ABSTRACT

Sorption-desorption of diuron to a subsurface material was investigated by a variety of batch reactor experiments. The time needed to reach sorption equilibrium was longer than 45 days, while desorption equilibrium was apparently approached within 7 days. Nonlinear sorption-desorption equilibrium and desorption hysteresis were observed. The Freundlich equation was found to describe sorption-desorption equilibria best, with a Freundlich sorption exponent of 0.66, and an average desorption exponent of 0.23. Complex pattern sorption-desorption experiments were performed. The results of these experiments showed that the sorption-desorption process may be described by a Freundlich model: sorption exponent, desorption exponent, and sorption capacity constant, and the maximum equilibrium value achieved. Several possible explanations to describe the observed hysteresis were investigated. Nonattainment of equilibrium, loss of solute, artifact of the experimental methods, sorption to nonsettling particles, centrifugation effects, accumulated measurement error, and presence of an implicit-sorbate were found not to be the major cause of desorption hysteresis. A two-site model was developed to describe the sorption and desorption rates. This model assumes that two types of reaction sites exist on the solid-phase—fast and slow sites. The fast-sites sorb solute rapidly inducing an instantaneous equilibrium. The slow-sites are simulated by a first order mass transfer model. The two-site model provided a reasonable fit of the observed data.

ACKNOWLEDGEMENTS

First of all, I want to thank my advisor, Dr. Cass T. Miller, for his constant encouragement and guidance.

Thanks to Dr. Lucy Sonnenberg, Alex Mayer, Jim Jersey, and Joe Pedit for their suggestions and assistance in developing analytical methods and experimental protocol.

To my husband, David, and my lovely children, Cindy and Michael, I couldn't have done it without your love and support.

Thanks to de Numours & Co. for providing the analytical grade diuron.

Finally, my sincere appreciation goes to the United States Geological Survey for their financial support of this research.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOTATION

ABS'	net absorbance.
C	fluid-phase solute concentration (M/L^3).
C_0	initial fluid-phase solute concentration (M/L^3).
C_e	equilibrium fluid-phase solute concentration (M/L^3).
C_{de}	desorption equilibrium fluid-phase solute concentration (M/L^3).
C_{se}	sorption equilibrium fluid-phase solute concentration (M/L^3).
C_{me}	maximum equilibrium fluid-phase solute concentration (M/L^3).
D	mass of compound dissolved (M).
f_{oc}	mass fraction of organic carbon (M/M).
K	Freundlich sorption capacity constant ($(L^3/M)^n$).
K_d	Freundlich desorption capacity constant ($(L^3/M)^n$).
K_{df}	Freundlich desorption capacity constant associated with fast-sites ($(L^3/M)^n$).
K_{ds}	Freundlich desorption capacity constant associated with slow-sites ($(L^3/M)^n$).
K_f	Freundlich capacity constant associated with fast-sites ($(L^3/M)^n$).
K_m	mass transfer coefficient ($1/T$).
K_{oc}	organic carbon normalized partition coefficient (L^3/M).
K_{ow}	octanol water partition coefficient.
K_p	linear equilibrium sorptive partition coefficient (L^3/M).
$K_{p,obs}$	observed equilibrium sorptive partition coefficient (L^3/M).
K_s	Freundlich sorption capacity constant ($(L^3/M)^n$).
K_{ss}	Freundlich sorption capacity constant associated with slow-sites ($(L^3/M)^n$).
$l, l+1$	old and new time level.
M	mass of soil in reactor (M).
M_p	mass of particle (M).
N	mass of compound sorbed to nonsettling particles (M).
n	Freundlich sorption intensity constant.
n_d	Freundlich desorption intensity constant.
n_f	Freundlich intensity constant associated with fast-sites.
n_s	Freundlich sorption intensity constant.
n_{ss}	Freundlich sorption intensity constant associated with slow-sites.
P	mass of compound sorbed to settleable particles (M).
q	solid-phase sorbate concentration (M/M).
q_{de}	desorption equilibrium solid-phase sorbate concentration (M/M).
q_e	equilibrium solid-phase sorbate concentration (M/M).
q_f	solid-phase sorbate concentration associated with fast-sites (M/M).
$q_{f,t=0}$	solid-phase sorbate concentration associated with fast-sites at $t = 0$ (M/M).
q_{me}	maximum equilibrium solid-phase sorbate concentration (M/M).

q_s	solid-phase sorbate concentration associated slow-sites (M/M).
q_{se}	sorption equilibrium solid-phase sorbate concentration (M/M).
q_{sse}	sorption equilibrium solid-phase sorbate concentration associated with slow-sites (M/M).
R	mass of solid to volume of solution ratio (M/L^3).
R_p	ratio of the diuron peak area to the DCB peak area.
t	time (T).
V	volume of solution (L^3).

ABBREVIATIONS

atrazine	6-chloro-N-ethyl-N′(1-methylethyl)-1,3,5-triazine-2,4-diamine
bromacil	5-bromo-6-methyl-3-(1-methylpropyl)2,4-(1H,3H)pyrimidinedione
2,4-D	(2,4-dichlorophenoxy)acetic acid
DDT	1,1′-(2,2,2-trichloroethylidene)bis[4-chlorobenzene]
diquat	6,7-dihydrodipyrido[1,2-2′,1′-c]pyrazinendiiumion
diuron	N′-(3,4-dichloropheny)-N,N-dimethylurea
fluridone	1′-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4-(1-H)-pyridinone
HCBP	2,4,5,2′,4′,5′-hexachlorobiphenyl
lindane	γ-1,2,3,4,5,6-hexachlorocyclohexane
linuron	N′-(3,5-dichloropheny)-N-methoxy-N-methylurea
paraquat	1,1′-dimethyl-4,4′-bipuridinium ion
PCB	polychlorinated biphenyl
picloram	4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid
prometone	6-methoxy-N,N′-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine
prometryn	N,N′-bis(1-metthylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine
2,4,5-T	(2,4,5-trichlorophenoxy)acetic acid

1 INTRODUCTION

1.1 Background and Motivation

Recently, more and more groundwater contamination has been reported, including leaking of subsurface storage tanks, leakage from the land disposal of hazardous waste, leaching of pesticides or herbicides applied to crops and lands, and so on. In order to prevent or remediate groundwater contamination, it is necessary to understand the fate and transport of contaminants in the subsurface environment.

Many physical, chemical, and biological processes are involved in the transport of contaminants in groundwater systems, including hydrodynamic transport, sorption/desorption, volatilization, biodegradation, hydrolysis, and retention by plant roots. Sorption is the physico-chemical process in which a substance is transferred from a liquid phase to a solid phase; the reverse reaction is called desorption. Sorption-desorption determines the relative fraction of the contaminant in the solid and liquid phase. The contaminant concentration in each phase will subsequently influence other processes. Therefore, it is important to know the sorptive characteristics of a contaminant to aquifer solids to predict contaminant transport.

Numerous investigations of organic solute sorption to aquifer solids have been done. Most of these investigations have focused on single solute sorption equilibrium. Some have focused on the desorption process— several finding desorption to be hysteretic or non-single valued. This non-singular characteristic of the solute phase distribution depends on the sorption history. When desorption hysteresis occurs, the solid-phase sorbate concentration at desorption equilibrium is different from— usually higher than— that predicted from the sorption equilibrium equation. If such behavior is manifest in the natural environment, any solute transport model that does not account for the hysteretic nature of sorption-desorption would produce inaccurate results. Therefore, it is important to have an understanding of hysteresis.

Several possible explanations have been advanced to describe the observed desorption hysteresis (Brusseau and Rao, 1989):

(1) Nonattainment of equilibrium

If sorption equilibrium is not attained before the desorption process begins, the obtained sorption isotherm is not the true isotherm. Thus desorption equilibrium obtained will be different from sorption equilibrium. Similarly, desorption hysteresis may be incorrectly inferred if sorption equilibrium is attained but desorption measurements are made on a system that has not achieved equilibrium.

(2) Loss of solute

Volatilization, chemical transformation (e.g. hydrolysis), sorption to the container wall, and biodegradation of the solute can occur during an equilibrium experiment. The solid-phase solute mass, hence concentration, is usually computed as the difference between the original mass in the system, minus the mass removed from the system, and minus the fluid-phase mass. Thus, any unaccounted for loss in mass results in an overestimation of the solute concentration on the solid-phase.

(3) Artifact of experimental method

The traditional method applied to investigate desorption equilibrium is the successive-dilution technique, which uses a series of centrifugation-dilution-resuspension steps. It has been reported that the repeated process of resuspension may cause weathering of the solids, giving additional sorption sites that will not be available under normal conditions (McCloskey and Bayer,1986). The hypothesis is that the solid-phase weathering increases the sorption capacity of the solid phase— leading to desorption hysteresis.

(4) Sorption to nonsettling particles

Failure to separate the dissolved organic matter (DOM), or nonsettling particles (NSP), in the supernatant from the solution phase by centrifugation can cause the washout of DOM. Because solvent extraction of a fluid-phase sample includes solute bound to colloidal particles, apparent sorption equilibrium fluid-phase concentrations are actually the sum of these two phases. If a large fraction of fine particles are removed during the sorption step, the apparent desorption equilibrium will result in a lower fluid-phase concentration for a given solid-phase concentration.

(5) Centrifugation effect

Repeated centrifugation may cause a partially irreversible compaction of the solids, which increases the time required to re-establish desorption equilibrium giving the impression of desorption hysteresis.

(6) Accumulated measurement error

Measurement error is another disadvantage of applying the successive-dilution method. This method may allow the small deviation of measurements in each step to accumulate to a large overall error after the sample is handled several times.

(7) Implicit-sorbate

The existence of an implicit-sorbate (unidentified organic substances) that is initially sorbed on the solids before the experiment starts and is released to the solution phase during the sorption and desorption steps may give an increasing amount of available sorption sites to an experimental solute. This increase of sorption sites may lead to apparent desorption hysteresis.

(8) Physical or chemical interactions

Part of the sorbed chemical (sorbate) may be physically or chemically bound to the solid phase during the sorption process. The bound sorbate may be desorbed only in part— when compared to the sorption equilibrium relationship— by lowering the fluid-phase concentration.

These potential causes of desorption hysteresis are described in more detail in chapter 2.

1.2 Objectives

The objectives of this research are:

(1) to investigate experimentally a variety of possible explanations of the desorption hysteresis phenomenon; and

(2) to develop a mathematical model to simulate the sorption-desorption process and to examine the predictive ability of the model.

2 LITERATURE REVIEW

This chapter will present a brief summary of research on rates and equilibrium of sorption-desorption, and desorption hysteresis. The literature reviewed includes discussion of types of sorption isotherms, linearity of isotherms, factors affecting sorption, characteristics of sorption-desorption processes (sorption-desorption rates), and explanations of desorption hysteresis.

2.1 Sorption Equilibria

2.1.1 Sorption equilibrium models

Sorption of organic compounds to natural sorbents has been described as mass transfer of compounds from a fluid-phase to a solid-phase. A solid-solute-solution system is at sorption equilibrium when the distribution of a solute between the solid-phase and the fluid-phase is no longer a function of time. The equilibrium relationship is described by a sorption equilibrium model, often referred to as a sorption isotherm model.

Both linear (Sabljic', 1987) and non-linear (Weber and Miller, 1989) sorption isotherms have been reported to describe the sorption equilibrium of organic compounds to natural sorbents . Four types of isotherms were devised, according to the shape of the isotherm curves, to characterize the sorption mechanism of solutes by sorbents (Giles et al., 1960). The S-type isotherm is characterized by cooperative sorption of solute (one-point attachment). The L-type isotherm, which is associated with a system in which specific bonding sites exist, is most commonly observed in sorption of organic compounds to solids. The H-type isotherm, which indicates that a solute is easily sorbed by a sorbent, is a special case of the L-type isotherm. The C-type isotherm is found in the sorption of solutes to porous media, usually within a narrow solute concentration range resulting in a linear isotherm (Weber and Miller, 1989).

The linear isotherm model is

$$q_e = K_p C_e \tag{2-1}$$

where q_e is the sorption equilibrium, mass-average, solid-phase sorbate concentration; K_p is a linear partition coefficient; and C_e is the sorption equilibrium, volume-average, solution-phase solute concentration.

The Freundlich equation is often used to describe the nonlinear sorption isotherm data for organic compounds in natural solid-water systems (Weber and Miller, 1989). It is expressed as

$$q_e = K C_e^n \tag{2-2}$$

where K is a sorption capacity constant and n is a sorption intensity constant.

2.1.2 Factors affecting sorption equilibrium

2.1.2.1 Solid properties

Many researchers have reported that K_p is positively correlated to the organic carbon content of the solid (Steen et al., 1978; Karickhoff et al., 1979; Peck et al., 1980; Brown and Flagg, 1981; Horzempa and DiToro, 1983; Nkedi-Kizza et al., 1983; Corwin and Farmer, 1984). The consensus of this work is that K_p is a linear function of organic carbon content. This is often expressed in equation form as

$$K_p = f_{oc} K_{oc} \tag{2-3}$$

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

It was also found that sorption of organic compounds to montmorillonite and kaolinite clay (low organic carbon content) may be approximated by the cation-exchange capacity of the solid (Weber and Weed, 1968; Mustafa and Gamar, 1972; Peck et al., 1980). In addition to cation-exchange capacity, surface area, charge density, and percent mineral content of the sorbent have also been reported to be correlated with the partition coefficient (Weber and Weed, 1968; Horzempa and DiToro, 1983; Corwin and Farmer, 1984; McCloskey and Bayer, 1986).

2.1.2.2 Solute properties

The partition coefficient that describes the linear equilibrium relationship can be estimated from the 1-octanol-water partition coefficient (K_{ow}) of the solute and the organic carbon content of the sorbent (Means et al., 1980; Schwarzenbach and Westall, 1981; Chiou et al., 1983; Karickhoff, 1984). Sabljic' (1987) summarizes equilibrium sorption data for a variety of natural systems, tabulates several empirical models for predicting sorption equilibrium, and presents an alternative predictive model based upon molecular connectivity of the solute.

Chiou et al. (1983) investigated the sorption of 12 aromatic compounds on a Woodburn soil and found that the extent of solute insolubility in water is the primary factor affecting the soil organic matter to water partition coefficient (K_{om}). Equilibrium isotherms of binary nonionic organic compounds indicated no competitive effect between two solutes (1,3-dichlorobenzene and 1,2,4-trichlorobenzene). This supported the hypothesis that sorption to the soil organic phase is a primary process for sorption of nonionic organic compounds on soil.

2.1.2.3 Temperature

Temperature was found to be inversely correlated to the partition coefficient of diuron by sediments (Peck et al., 1980). On the other hand, Horzempa and DiToro (1983) reported a positive relationship between the temperature and the partition coefficient of PCB to sediments. This contradiction was attributed to factors other than sorption equilibrium (e.g. kinetics, solubility etc.).

2.1.2.4 Solid/solution ratio

Solid-solution ratio was found inversely related to the sorption coefficient (O'-Connor and Connolly, 1980; Koskinen and Cheng, 1983; Higgo and Rees, 1986). This relationship has been termed the solids effect. A solid-solid interaction may be mediating the sorption process, resulting in the observed solids effect. Increasing the solids concentration may increase the nonsettling particle concentration in the solution phase. Sorption to nonsettling particles can cause part of the sorbate to remain in the apparent solution phase, therefore lowering the sorption capacity constant. The solids effect was found most pronounced for strongly sorbing solutes. For weekly sorbing solutes, the partition coefficient remained constant regardless of the solids concentration (O'Connor and Connolly, 1980).

2.2 Desorption Equilibria

Desorption is the reverse of sorption. It occurs when the solid-phase sorbate concentration exceeds the level that would be in equilibrium with the fluid-phase solute concentration. A decrease of solution-phase solute concentration, a change of solution composition, and a change of temperature are the major causes of desorption (Miller, 1984).

Like sorption, the desorption process reaches a final distribution of solute between the solid-phase and the solution-phase at equilibrium. Many contaminant transport models assume that desorption equilibria may be described by the same equilibrium relationship as sorption equilibria. However, several researchers (van Genuchten et al., 1974; Koskinen et al., 1979; Peck et al., 1980; DiToro and Horzempa, 1982, 1983; Koskinen and Chen, 1983; Isaacson and Frint, 1984; Corwin and Farmer, 1984; Curl and Keoleian, 1984; Miller, 1984; Gschwend and Wu, 1985; Bowman and Sans, 1985; Jaffe, 1986; Uchrin and Mangels, 1987; Hermosin et al., 1987; and McCloskey and Bayer, 1987) have observed that the desorption process is hysteretic or nonsingular, i.e. desorption isotherms are different from the sorption isotherm (see Table 2-1).

The Freundlich sorption-desorption equilibrium model has been used to describe desorption hysteresis

$$q_{se} = K_s C_{se}^{n_s} \tag{2–4}$$

$$q_{de} = K_d C_{de}^{n_d} \tag{2–5}$$

and

Table 2-1 List of Reported Linearity and Desorption Hysteresis of Sorption-Desorption Isotherm

Author	Year	Solute	Solid	Linearity	Desorption Hysteresis
Schwarzenbach & Westall	1981	1,4-dimethylbenzene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	1,3,5-trimethylbenzene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	1,2,3-trimethylbenzene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	1,2,4,5-tetramethylbenzene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	1,4-dimethylbenzene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	n-butylbenzene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	tetrachloroethylene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	chloroethylene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	1,4-dichlorobenzene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	1,2,4-trichlorobenzene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	1,2,3-trichlorobenzene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	1,2,4,5-tetrachlorobenzene	sediments, kaolin	L	N
Schwarzenbach & Westall	1981	1,2,3,4-tetrachlorobenzene	sediments, kaolin	L	N
Karickhoff et al.	1979	pyrene	Doe Run Coarse Silt	L	N
Karickhoff et al.	1979	methoxychlor	Doe Run Coarse Silt	L	N
Gschwend & Wu	1985	PCB	washed sediment	L	N
Peck et al.	1980	diuron	sediments	L	Y
Uchrin & Mangels	1987	benzene	soils	L	Y
Corwin & Farmer	1984	bromacil	sediment	L	Y
Gschwend & Wu	1985	PCB	unwashed sediment	L/NL	Y
Curl & Keoleian	1984	atrazine	Ca-montmorillonite	L/NL	Y
Jaffe	1986	malathion	sediment	L/NL	Y
DiToro & Horzempa	1982,1983	HCBP	sediment	L/NL	Y
Koskinen et al.	1979	2,4,5-T	soils	NL	Y
Bowman & Sans	1985	chlorpyrifos	soil	NL	Y
Bowman & Sans	1985	DDT	soil	NL	Y
Bowman & Sans	1985	dieldrin	soil	NL	Y
Bowman & Sans	1985	diuron	soil	NL	Y
Bowman & Sans	1985	fensulfothion sulfone	soil	NL	Y
Bowman & Sans	1985	fonofos	soil	NL	Y
Bowman & Sans	1985	2,4-D	soil	NL	Y
Bowman & Sans	1985	parathion	soil	NL	Y
Bowman & Sans	1985	picloram	soil	NL	Y
Bowman & Sans	1985	prometryn	soil	NL	Y
Bowman & Sans	1985	hexachlorobiphenyl	soil	NL	Y
van Genuchten et al.	1974	picloram	sediment	NL	Y
Koskinen & Chen	1983	2,4,5-T	soil	NL	Y
Isaacson & Frint	1984	phenolic compounds	sediment	NL	Y
Hermosin et al.	1987	maleic hydrazide	soils	NL	Y
Uchrin & Mangels	1987	benzene	soils	NL	Y
McCloskey & Bayer	1987	fluridone	soils	NL	Y

L = linear sorption/desorption isotherms
L/NL = linear sorption isotherm, nonlinear desorption isotherm
NL = nonlinear sorption/desorption isotherms
N = no desorption hysteresis observed
Y = desorption hysteresis observed

$$K_d = K_s C_{me}^{n_s - n_d} \tag{2-6}$$

where q_{se} is the sorption equilibrium, mass-average, solid-phase sorbate concentration; q_{de} is the desorption equilibrium, mass-average, solid-phase sorbate concentration; C_{se} is the sorption equilibrium, volume-average, solution-phase solute concentration; C_{de} is the desorption equilibrium, volume-average, solution-phase solute concentration; C_{me} is the maximum equilibrium, volume-average, solution-phase solute concentration; K_s is a sorption capacity constant; K_d is a desorption capacity constant; n_s is a sorption intensity constant; and n_d is a desorption intensity constant. A typical sorption-desorption isotherm that includes hysteresis is shown in Figure 2-1.

For the Freundlich desorption equilibrium model, the desorption equilibrium path is dependent upon the maximum solid-phase sorbate concentration. Different desorption capacity constants (K_d) correspond to different sorption equilibrium concentrations (q_{se}, C_{se}).

Brusseau and Rao (1989) presented a normalization procedure to simplify the desorption isotherms. In this procedure, the desorption series were normalized to derive one equivalent desorption isotherm by using the equation

$$q_{de}/q_{me} = (C_{de}/C_{me})^{n_d} \tag{2-7}$$

where q_{me} is the maximum equilibrium solid-phase sorbate concentration; and C_{me} is the maximum equilibrium solution-phase solute concentration. This equation is predicated upon the assumption that $n_d \neq f(C_{me})$. An example normalized Freundlich equilibrium model is illustrated by Figure 2-2.

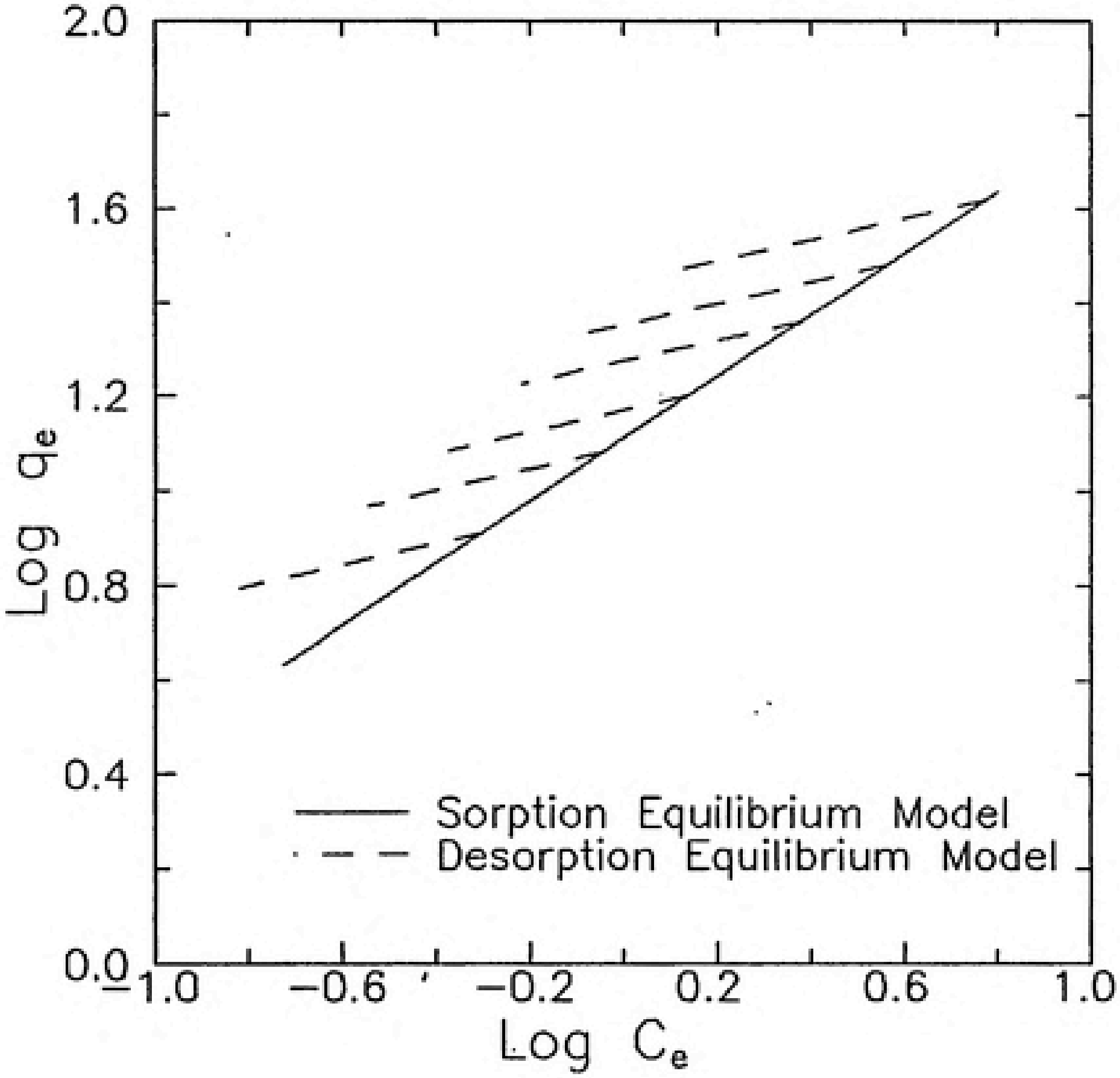

Figure 2-1 Hysteretic Freundlich Sorption-Desorption Equilibrium Model

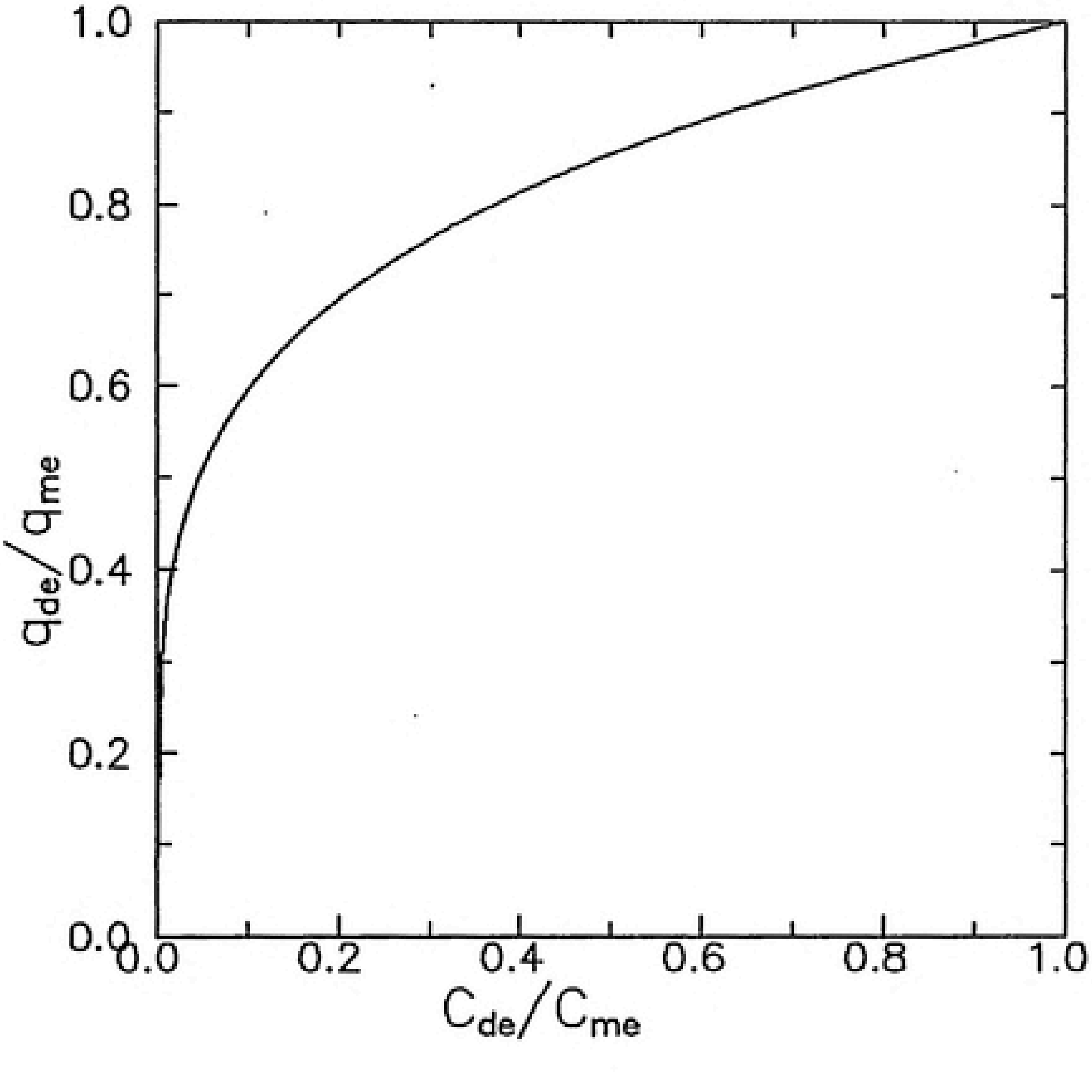

Figure 2-2 Normalized Freundlich Desorption Equilibrium Model

2.3 Sorption Rates

The rate of the sorption process is important in assessing contaminant transport in groundwater systems, because it determines the time required to reach sorption equilibrium. If the sorption rate is rapid, an assumption of instantaneous equilibrium between the solute and the solid is feasible— greatly simplifying the analysis of contaminant transport in such systems. The rate of sorption is dependent on both solute properties and solid characteristics. An inverse relationship was noted between the octanol-water partition coefficient of a solute and the time required to reach equilibrium (Wu and Gschwend, 1986). It may take a long time (months to years) for some hydrophobic solute-natural solid systems to reach true sorption equilibrium (Miller, 1984; Karickhoff, 1984; Coates and Elzerman, 1986). Reported times required to reach sorption equilibrium have ranged from a few minutes to years (see Table 2-2).

