range of initial input concentrations was adequate in describing the batch results. Recovery of applied atrazine based on six successive desorptions and the addition alextraction with pure methanol accounted for $63.67 \pm 4.38\%$ of that adsorbed over the entire input concentration range. Atrazine recovery for the different initial atrazine input concentrations was found to be concentration-independent except for the lowest C_i (3.37

µg mL^{-1}). The estimated atrazine adsorption capacity by sugarcane mulch residue of 2430 µg g^{-1} is more than one magnitude higher than the value of atrazine adsorption by a Sharkey clay soil. The use of a multireaction model proved successful in describing the atrazine mobility in the columns with mulch on top of the soil layer and was in close agreement with measured results.

5.5   References

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CHAPTER 6: CONCLUSIONS

Deltamethrin retention and mobility were studied in reference sand and four soils with different organic matter, clay contents and pH values. Adsorption-desorption results exhibited strong retention for all soils studied. Adsorption was positively correlated with increasing cation-exchange capacity (CEC) and decreasing soil pH. After 1 d of reaction, more than 90% of applied deltamethrin was adsorbed by Mahan sandy clay loam and Sharkey clay soils, where clay is the main component of soils to adsorb deltamethrin. In contrast, the lowest retention was observed for a nonacidic Vacherie sandy loam soil (pH of 7.6 and clay content of 2%) with relatively high organic matter content (2.51%). Deltamethrin adsorption by the different soils was quantified by the distribution parameters (K_d) and the Freundlich coefficients (K_f) as derived from the adsorption isotherms. Moreover, our results indicate that, with the exception of the reference sand material, adsorption was not time-dependent. The extent of recovery or desorption of deltamethrin adsorbed varied among soils and input concentrations. The total desorbed deltamethrin (resulted from six successive dilution steps) as percent of amount adsorbed ranged from 0.20% for Mahan sandy clay loam (O.M = 0.96%) to 32.9% for Vacherie sandy loam. Nevertheless, for all soils, the total amount retained, following desorption, ranged from 78 to 97% of total input. The only exception was for Vacherie soil which showed highest recovery and the lowest amount retained (39.5% of input). This high recovery for Vacherie soil may be due to solubilization effect of dissolved carbon (DOC), as well as the decrease of pH-dependent charge at high pH. Strong hysteresis behavior of deltamethrin adsorption-

desorption was observed for all soils as illustrated by apparent discrepancies between the adsorption and desorption isotherms.

The results of deltamethrin transport experiments indicated that the synthetic pyrethroid insecticide deltamethrin has extremely low mobility and strong retention in the soil columns. After leaching 80 pore volumes of 0.005 M $CaCl_2$ solution, which is equivalent to approximately 2500 mm rainfall, the amount of deltamethrin leached out from each soil column was small and ranged only from 3 to 8% of the total amount applied, and the amount varied among soils. For clay soil and loamy soil, over 90% of deltamethrin remained where it was applied. The mobility of deltamethrin can be facilitated in soils with high content of organic matter due to the enhanced solubility of deltamethrin by dissolved organic carbon. DOC may act as co-solvent in dissolution of deltamethrin in precipitated forms. Relatively higher mobility of deltamethrin was observed for a nonacid sandy soil with pH of 7.6 and clay content of 2% (Vacherie). The use of a multireaction and transport model (MRTM) proved successful in describing the BTC from the reference sand column and in close agreement with measured deltamethrin results. Based on its extreme low mobility in soils, along with the strong adsorption and low recovery from batch experiment, deltamethrin may be considered not susceptible to leaching from the soil profile, and thus low risk of ground water contamination.

In this study, the characteristics of sugarcane mulch residue for atrazine based on adsorption-desorption and transport in the soil environment was also investigated. An adsorption kinetic-batch method was used to quantify retention of mulch for a wide range of atrazine concentrations and reaction times. Adsorption as well as desorption of

atrazine by the mulch residue exhibited extensive kinetic behavior. Adsorption isotherms appeared linear for all retention times. A linear multireaction model which accounted for reversible equilibrium and kinetic retention along with a consecutive irreversible reaction described both adsorption and desorption of atrazine retention results (r^2=0.99) The estimated atrazine adsorption capacity by sugarcane mulch residue (2430 μg g^{-1}) is more than one magnitude higher than that of atrazine adsorption by a Sharkey clay soil.

A kinetic multireaction model was successful in describing the kinetic behavior of metolachlor adsorption and desorption by Sharkey clay and Commerce silty loam, as well as atrazine by sugarcane mulch residue. However, for metolachlor retention by soils, the parameters estimated from individual fitting for each initial input concentration provided better prediction than parameters estimated from overall fitting for the entire concentrations. Atrazine retention by sugarcane mulch residue which was characterized by strong kinetic retention was also well described by the multireaction model. It is important to point out that parameters estimated from the individual fitting and overall fitting was found to be not significantly different. Therefore, one set of parameters estimated from data set, including entire initial concentration range as well as both adsorption and desorption, adequately described the results of atrazine retention by sugarcane mulch residue. Although K_d value for atrazine adsorption by sugarcane mulch residue is one magnitude higher than that in soils, atrazine adsorbed by crop residue is more susceptible for desorption. The larger K_d value for mulch residue than for soils is due to the increase of equilibrium and kinetic retention. The MRM parameter

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for irreversible retention was similar for atrazine adsorption by soil and sugarcane mulch residue.

In this study, a new approach for desorption isotherms is presented. Specifically, families of desorption isotherms were presented in two different ways; namely the traditional type of successive desorptions, and the other is based on time-dependent desorptions (newly proposed). This resulted in two different sets of model parameter estimates for desorption. The main advantage of the time-dependent type isotherms is that often the case there is no significant difference of N for adsorption and desorption such as this study for metolachlor in Sharkey and Commerce soils,. Thus K_f becomes the only significant parameter when simulation of adsorption and desorption processes are sought. On the other hand, parameters from successive isotherms provide an understanding of the distribution of a herbicide between soil and solution for a given initial (input) concentration (Bowman and Sans, 1985). Another advantage of the time-dependent desorption isotherm is that the isotherm definition remains unaltered, and when an isotherm is measured based on laboratory adsorption-desorption experiments or based on field measurements equal reaction times should be maintained. Data sets based on the traditional or successive desorption isotherms no longer satisfies the requirement of an isotherm, instead time-dependent or kinetic desorption results are often presented.

Freundlich parameters can be derived from the two types of desorption isotherms. A hysteresis (λ) coefficient based on the difference in the area between adsorption and desorption isotherms was proposed. The coefficient was capable of quantifying hysteresis for both types of desorption isotherms. For the time-dependent desorption

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isotherms, from desorption step one (24 h) to desorption step six (144 h), λ values ranged from 30.2 to 164.1 and from 39.0 to 217.5 for metolachor desorption from Sharkey clay and Commerce silty loam, respectively. Moreover, the λ values changed from 61.26 to 1274.9 for desorption step one (24 h) to step six (144 h) for atrazine desorption from sugarcane mulch residue.

VITA

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