2.4 Desorption Rates

Desorption rate has often been assumed to be the same as the sorption rate in equilibrium studies performed to date (Mustafa and Gamar, 1972; van Genuchten et al., 1974; Karickhoff et al., 1979; Koskinen et al., 1979; Peck et al., 1980; Schwarzenbach and Westall, 1981; DiToro and Horzempa, 1982, 1983; Koskinen and Chen, 1983; Corwin and Farmer, 1984; Bouchard and Lavy, 1985; Bowman and Sans, 1985; Gschwend and Wu, 1985; Jaffe, 1986; Hermosin et al., 1987; McCloskey and Bayer, 1987). But the actual desorption rate could be faster or slower than the sorption rate (Hance, 1967; Isaacson and Frink, 1984; Bouchard and Lavy, 1985). It has been reported that desorption rates are dependent on the sorption age of the sorbate, with faster desorption rates noted for shorter sorption age (DiToro and Horzempa, 1982; Karickhoff, 1984; Miller, 1984; Coates and Elzerman, 1986). Coates and

Table 2-2 List of Reported Sorption Equilibration Times in Sorption-Desorption Experiments

Author	Year	Solute	Solid	Equilibration Time
Dao & Lavy	1987	aniline	soil	10 minutes
Dao & Lavy	1987	diuron	soil	30 minutes
Weber & Weed	1968	diquat	montmorillonite,	1 hour
Weber & Weed	1968		kaolinite	1 hour
Weber & Weed	1968	paraquat	montmorillonite,	1 hour
Weber & Weed	1968		kaolinite	1 hour
Weber & Weed	1968	prometone	montmorillonite,	1 hour
Weber & Weed	1968		kaolinite	1 hour
Adams & Li	1971	lindane	soils	90 minutes
Wauchope & Myers	1985	atrazine	sediments	2 hours
Wauchope & Myers	1985	linuron	sediments	2 hours
DiToro & Horzempa	1982,1983	HCBP	sediments	3 hours
Dao & Lavy	1987	aniline	soil	3 to 5 hours
Dao & Lavy	1987	diuron	soil	3 to 5 hours
Karickhoff et al.	1979	naphthalene	sediments	4 to 8 hours
Karickhoff et al.	1979	2-methylnaphthalene	sediments	4 to 8 hours
Karickhoff et al.	1979	phenanthrene	sediments	4 to 8 hours
Karickhoff et al.	1979	benzene	sediments	4 to 8 hours
Hermosin et al.	1987	maleic hydrazide	22 soils	4 hours
Isaacson & Frint	1984	phenolic compounds	sediments	100 to 3000 minutes
van Genuchten et al.	1974	picloram	Ca-saturated soil	5 hours
Bouchard & Lavy	1985	hexazinone	soils	6 to 12 hours
Jaffe	1986	malathion	sediment	12 hours
Rogers et al.	1980	benzene	montmorillonite	16 hours
Schwarzenbach & Westall	1981	1,4-dimethylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,3,5-trimethylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,3-trimethylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,4,5-tetramethylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,4-dimethylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	n-butylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	tetrachloroethylene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	chloroethylene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,4-dichlorobenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,4-trichlorobenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,3-trichlorobenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,4,5-tetrachlorobenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,3,4-tetrachlorobenzene	sediments, kaolin	18 hours
Karickhoff et al.	1979	pyrene	sediments	24 hours
Karickhoff et al.	1979	methoxychlor	sediments	24 hours
Karickhoff et al.	1979	anthracene	sediments	24 hours
Karickhoff et al.	1979	9-methylanthracene	sediments	24 hours
Karickhoff et al.	1979	tetracene	sediments	24 hours
Karickhoff et al.	1979	hexachlorobiphenyl	sediments	24 hours
Koskinen et al.	1979	2,4,5-T	soils	24 hours

Table 2-2 continued

Author	Year	Solute	Solid	Equilibration Time
Bowman & Sans	1985	chlorpyrifos	soils	24 hours
Bowman & Sans	1985	DDT	soils	24 hours
Bowman & Sans	1985	dieldrin	soils	24 hours
Bowman & Sans	1985	diuron	soils	24 hours
Bowman & Sans	1985	fensulfothion sulfone	soils	24 hours
Bowman & Sans	1985	fonofos	soils	24 hours
Bowman & Sans	1985	2,4-D	soils	24 hours
Bowman & Sans	1985	parathion	soils	24 hours
Bowman & Sans	1985	picloram	soils	24 hours
Bowman & Sans	1985	prometryn	soils	24 hours
Mustafa & Gamar	1972	diuron	soils	24 hours
Peck et al.	1980	diuron	sediments	24 hours
Nkedi-kizza et al.	1987	atrazine	soil	24 hours
Nkedi-kizza et al.	1987	aniline	soil	24 hours
Koskinen & Chen	1983	2,4,5-T	soil	24 hours
Chiou et al.	1983	benzene	soil	24 hours
Chiou et al.	1983	ethylbenzene	soil	24 hours
Chiou et al.	1983	chlorobenzene	soil	24 hours
Chiou et al.	1983	anisole	soil	24 hours
Chiou et al.	1983	1,2-dichlorobenzene	soil	24 hours
Chiou et al.	1983	1,3-dichlorobenzene	soil	24 hours
Chiou et al.	1983	1,4-dichlorobenzene	soil	24 hours
Chiou et al.	1983	1,2,4-trichlorobenzene	soil	24 hours
Chiou et al.	1983	2-PCB	soil	24 hours
Chiou et al.	1983	2,2'-PCB	soil	24 hours
Chiou et al.	1983	2,4'-PCB	soil	24 hours
Chiou et al.	1983	2,4,4'-PCB	soil	24 hours
Corwin & Farmer	1984	bromacil	sediment	48 hours
Corwin & Farmer	1984	diquat	sediment	48 hours
Gschwend & Wu	1985	PCB	sediment	48 hours
Weber & Miller	1988	nitrobenzene	aquifer sands	100 hours
Weber & Miller	1988	lindane	aquifer sands	100 to 200 hours
McCloskey & Bayer	1987	fluridone	soil	6 days
Miller	1984	lindane	soils	longer than 7 days
Karickhoff	1984	organic pollutants	sediment or soil	weeks to months
Coates & Elzerman	1986	PCB congeners	sediment	weeks to years

Elzerman (1986) also indicated that if the desorption process was initiated after attainment of sorption equilibrium, the desorption rate for a hydrophobic solute as a function of sorbent concentration should be constant if particles did not aggregate. However, if particle aggregation occurred during the sorption-desorption process, the desorption rate would become slower due to the increasing length of diffusion path. Reported desorption equilibration times in sorption-desorption experiments are listed in Table 2-3.

2.5 Desorption Hysteresis Theories

The mechanism of desorption hysteresis is not well understood; several possible explanations to describe this phenomenon include nonattainment of equilibrium, loss of solute, artifact of experimental method, sorption to nonsettling particles, centrifugation effects, accumulated measurement error, presence of implicit-sorbate, and physical or chemical interactions. This section will briefly summarize each of these theories.

2.5.1 Nonattainment of equilibrium

If sorption equilibrium is not established before the desorption process is initiated, the observed sorption relationship is not the true equilibrium distribution. Thus, the desorption relationship obtained will be different from the obtained sorption isotherm. Miller (1984) observed desorption hysteresis in experiments of short equilibration times (24 to 48 hours), but no desorption hysteresis was observed in experiments of longer equilibration times (7 to 20 days).

The hysteresis found in sorption-desorption isotherms could also be due to the diffusion of solute into the solid particles; therefore, a much longer time was required for the sorbate to diffuse from the sorbed site to the solution (Wu and Gschwend, 1986; McCloskey and Bayer,1986). Thus, a desorption rate may be slower than the

Table 2-3 List of Reported Desorption Equilibration Times in Sorption-Desorption Experiments

Author	Year	Solute	Solid	Equilibration Time
DiToro & Horzempa	1982,1983	HCBP	sediments	2 hours
van Genuchten et al.	1974	picloram	Ca-saturated soil	5 hours
Bouchard & Lavy	1985	hexazinone	soils	6 hours
Hermosin et al.	1987	maleic hydrazide	22 soils	12 hours
Jaffe	1986	malathion	sediment	12 hours
Schwarzenbach & Westall	1981	1,4-dimethylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,3,5-trimethylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,3-trimethylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,4,5-tetramethylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,4-dimethylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	n-butylbenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	tetrachloroethylene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	chloroethylene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,4-dichlorobenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,4-trichlorobenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,3-trichlorobenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,4,5-tetrachlorobenzene	sediments, kaolin	18 hours
Schwarzenbach & Westall	1981	1,2,3,4-tetrachlorobenzene	sediments, kaolin	18 hours
Mustafa & Gamar	1972	diuron	soils	24 hours
Peck et al.	1980	diuron	sediments	24 hours
Koskinen & Chen	1983	2,4,5-T	soil	24 hours
McCloskey & Bayer	1987	fluridone	soils	24 hours
Karickhoff et al.	1979	pyrene	Doe Run Coarse Silt	24 hours
Karickhoff et al.	1979	methoxychlor	Doe Run Coarse Silt	24 hours
Koskinen et al.	1979	2,4,5-T	soils	24 hours
Bowman & Sans	1985	Chlorpyrifos	soils	24 hours
Bowman & Sans	1985	DDT	soils	24 hours
Bowman & Sans	1985	dieldrin	soils	24 hours
Bowman & Sans	1985	diuron	soils	24 hours
Bowman & Sans	1985	fensulfothion sulfone	soils	24 hours
Bowman & Sans	1985	fonofos	soils	24 hours
Bowman & Sans	1985	2,4-D	soils	24 hours
Bowman & Sans	1985	parathion	soils	24 hours
Bowman & Sans	1985	picloram	soils	24 hours
Bowman & Sans	1985	prometryn	soils	24 hours
Bowman & Sans	1985	hexachlorobiphenyl	soils	24 hours
Corwin & Farmer	1984	bromacil	sediment	48 hours
Corwin & Farmer	1984	diquat	sediment	48 hours
Gschwend & Wu	1985	PCB	sediment	48 hours
Miller	1984	lindane	soils	longer than 7 days
Coates & Elzerman	1986	PCB (less than 4 Cl atoms)	sediment	6 weeks
Coates & Elzerman	1986	PCB (more than 6 Cl atoms)	sediment	months to years

corresponding sorption rate (Hance, 1967; Isaacson and Frink,1984; Bouchard and Lavy,1985), and a longer time would be required to reach desorption equilibrium. If the desorption equilibrium is not attained, solid-phase concentration would be higher than the true equilibrium value— giving a solute phase distribution suggesting hysteresis. Under such conditions, the calculated sorbate concentration would be greater than the true equilibrium sorbate concentration, causing the deviation of desorption isotherms from the sorption isotherm (Corwin and Frint, 1984).

2.5.2 Loss of solute

Loss of solute has been reported as a key reason for desorption hysteresis. During the sorption-desorption experiments, volatilization, biodegradation, chemical decomposition, and sorption to the container walls can cause loss of solute. Due to the mass-balance method usually used to compute the sorbate concentration, any solute lost will be assumed to exist on the solid phase. This will result in an overestimation of the sorbate concentration and apparent desorption hysteresis (Koskinen, O'Connor and Cheng,1979; Rogers, McFarlane and Cross, 1980; Bouchard and Lavy, 1985; Hermosin, Cornejo and Rodriguez, 1987).

2.5.3 Artifact of experimental method

The use of the suspension-centrifugation-resuspension method in batch reactor sorption-desorption isotherm experiments has been reported as a possible cause of hysteresis. The repeated suspension may cause weathering of the solid thereby increasing available sorption sites. Also, the repeated washing of the solids (adding a solute-free solution to the decanted soil sample) may alter the organic matter of the solid and reveal additional sorption sites. Both procedures may increase the sorption capacity causing apparent hysteresis (Koskinen and Cheng, 1983).

2.5.4 Sorption to nonsettling particles

Sorption of solutes on nonsettling organic particles (NSPs) may also cause apparent desorption hysteresis. Sorbates sorbed to soluble organics or colloidal particles may not be separated by centrifugation and could thus be incorrectly reported as free chemicals in solution. Under such circumstances, the apparent sorption equilibrium solute concentration actually includes both free solute and solute sorbed to colloidal particles, thus overestimating the sorption equilibrium solute concentration. Also, nonsettling organic particles may be removed from the system during decanting of the soil samples, resulting in a smaller amount of NSPs remaining in the batch reactor. A decrease in NSPs during desorption steps can lead to lower apparent fluid-phase concentrations compared to the apparent sorption equilibrium relationship, hence apparent hysteresis. Both of the above situations can cause erroneous equilibrium interpretations (O'Connor and Connolly, 1980).

Gschwend and Wu (1985) described the NSP effect by presenting the equation

$$K_{p,obs} = \frac{P/M_p}{(D+N)/V} \tag{2-8}$$

where $K_{p,obs}$ is the observed partition coefficient; P is the mass of compound sorbed to settleable particles; M_p is the mass of particles; D is the mass of compound dissolved; N is the mass of compound sorbed to NSPs; and V is the volume of water.

If the suspended solid loadings are small, such that $D \gg N$, then $K_{p,obs} \approx K_p$. However, if the suspended solid loadings are large such that D is not much greater than N, then $K_{p,obs} < K_p$. Gschwend and Wu conducted sorption-desorption equilibrium studies using both unwashed sediments and prewashed sediments (low NSP loading). Apparent desorption hysteresis was found for unwashed sediments but no desorption hysteresis was observed in the prewashed sediment-water system.

2.5.5 Centrifugation effect

Browman and Sans (1985) investigated the cause of hysteresis by using the consecutive-desorption method (which uses a series of centrifugation steps) and a single-dilution method (which uses centrifugation only once for all samples). The results showed that the isotherm obtained using the single-dilution method exhibited considerably less hysteresis than the isotherm obtained using the consecutive-desorption method. They postulated that repeated centrifugation might cause a partially irreversible compaction of the solids, which would greatly increase the desorption time required to re-establish equilibrium.

2.5.6 Accumulated measurement error

The consecutive-desorption (or successive-dilution) technique applied in desorption isotherm studies requires several successive sampling steps. Individual measurement error in each step may accumulate to give a large overall error, resulting in a deviation of desorption isotherms from the sorption isotherm (Brusseau and Rao, 1989).

2.5.7 Presence of implicit-sorbate

Curl and Keoleian (1984) presented an implicit-sorbate model to explain the hysteresis in sorption-desorption of organic chemicals to natural sorbents. The model is based on competitive sorption between two sorbates, the one under study and the implicit one which was initially sorbed on the sorbent. The implicit-sorbate could be any unidentified organic substances that were sorbed on the sorbent before the experiment started. During the sorption-desorption experiments, the implicit-sorbate desorbs and reveals more sites for the solute under study, thus increasing the sorption of the solute.

2.5.8 Physical or chemical interactions

Horzempa and DiToro (1982,1983) investigated the reversibility of sorption-desorption of hexachlorobiphenyl (HCBP) on sediment, and postulated a two-component theory. Nonattainment of equilibrium, loss of solute, and centrifugation effects were found not to be the causes of desorption hysteresis. They attributed the desorption hysteresis to the formation of HCBP-sediment bonds of different strengths, described by a readily desorbed reversible component and a component resistant to desorption.

The related research about desorption hysteresis is briefly summarized in Table 2-4.

Table 2-4 Summary of Desorption Hysteresis Theories

Author	Year	Solute	Solid	Explanation of Desorption Hysteresis
Koskinen et al.	1979	2,4,5-T	soils	loss of solute (biochemical degradation)
DiToro & Horzempa	1982,1983	HCBP	sediments	formation of HCBP-sediment bonds of different strengths (reversible + resistant components)
Koskinen & Chen	1983	2,4,5-T	Palouse silt loam soil	artifact of experimental method, physical/chemical properties of the soil/water system were changed in sorption-desorption processes
Isaacson & Frint	1984	phenolic compounds	sediment	nonattainment of equilibrium, a fraction of sorbate was irreversibly held by sediment
Corwin & Farmer	1984	bromacil, diquat	sediment	nonattainment of equilibrium
Curl & Keoleian	1984	atrazine	Ca-montmorillonite	presence of implicit-sorbate
Gschwend & Wu	1985	PCB	sediment	sorption to non-settling particles incomplete phase separation
Bowman & Sans	1985	chlorpyrifos, DDT, dieldrin, diuron, fensulfothion sulfone, fonoofos, picloram parathion, prometry, 2,4-D, hexachlorobipyenul	soils	centrifugation effect compact of sorbent by centrifugal force, loss of sorbate, instability of solute in soil-water system
Jaffe	1986	malathion	sediment	sorption to non-settling particles
Hermosin et al.	1987	maleic hydrazide	soils	loss of solute (precipitation and/or biodegradation)
McClosdey & Bayer	1987	fluridone	soils	weathering of soil, intraparticle diffusion, nonattainment of equilibrium

3 MATERIALS AND METHODS

3.1 Materials

3.1.1 Solid

A subsurface solid sample (Wagner) was collected from Ann Arbor, Michigan. The Wagner sample was air-dried and passed through a 2-mm sieve before use. The physical and chemical properties of the Wagner material are listed in Table 3-1. A grain size distribution diagram of the Wagner material is shown in Figure 3-1. Grain size analysis of the Wagner sample was done by fractioning with sieves of different opening sizes. Organic carbon content of the Wagner sample was analyzed by the ampule method with an O.I. Corporation Model 700 TOC analyzer. The cation-exchange capacity was determined by the sodium saturation method (Black, 1965). Detailed experimental procedures for the determination of the organic carbon content and the cation-exchange capacity are described in Appendix I and II, respectively.

3.1.2 Solute

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] is a herbicide of relatively low water solubility (42 mg/l at $25°C$) and is widely used for selective long-term weed control on crops such as asparagus, citrus, cotton, pineapple, sugar cane, temperate

Table 3-1 Physical and Chemical Properties of the Wagner Material

Median grain size diameter	0.45 mm
Grain size uniformity coefficient	2.476
Organic carbon content	1.2 %
Cation-exchange capacity	3 meq./100 g soil

tree and bush fruits. The mean value of log K_{ow} (octanol-water partition coefficient) of diuron is 2.92 (Hansch and Leo, 1979). Phototoxic residues of diuron in soil disappeared within one season at application rates of 0.6 to 4.8 kg/ha (The Pesticide Manual, 1983). Its rate of hydrolysis is negligible at ordinary temperatures and neutral pH . It decomposes at 180 to 190°C and is degraded in soil by demethylation, 50% loss was reported in 90 to 180 days (Sheets, 1964). Diuron is a stable chemical of fairly long persistence in soil. Since it is highly persistent in soil, it constitutes a possible residue hazard.

Preliminary studies showed diuron is non-volatile (the vapor pressure of diuron at $50°C$ is 3.1×10^{-6} mm Hg), doesn't degrade in a buffer solution of pH 8.42, and can be analyzed by gas chromatography or UV spectroscopy. Diuron was chosen as the target compound for this work because it is easy to handle in lab experiments, convenient to analyze for concentration, and potentially a hazardous residue in subsurface systems. Analytical grade diuron (98%) was obtained from de Nemours & Co. and it was used as received.

3.1.3 Reagents

3.1.3.1 Buffer solutions

A buffer solution was used as the blank solution (herbicide free) for all exper-

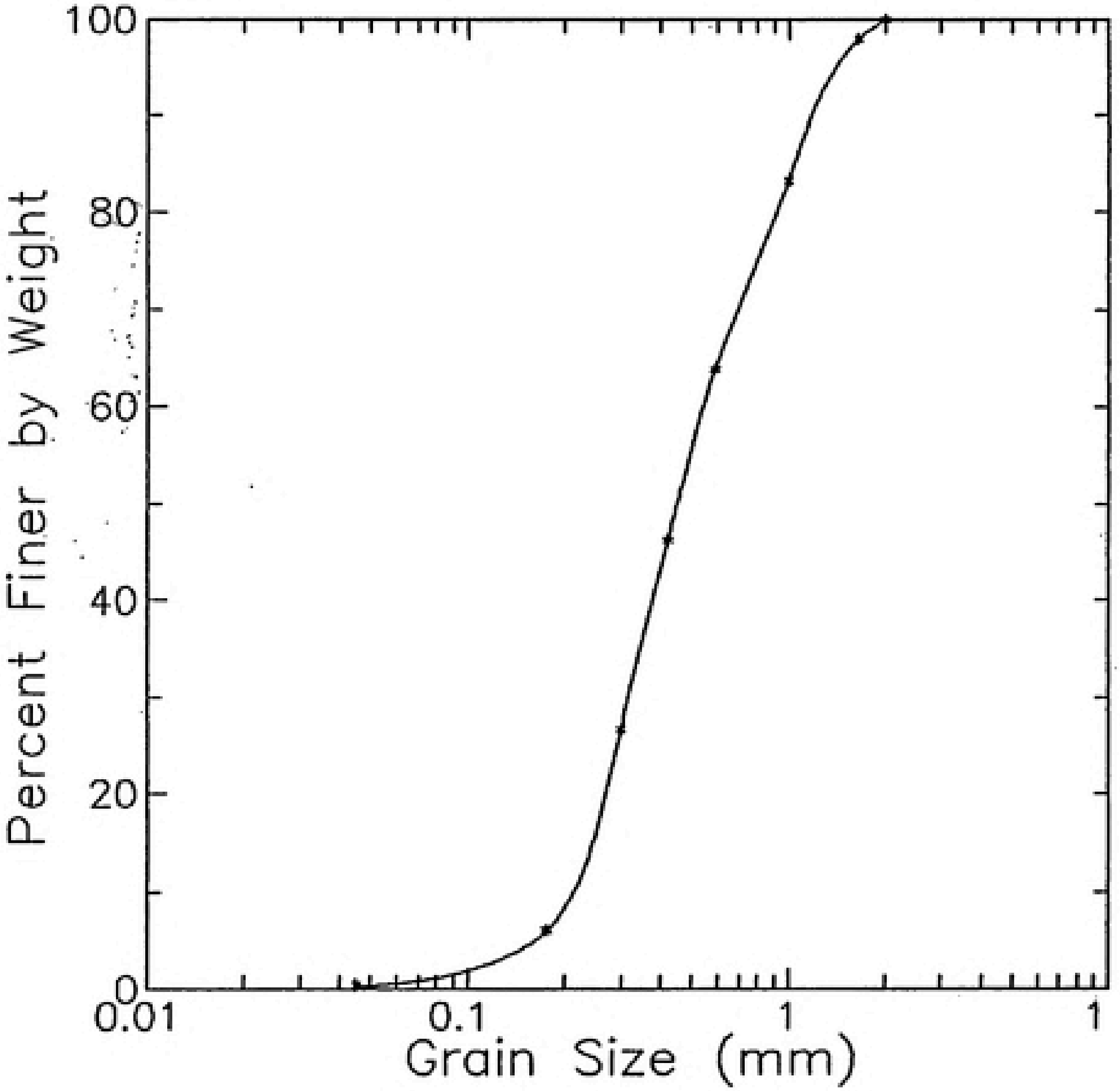

Figure 3-1 Grain Size Distribution Diagram of the Wagner Material

iments. It contained tetraborate, calcium chloride dihydrate, and sodium azide. Tetraborate was used in the experiment as a buffer to control the change of pH in the batch systems. Calcium chloride dihydrate was added to the buffer solution to help obtain good separation of solids from the solution, while sodium azide was used to inhibit biodegradation in the system.

The buffer solutions were made of 0.005 M A.C.S. grade calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), 0.005 M A.C.S. grade sodium borate ($Na_2B_4O_7 \cdot 10H_2O$), and 0.005 M purified sodium azide (NaN_3). The pH of the buffer solution was adjusted to 8.42 by adding concentrated hydrochloric acid (HCl).

3.1.3.2 Diuron standards

Diuron standards were made by dissolving diuron in the buffer solution.

3.1.4 Glassware

Kimax glass centrifuge bottles were used as the bottle point reactors. The centrifuge bottles and sample vials were soaked in Alconox cleaning solution overnight, brushed 15 times with tufted-end brushes, then rinsed approximately 10 times, and air-dried for two days or oven-dried overnight before use.

All other glassware was acid-washed with Nochromix in sulfuric acid, rinsed with distilled water at least ten times, then air-dried for two days or oven-dried overnight.

3.2 Bottle-Point Methods

A bottle-point technique that uses a tumbled glass centrifuge bottle for each data point was applied to investigate the sorption of diuron to the Wagner material. Several studies using this method were performed:

(1) A degradation study was performed to examine if there was any degradation of

the solute in the solution phase. A study was performed to observe the effect of sodium azide on inhibiting the rate of biodegradation of diuron in the presence of the Wagner material.

(2) Sorption rate studies were performed to obtain the time required to reach sorption equilibrium.

(3) Desorption rate studies were conducted to determine the time needed to establish desorption equilibrium.

(4) Sorption-desorption equilibrium studies were performed.

(5) A study was conducted to observe the effect of sorption age on the rate of desorption.

(6) A study was performed to investigate the effect of initial solute concentration on the rate of desorption.

(7) Complex concentration history sorption-desorption equilibrium experiments were conducted to investigate non-ideal sorption-desorption behavior.

(8) A single-dilution method was applied to a desorption equilibrium study to observe the effect of centrifugation and dissolved organic matter (DOM) removal on desorption.

3.2.1 Degradation study

A diuron stock solution of 14 mg/l was made in the standard buffer solution. Two sets of sample vials were filled with the stock solution and the buffer solution, capped with teflon-lined caps, and stored in a covered black box at room temperature. At different times, samples were taken out of the box and analyzed by UV absorption spectroscopy, and then put back into the box for subsequent sampling and analysis. The absorbance of the samples were recorded and the concentration of the stock solution was calculated.

The effect of including sodium azide in the system was investigated by conducting two parallel sorption rate studies, with and without azide in the soil/solution system. The study lasted for a period of 20 days.

3.2.2 Sorption rate studies

The experimental procedure used for sorption rate studies was:

(1) 10 g of Wagner material and 10 ml of buffer solution were put in each 35-ml centrifuge bottle, capped with teflon-lined screw caps, and the solid was hydrated for a minimum of 12 hours;

(2) 10 ml of 28 mg/l diuron stock solution was added to each bottle to obtain a solid-solution ratio of 1:2 and an initial diuron concentration of 14 mg/l, which is one third of diuron solubility in water (10 ml of buffer solution instead of diuron stock solution were added to the blanks);

(3) the tightly capped bottles were then put on a tumbler to ensure mixing of the solid material and the solution;

(4) at different times, the samples were taken off the tumbler, and centrifuged at 2500 rpm for 30 minutes; and

(5) supernatants were decanted and saved for the diuron concentration analysis.

A high initial concentration (28 mg/l) long-term sorption rate study was conducted in the same way, but 10 g of soil, 4 ml of buffer and 16 ml of 35 mg/l stock solution were used for each diuron sample in the experiment.

3.2.3 Desorption rate studies

The desorption rate studies were conducted following the same procedure as the sorption rate studies, except a 10-day sorption period was allowed for all samples. Following the sorption period:

(1) the samples were centrifuged, and 15 ml of supernatant was replaced with 15 ml of buffer solution;

(2) the solid-solution mixtures were tumbled again, sets of bottles were removed at different times then recentrifuged; and

(3) the supernatants were removed and analyzed for diuron concentrations.

3.2.4 Sorption-desorption equilibrium studies

Sorption-desorption equilibrium studies were performed using the following protocol:

(1) 15 g of solids and 30 ml of solution of different diuron concentrations (2 to 28 mg/l) were prepared (6 ml of buffer solution was used to hydrate the solid) in the centrifuge bottles;

(2) samples were tumbled for 44 days then centrifuged; 25 ml of the supernatant was removed and saved for diuron concentration analysis; 25 ml of buffer solution was added to each bottle;

(3) the bottles were then put on tumbler again for another seven days then re-centrifuged;

(4) 25 ml of supernatant was replaced with 25 ml of buffer solution, the supernatants were saved for diuron concentration analysis, the soil-solution mixtures were put on the tumbler, re-equilibrated and then re-centrifuged; and

(5) the process was repeated for a total of four desorption steps.

3.2.5 Sorption age study

A sorption age study was conducted following the same procedure as the desorption rate study except the sorption times of the samples were 1, 10, and 20 days.

3.2.6 Initial concentration study

An initial concentration study was conducted following the same procedure as the desorption rate study except that three different initial solute concentrations of 7, 14, and 21 mg/l were used.

3.2.7 Other sorption-desorption equilibrium studies

(1) A short-term sorption-desorption equilibrium study was conducted following the same procedure of the sorption-desorption equilibrium study, but initial concentrations of 2 to 14 mg/l, a sorption equilibration time of 10 days, and a desorption equilibration time of 5 days were used.

(2) Two sets of samples of initial concentrations of 14 mg/l and 9.3 mg/l were used in the sorption-desorption-consecutive sorption-consecutive desorption (SDSD) study. The procedure of this study is basically the same as that of sorption-desorption equilibrium study. Following the initial sorption equilibration:

   a. 25 ml of the supernatant was removed and saved for diuron concentration analysis; 25 ml of buffer solution was added to the bottle;
   b. the bottles were then put on the tumbler again for another 5 days then re-centrifuged;
   c. 25 ml of the supernatant was replaced with 25 ml of 2.8 mg/l stock solution, the supernatants were saved for diuron concentration analysis, the soil-solution mixtures were put on the tumbler for another 10 days then re-centrifuged;
   d. 20 ml of the supernatant was replaced with 20 ml of 4.2 mg/l stock solution, the supernatants were saved for diuron concentration analysis, the soil-solution mixtures were put on the tumbler,re-equilibrated and re-centrifuged;
   e. 20 ml of the supernatant was replaced with 20 ml of 5.6 mg/l stock solution, the supernatants were saved for diuron concentration analysis, the soil-solution mixtures were put on the tumbler,re-equilibrated and re-

centrifuged;

   f. 20 ml of the supernatant was replaced with 20 ml of 14 mg/l stock solution, the supernatants were saved for diuron concentration analysis, the soil-solution mixtures were put on the tumbler,re-equilibrated and recentrifuged;

   g. 25 ml of the supernatant was removed and saved for diuron concentration analysis; 25 ml of buffer solution was added to the bottle; the bottles were then put on the tumbler again for another 5 days then re-centrifuged; and

   h. the desorption process was repeated for another two times.

(3) A Sorption-desorption-consecutive sorption (SDDS) study was performed. The procedure of this study is similar to the procedure of the SDSD study. Following the initial sorption equilibration:

   a. 25 ml of the supernatant was removed and saved for diuron concentration analysis; 25 ml of buffer solution was added to the bottle; the bottles were then put on the tumbler again for another 5 days then re-centrifuged;

   b. the above desorption process was repeated again;

   c. 25 ml of the supernatant was removed and saved for diuron concentration analysis; 25 ml of 7 mg/l stock solution was added to the bottle; the bottles were then put on the tumbler again for another 10 days then re-centrifuged; and

   d. the above sorption process was repeated for another two times.

3.2.8 Single-dilution desorption equilibrium study

A single dilution desorption equilibrium experiment was performed using the following method:

(1) 3.5 g of Wagner solid and 3.5 ml of buffer solution were put in each of 16 centrifuge bottles and the solids were hydrated for a minimum of 12 hours;

(2) 3.5 ml of 28 mg/l stock solution were added to eight diuron samples while 3.5 ml of buffer solution were added to the other eight blank samples, all samples were then tumbled to allow complete mixing for ten days;

(3) after ten days of sorption, two diuron samples and two blank samples were centrifuged, and the supernantants were saved for determination of UV absorbance;

(4) 10 ml, 20 ml, and 30 ml of buffer solution were added to the remaining bottles after the ten-day sorption to dilute the liquid-phase concentrations further; and

(5) after a five-day desorption period, the samples were centrifuged, and the supernatants were saved for UV spec analysis.

3.3 Extraction Methods

3.3.1 Solid-phase extractions

Solid-phase extractions were performed on several samples at the end of some experiments to check if there was any loss of sorbate during the experimental period. It has been reported that methanol and acetone are much better extracting solvents than water for extracting organic compounds from solids (Ho and Daw, 1988). But acetone-extraction was not feasible in this research because it exerts a very high background absorbance at the wavelength of interest. Therefore, methanol was used as the extracting solvent in the solid extraction experiment. The following procedure was used:

(1) Solid-solution samples were first centrifuged then decanted as completely as possible;

(2) 25 ml of methanol were added to the decanted samples, and the samples were then put on tumbler for one day;

(3) step 1 and 2 were repeated two more times and the supernatants were saved

in 100-ml volumetric flasks;

(4) to each 100-ml volumetric flask, enough methanol was added to bring the volume of the sample to 100 ml;

(5) diuron methanol standards were prepared by dissolving diuron in methanol;

(6) the absorbance of methanol samples and standards were measured; and

(7) the diuron mass that was extracted was computed and compared to the original mass of diuron in the system.

3.3.2 GC solvent extraction

Aqueous samples were extracted with hexane before performing GC analysis using the following procedure:

(1) 5 ml of an aqueous sample and 5 ml of hexane were put in a sample vial, and capped with teflon-lined cap;

(2) the sample was mixed for three minutes to allow complete extraction.

(3) the solvent sample was stored in a refrigerator after shaking; and

(4) the solvent samples were warmed to room temperature before performing GC analysis, and one μl of the upper-level liquid (hexane with diuron) was injected into a GC for diuron concentration analysis.

3.4 Analytical Methods

Diuron can be analyzed by gas chromatography (GC) or ultra violet spectrophotometry (UV spec). For the GC method, the diuron solvent samples were analyzed on a Hewlett Packard 5890 gas chromatograph fitted with a 30-m, DB5 capillary column and an electron capture detector. The operating conditions are listed in Table 3-2.

Dichlorobenzene (DCB) was used as the internal standard. The ratio of di-

Table 3-2 The Operating Conditions of Diuron GC Analysis

Injector temperature	275 degree C
Detector temperature	300 degree C
Oven temperature	170 degree C, isothermal
Column flowrate	1.63 ml/min
Split flowrate	35 ml/min
Purge flowrate	4.05 ml/min

uron peak area to DCB peak area (R_p) for each injected sample was computed. The correlation between the ratio of peak areas (R_p) and the diuron concentration of standards (C) was determined by performing a nonlinear regression on these collected data. The calibration curve was found to be

$$R_p = -0.0027C^2 + 0.1356C + 0.0265 \tag{3-1}$$

The R_p of each sample was computed and used to determine the diuron concentration via the calibration curve.

For the UV method, the liquid-phase concentrations of diuron were determined by measuring the UV light absorbance on a Perkin-Elmer Lambda 3 spectrophotometer. The diuron in distilled, deionized water was found to exhibit maximum absorbance at 210 nm and 248 nm, while the buffer solution exhibited a maximum absorbance at 220 nm due to the presence of azide (see Figure 3-2). The absorbance at 248 nm was used through all the studies for calculating diuron concentrations to minimize the azide interference.

Preliminary studies showed background interference existed due to sodium azide in the solutions and organic matter released from the soils. To eliminate background interference, two blanks were carried along with each sample point. The blanks were made with the same procedure in the studies except the diuron stock solutions were replaced with the same amount of buffer solutions.

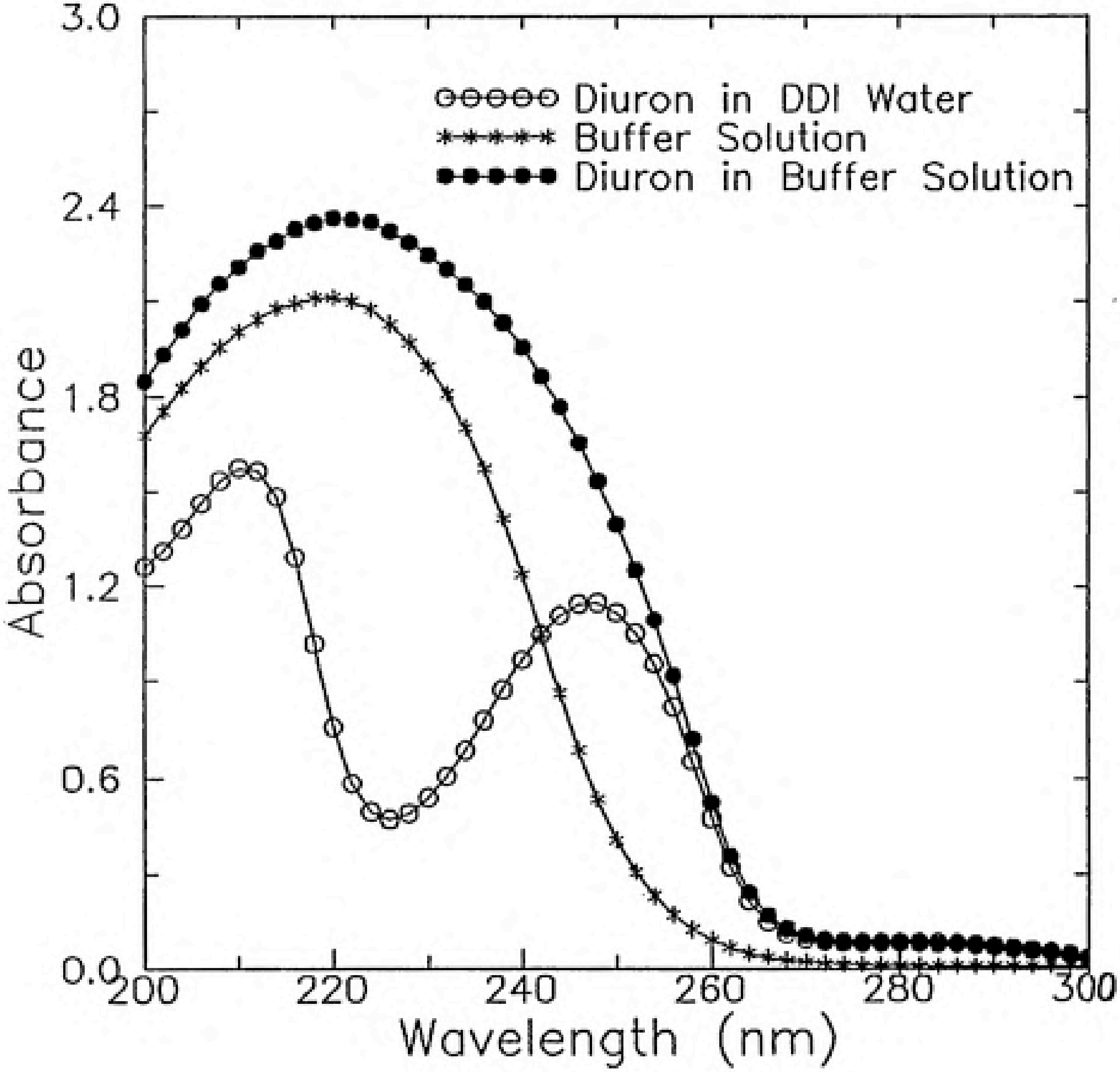

Figure 3-2 UV Response of Diuron and Azide

The measured absorbance of diuron standards was subtracted by the absorbance of the buffer solution with which the standards were made, giving a net absorbance. The correlation between the net absorbance (ABS') and the concentration of standards (C) was determined by performing a nonlinear regression on all the absorbance data of the standards collected during the experimental period. The calibration curve was found to be

$$ABS' = -0.00049C^2 + 0.08C - 0.002 \tag{3-2}$$

The measured absorbance of each sample was subtracted by the corresponding absorbance of the blanks. The net absorbance of each sample was used to compute the diuron concentration via the calibration curve. The amount of diuron that disappeared from the solution was assumed to be sorbed by the solids. The amount of diuron measured in the solution in excess of the amount of diuron in the solution at the beginning of the desorption process was assumed to be desorbed.

Figure 3-3 and Figure 3-4 show the comparison of experimental data obtained with the GC method and the UV method. The agreement between these two methods was good. The UV method was applied to all other studies in this research because solvent extraction was needed for the GC method, while aqueous solutions were used directly for the UV-spec method, and preliminary studies showed that the UV method gave a more consistent results than the GC method.

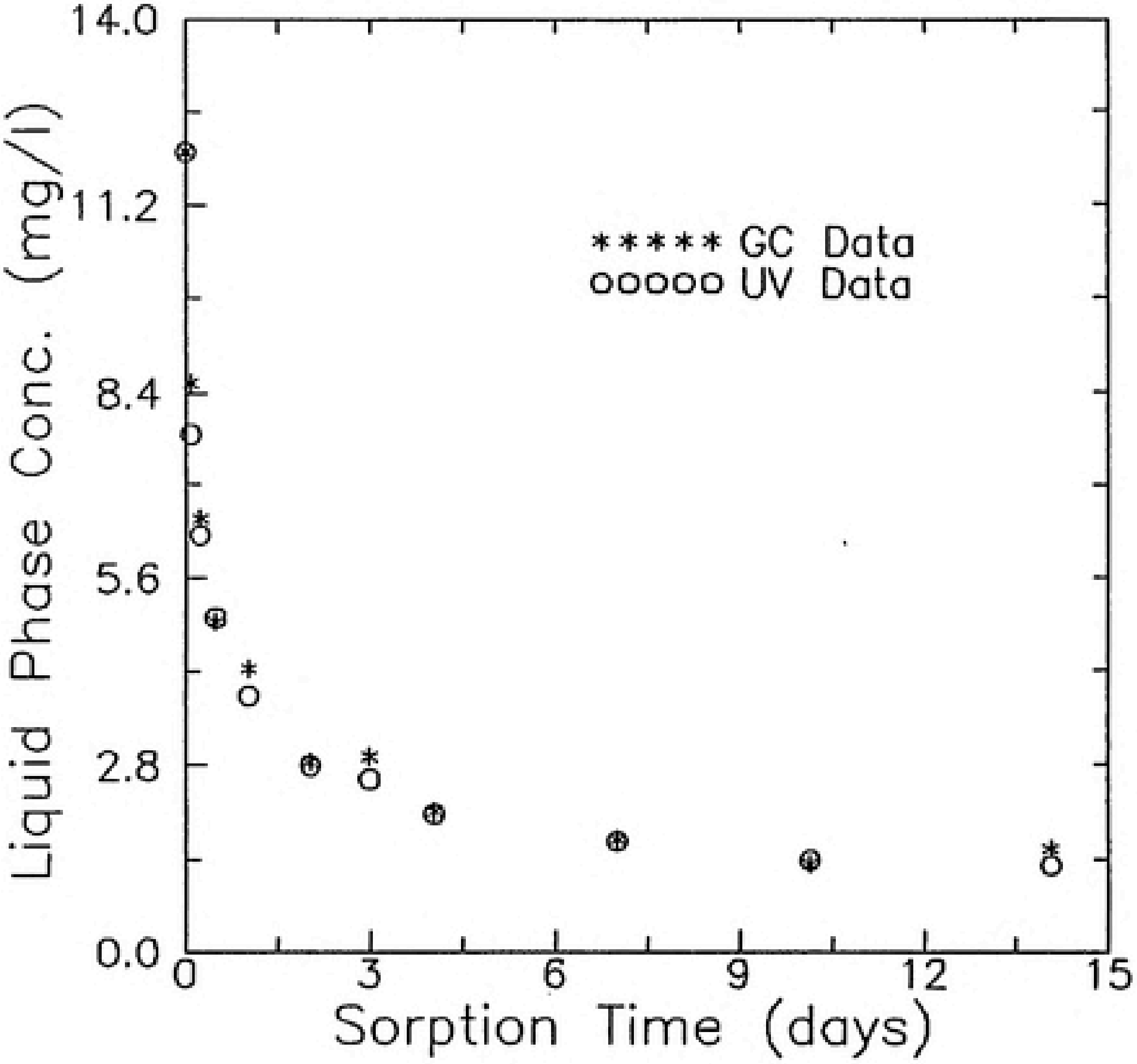

Figure 3-3 Comparison of UV data and GC data (I)

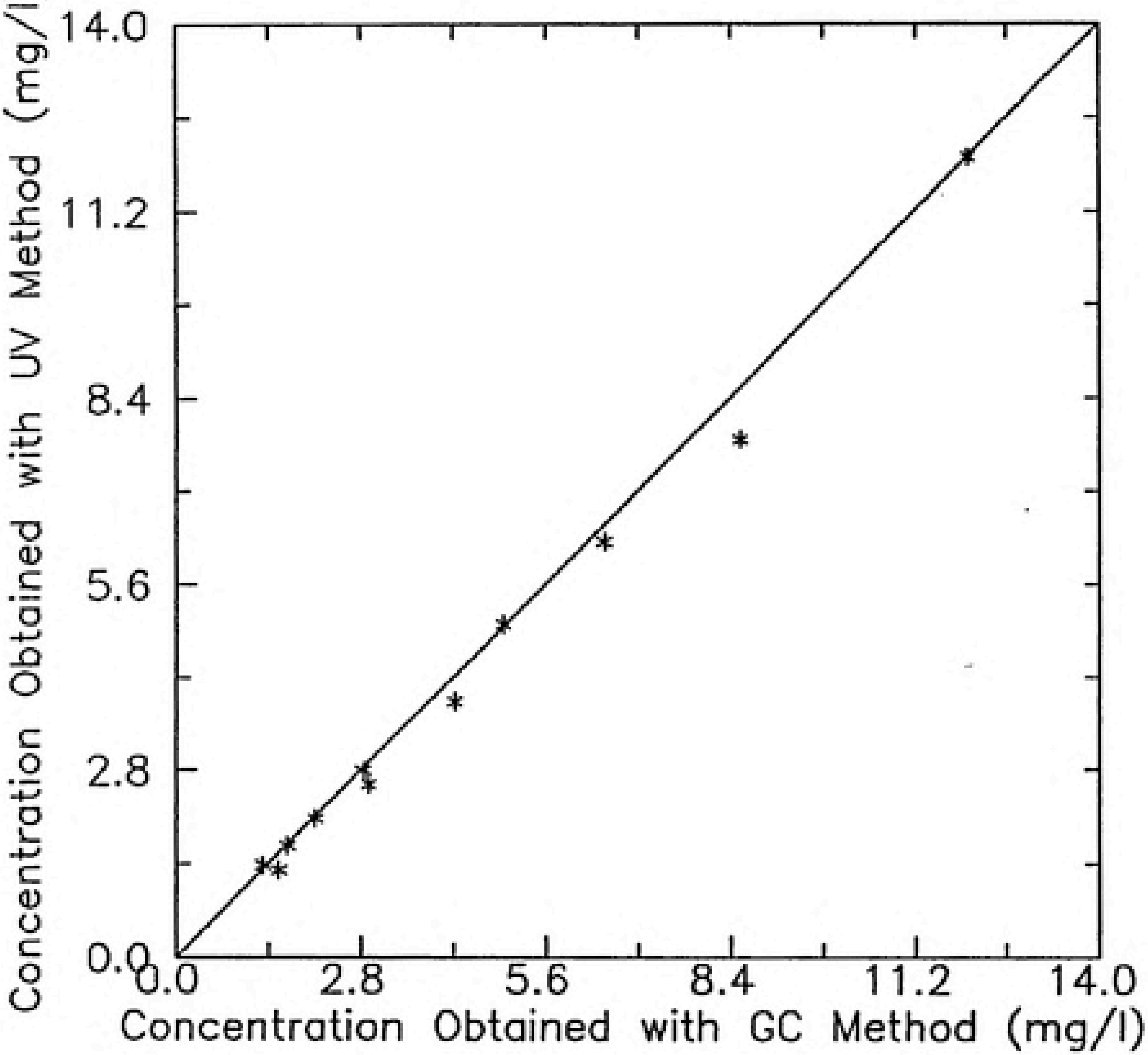

Figure 3-4 Comparison of UV data and GC data (II)

4 EXPERIMENTAL RESULTS AND DISCUSSION

This chapter will present all the experimental results in the same order as the experimental methods were presented in section 3.2 (pp. 3-4). The experimental conditions for all those studies are summarized in Table 4-1. All sample data points of the rate studies are the average of two replicates and all sample data points of equilibrium studies are the average of four replicates.

4.1 Degradation Study

A study was performed to investigate the effect of solute degradation in the Wagner-diuron system. A batch reactor method described in the methods section was used to evaluate the change in solute concentration that occurred over 69 days. The results of this experiment showed no evidence of loss of diuron (liquid phase only, no solids) during a period of 69 days (see Figure 4-1).

An experiment was performed to investigate the effect of azide on inhibiting biodegradation in the Wagner-diuron system. The result of this experiment did not show that azide had any significant effect in the Wagner-diuron system (Figure 4-2).

Solid-phase extractions were performed on samples that were suspended for 44 to 80 days. The average recovery of diuron from the soils was 95%, which indicated that there was little biodegradation in the solid/water system (see Table 4-2).

It has been reported that herbicide sorbed on soil surfaces is protected from

Table 4-1 List of Experimental Conditions

Experiment Name	Description	Sorption Time (d)	Desorption Time (d)	M/V	Analytical Method	Co (mg/l)
DGD	solute degradation study				UV	14
D-K	sorption kinetics study	15		1:1	GC & UV	12
SR1	sorption kinetics study	20		1:1	GC	14
SR4	sorption kinetics study	23		1:2	UV	14
SR5	sorption kinetics study	75		1:2	UV	28
AZ	study of azide effect	20		1:2	UV	14
A1	desorption kinetics study	1	19	1:2	UV	14
DR2	desorption kinetics study	10	6	1:2	UV	14
A20	desorption kinetics study	20	24	1:2	UV	14
D-C	desorption kinetics study	10	21	1:2	UV	7,14,21
RI	sorption-desorption equilibrium study	44	7	1:2	UV	2-27
ISO	sorption-desorption equilibrium study	10	5	1:2	UV	2-14
SDDS	sorption-desorption equilibrium study	10	5	1:2	UV	9,14
SDSD	sorption-desorption equilibrium study	10	5	1:2	UV	9,14
DILU	desorption isotherm study	10	5	1:2	UV	14

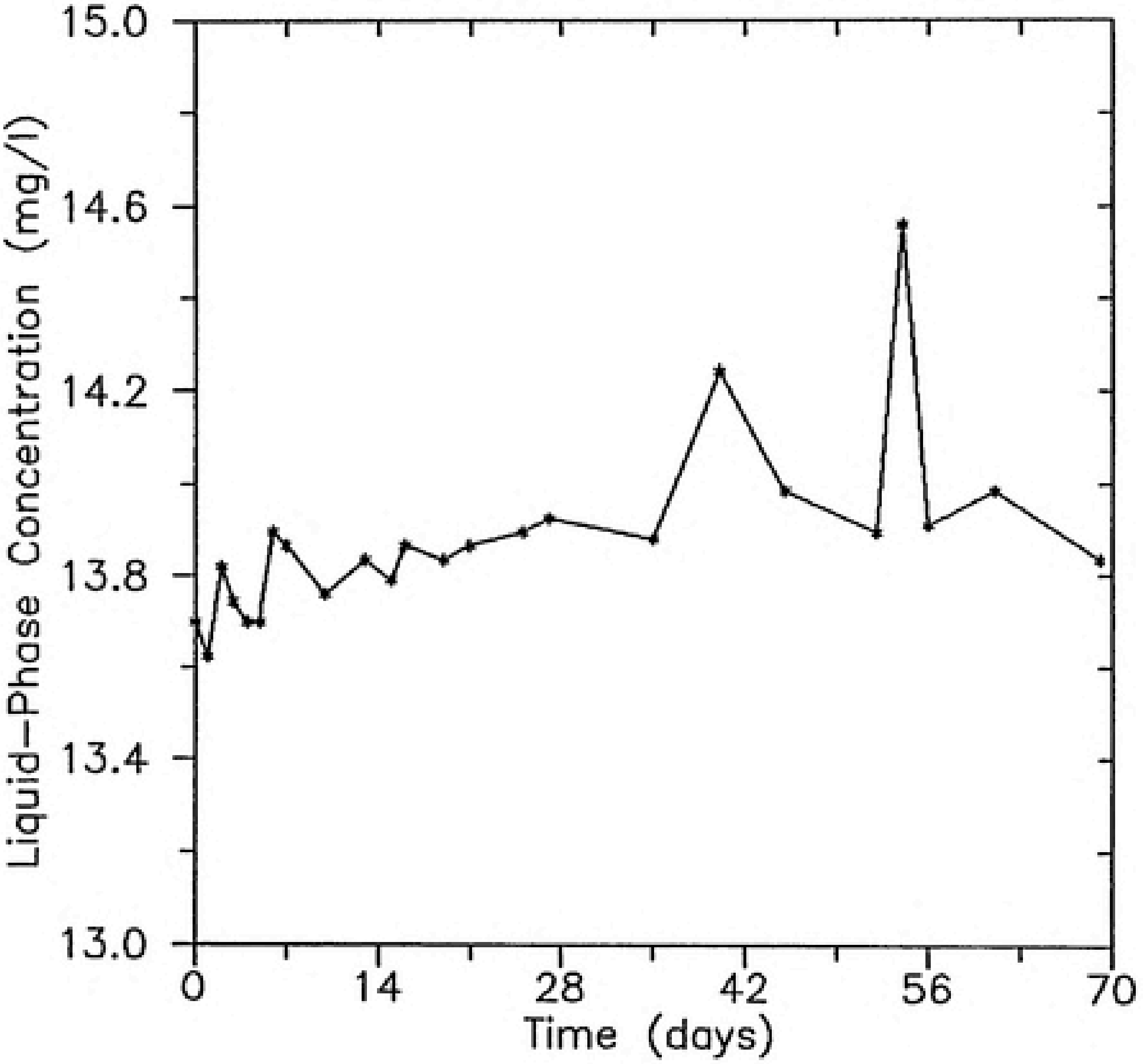

Figure 4-1 Result of Liquid-Phase Solute Degradation Test

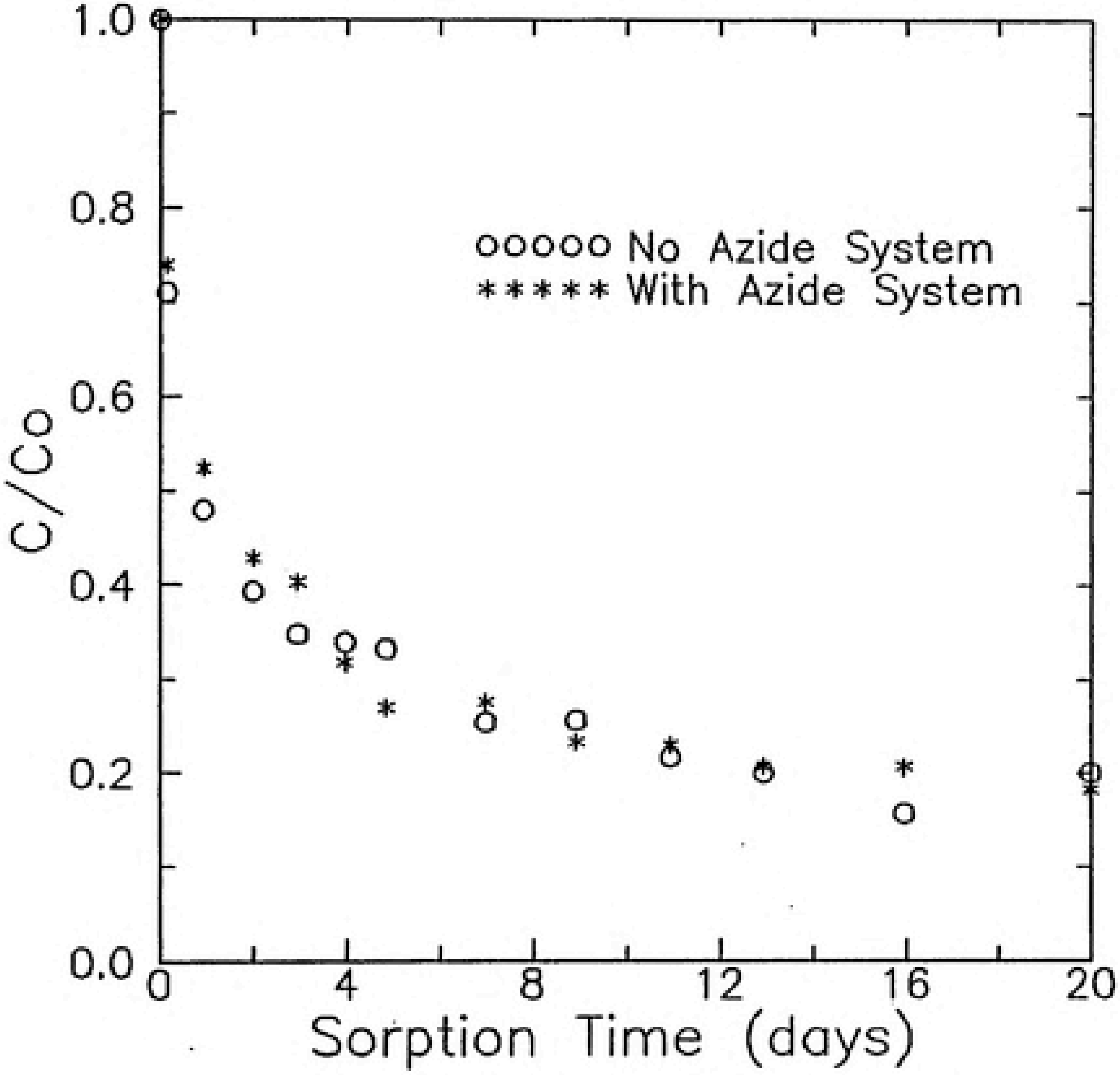

Figure 4-2 Effect of Azide on the Rate of Sorption

Table 4-2 Soil Extraction Recoveries

Sample Name	Total Suspension Time (days)	Diuron Recovery
SR5-18	55	90.77 %
SR5-22	75	98.83 %
A20-12	44	96.85 %
SDS1	80	92.17 %
SDS2	80	95.59 %
	average =	94.84 %

biological mineralization (Ogram et al., 1985). Dao and Lavy (1987) also reported that diuron was not susceptible to microbial degradation in short-term studies. These reports support the finding that little degradation occurred in the sorption-desorption experiments.

4.2 Sorption Rate Studies

4.2.1 Solid concentration effect

In order to have the resulting diuron concentrations fall in the detection limits of the instrument, a proper solid to solution ratio must be found. Two sorption rate studies of solid to solution ratio (M/V, mass of solid to volume of solution) of 1:1 and 1:2 were conducted. The results (Figure 4-3) showed that the higher solid concentration experiment (M/V=1:1) reached apparent equilibrium faster than the lower one. The final liquid phase diuron concentrations were about one fourth of the initial concentration in the M/V=1:2 experiment, which gave a clear view of experimental results during the sorption process. Thus, a solid to solution ratio of 1:2 was used in all other experiments in this research.

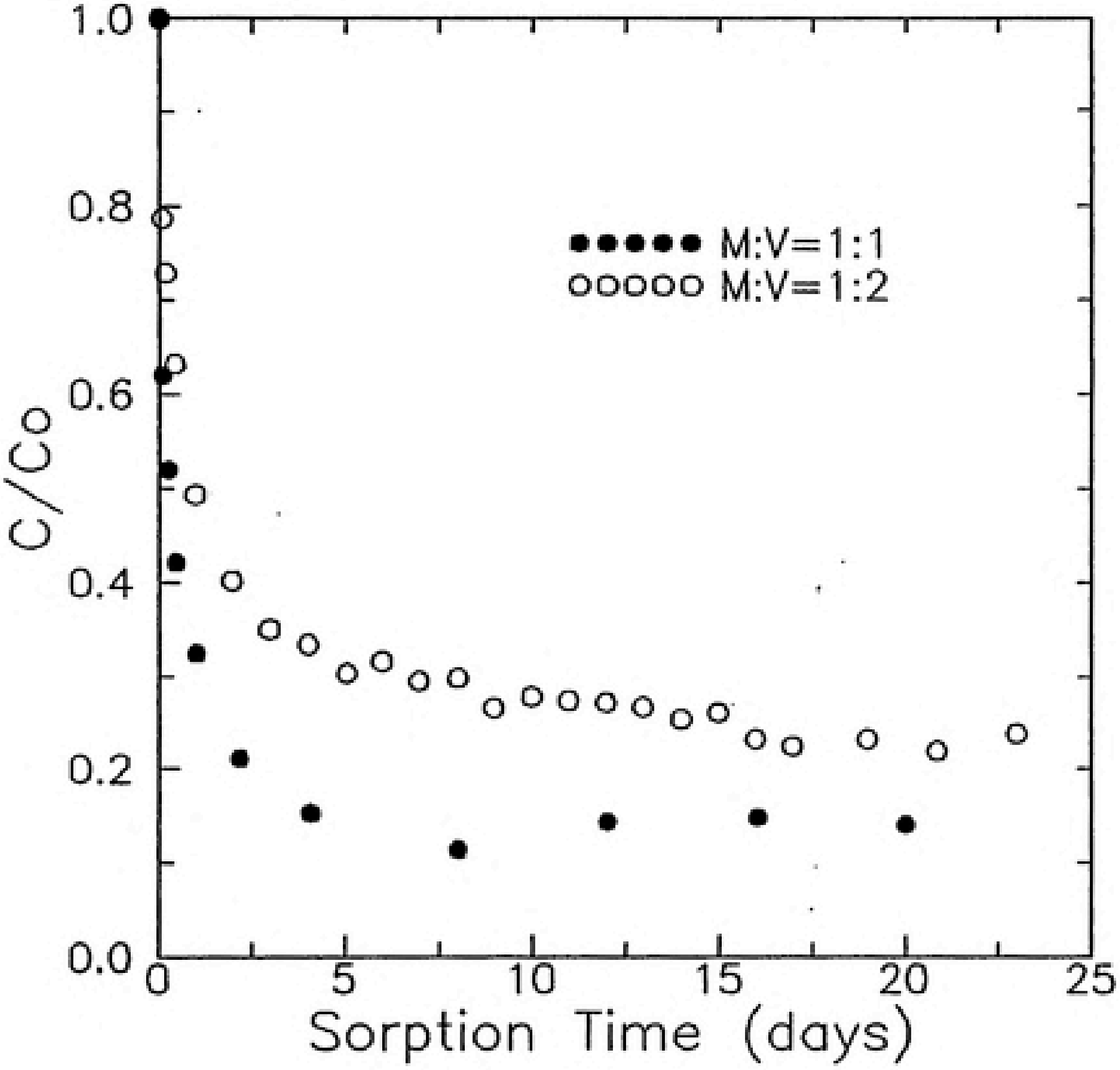

Figure 4-3 Effect of Solids Concentration on the Rate of Sorption

4.2.2 Initial concentration study

Two sorption rate experiments of initial concentrations (C_0) of 14 mg/l and 28 mg/l respectively were performed to investigate the effect of initial concentration on sorption rate. Both sorption processes were characterized by an initial rapid sorption rate followed by a much slower sorption rate (Figure 4-4). This phenomenon had also been observed in other research (Karickhoff, 1984; Miller, 1984; Miller and Weber, 1986; Dao and Lavy, 1987). Comparison of the results of these two experiments shows that the time required to approach sorptive equilibrium is a function of the initial concentration.

More than 95 percent of the solute that would be sorbed at sorption equilibrium had already been sorbed in the first ten days in the sorption rate experiment with an initial concentration of 14 mg/l. Although the sorption rate experiment performed with an initial concentration of 28 mg/l was conducted for 75 days, it seems that the uptake of diuron by the solid phase was still occurring at a very slow rate. This might be due to the constant agitation used in the batch reactor method, which caused weathering of the solids, increasing the surface area of the solids, and resulting in an increasing sorption capacity. Also, as the time of exposure to the solids increases, solute diffusion into the less accessible sites on the solid particles may occur. This suggests that even though an apparent equilibrium was obtained rapidly, the approach to the actual equilibrium might require an extremely long time (McCloskey and Bayer, 1986).

4.3 Desorption Rate Studies

4.3.1 Sorption age effect on desorption rate

The rate of desorption was studied using the methods previously presented for

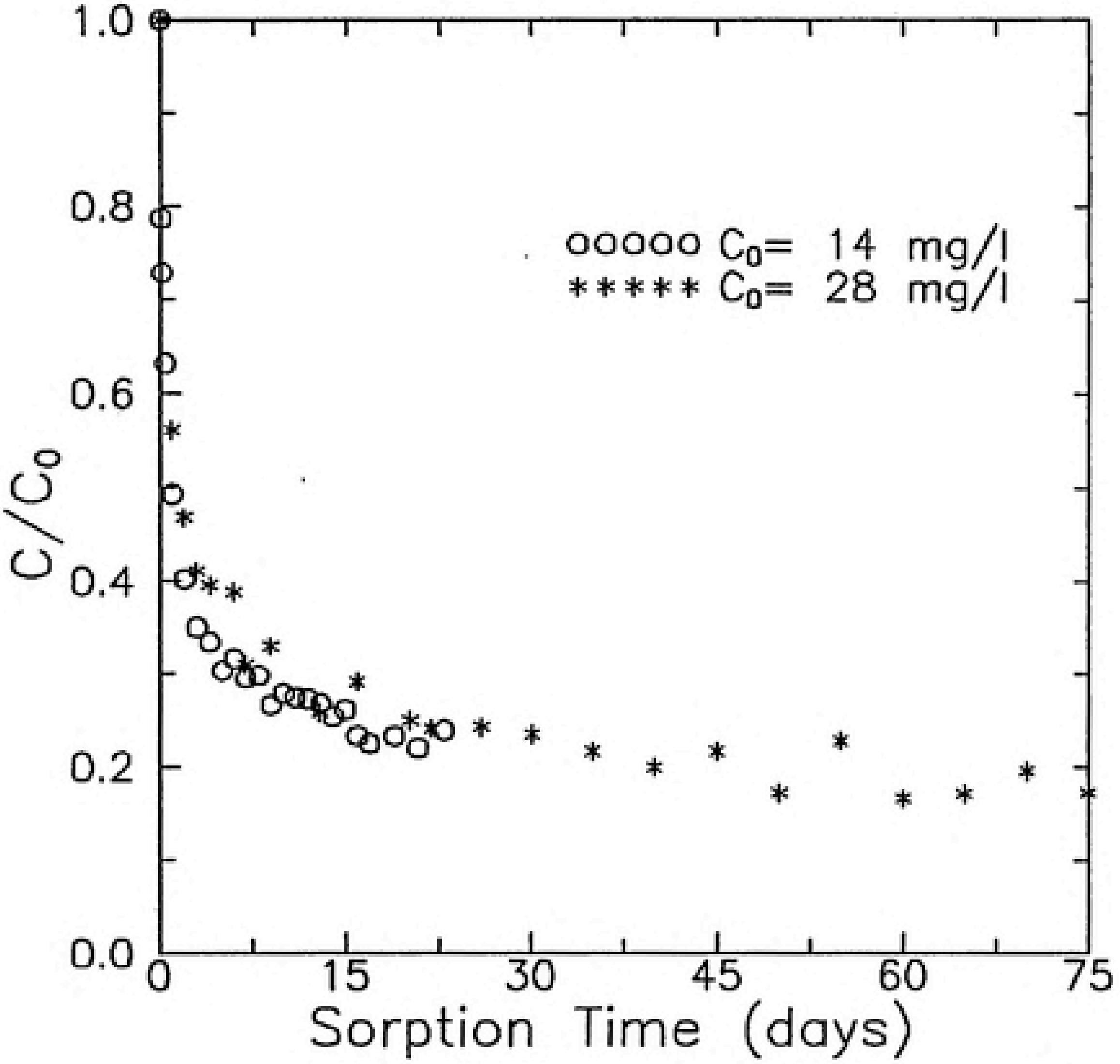

Figure 4-4 Sorption Rate Studies

a sorption age of 1 day, 10 days, and 20 days. The results are displayed in Figure 4-5 and show that diuron was readily desorbed with a desorption rate apparently faster than the sorption rate. Desorption of diuron approached equilibrium within five days after a 10-day sorption. A short sorption age did affect the desorption rate resulting in an initial rapid desorption followed by a slow sorption as shown in Figure 4-5 for the sorption age of one day desorption rate data. This phenomenon may be related to an intraparticle diffusive process. When the sorption time is very short, the solute does not have enough time to diffuse into the porous media. Thus, the decrease of the concentration of the bulk solution caused the quick release of the sorbate that was sorbed on the surface of the sorbent. Given enough time, the solute was re-sorbed and diffused into the porous media. The short sorption age (one day) desorption process reached the desorption equilibrium at a desorption time of about 10-15 days, which compares with the result of the sorption rate study conducted with an initial concentration of 14 mg/l.

4.3.2 Effect of initial concentration on desorption rate

Desorption rate studies were performed for three different initial concentrations 7, 14, and 21 mg/l. The results of these three experiments showed that initial concentration did not have much effect on the rate of desorption (Figure 4-6).

4.4 Sorption-Desorption Equilibrium Studies

The consecutive-desorption method was applied in a sorption-desorption equilibrium study with the initial concentrations for the sorption step ranging from 2 mg/l to 27 mg/l, a sorption time of 44 days, and desorption time of 7 days in each desorption stage. The use of a sorption equilibration time of 44 days and desorption equilibration time of 7 days were based on the results of previously-presented rate studies. The nonlinear Freundlich equation was found to describe sorption equilib-

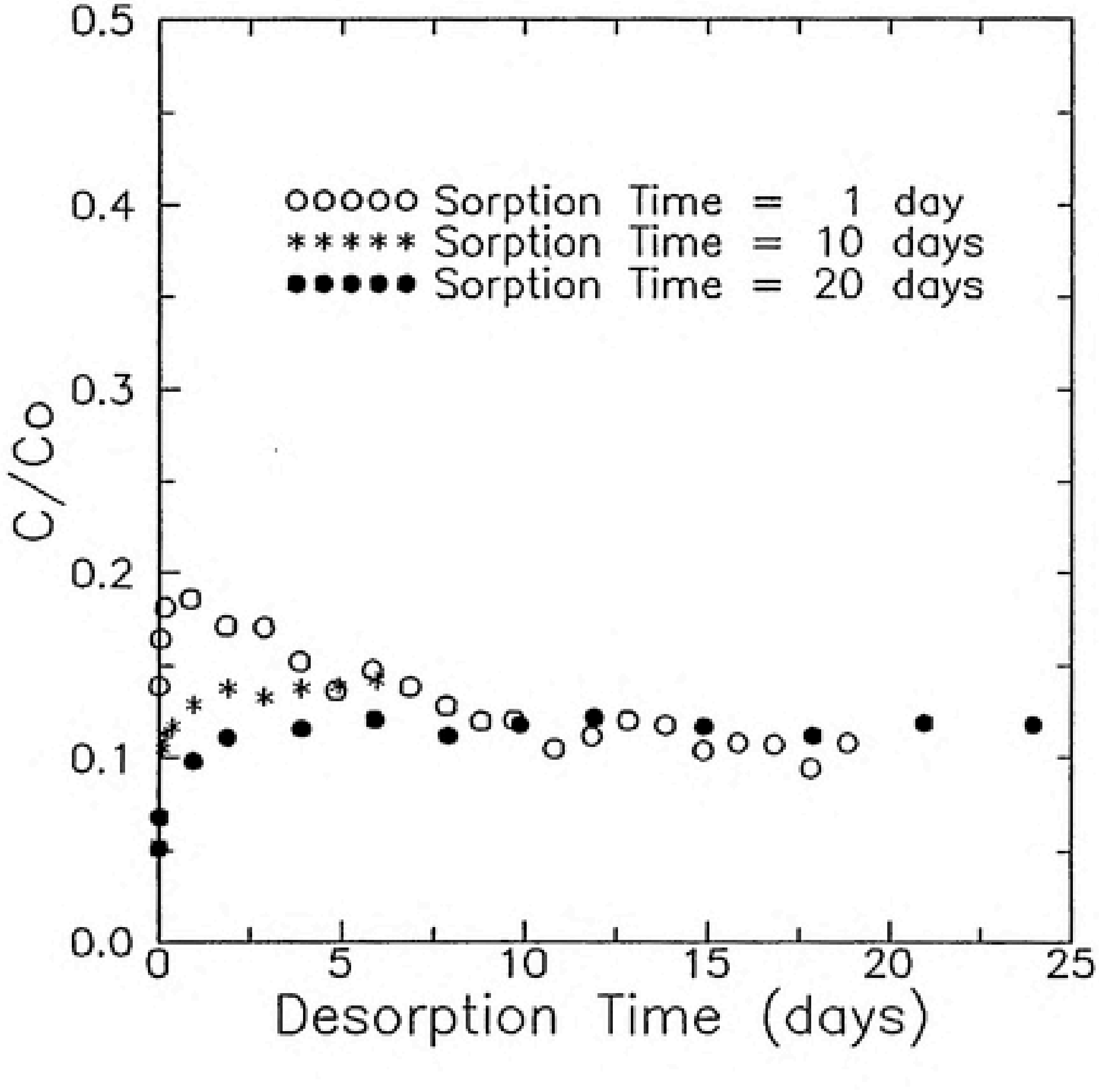

Figure 4-5 Effect of Sorption Age on Desorption Rate

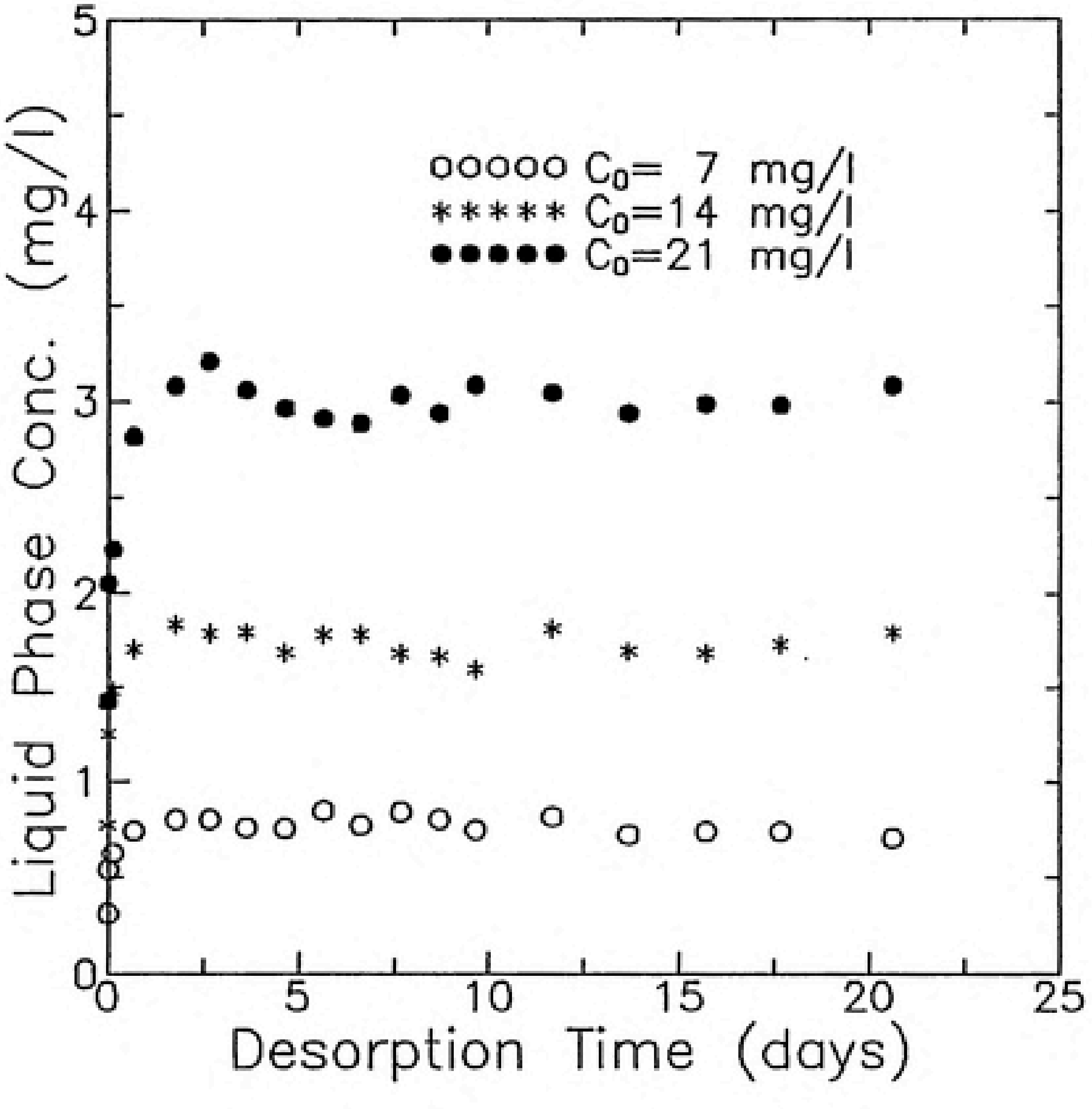

Figure 4-6 Effect of Initial Concentration on Desorption Rate

ria best, with a Freundlich sorption capacity constant (K_s) of 12.87 and a sorption intensity constant (n_s, slope of $\log q_e$ vs $\log C_e$ plot) of 0.657.

As shown in Figure 4-7, desorption hysteresis was observed in this experiment. The desorption intensity constants of the desorption isotherms are listed in Table 4-3. The average of the desorption intensity constants (0.226) was used to plot the desorption isotherms in Figure 4-7.

Table 4-3 List of Freundlich Desorption Intensity Constants

Sorption equilibrium concentration Cse (mg/l)	Desorption intensity constant n_d
0.495	0.189
0.882	0.221
1.376	0.241
2.274	0.232
3.492	0.230
6.337	0.242

Another short-term sorption-desorption isotherm study with initial concentrations ranging from 2 mg/l to 14 mg/l was also conducted. Since sorption-desorption of lower initial concentrations does not need as much time as that of higher initial concentrations to reach equilibrium, a sorption time of 10 days and a desorption time of five days in each sorption-desorption stage were applied in this experiment. The result of this study (see Figure 4-8) gave an average n_d of 0.261, although clearly equilibrium conditions were not met for the sorptive portion of the investigation.

The difference of n_d from n_s is 0.431 in the long-term sorption-desorption isotherm study. The difference of n_d from n_s in the short-term sorption-desorption isotherm study is 0.362. It seems nonattainment of equilibrium was not a ma-

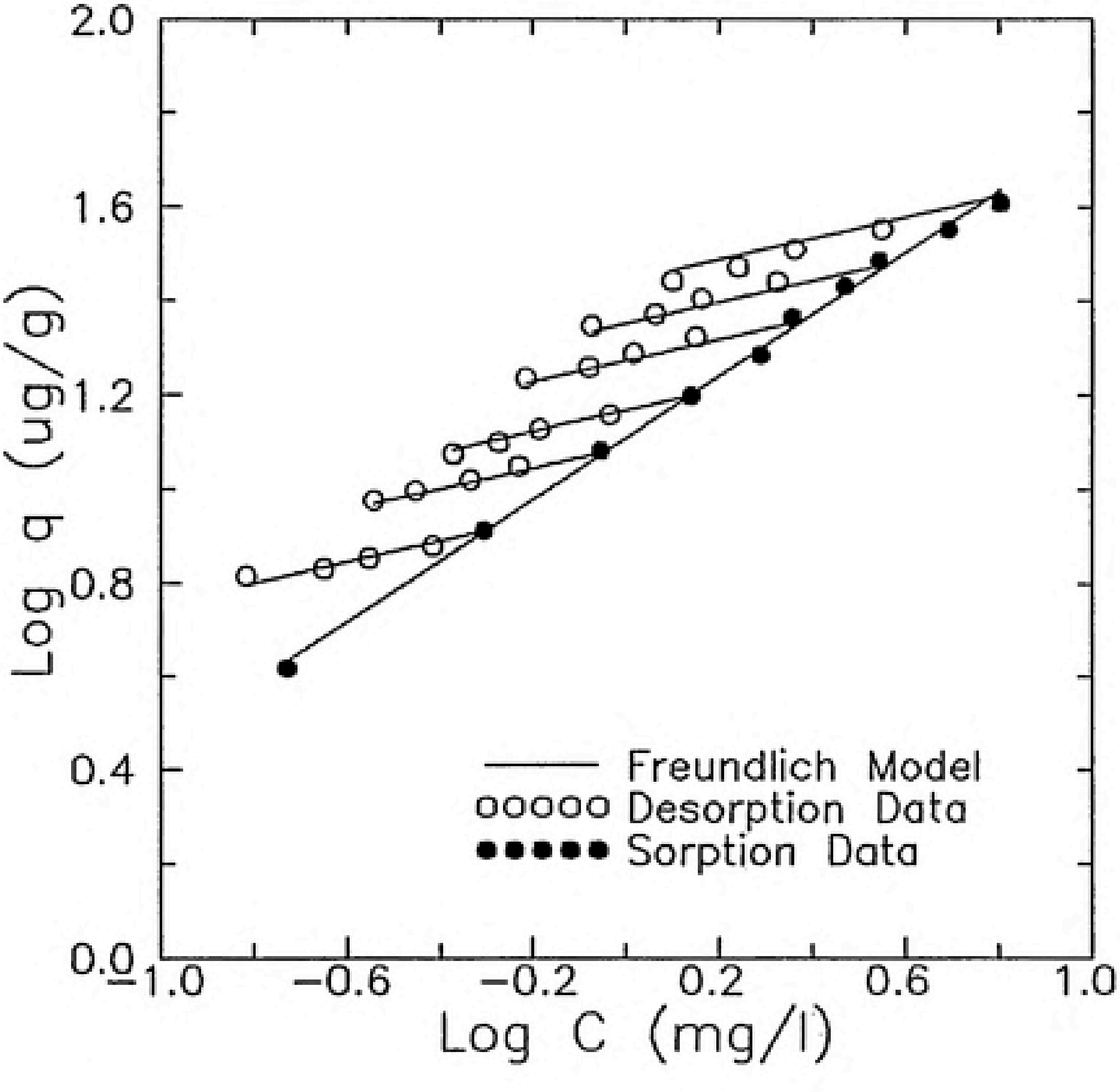

Figure 4-7 Sorption-Desorption Equilibrium

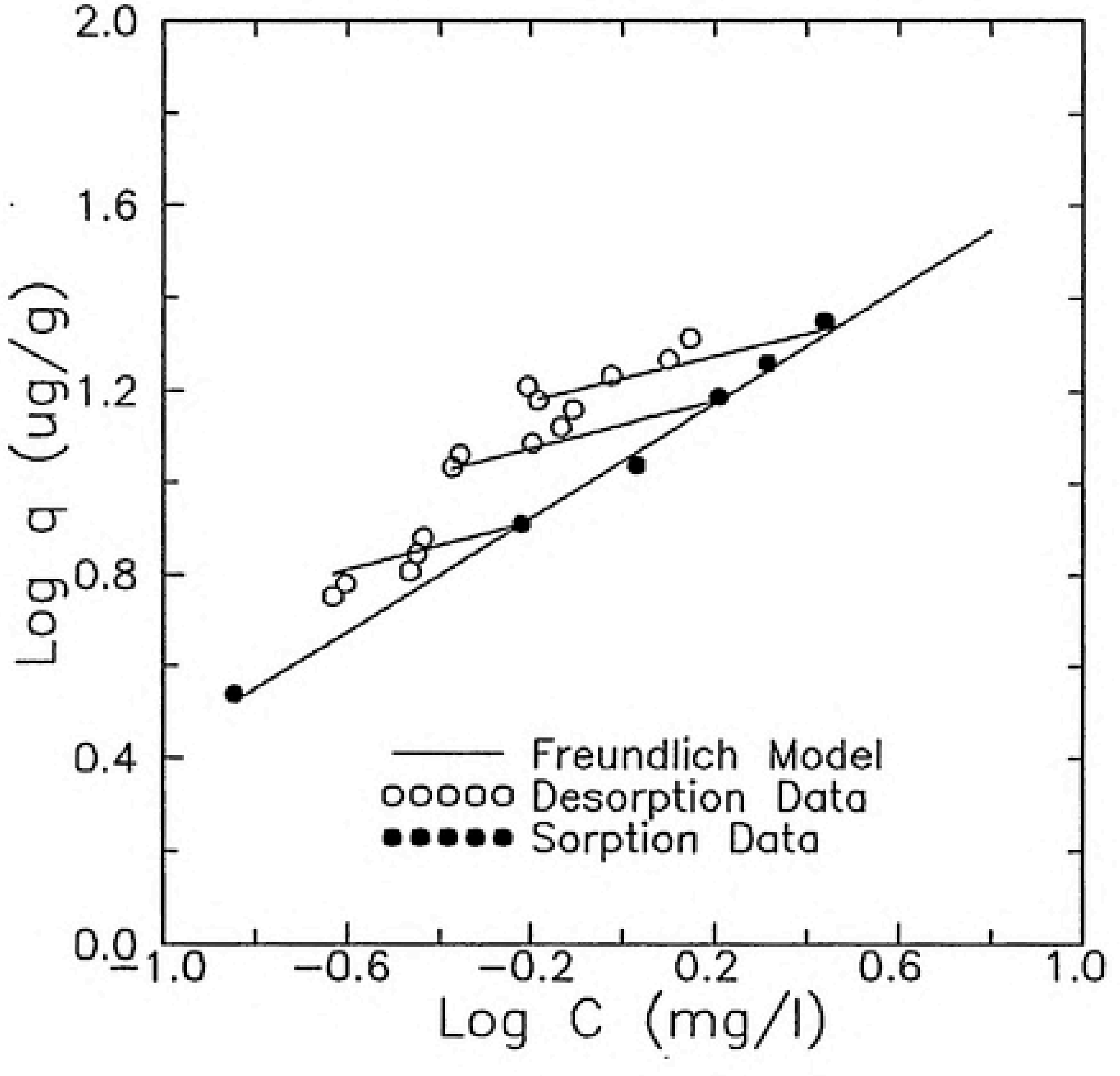

Figure 4-8 Short-Term Sorption-Desorption Equilibrium

jor factor for hysteresis in this case because the experimental data showed longer equilibration time gave even greater hysteresis.

4.5 Complex Pattern Sorption-Desorption Studies

The reversibility of sorption-desorption was investigated by conducting two sorption-desorption-resorption (SDDS and SDSD) studies. The SDDS study was performed with initial sorption followed by two steps of desorption and then three steps of successive-sorption. The result showed the initial sorption data were a little bit off the sorption isotherm line, the desorption data followed the desorption isotherm, and the successive-resorption data correlated to the sorption isotherm quite well (see Figure 4-9).

A SDSD study was conducted with an initial sorption followed by one step of desorption, five steps of consecutive-sorption and three steps of consecutive-desorption. The consecutive-desorption process was initiated after five steps of the consecutive-sorption. The experimental data (Figure 4-10) showed desorption hysteresis still existed between the re-desorption and the re-sorption processes.

The results of the SDDS and the SDSD studies indicated that sorption-desorption is reversible following the sorption-desorption isotherms. This reversibility excludes sorption to nonsettling materials as a cause of hysteresis for the system investigated here.

4.6 Single-Dilution Study

A desorption isotherm study using the single-dilution method was conducted to investigate the effect of multiple centrifugation.

The slope of the desorption isotherm obtained by using this method was 0.319, while the slope of the desorption isotherm obtained by using the consecutive-

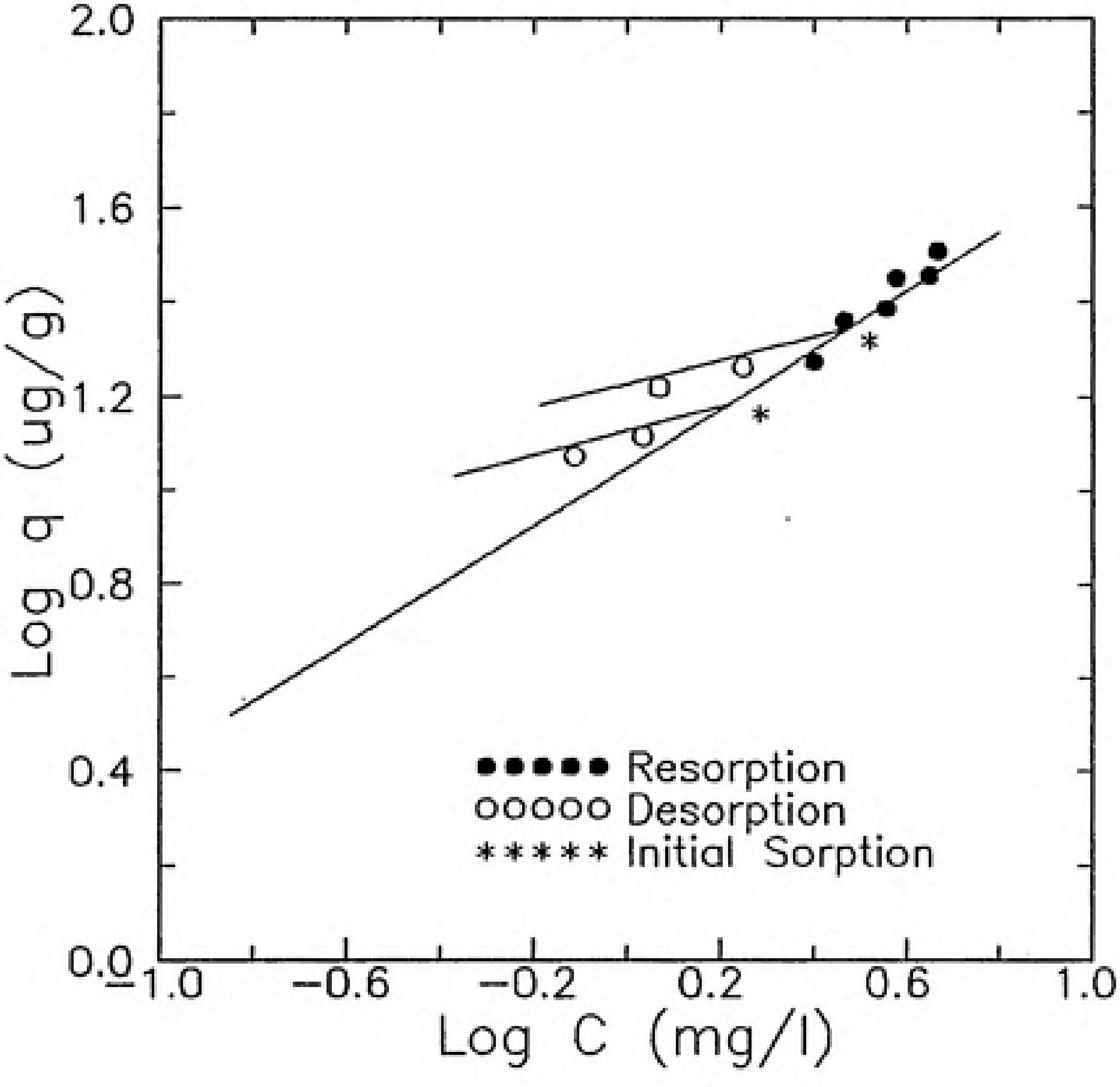

Figure 4-9 Comparison of SDDS Data to Sorption-Desorption Equilibrium Model

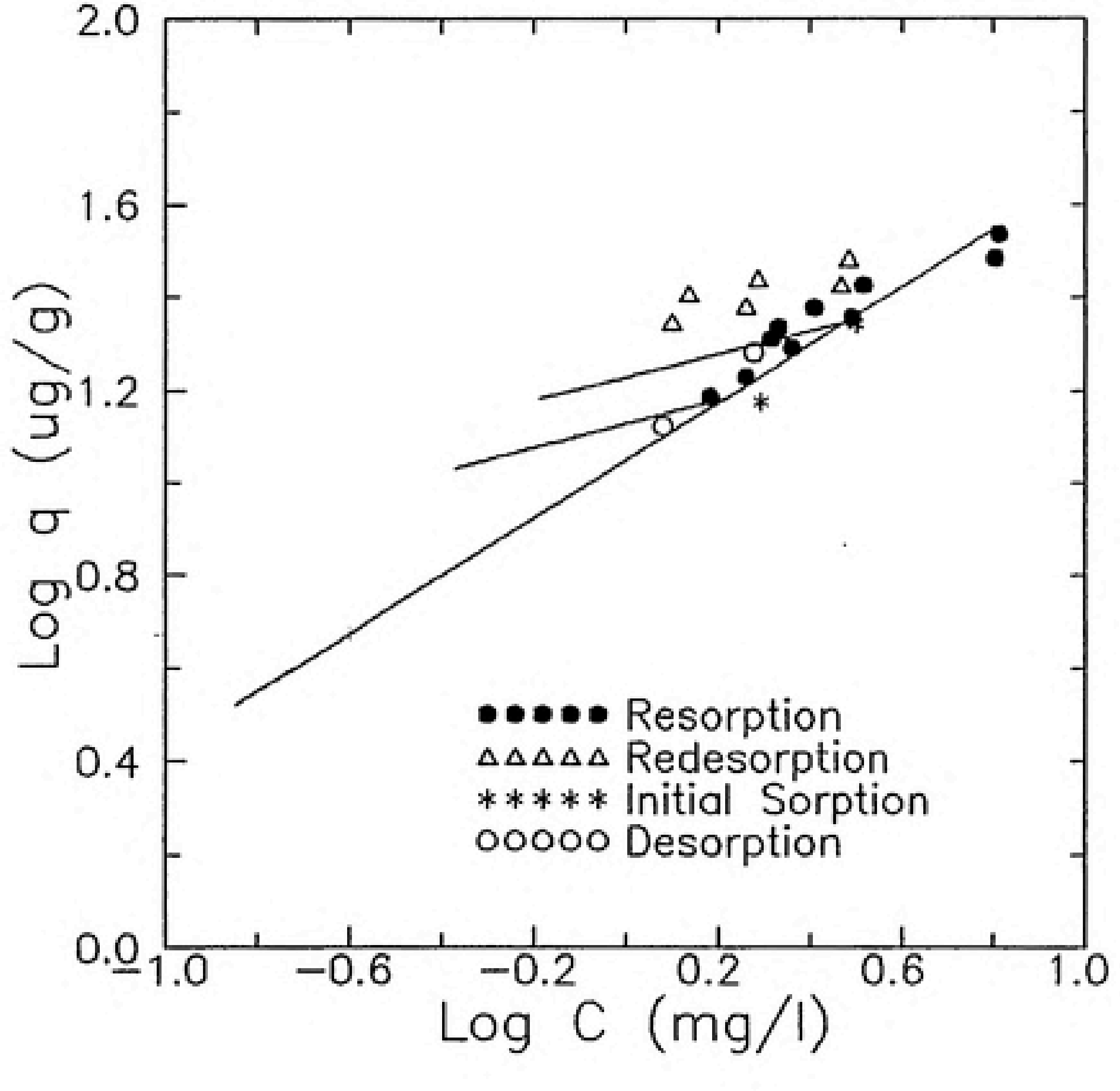

Figure 4-10 Comparison of SDSD Data to Sorption-Desorption Isotherm Data

desorption method was 0.261 (Figure 4-11). This indicates that there was some effect of these two different methods on the desorption isotherms obtained. The volume of solution in the sorption stage in the single-dilution method was 7 ml, which was a small volume compared to the 30-ml solution volume used in the consecutive-desorption method. This small solution volume might cause poor mixing, resulting in the different results of the two experiments. Also, the centrifugal force might cause a partially irreversible compaction of the solid, thus part of the sorbate may require a longer time to desorb or would not desorb at all (resistant component was formed during centrifugation). The other possibility is that the consecutive-desorption method applied the centrifugation-resuspension processes too many times. Thus, the solid characteristics were changed (washing out organic matter, weathering of soils), which in turn changed the sorption property of the soil. It should also be observed that sorption equilibrium was clearly not obtained in this experiment.

4.7 Normalized Desorption Equilibrium Model

The normalization procedure presented by Brusseau and Rao (1989) was applied to analyze the sorption-desorption isotherm data to generate an equivalent desorption isotherm as shown in Figure 4-12. A similar trend of data was observed. The equation of the best fit curve is

$$q_{de}/q_{me} = (C_{de}/C_{me})^{0.207} \tag{4-1}$$

The value of n_d (0.207) is very close to the average value of desorption isotherm slopes (0.226) in the sorption-desorption isotherm study. Experimental data of the SDSD, SDDS, and the single-dilution method were also analyzed with the normalization procedure. The results are shown in Figure 4-13.

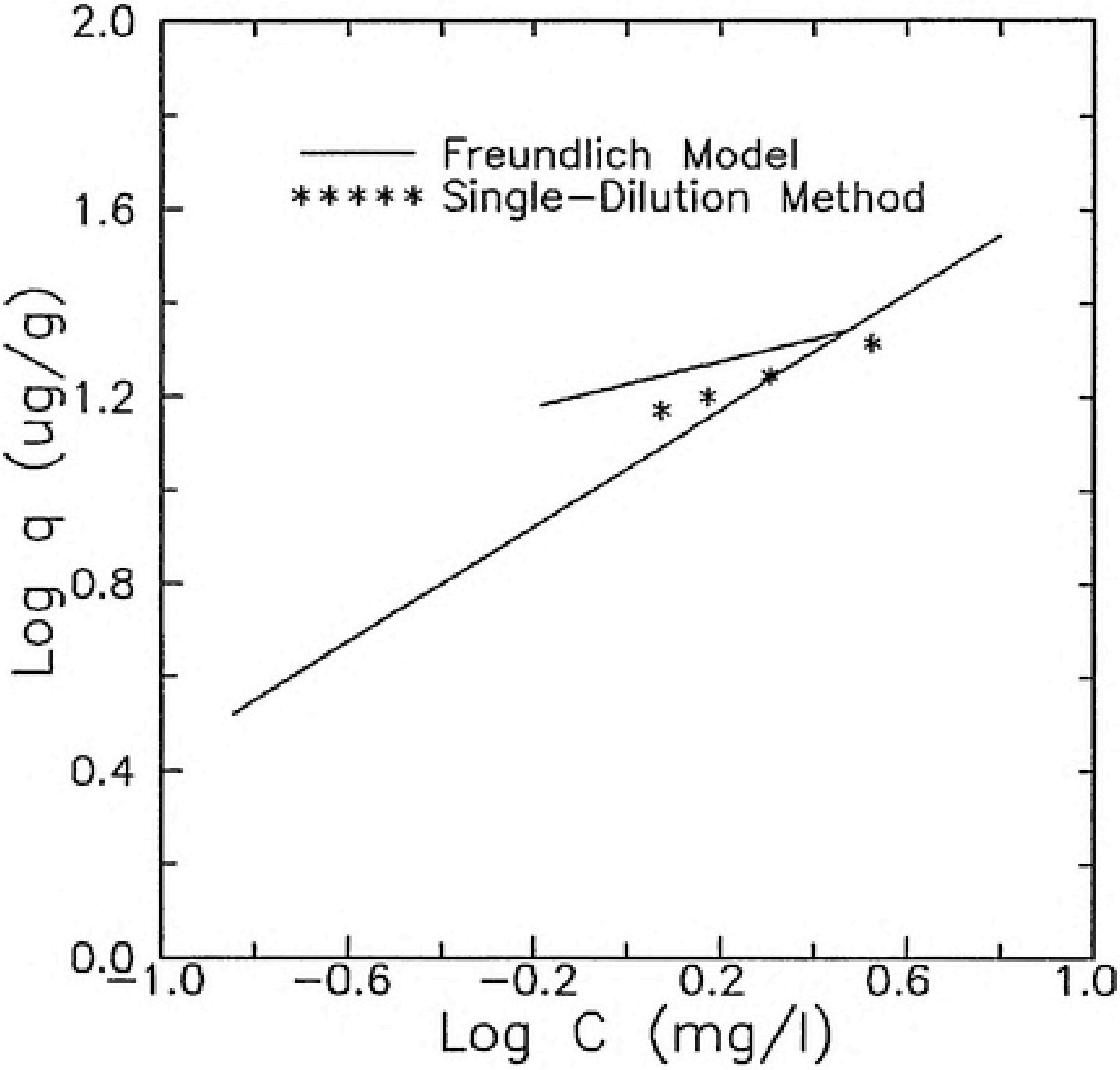

Figure 4-11 Comparison of Single-Dilution Data to Consecutive-Desorption Model

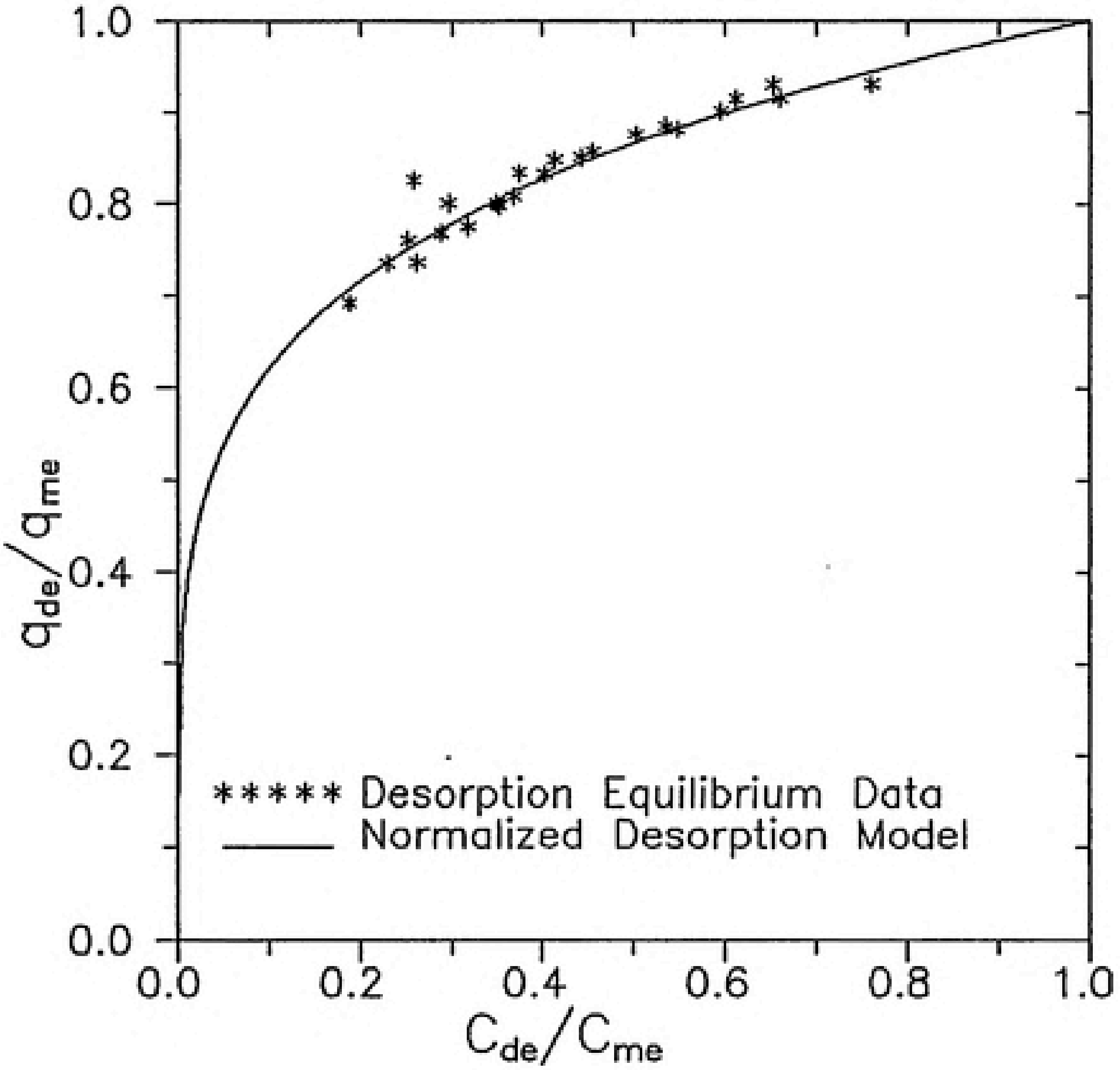

Figure 4-12 Normalized Desorption Data and Model Comparison

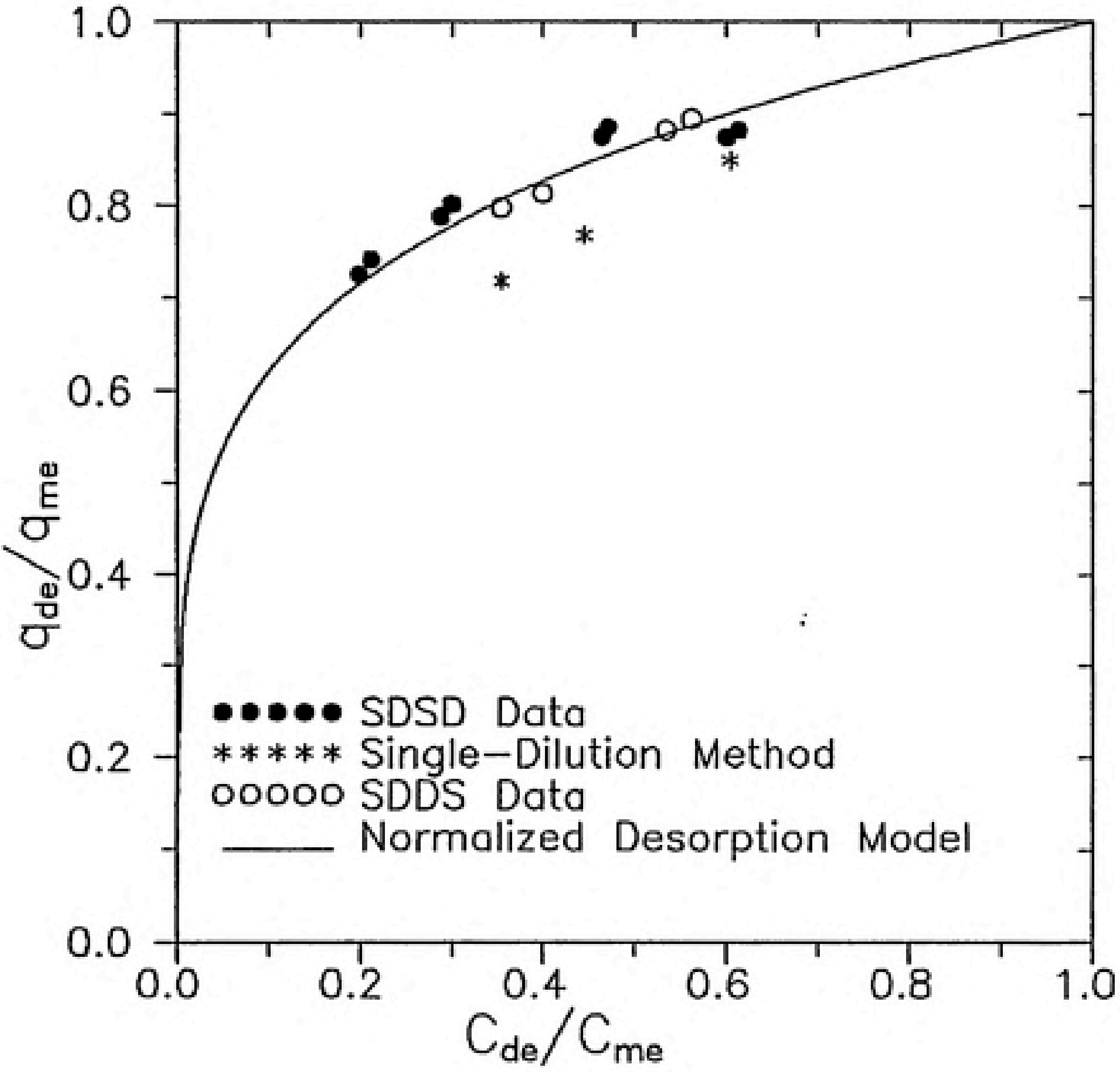

Figure 4-13 Comparison of Results from Different Desorption Equilibrium Studies

A sorption time of 10 days and a desorption time of 5 days were applied to the SDSD and SDDS experiments, while a sorption time of 44 days and a desorption time of 7 days were used in the sorption-desorption isotherm study. Although different equilibration times were used in these experiments, the experimental data correlated very well (see Table 4-4). This indicates that the experimental data of the SDSD and SDDS experiments was very close to the equilibrium data. The SDDS and the SDSD data fit the normalized desorption equilibrium curve quite well but single-dilution data did not follow that desorption curve. This result was not totally unexpected, since the previous data presentation showed a deviation from the long-term sorption-desorption equilibrium relationship.

Table 4-4 List of Freundlich Constants in Sorption-Desorption Equilibrium Experiments

Experiment Name	Description	Sorption Time (days)	Desorption Time (days)	Sorption Capacity Constant, Ks	Sorption Intensity Constant, ns	Desporption Intensity Constant, nd
RI	Sorption-Desorption Equilibrium Study	44	7	12.9	0.657	0.226
RI	Normalized RI data	44	7			0.207
ISO	Short-Term Sorption-Desorption Equilibrium Study	10	5	11.2	0.624	0.262
SDDS	Sorption-Desorption Equilibrium Study	10	5	10.0	0.731	0.218
SDSD	Sorption-Desorption Equilibrium Study	10	5			0.195
DILU	Desorption Equilibrium Study with Single-Dilution Method	10	5			0.319

4.8 Desorption Hysteresis

The desorption of diuron for the Wagner-diuron system was found to be hysteretic. The equilibration times used in a sorption-desorption isotherm study was 44 days for the sorption and 7 days for the desorption. These are pretty long equilibration times compared to those used in other research (see Table 2-2, Table 2-3). A short-term sorption-desorption isotherm study was performed using a sorption equilibration time of 10 days and desorption equilibration time of 5 days. These short-term sorption-desorption isotherms were found to be less hysteretic. It seems that nonattainment of equilibrium was not the cause of the observed desorption hysteresis.

According to the results of degradation test, there was no evidence of loss of diuron in the liquid-phase. The results from the azide-effect experiment and solid-phase extractions showed that there was little biodegradation in the Wagner-diuron system used in this research. Therefore, loss of solute is not a major factor contributing to the apparent hysteresis either.

The long-term sorption-desorption equilibrium study showed greater hysteresis than the short-term sorption-desorption equilibrium study. A possible explanation is that the consecutive-desorption technique used in the desorption equilibrium experiments caused solid-phase weathering (although the tumbling speed was slow), increasing the sorption capacity and leading to the greater desorption hysteresis. But this is not the major cause of the desorption hysteresis because the hysteresis phenomenon was still observed in the short-term sorption-desorption isotherm study.

Sorption to nonsettling particles was found not a feasible explanation of the desorption hysteresis in this research. First of all, the solid used in the experiments was a sand-size material, not sediment, and the grain size distribution (Figure 3-1) showed that there was a small fine fraction. Also, if sorption to nonsettling particles did play a role in the sorption-desorption equilibrium experiments, the sorption-desorption isotherms would not be reversible. But the results from the SDSD and SDDS experiments indicated that the sorption-desorption isotherms were reversible.

The centrifugation effect was investigated by comparing the experimental results of the single-dilution method to the consecutive-desorption method. The slope of the desorption isotherm obtained with the single-dilution method was a little bit greater than the one obtained with the consecutive-desorption method. This might be due to the small solution volume used in the sorption portion in the single-dilution experiment resulting in a poor mixing of the solid-solution mixture. Also, the repeated centrifugation might cause a partially irreversible compaction of the solids, leading to a greater hysteresis. However, centrifugation effect is not the only or major cause of hysteresis because the hysteresis phenomenon was also found in the desorption experiment using the single-dilution method.

Brusseau and Rao (1989) reported that the accumulated measurement error of each sampling step could lead to the deviation of the desorption isotherms from the sorption isotherm. However, it is not applicable in this research because the results of solid-phase extractions showed an average recovery of 95%, which indicated that the experimental error was not significant.

The implicit-sorbate model describes that the increasing sorption capacity is due to an increase in sorption sites that were previously occupied by the implicit-sorbate, and were revealed during the desorption process. According to this explanation, the sorption capacity would increase after the implicit-sorbate was desorbed. But the results of the SDDS experiment showed that the sorption equilibrium still followed the sorption isotherm after two steps of desorption equilibria were established (see Figure 4-9). Therefore, the implicit-sorbate model is not a feasible explanation of hysteresis observed in this research.

In summary, all the above discussion of possible explanations of hysteresis were found not to be the major causes of hysteresis. Physical or chemical interactions might occur during the sorption-desorption process causing the formation of tightly sorbed component. Several mechanisms were postulated for the sorption of diuron by soils, including physical sorption by van der Waals force and hydrogen bonding that occur via the carbonyl oxygen and the amino hydrogen of diuron (Mustafa and Gamar, 1972). Farmer and Ahlrichs (1969) also reported that sorption of diuron on montmorillonite (low organic matter content) may be attributed to an interaction of the carbonyl of the herbicide with exchangeable cations on surface of the soil. Therefore, sorption of diuron by soils may not be considered as pure hydrophobic sorption. It could have included chemisorption which generally exhibits resistant desorption (Brusseau and Rao, 1989). Diffusion into the porous solids during the sorption process has been postulated as a sorption mechanism (Miller, 1984; Wu and Gschwend, 1988; Brusseau and Rao, 1989). A possible mechanism leading to desorption hysteresis could be a result of a diffusional process whereby molecular hindrance occurs in small pore openings of the organic fraction.

5 MODELING OF EXPERIMENTAL RESULTS AND DISCUSSION

5.1 Model Development

5.1.1 Basic assumptions

The sorption process was observed to have an initial fast rate followed by a slower rate. This phenomenon coincides with other reported descriptions of the sorption process (Karickhoff, 1984; Miller, 1984; Miller and Weber, 1986; Dao and Lavy, 1987). A two-site model has been proposed to describe this process, assuming two types of solid-phase reaction sites— those that appeared to sorb solute rapidly (fast-sites) inducing an instantaneous equilibrium, and those that appeared to sorb solute more slowly (slow-sites). Slow-site sorption is characterized by a mass transfer coefficient, K_m (Cameron and Klute, 1977; Karickhoff, 1980).

5.1.2 Derivation of algorithm

The Freundlich isotherm relationship was applied based on the results of sorption-desorption isotherm experiments

$$q_e = KC_e^{n} \tag{5–1}$$

where q_e is equilibrium mass-average, solid-phase sorbate concentration; C_e is equilibrium volume-average, liquid-phase solute concentration; K is a sorption capacity constant; n is a sorption intensity constant.

Since the fast-sites are assumed to be at equilibrium, the chain rule can be used to relate the solid-phase and liquid-phase concentration

$$\frac{dq_f}{dt} = \frac{dq_f}{dC}\frac{dC}{dt} \tag{5-2}$$

also

$$q_f = K_f C^{n_f} \tag{5-3}$$

$$\frac{dq_f}{dt} = n_f K_f C^{n-1}\frac{dC}{dt} \tag{5-4}$$

where q_f is the mass-average, solid-phase sorbate concentration associated with the fast-sites; K_f if the Freundlich sorption capacity constant for the fast-sites; n_f is the Freundlich sorption intensity constant for the fast-sites.

For slow-sites,

$$\frac{dq_s}{dt} = K_m(q_{sse} - q_s) \tag{5-5}$$

$$q_{sse} = K_{ss}C_e{}^{n_{ss}} \tag{5-6}$$

where q_s is the mass-average, solid-phase sorbate concentration associated with the slow-sites or the rate-controlled reaction; K_m is a mass-transfer coefficient; q_{sse} is the sorption equilibrium, solid-phase sorbate concentration associated with the slow-sites; K_{ss} is the Freundlich sorption capacity constant for the slow-sites; n_{ss} is the Freundlich sorption intensity constant for the slow-sites.

Substituting equation 5-6 to 5-5 gives

$$\frac{dq_s}{dt} = K_m(K_{ss}C^{n_{ss}} - q_s) = K_m K_{ss} C^{n_{ss}} - K_m q_s \tag{5–7}$$

assuming

$$n_{ss} = n_f = n \tag{5–8}$$

allows for

$$\frac{dq}{dt} = \frac{dq_f}{dC}\frac{dC}{dt} + \frac{dq_s}{dt} \tag{5–9}$$

$$\frac{dq}{dt} = nK_f C^{n-1}\frac{dC}{dt} + K_m K_{ss} C^n - K_m q_s \tag{5–10}$$

also,

$$q = (C_0 - C)/R \tag{5–11}$$

where C_0 is the initial fluid-phase solute concentration; R is the ratio of the mass of solid to the volume of solution. gives

$$\frac{dC}{dt} = -R\frac{dq}{dt} \tag{5–12}$$

combining equation 5-10 and 5-12 gives

$$\frac{dC}{dt} = -R[nK_f C^{n-1}\frac{dC}{dt} + K_m K_{ss} C^n - K_m q_s] \tag{5–13}$$

expanding and rearranging equation 5-13 gives

$$(1 + RnK_f C^{n-1})\frac{dC}{dt} + RK_m K_{ss} C^n - RK_m q_s = 0 \qquad (5\text{–}14)$$

Applying the implicit finite difference method to equation 5-14 gives

$$(1 + RnK_f C_{l+1}^{n-1})\frac{C_{l+1} - C_l}{\Delta t} + RK_m K_{ss} C_{l+1}^n - RK_m q_{s,l+1} = 0 \qquad (5\text{–}15)$$

where l,and l+1 indicate old and new time level, respectively.

Rearranging equation 5-15 gives

$$C_{l+1} - \Delta t K_m R q_{s,l+1} = (1 + RnK_f C_{l+1}^{n-1})C_l - (\Delta t R K_m K_{ss} + RnK_f)C_{l+1}^n \quad (5\text{–}16)$$

Applying the implicit finite difference method to equation 5-7 gives

$$\frac{q_{s,l+1} - q_{s,l}}{\Delta t} = K_m K_{ss} C_{l+1}^n - K_m q_{s,l+1} \qquad (5\text{–}17)$$

rearranging equation 5-17 gives

$$(1 + K_m \Delta t) q_{s,l+1} = q_{s,l} + \Delta t K_m K_{ss} C_{l+1}^n \qquad (5\text{–}18)$$

A FORTRAN program was written to compute C and q at any time t during the sorption-desorption process by applying equations 5-16 and 5-18. The nonlinear terms, C_{l+1}^{n-1} and C_{l+1}^n, were computed by using the Picard iteration method.

The program first read the values of parameters that were related to the simulating system (e.g. sorption-desorption Freundlich constants, initial concentration, sorption time, desorption time, tolerance of Picard iteration, desorption steps of the isotherm simulation, etc.). These parameters were then printed out for the checking of the input data.

The fluid-phase concentration at $t = 0$ which was different from C_0 due to the fast-site sorption was computed first. The fluid-phase concentration at any time t was then computed and the equilibrium concentrations were printed out.

If the simulation was for the sorption rate process (IRATE=1), the experimental data of the sorption rate experiment were read in and the SSE was computed and printed out. If the simulation was not for the sorption rate process, the program continued simulating the desorption process.

The desorption process (IRATE=2) was initiated by replacing a portion of the liquid with the solute-free solution. The concentrations were computed using the desorption capacity constants for the fast-sites and the slow-sites (K_{df}, K_{ds}) and the desorption intensity constant (n_d).

The type of simulation was checked at the end of the simulation of the desorption process. If a simulation of the sorption-desorption equilibrium was desired, the desorption process would be repeated until the number of repetitions (I) equaled the number of the desorption steps.

The flowchart of algorithm of the FORTRAN program is shown in Figure 5-1.

5.1.3 Model validation

The computer program was validated by comparing the analytical solution for the case of a linear isotherm (Weber and Miller, 1988) to the numerical solution. Figure 5-2 shows the result of the case where fast-sites were 11.35% of total sorption sites. The results showed the numerical solution fits very well to the analytical solution. For the nonlinear case, validation was performed by calculating a mass balance and checking the equilibrium concentrations.

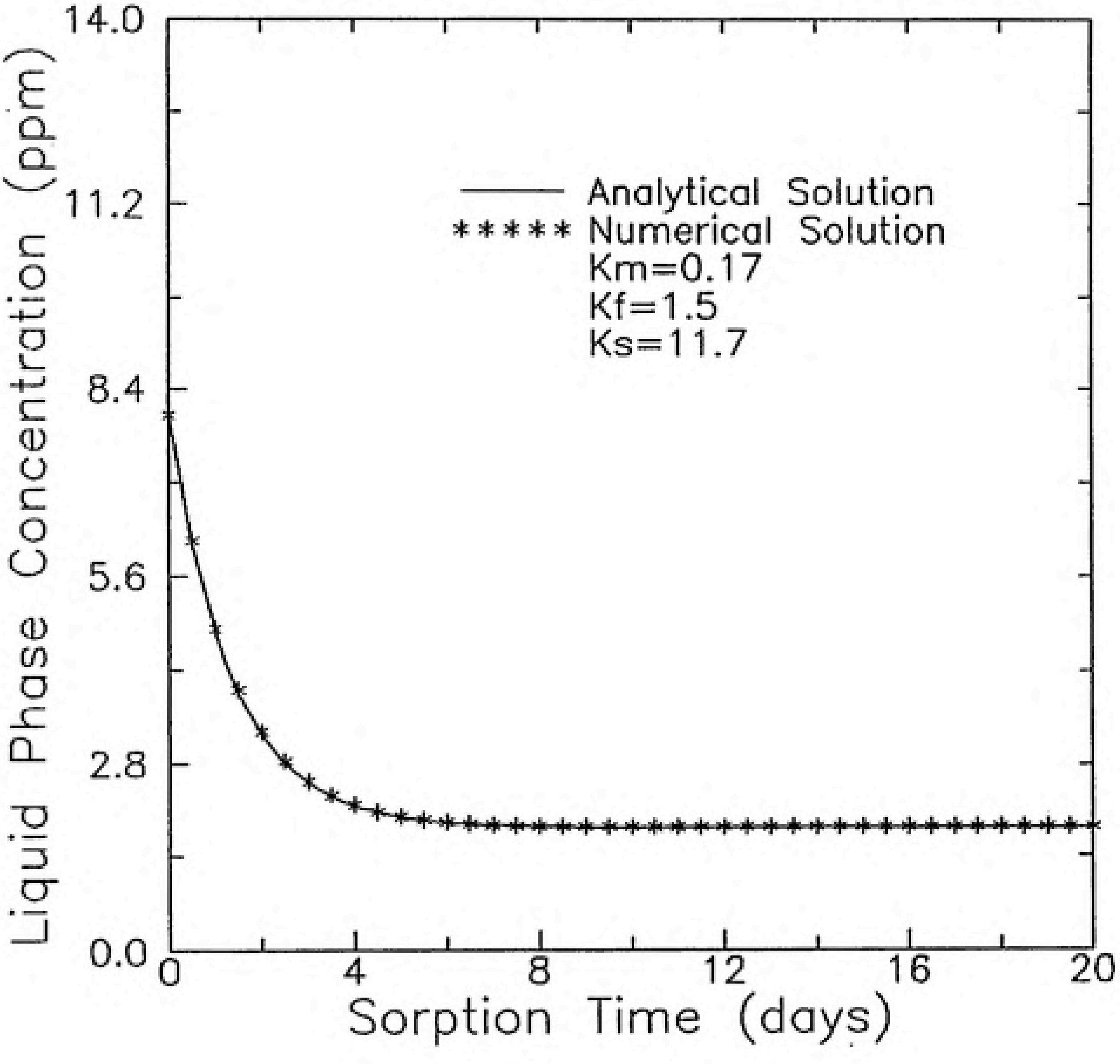

Figure 5-2 Validation of the Two-Site Model

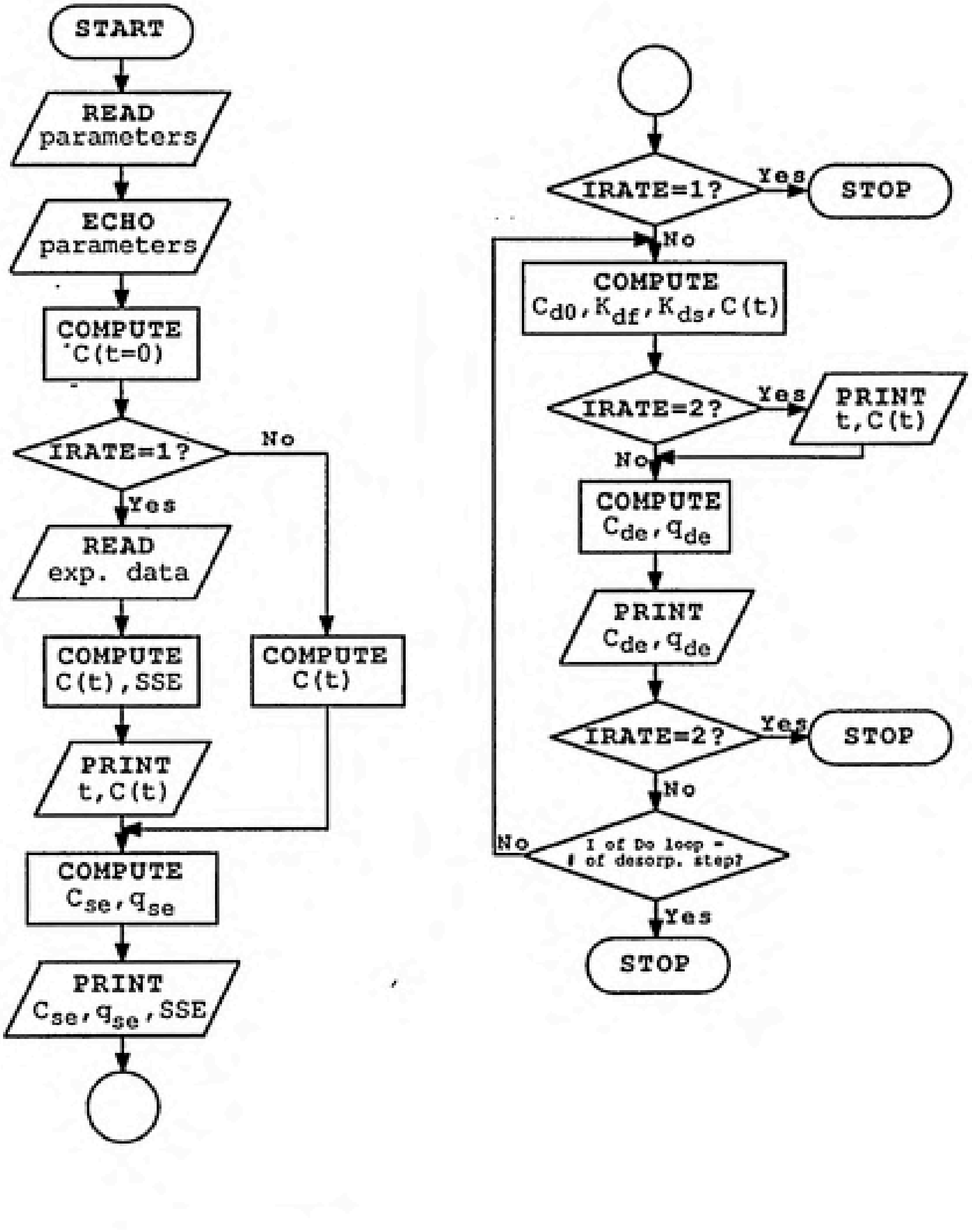

Figure 5-1 Flowchart of Algorithm

5.2 Model Parameters Determination

The values of Freundlich sorption equilibrium model parameters, obtained from the sorption-desorption isotherm study were used for model simulations. The sorption capacity constant for the fast-sites was obtained by using the first sorption rate data point (sorption time of two hours) as the instantaneous liquid-phase solute concentration at $t = 0$, since two hours is a very short period compared to 23 days. K_f was computed by the equation

$$q_{f,t=0} = K_f C_{t=0}^n \tag{5-19}$$

where

$$q_{f,t=0} = \frac{C_0 - C_{t=0}}{R} \tag{5-20}$$

The value of K_f was found to be 1.64, i.e. 13% of the total sorption sites were fast-sites.

The value of the mass-transfer coefficient (K_m) was then determined by entering different possible values of K_m, and computing the SSE between the experimental data and model result, and noting the region of minimum error. The best fit was found with $K_m = 0.13$/day for both sorption rate studies (Figure 5-3).

5.3 Comparison of Experimental Data and Model Prediction

Using the predetermined values of the equilibrium parameters, the model was fit to the sorption rate studies of $Co = 14$ mg/l and $Co = 28$ mg/l (see Figures 5-4 and 5-5).

For the sorption rate study conducted with $C_0 = 14$ mg/l , the model didn't fit very well to the experimental data. Because the isotherm parameters used in

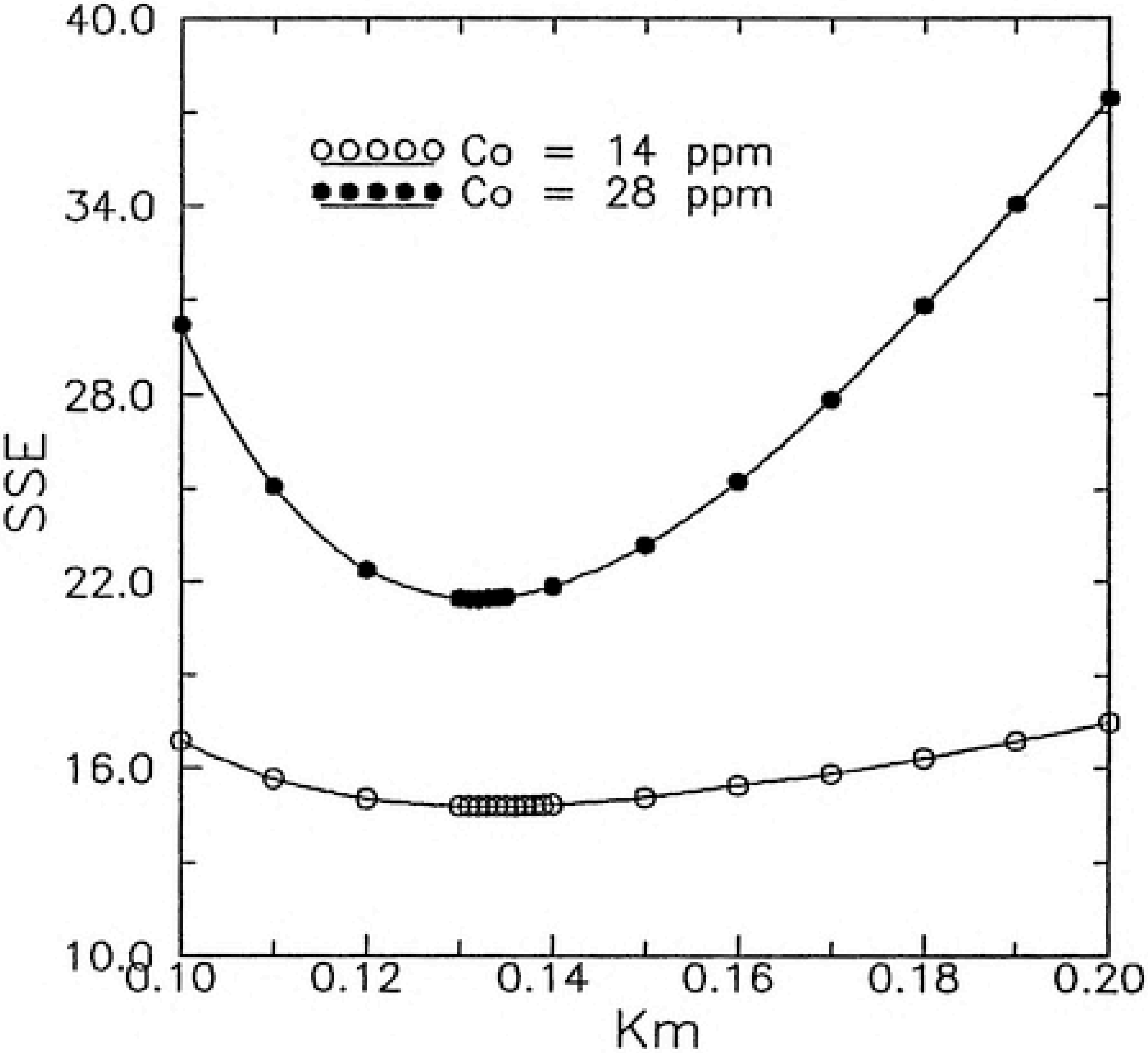

Figure 5-3 SSE as a Function of Km

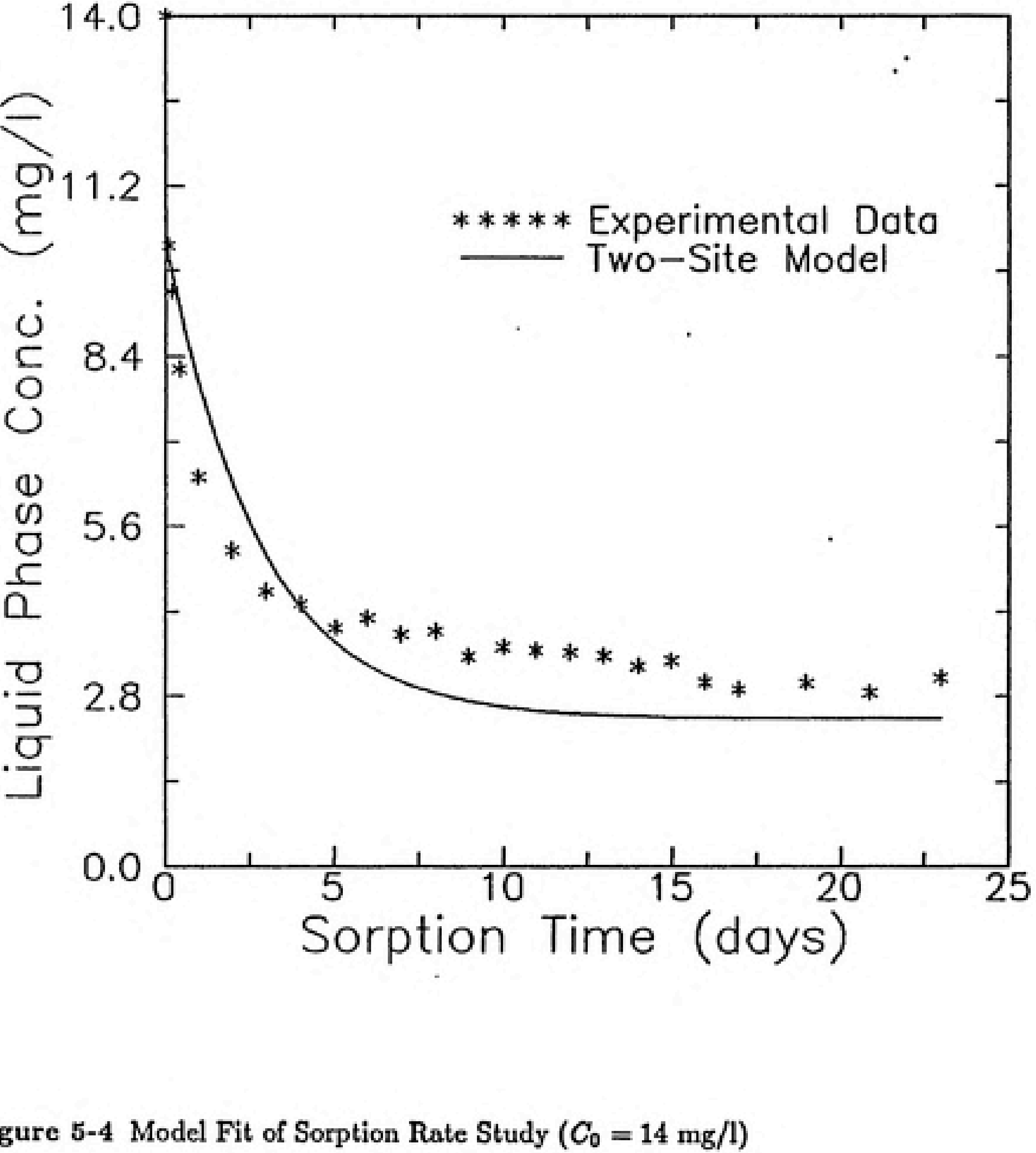

Figure 5-4 Model Fit of Sorption Rate Study ($C_0 = 14$ mg/l)

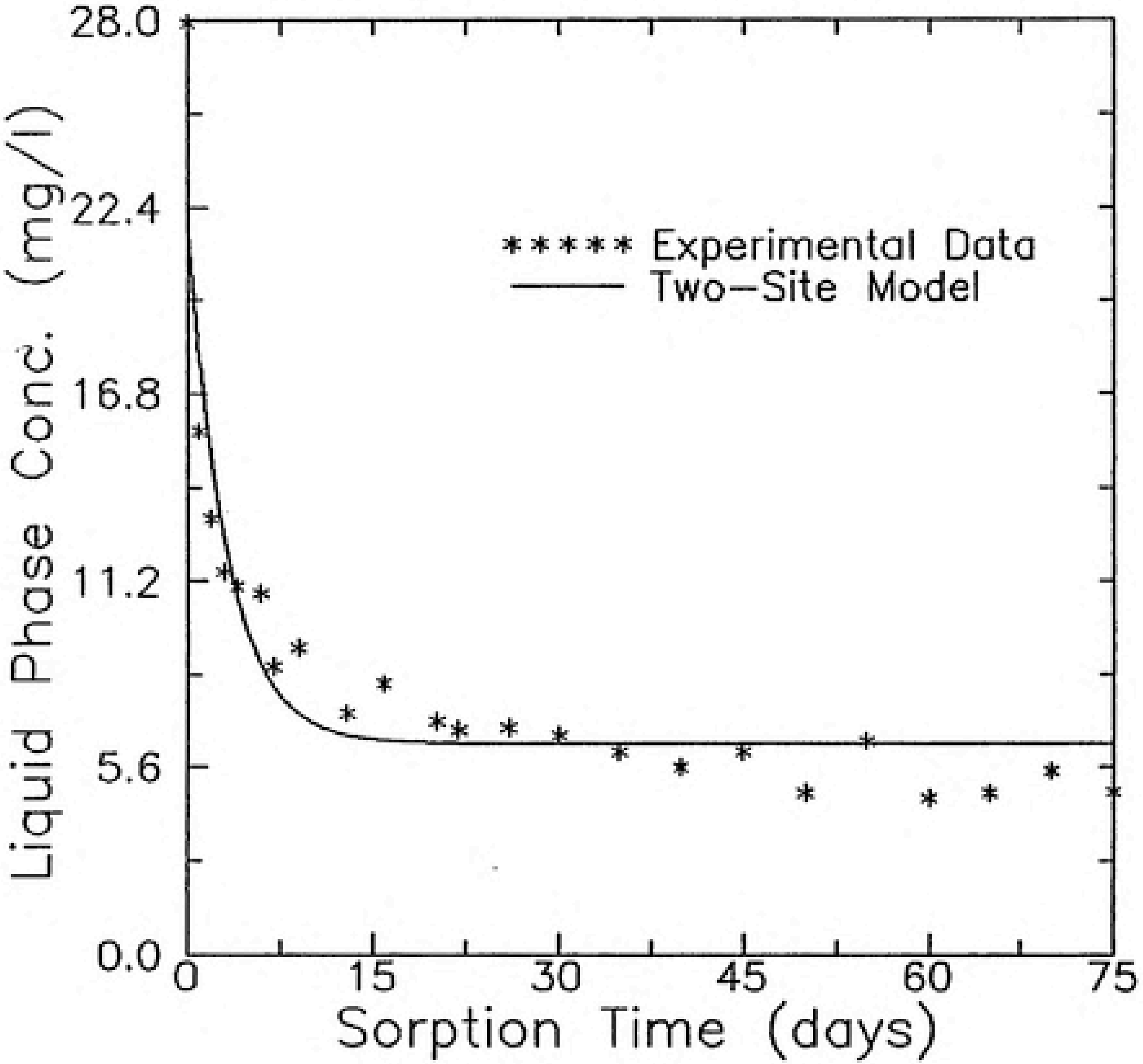

Figure 5-5 Model Fit of Sorption Rate Study ($C_0 = 28$ mg/l)

the model were obtained from a sorption equilibrium experiment performed for a sorption time of 44 days, which gave a higher sorption capacity constant, the predicted sorption equilibrium concentration was lower than the experimental data.

For the C_0 = 28 mg/l sorption rate study, the model fit the experimental data quite well for sorption time of 0 to 45 days. But after that, the predicted concentrations were higher than the experimental data. This is reasonable because a 44-day sorption isotherm was applied to interpret the sorption data that was not at equilibrium by that time.

The model fit of the desorption rate study with $K_{df}/K_d = 0.13$ or 0.45 and $K_m = 0.13$ or 0.35 is shown in Figure 5-6. The experimental data showed the desorption rate of diuron was faster than the sorption rate. The model predicted that the desorption rate (which is the same as the predicted sorption rate) was slower than the desorption rate given by experimental data. This deviation could result from a change of mass-transfer coefficient or the change of fraction of fast-sites to total sorption sites. The model fit of desorption rate study with the same ratio of K_{df}/K_d as that in sorption (0.13), but with K_m=0.35 in the desorption process is the best of the three simulations, indicating that the desorption rate is different from the sorption rate, a different K_m should be used for the desorption process.

The two-site model fit the sorption-desorption isotherm study data accurately (Figure 5-7). This is expected since the value of parameters used in the model were obtained from the isotherm study, they should give the same results.

The value of parameters used in the sorption-desorption simulations are listed in Table 5-1.

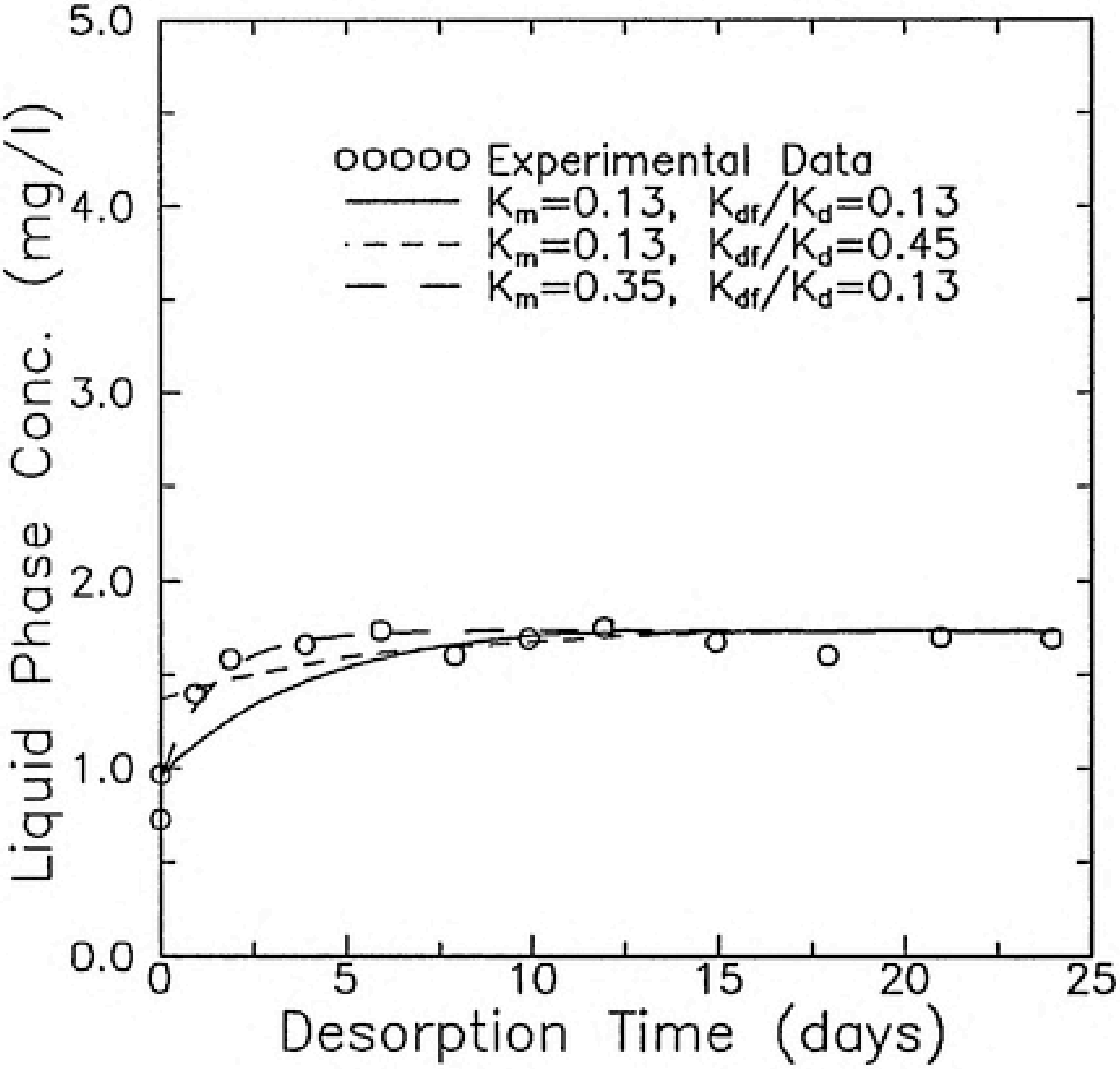

Figure 5-6 Model Fit of Desorption Rate

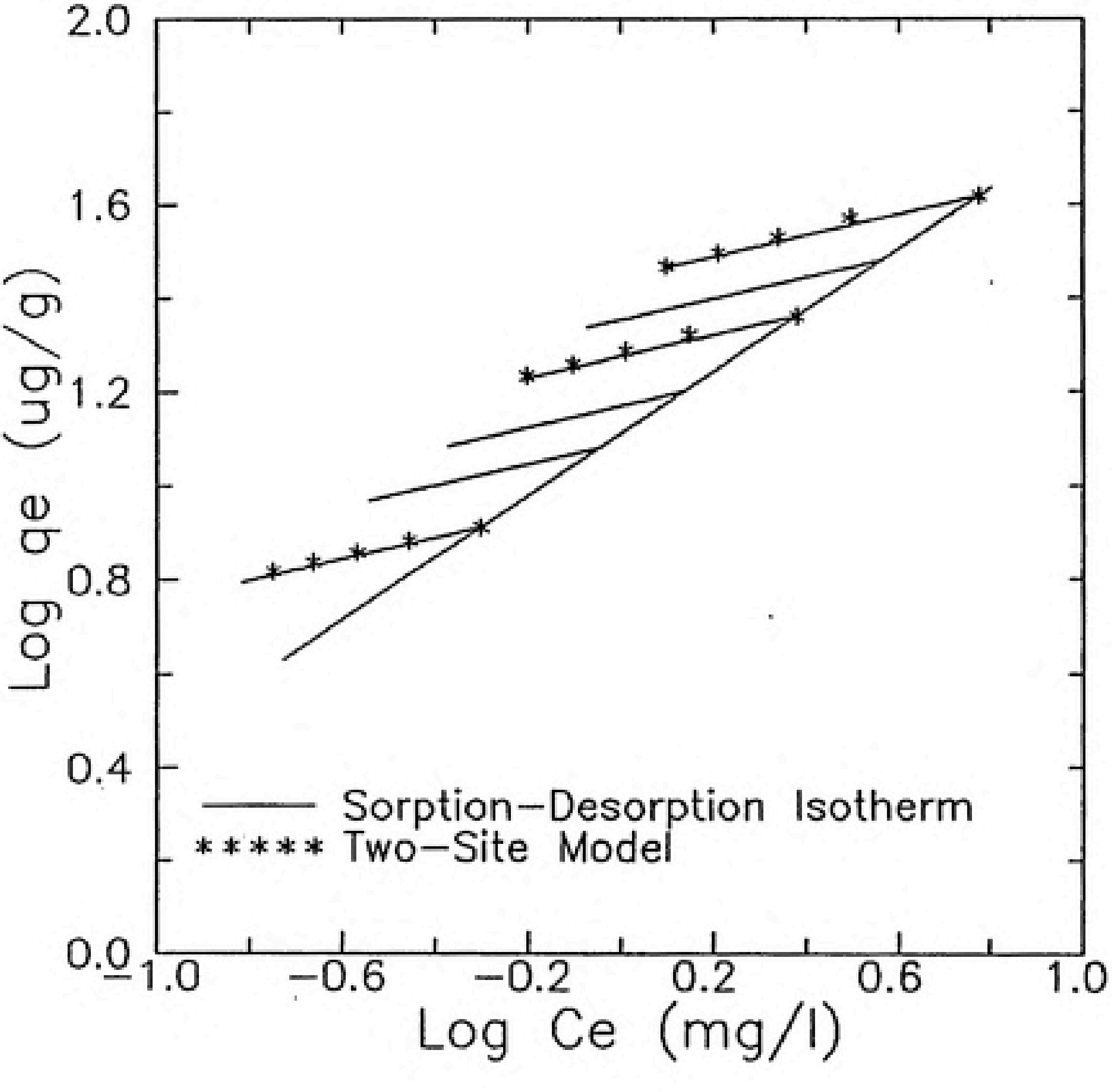

Figure 5-7 Model Fit of Sorption-Desorption Equilibrium Data

Table 5-1 List of Parameters Used in the Sorption-Desorption Simulations

	Sorption				Sorption	Desorption				Desorption	
Name of Simulation	n	Kf	Ks	Km	Time (d)	n	Kf	Ks	Km	Time (d)	Figure
Sorption Kinetics	1	1.5	11.71	0.17	20						5-2
Sorption Kinetics	0.65	1.64	11.23	0.1-0.2	23,44						5-3
Sorption Kinetics	0.65	1.64	11.23	0.13	23						5-4
Sorption Kinetics	0.65	1.64	11.23	0.13	75						5-5
Desorption Kinetics	0.65	1.64	11.23	0.13	20	0.226	2.46	16.45	0.13	24	5-6
Desorption Kinetics	0.65	1.64	11.23	0.13	20	0.226	8.51	10.40	0.13	24	
Desorption Kinetics	0.65	1.64	11.23	0.13	20	0.226	2.46	16.45	0.35	24	
Sorption-Desorption Equilibrium	0.65	1.64	11.23	0.13	44	0.226	2.46	16.45	0.13	7	5-7

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Several conclusions can be drawn from the results of the sorption-desorption experiments in this research. These conclusions include

(1) Desorption hysteresis was observed in the diuron sorption-desorption equilibrium experiment.

(2) Sorption-desorption data were found to fit a Freundlich model with the exponent and the capacity coefficient determined from the maximum historical equilibrium point.

(3) Nonattainment of equilibrium, loss of solute, artifact of experimental method, sorption to nonsettling particles, centrifugation effect, accumulated measurement error, and presence of implicit-sorbate were found not to be the major cause of desorption hysteresis.

(4) The two-site model described sorption kinetics reasonably well.

(5) The mass transfer coefficient obtained in the sorption rate study provided a less accurate prediction of desorption rate data than of the sorption rate data.

6.2 Recommendations

(1) Different results of desorption equilibrium were observed using the consecutive-desorption method and the single-dilution method. The reason causing this

result should be further investigated.

(2) One-dimensional column experiments should be used to compare the degree of hysteresis between batch and flow-through systems.

REFERENCES

Adams, R.S. and P. Li, Soil Properties Influencing Sorption and Desorption of Lindane, *Soil Sci. Soc. Amer. Proc., 35, pp. 78–81*, 1971.

Black, C.A., Methods of Soil Analysis, *American Society of Agronomy, serial no. 9, pp. 891–901*, 1965.

Bouchard, D.C. and T.L. Lavy, Hexazinone Adsorption-Desorption Studies with Soil and Organic Adsorbents, *J. Environ. Qual., 14(2), pp. 181–186*, 1985.

Bowman, B.T. and W.W. Sans, Partitioning Behavior of Insecticides in Soil-Water Systems: I. Adsorbent Concentration Effects, *J. Environ. Qual., 14(2), pp. 265–269*, 1985.

Bowman, B.T. and W.W. Sans, Partitioning Behavior of Insecticides in Soil-Water Systems: II. Desorption Hysteresis Effects, *J. Environ. Qual., 14(2), pp. 270–273*, 1985.

Brown, D.S. and E.W. Flagg, Empirical Prediction of Organic Pollutant Sorption in Neutral Sediments, *J. Environ. Qual., 10, pp. 382–386*, 1981.

Brusseau, M.L. and P.S.C. Rao, Sorption Nonideality During Organic Contaminant Transport in Porous Media, *Critical Reviews in Environ. Control, 19, pp. 33–99*, 1989.

Cameron, D.R. and A. Klute, Convective-Dispersive Solute Transport with a Combined Equilibrium and Kinetic Adsorption Model, *Water Resources Research, 13(1), pp. 183– 188*, 1977.

Chiou, C.T., P.E. Porter, and D.W. Schmedding, Partition Equilibria of Nonionic Organic Compounds between Soil Organic Matter and Water, *Environ. Sci. and Technol., 17, pp. 227–231*, 1983.

Coates, J.T. and A.W Elzerman, Desorption Kinetics for Selected PCB Congeners from River Sediments, *J. of Contaminant Hydrology, 1, pp. 191–210*, 1986.

Corwin, D.L. and W.J. Farmer, Nonsingle-Valued Adsorption- Desorption of Bromacil and Diquat by Freshwater Sediments, *Environ. Sci. and Technol., 18, pp. 507–514*, 1984.

Curl, R.L. and G.A. Keolelan, Implicit-Adsorbate Model for Apparent Anomalies with Organic Adsorption on Natural Adsorbents, *Environ. Sci. and Technol., 18, pp. 916–922*, 1984.

Dao, T.H., D.B. Marx, T.L. Lavy, and J. Dragun, Effect, and Statistical Evaluation, of Soil Sterilization on Aniline and Diuron Adsorption Isotherms, *Soil Sci. Soc. Am. J., 46, pp. 963-969*, 1982.

Dao, T.H. and T.L. Lavy, A Kinetic Study of Adsorption and Degradation of Aniline, Benzoic Acid, Phenol, and Diuron in Soil Suspensions, *Soil Science, pp. 66-71*, 1987.

DiToro, D.M. and L.M. Horzempa, Reversible and Resistant Components of PCB Adsorption-Desorption: Isotherms, *Environ. Sci. and Technol., 16(9), pp. 594-602*, 1982.

DiToto, D.M., A Particle Interaction Model of Reversible Organic Chemical Sorption, *Chemosphere, 14(10), pp. 1503- 1538*, 1983.

Gerstl, Z. and C.S. Helling, Evaluation of Molecular Connectivity as a Predictive Method for the Adsorption of Pesticides by Soils, *Environ. Sci. Health, 22(1), pp. 55-69*, 1987.

Giles, C.H., T.H. MacEwan, S.N. Nakhwa, and D. Smith, Studies in Adsorption. Part XI. A System of Classification of Solution Adsorption Isotherms, and Its Use in Diagnosis of Adsorption Mechanisms and in Measurement of Specific Surface Areas of Solids, *J. Chem. Soc., pp. 3973-3993*, 1960.

Gschwend, P.M. and S.C. Wu, On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants, *Environ. Sci. and Technol., 19, pp. 90-96*, 1985.

Hansch, C. and A.J. Leo, Substituent Constants for Correlation Analysis in Chemistry and Biology, *Wiley-Interscience*, 1979.

Hermosin, M.C., J.C., and J.L. Perez Rodriguez, Adsorption and Desorption of Maleic Hydrazide as a Function of Soil Properties, *Soil Sci., 144(4), pp. 250-256*, 1987.

Higgo, J.J.W. and L.V.C. Rees, Adsorption of Actinides by Marine Sediments: Effect of the Sediment/Seawater Ratio on the Measured Distribution ratio, *Environ. Sci. and Technol., 20, pp. 483-490*, 1986.

Ho, P.C. and C.S. Daw, Adsorption and Desorption of Dinitrotoluene on Activated Carbon, *Environ. Sci. and Technol., 22(8), pp. 919-924*, 1988.

Horzempa, L.M. and D.M. DiToro, The Extent of Reversibility of polychlorinated Biphenyl Adsorption, *Water Research, 17(8), pp. 851-859*, 1983.

Isaacson, P.J. and C.R. Frink, Nonreversible Sorption of Phenolic Compounds by Sediment Fractions: The Role of Sediment Organic Matter, *Environ. Sci. and Technol., 18, pp. 43-48*, 1984.

Jaffe, P.R., Modeling Sorbing Chemicals: Considering the Nonsingular Adsorption-Desorption Isotherm, *J. Environ. Sci. Health, A21(1), pp. 55–69*, 1986.

Karickhoff, S.W., D.S. Brown, and T.A. Scott, Sorption of Hydrophobic Pollutants on Natural Sediments, *Water Research, 13, pp. 241–248*, 1979.

Karickhoff, S.W., Organic Pollutant Sorption in Aquatic Systems, *J. Hydraulic Eng., 110(6), pp. 707–733*, 1984.

Karickhoff, S.W., D.S. Brown, and T.A. Scott, Sorption of Hydrophobic Pollutants in Natural Sediments, *Water Research, 13, pp. 241–248*, 1979.

Koskinen, W.C. and H.H. Cheng, Effects of Experimental Variables on 2,4,5-T Adsorption-Desorption in Soil, *J. Environ. Qual., 12(3), pp. 325–330*, 1983.

Koskinen, W.C., G.A. O'Connor, and H.H. Cheng, Characterization of Hysteresis in the Desorption of 2,4,5-T from Soils, *Soil Sci. Soc. Am., 45, pp. 871–874*, 1979.

McCloskey, W.B. and D.E. Bayer, Thermodynamics of Fluridone Adsorption and Desorption on Three California Soils, *Soil Sci. Soc. Am. J., 51, pp. 605–611*, 1987.

Means, J.C., S.G. Wood, J.J. Hassett, W.L. Barwart, Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils, *Environ. Sci. and Technol., 14, pp. 1524–1528*, 1980.

The Merck Index: An Encyclopedia of Chemicals, Drugs and Biologicals, 10th edition, Published by Merck & Co., Inc. Rahway, NJ. USA, , 1983.

Miller, C.T., Modeling of Sorption and Desorption Phenomena for Hydrophobic Organic Contaminants in Saturated Soil Environments, *Ph.D. dissertation, University of Michigan*, 1984.

Miller, C.T. and W.J. Weber, Sorption of Hydrophobic Organic Pollutants in Saturated Soil Systems, *J. of Contaminant Hydrology, 1, pp. 243–261*, 1986.

Mustafa, M.A. and Y. Gamar, Adsorption and Desorption of Diuron as a Function of Soil Properties, *Soil Sci. Soc. Amer. Proc., 36, pp. 561–564*, 1972.

Nkedi-Kizza, P., P.S.C. Rao, and J.W. Johnson, Adsorption of Diuron and 2,4,5-T on Soil Particle-size Separates, *J. Environ. Qual., 12(2), pp. 195–197*, 1983.

Nkedi-Kizza, P., P.S.C. Rao, and A.G. Hornsby, Influence of Organic Cosolvents on Leaching of Hydrophobic Organic Chemicals through Soils, *Environ. Sci. Technol., 21(11), pp. 1107–1111*, 1987.

O'Connor, D.J. and J.P. Connolly, The Effect of Concentration of adsorbing Solids on the Partition Coefficient, *Water Research, 14, pp. 1517–1523*, 1980.

Ogram, A.V., R.E. Jessup, L.T. Ou, and P.S.C. Rao, Effects of Sorption on Biological Degradation Rates of 2,4-D in Soils, *Appl. Environ. Microbiol., 49, pp. 582–587*, 1985.

Operation Procedures and Service Manual of Model 700 TOC Analyzer, O.I. Corporation.

Peck, D.E., D.L. Corwin, and W.J. Farmer, Adsorption-Desorption of Diuron by Freshwater Sediments, *J. Environ. Qual., 9(1), pp. 101–106*, 1980.

The Pesticide Manual: A World Compendium, 7th edition, Thornton Heath: British Crop Protection Council, 1983.

Rogers, R.D., J.C. McFarlane, and A.J. Cross, Adsorption and Desorption of Benzene in Two Soils and Montmorillonite Clay, *Environ. Sci. Technol., 14(4), pp. 457–460*, 1980.

Sabljic', A., On the Prediction of Soil Sorption Coefficients of Organic Pollutants from Molecular Structure: Application of Molecular Topology Model, *Environ. Sci. and Technol., 21, pp. 358–366*, 1987.

Schwarzenbach, R.P. and J. Westall, Transport of Nonpolar Organic Compounds from Surface Water to Groundwater. Laboratory Sorption Studies, *Environ. Sci. and Technol., 15(11), pp. 1360– 1367*, 1981.

Sheets, T.J., Review of Disappearance of Substituted Urea Herbicides from Soil, *Agron. J., 47,93*, 1955.

Steen, W.C., D.F. Paris and G.L. Baughman, Partition of Selected Polychlorinated Biphenyl to Natural Sediments, *Water Research, 12, pp. 655–657*, 1978.

Uchrin, C.G. and G. Mangels, Sorption Equilibria of Benzene and Toluene on Two New Jersey Coastal Plain Ground Water Aquifer Solids, *J. Environ. Sci. Health, A22(8), pp. 743– 758*, 1987.

Van Genuchten, M.T., J.M. Davidson, and P.J. Wierenga, An Evaluation of Kinetic and Equilibrium Equations for the Prediction of Pesticide Movement Through Porous Media, *Soil Sci. Soc. Amer. Proc., 38, pp. 29–35*, 1974.

Wauchope, R.D. and R.S. Myers, Adsorption-Desorption Kinetics of Atrazine and Linuron in Freshwater-Sediment Aqueous Slurries, *J. Environ. Qual., 14(1), pp. 132–136*, 1985.

Weber, J.B. and S.B. Weed, Adsorption and Desorption of Diquat, Paraquat, and Prometone by Montmorillonitic and Kaolinitic Clay Minerals, *Soil Sci. Soc. Am. Proc., 32, pp. 485– 487*, 1968.

Weber, W.J. and C.T. Miller, Modeling the Sorption of Hydrophobic Contaminants by Aquifer Materials-I, *Water Research, 22(4), pp. 457–464*, 1988.

Weber, J.B. and C.T. Miller, Organic Chemical Movement over and through Soil, *Soil Sci. Soc. of America and American society of Agronomy, 22, pp. 305–333*, 1989.

Wu, S.C. and P.M. Gschwend, Numerical Modeling of Sorption Kinetics of Organic Compounds to Soil and Sediment Particles, *Water Resources Research, ,24(8), pp. 1373–1383*,1988.

Wu, S.C. and P.M. Gschwend, Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments and Soils, *Environ. Sci. and Technol., 20, pp. 717–725*, 1986.

APPENDIX I

The Analytical Method of the Organic Carbon Content of Solids

The Analytical Method of the Organic Carbon Content of Solids

The organic carbon content of the solid was analyzed by ampule method with O.I. Corporation Model 700 TOC analyzer.

For each sample, varying amounts of soil were placed in an ampule of 10 ml. capacity and 2.2 ml of acidified persulfate solution (1 ml of 100 g/l sodium persulfate and 0.2 ml of 5% phosphoric acid and 1 ml distilled deionized water) were added. The ampules were then purged with oxygen to remove inorganic carbon and ambient carbon dioxide, then were flame sealed. The sealed ampules were put in an oven at 90 to 100°C and heated for three days resulting in the quantitative oxidation of organic carbon. The carbon dioxide produced was then purged from the ampule onto a molecular sieve trap where it accumulated during purging. After a specified purge time (2.5 minutes) the trap was placed in line with a non-dispersive infrared analyzer and was rapidly heated to desorb the trapped carbon dioxide. The carbon dioxide detected was equivalent to the mass of TOC in the sample and was determined by comparison with standards which were made with 1 ml of 100 g/l sodium persulfate, 0.2 ml 5% phosphoric acid, and 1 ml 25 mg/l potassium biphthalate (Operation Procedures and Service Manual of Model 700 TOC analyzer, O. I. Corporation).

APPENDIX II

The Analytical Method of the Cation-Exchange Capacity of Solids

The Analytical Method of the Cation-Exchange Capacity of Solids

The cation-exchange capacity of the solid was determined by the sodium saturation method (Black, 1965). The experimental procedure used for this method was:

1. For each sample, 6 g of Wagner sample was put in a 37-ml round-bottom centrifuge bottle;
2. 33 ml of 1.0 N NaOAc solution were added to the bottle;
3. the capped bottle was then shaken in a mechanical shaker at 150 rpm for five minutes, and then centrifuged at 2500 rpm for 15 minutes;
4. the supernatant was decanted and the extraction process was repeated three times;
5. the samples were then washed with three 33-ml portions of 99% isopropyl alcohol in the same manner as that in step 2 and 3;
6. using the shaking and centrifugation procedure of the previous steps, the adsorbed Na was replaced with three 33-ml portions of NH_4OH reagent;
7. the supernatants were decanted and saved in a 100-ml volumetric flask;
8. the solution in the flask was then diluted to volume with NH_4OAc reagent.
9. each sample was then acidified with 1 ml 10% HNO_3 and saved in a refrigerator; and
10. the concentration of Na was determined with a Perkin-Elmer Model 560 atomic absorption spectrophotometer. The results were expressed in meq. per 100 g of air-dried soil.

APPENDIX III

Experimental Data

I. Effect of Azide on Inhibiting Biodegradation Study (AZ)

Time (days)	No Azide System C/Co	With Azide System C/Co
0.000	1.000	1.000
0.142	0.711	0.739
0.941	0.480	0.525
2.003	0.393	0.429
2.955	0.348	0.403
3.962	0.339	0.317
4.851	0.332	0.270
6.993	0.254	0.276
8.924	0.257	0.234
10.943	0.217	0.230
12.951	0.200	0.208
15.962	0.157	0.207
19.969	0.201	0.182

II. Sorption Kinetics Study (D-K)

Time (days)	GC Data Conc. (mg/l)	UV Data Conc. (mg/l)
0.000	12.000	12.000
0.083	8.551	7.771
0.236	6.484	6.242
0.491	4.950	5.003
1.028	4.234	3.836
2.021	2.843	2.795
2.990	2.923	2.591
4.042	2.116	2.074
7.007	1.696	1.670
10.139	1.320	1.378
14.056	1.550	1.304

III. Sorption Rate Study I. (SR4, Co=14 mg/l)

Time (days)	Conc. (mg/l)	C/Co
0.000	14.000	1.000
0.083	10.217	0.730
0.167	9.456	0.675
0.417	8.195	0.585
0.986	6.411	0.458
1.979	5.214	0.372
2.986	4.536	0.324
4.007	4.332	0.309
5.042	3.930	0.281
5.986	4.094	0.292
6.979	3.825	0.273
8.000	3.871	0.277
8.979	3.452	0.247
9.993	3.609	0.258
10.979	3.557	0.254
11.983	3.524	0.252
12.983	3.466	0.248
14.000	3.296	0.235
14.986	3.387	0.242
15.979	3.030	0.216
16.979	2.919	0.209
18.909	3.023	0.216
20.865	2.855	0.204
22.972	3.101	0.222

IV. Sorption Rate Study II. (SR5, Co=28 mg/l)

Time (days)	Conc. (mg/l)	C/Co
0.000	27.915	1.000
0.962	15.675	0.562
1.944	13.081	0.469
2.976	11.478	0.411
4.003	11.036	0.395
5.955	10.841	0.388
6.969	8.641	0.310
8.972	9.202	0.330
12.955	7.216	0.258
15.910	8.126	0.291
20.219	6.969	0.250
21.962	6.717	0.241
25.983	6.785	0.243
30.073	6.561	0.235
34.946	6.060	0.217
39.941	5.582	0.200
44.962	6.066	0.217
50.017	4.821	0.173
54.955	6.371	0.228
59.993	4.662	0.167
64.955	4.808	0.172
69.962	5.481	0.196
74.958	4.841	0.173

V. Effect of Sorption Age on Desorption Rate Study I. (A1, Sorption Age=1 day)

Time (days)	Conc. (mg/l)	C/Co
0.000	1.898	0.139
0.042	2.242	0.164
0.153	2.474	0.181
0.858	2.532	0.186
1.858	2.338	0.171
2.896	2.326	0.170
3.861	2.075	0.152
4.851	1.864	0.137
5.854	2.011	0.147
6.868	1.890	0.139
7.864	1.749	0.128
8.827	1.634	0.120
9.740	1.641	0.120
10.826	1.430	0.105
11.847	1.526	0.112
12.840	1.641	0.120
13.868	1.609	0.118
14.903	1.418	0.104
15.845	1.475	0.108
16.845	1.462	0.107
17.847	1.284	0.094
18.847	1.475	0.108

VI. Effect of Sorption Age on Desorption Rate Study II. (DR2, Sorption Age=10 days)

Time (days)	Conc. (mg/l)	C/Co
0.000	0.736	0.053
0.083	1.469	0.105
0.167	1.577	0.113
0.392	1.641	0.117
0.958	1.806	0.129
1.917	1.928	0.138
2.906	1.864	0.133
3.903	1.934	0.138
4.910	1.941	0.139
5.958	1.992	0.142

VII. Effect of Sorption Age on Desorption Rate Study III.
(A20, Sorption Age=20 days)

Time (days)	Conc. (mg/l)	C/Co
0.000	0.728	0.051
0.021	0.968	0.068
0.944	1.399	0.098
1.885	1.583	0.111
3.904	1.660	0.116
5.913	1.736	0.121
7.910	1.602	0.112
9.889	1.692	0.118
11.913	1.749	0.122
14.910	1.672	0.117
17.903	1.602	0.112
20.948	1.698	0.119
23.930	1.692	0.118

VIII. Effect of Initial Concentration on Desorption Rate Study
(Cmax, Sorption Time=10 days)

	Co=7mg/l	Co=14mg/l	Co=21mg/l
Time (days)	Conc. (mg/l)	Conc. (mg/l)	Conc. (mg/l)
0.000	0.311	0.772	1.427
0.021	0.539	1.253	2.050
0.135	0.621	1.481	2.229
0.680	0.740	1.704	2.816
1.771	0.803	1.838	3.082
2.674	0.803	1.787	3.212
3.642	0.759	1.794	3.062
4.656	0.753	1.685	2.965
5.660	0.848	1.781	2.913
6.642	0.772	1.781	2.887
7.674	0.841	1.679	3.036
8.701	0.803	1.666	2.939
9.653	0.747	1.596	3.088
11.667	0.816	1.813	3.049
13.670	0.721	1.692	2.939
15.680	0.740	1.685	2.991
17.653	0.740	1.730	2.984
20.608	0.702	1.794	3.088

IX. Sorption-Desorption Equilibrium Study
(Sorption Time=44 days, Desorption Time=7 days)
(RI, Co=2 to 27 mg/l)

Sample name	Initial Conc. (mg/l)	Sorption Equil. Conc.	1st Desorp. Equil. Conc.	2nd Desorp. Equil. Conc.	3rd Desorp. Equil. Conc.	4th Desorp. Equil. Conc.
RI-1	2.261	0.187				
RI-2	4.583	0.495	0.385	0.281	0.225	0.153
RI-3	6.935	0.882	0.589	0.463	0.354	0.288
RI-4	9.280	1.376	0.923	0.652	0.553	0.426
RI-5	11.601	1.941				
RI-6	13.852	2.274	1.411	1.037	0.832	0.608
RI-7	16.460	2.945				
RI-8	18.814	3.492	2.110	1.449	1.154	0.844
RI-9	22.795	4.921				
RI-10	26.714	6.337	3.534	2.300	1.739	1.259

X. Short-Term Sorption-Desorption Equilibrium Study
(Sorption Time=10 days, Desorption Time=5 days)
(ISO, Co=2 to 14 mg/l)

Sample Name	Co (mg/l)	Sorption Equil. Conc.	1st Desorp. Equil. Conc.	2nd Desorp. Equil. Conc.	3rd Desorp. Equil. Conc.	4th Desorp. Equil. Conc.	5th Desorp. Equil. Conc.
ISO-1	1.870	0.143					
ISO-2,3	4.660	0.600	0.368	0.357	0.344	0.250	0.234
ISO-4	6.530	1.070					
ISO-5,6	9.330	1.613	0.779	0.732	0.633	0.441	0.426
ISO-7	11.200	2.056					
ISO-8,9	14.000	2.740	1.397	1.255	0.942	0.621	0.652

XI. Sorption-Desorption Equilibrium Study
(SDDS, Sorption Time=10 days, Desorption Time=5 days)

Sample name	Initial Conc. (mg/l)	Sorption Equil. Conc.	1st Desorp. Equil. Conc.	2nd Desorp. Equil. Conc.	1st Re-sorb. Equil. Conc.	2nd Re-sorb. Equil. Conc.	3rd Re-sorb. Equil. Conc.
SDDS-1	9.21	1.931	1.085	0.772	2.522	3.603	4.46
SDDS-2	13.716	3.316	1.771	1.173	2.923	3.792	4.642

XII. Sorption-Desorption Equilibrium Study
(SDSD, Sorption Time=10 days, Desorption Time=5 days)

Sample name	Initial Conc. (mg/l)	Sorption Equil. Conc.	Desorp. Equil. Conc.	1st Re-sorb. Equil. Conc.	2nd Re-sorb. Equil. Conc.	3rd Re-sorb. Equil. Conc.	4th Re-sorb. Equil. Conc.	5th Re-sorb. Equil. Conc.	1st Re-desorp. Equil. Conc.	2nd Re-desorp. Equil. Conc.	3rd Re-desorp. Equil. Conc.
SDSD-1	9.47	1.97	1.208	1.526	1.826	2.297	3.098	6.344	2.942	1.829	1.265
SDSD-2	14.108	3.162	1.899	2.072	2.149	2.567	3.286	6.476	3.052	1.944	1.37

XIII. Single-Dilution Study
(Sorption Time=10 days, Desorption Time=5 days)
(DILU)

Sample name	Equilibrium Conc. (mg/l)
DILU-Co	13.701
DILU-1	3.342
DILU-2	2.018
DILU-3	1.488
DILU-4	1.183

APPENDIX IV

FORTRAN Code

```
$DEBUG
      PROGRAM BATCH
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                                                                      C
C     THIS PROGRAM COMPUTES SOLUTION-PHASE SOLUTE CONCENTRATIONS,      C
C     AND SOLID-PHASE SORBATE CONCENTRATIONS DURING SORPTION-          C
C     DESORPTION PROCESS IN THE BATCH REACTOR. IT ALSO COMPUTES THE    C
C     SUM OF THE SQUARES OF ERROR BETWEEN THE ENTERED EXPERIMENTAL     C
C     DATA AND RESULT OF SIMULATION.                                   C
C                                                                      C
C     PARAMETER    PRECISION     DESCRIPTION                           C
C     ---------    ---------     -----------                           C
C     C            REAL*8        SOLUTION-PHASE SOLUTE CONCENTRATION   C
C     C0           REAL*8        INITIAL C                             C
C     CNEW         REAL*8        C AT NEW TIME STEP                    C
C     CRATIO       REAL*8        RATIO OF INITIAL C AT DESORPTION TO   C
C                                EQUILIBRIUM C AT SORPTION EQUILIBRIUM C
C     DT           REAL*8        TIME STEP                             C
C     IRATE        INTEGER*4     INDICATOR FOR TYPE OF REACTION        C
C                                (IRATE=1 FOR SORPTION RATE, IRATE=2   C
C                                 FOR DESORPTION RATE, IRATE=3 FOR     C
C                                 SORPTION-DESORPTION EQUILIBRIUM)     C
C     KD           REAL*8        FREUNDLICH DESORPTION CAPACITY CONST. C
C     KF           REAL*8        FREUNDLICH CAPACITY CONST. FOR FAST-  C
C                                SITE                                  C
C     KM           REAL*8        MASS TRANSFER COEFFICIENT             C
C     KS           REAL*8        FREUNDLICH CAPACITY CONST. FOR SLOW-  C
C                                SITE                                  C
C     ND           REAL*8        FREUNDLICH ENERGY CONST. FOR DESORP-  C
C                                TION                                  C
C     NS           REAL*8        FREUNDLICH ENERGY CONST. FOR SORPTION C
C     NSTEP        INTEGER*4     NUMBER OF DESORPTION STEPS            C
C     NT           INTEGER*4     NUMBER OF TIME STEPS OF REACTION      C
C     Q            REAL*8        SOLID-PHASE SORBATE CONCENTRATION     C
C     QE           REAL*8        EQUILIBRIUM Q                         C
C     QF           REAL*8        Q FOR FAST-SITE COMPONENT             C
C     QS           REAL*8        Q FOR SLOW-SITE COMPONENT             C
C     QSNEW        REAL*8        QS AT NEW TIME STEP                   C
C     R            REAL*8        RATIO OF MASS OF SOLID TO VOLUME OF   C
C                                SOLUTION                              C
C     SOLID        REAL*8        MASS OF SOLID                         C
C     TDESORB      REAL*8        DESORPTION TIME                       C
C     TOLER        REAL*8        TOLERANCE FOR PICARD ITERATION        C
C     TRY          REAL*8        GUESS OF C FOR NONLINEAR CALCULATION  C
C     TSORB        REAL*8        SORPTION TIME                         C
C     TSTEP        REAL*8        NUMBER OF TIME STEPS BETWEEN TWO      C
C                                SUCCESSIVE OUTPUTS                    C
C     VOL          REAL*8        VOLUME OF SOLUTION                    C
C                                                                      C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 NS,KM,KS,KF,ND,KD
```

```
      COMMON / B1 / KM,NS,KF,KS,DT,NT,SOLID,VOL,TOLER
      COMMON / B2 / IRATE,C0,R,TSTEP
      COMMON / B3 / C,Q,QS,QF,CNEW,QSNEW,QE,TRY
      COMMON / B5 / TSORB,TDESORB,CRATIO,NSTEP
C
      CALL READ
      CALL ECHO
C
C-----INITIALIZATION
C
      C=C0
      Q=0.D00
      QS=0.D00
      QF=0.D00
      CNEW=0.D00
      QSNEW=0.D00
      R=SOLID/VOL
C
C-----SORPTION
C
      NT=INT(TSORB/DT)+1
      TRY=C
      CALL SORB
      IF ( IRATE .EQ. 1 ) STOP
C
C-----DESORPTION
C
      NT=INT(TDESORB/DT)+1
      C0=C*CRATIO
      C=C0
      TRY=C
      CALL DESORB
      IF ( IRATE .EQ. 2 ) STOP
      DO 100 I=2,NSTEP
      C0=C*CRATIO
      C=C0
      TRY=C
      CALL DESORB
  100 CONTINUE
C
C
      STOP
      END

      SUBROUTINE READ
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 NS,ND,KM,KS,KF,KD
C
      COMMON / B1 / KM,NS,KF,KS,DT,NT,SOLID,VOL,TOLER
      COMMON / B2 / IRATE,C0,R,TSTEP
      COMMON / B4 / ND,KD
      COMMON / B5 / TSORB,TDESORB,CRATIO,NSTEP
C
```

```
      READ(1,1000) NS,KM,KF,KS,DT,SOLID,VOL,TSORB
      READ(1,2000) C0,CRATIO,TDESORB,ND,KD,TOLER
      READ(1,3000) IRATE,NSTEP,TSTEP
C
 1000 FORMAT(8F10.4)
 2000 FORMAT(6F10.4)
 3000 FORMAT(2I4,2X,F10.4)
C
      RETURN
      END

      SUBROUTINE ECHO
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 NS,ND,KF,KS,KM,KD
C
      COMMON / B1 / KM,NS,KF,KS,DT,NT,SOLID,VOL,TOLER
      COMMON / B2 / IRATE,C0,R,TSTEP
      COMMON / B4 / ND,KD
      COMMON / B5 / TSORB,TDESORB,CRATIO,NSTEP
C
      WRITE(2,1000)
      WRITE(2,2000) NS,KM,KF,KS,DT,SOLID,VOL,TSORB,C0,CRATIO,
     &             TDESORB,ND,KD,TOLER,TSTEP
      WRITE(2,3000) IRATE,NSTEP
C
 1000 FORMAT(10X,'SORPTION/DESORPTION SIMULATION OF BATCH REACTOR'/
     &       15X,'WITH TWO-SITES MODEL'//)
 2000 FORMAT(5X,'FREUNDLICH ENERGY CONSTANT              NS=   ',F10.4/
     &       5X,'MASS TRANSFER COEFFICIENT               KM=   ',F10.4/
     &       5X,'CAPACITY CONSTANT FOR FAST-SITE         KF=   ',F10.4/
     &       5X,'CAPACITY CONSTANT FOR SLOW-SITE         KS=   ',F10.4/
     &       5X,'TIME INCREMENT                          DT=   ',F10.4/
     &       5X,'MASS OF SOIL                            SOLID=',F10.4/
     &       5X,'VOLUME OF SOLUTION                      VOL=  ',F10.4/
     &       5X,'DURATION OF SORPTION PROCESS            TSORB=',F10.4/
     &       5X,'INITIAL LIQUID PHASE CONCENTRATION      C0=   ',F10.4/
     &      5X,'RATIO OF LIQUID PHASE CONC. AT BEGINNING OF DESORPTION'/
     &      5X,'TO THE CONC. AT THE END OF SORPTION    CRATIO=',F10.4/
     &      5X,'DURATION OF DESORPTION PROCESS        TDESORB=',F10.4/
     &      5X,'FREUNDLICH ENERGY CONSTANT FOR DESORPTION ND=  ',F10.4/
     &      5X,'CAPACITY CONST. FOR DESORPTION            KD=  ',F10.4/
     &      5X,'TOLERANCE FOR PICARD ITERATION          TOLER=',F10.4/
     &      5X,'NUMBER OF TIME STEPS BETWEEN TWO SUCCESSIVE OUTPUTS'/
     &      5X,'                                        TSTEP=',F10.4)
 3000 FORMAT(5X,'INDICATOR FOR RATE STUDY                IRATE=',I4/
     &       5X,'NUMBER OF DESORPTION STEPS              NSTEP=',I4)
C
      RETURN
      END

      SUBROUTINE SORB
C
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
      REAL*8 NS,ND,KM,KF,KS,KD
C
      DIMENSION DATT(24),DATC(24)
      COMMON / B1 / KM,NS,KF,KS,DT,NT,SOLID,VOL,TOLER
      COMMON / B2 / IRATE,C0,R,TSTEP
      COMMON / B3 / C,Q,QS,QF,CNEW,QSNEW,QE,TRY
C
C-----COMPUTE LIQUID PHASE CONCENTRATION AT T=0
C
      ITER=0
  100 CNEW=C0-KF*R*(TRY)**NS
      ERROR=ABS(CNEW-TRY)
      IF ( ERROR .GT. TOLER ) THEN
     ITER=ITER+1
     TRY=ABS(CNEW)
     WRITE(*,1000) ITER
     GOTO 100
      ENDIF
      TIME=0.D00
      C=CNEW
      Q=(C0-C)/R
      WRITE(3,2000)TIME,C
C
C-----READ EXPERIMENTAL DATA
C
      IF ( IRATE .EQ. 1 ) THEN
     DO 200 I=1,24
        READ(4,3000) DATT(I),DATC(I)
  200   CONTINUE
      ENDIF
     SSE=0.D00
     ISSE=1
C
C-----SOLVE FOR CNEW
C
      DO 300 I=1,NT
     ITER=0
  400   QSNEW=(QS+DT*KM*KS*TRY**NS)/(1.+KM*DT)
     CNEW=DT*KM*R*QSNEW+(1.+R*NS*KF*TRY**(NS-1.))*C
     &       -(DT*R*KM*KS+R*NS*KF)*TRY**NS
C
C-----CHECK IF ERROR < TOLERANCE FOR PICARD ITERATION
C
     ERROR=ABS(CNEW-TRY)
     IF ( ERROR .GT. TOLER ) THEN
       ITER=ITER+1
       TRY=ABS(CNEW)
       WRITE(*,1000) ITER
       GOTO 400
     ENDIF
     IF ( IRATE .EQ. 1 ) THEN
       TIME=DT*I
C
C-----CHECK AND COMPUTE SUM OF SQUARE ERROR
```

```
C
         IF( ABS(TIME-DATT(ISSE))  .LT.  DT/2.0 ) THEN
           SSE=SSE+ABS(CNEW-DATC(ISSE))**2.0
           ISSE=ISSE+1
         ENDIF
C
C-----CHECK AND PRINT OUT CONCENTRATIONS AT DESIRED TIMES
C
         CKSTEP=I/TSTEP
         CK=ABS(CKSTEP-INT(CKSTEP))
         IF ( CK .LE. 0.00001 ) THEN
            WRITE(3,4000) TIME,CNEW
         ENDIF
       ENDIF
       C=CNEW
       QS=QSNEW
  300 CONTINUE
      QE=(C0-CNEW)/R
      QF=KF*C**NS
      WRITE(3,5000) C,QE,SSE
C
 1000 FORMAT(2X,'ITER=',I4)
 2000 FORMAT(2E10.4)
 3000 FORMAT(2F10.3)
 4000 FORMAT(F10.4,E10.4)
 5000 FORMAT(3E10.4)
C
      RETURN
      END

      SUBROUTINE DESORB
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 NS,ND,KM,KF,KS,KD,KDF,KDS
C
      COMMON / B1 / KM,NS,KF,KS,DT,NT,SOLID,VOL,TOLER
      COMMON / B2 / IRATE,C0,R,TSTEP
      COMMON / B3 / C,Q,QS,QF,CNEW,QSNEW,QE,TRY
      COMMON / B4 / ND,KD
C
C
      KDF=KF/(KF+KS)*KD
      KDS=KS/(KF+KS)*KD
C
C-----COMPUTE LIQUID PHASE CONCENTRATION AT Td=0
C
      ITER=0
  100 QF1=KDF*TRY**ND
      CNEW=C0+(QF-QF1)*R
C
C-----CHECK IF ERROE < TOLERANCE FOR PICARD ITERATION
C
      ERROR=ABS(CNEW-TRY)
      IF ( ERROR .GT. TOLER ) THEN
```

```
      ITER=ITER+1
      WRITE(*,1000) ITER
      TRY=ABS(CNEW)
      GOTO 100
       ENDIF
       TIME=0.D00
       C=CNEW
       Q=QE+(C0-C)/R
       WRITE(3,2000)TIME,C
       TRY=C
       DO 200 I=1,NT
C
C-----SOLVE FOR CNEW
C
       ITER=0
  300    QSNEW=(QS+DT*KM*KDS*TRY**ND)/(1.+KM*DT)
      CNEW=DT*KM*R*QSNEW+(1.+R*ND*KDF*TRY**(ND-1.))*C
      &       -(DT*R*KM*KDS+R*ND*KDF)*TRY**ND
C
C-----CHECK IF ERROR < TOLERANCE FOR PICARD ITERATION
C
      ERROR=ABS(CNEW-TRY)
      IF ( ERROR .GT. TOLER ) THEN
        ITER=ITER+1
        WRITE(*,1000) ITER
        TRY=ABS(CNEW)
        GOTO 300
      ENDIF
      IF ( IRATE .EQ. 2 ) THEN
        TIME=DT*I
C
C-----CHECK AND PRINT OUT CONCENTRATIONS AT DESIRED TIMES
C
        CKSTEP=I/TSTEP
        CK=ABS(CKSTEP-INT(CKSTEP))
        IF ( CK .LE. 0.00001 ) THEN
           WRITE(3,3000) TIME,CNEW
        ENDIF
      ENDIF
      C=CNEW
      QS=QSNEW
  200 CONTINUE
       QF=KDF*C**ND
       QE=QE+(C0-C)/R
       WRITE(3,4000) C,QE
C
 1000 FORMAT(2X,'ITER=',I4)
 2000 FORMAT(2E10.4)
 3000 FORMAT(F10.4,E10.4)
 4000 FORMAT(2E10.4)
C
       RETURN
       END
```