INFORMATION TO USERS

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

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

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

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

Bell & Howell Information and Learning
300 North Zeib Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI®
RICE UNIVERSITY

Impact of Irreversible Sorption on Sediment Quality

by

Wei Chen

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE
Doctor of Philosophy

Approved, Thesis Committee

Mason B. Tomson, Director
Professor, Environmental Science and Engineering

Philip B. Bedient
Professor, Environmental Science and Engineering

Clarence A. Miller
Louis Calder Professor, Chemical Engineering

Houston, Texas
September, 1999
Abstract

Impact of Irreversible Sorption on Sediment Quality

by

Wei Chen

Irreversible sorption has been widely observed for hydrophobic organic contaminants in natural sediments. It is a complicated process and impacts sediment quality and contaminated sediment management. In this research, experiments were conducted to further understand the nature of irreversible sorption and the mechanism(s) controlling this process.

The unique characteristics of the irreversible compartment were delineated with the sorption and desorption of five chlorinated benzenes in four natural sediments. It was observed that each chemical-sediment combination exhibited a fixed amount of maximum irreversible sorption capacity, \( q_{\text{max}}^{\text{irr}} \). However, the organic carbon based partition coefficient associated with the irreversible compartment was essentially constant for different chemical-sediment combinations -- \( K_{\text{oc}}^{\text{irr}} = 10^{5.4250.17} \). The desorption behaviors were modeled with an irreversible sorption model, in which a Langmurian-type expression (representing the irreversible fraction) was added to the linear model. For the sorption and desorption of different compounds in the same sediment \( q_{\text{max}}^{\text{irr}} \) seems to be related to both \( K_{\text{ow}} \) and solubility. For sorption and
desorption of the same compound in different sediments $q_{\text{rr}}^{\text{max}}$ depends mainly on sediment organic carbon content ($f_{\infty}$), but may also be affected by the origin of the sediments. The release from the irreversible compartment was not affected by a number of factors, such as extended desorption time, competitive sorption, caustic treatment of sediments, and external mechanic forces. Many observations in this research suggest that sorption and desorption of hydrophobic organic contaminants in natural sediments are not controlled by the same mechanism, and irreversible sorption may be partly due to the association of organic sorbate molecules to some highly insoluble and hydrophobic materials in sediments.

Irreversible sorption greatly affects the fate and transport of contaminants in surface and subsurface environments -- it causes contaminants to persist in soils and sediments, and it also reduces the efficiency of pump and treat and bioremediation. Nevertheless, the same process could also greatly reduce the ecological and human-health risks of contaminated sediments. Thus, it is necessary to establish risk-based sediment quality standards, which could be of enormous economical impact. Also, to quantitatively address the impact of irreversible sorption on sediment quality, a one-dimensional solute-transport model was developed. This simple model could provide valuable support for environmental decision making.
Acknowledgement

It is with great gratitude that I herein acknowledge the help of the following people, without whom I could not complete this work. It is only fitting to begin with Dr. Mason Tomson, my advisor. During my graduate study, Dr. Tomson has given me tremendous guidance, support, and faith in my academic and personal lives. It was Dr. Tomson who convinced me to continue on my doctoral study when I doubted my future. I would like to give special thanks to my thesis committee members, Dr. Philip Bedient and Dr. Clarence Miller, both have provided invaluable oversight and assistance for my thesis. Dr. Amy Kan has been an incredible support for my graduate study. I greatly appreciate her time, patience, insights, and continual guidance to have my work completed. My friends Mr. Kalyan Lakshmanan and Ms. Xiaohui Wang, both are brilliant graduate students and are extremely proficient in computer languages, have helped to implement the ISAST model. I also want to acknowledge everyone else who have contributed to this work.

The Hazardous Substance Research Center, South & Southwest, under U.S. EPA has generously funded this research. Eleanor and Mills Bennette Fellowship Foundation has provided financial assistantship for my last year of graduate study.
Table of Contents

Abstract ii

Acknowledgments iv

Table of Contents v

List of Tables ix

List of Figures xi

1 Introduction 1

1.1 Problem Statement 1

1.2 Research Objective and Approach 7

2 Literature Review 11

2.1 Adsorption and Desorption 11

2.1.1 Concept of Adsorption and Desorption 11

2.1.2 Adsorption Equilibrium 12

2.1.3 Adsorption and Desorption Isotherms 17

2.2 Adsorption to Natural Soil and Sediment 23

2.2.1 Physical-Chemical Properties of Soil and Sediment Constitutes 23
2.2.2 Complex Adsorption Behavior of HOCs Caused by Sorbent Heterogeneity

2.3 Irreversible Adsorption

2.3.1 Evidence of Irreversible Adsorption

2.3.2 Proposed Mechanisms for Irreversible Sorption

2.3.3 Factors Affecting Adsorption and Desorption in Natural Sediment

2.4 Impact of Irreversible Adsorption

3 Characteristics of Irreversible Sorption

3.1 Introduction

3.2 Experimental

3.2.1 Sorbates and Chemicals

3.2.2 Tenax TA Resin

3.2.3 Sediments

3.2.4 Analytical Methods

3.2.5 Sorption and Desorption Experiments

3.2.6 Solution and Solid Phase Concentrations

3.2.7 Quality Control

3.3 Results

3.3.1 Sorption and Resistant Desorption
3.3.2 Irreversible Partition Coefficient, $K_{oc}^{irr}$, and Irreversible Sorption Capacity, $q_{max}^{irr}$

3.4 Discussion

3.4.1 Justification of Experimental Protocols

3.4.2 Sorption and Desorption Isotherms

3.4.3 Dependency of $K_{oc}$ and $K_{oc}^{irr}$ on $K_{ow}$

3.4.4 Dependency of $q_{max}^{irr}$ on $K_{ow}$ and $f_{oc}$

3.5 Summary

4 Mechanistic Aspects of Irreversible Sorption

4.1 Introduction

4.2 Experimental

4.2.1 Sorbates and Sediments

4.2.2 Radio-Active Analysis

4.2.3 Competitive Sorption

4.2.4 Caustic Treatment

4.2.5 External Mechanic Force

4.3 Results

4.3.1 Effect of Competitive Sorption

4.3.2 Caustic Effect on Desorption
List of Tables

Table 3.1: Summary of sediment properties 107

Table 3.2: Experimental protocols 108

Table 3.3: Physical and chemical properties of the five chlorinated benzenes used in sorption and desorption experiments. Data were obtained and calculated from Schwarzenbach et al. (1992). 109

Table 3.4: Summary of the results of sorption and desorption experiments, including solid phase concentrations at the end of sorption and desorption cycles, respectively; observed partition coefficients in sorption; observed apparent partition coefficients associated with the resistant fraction; and the irreversible sorption capacities. 110

Table 4.1: Experimental protocols 148

Table 4.2: Summary of competitive sorption effect on the release of sorbed compounds, including the effect of naphthalene on the release of 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene from Lake Charles sediment, and the effect of trans-cinnamic acid on the release of naphthalene and 1,4-dichlorobenzene, respectively, from Dickinson sediment. 149
Table 5.1: Summary of field observations and modeling input parameters used to construct Figure 5.1. Field data were obtained and reconstructed from McGroddy et al. (1996).

Table 5.2: Summary of field observations and modeling input parameters used to construct Figure 5.2. Field data were obtained and derived from Pereira et al. (1988).
List of Figures

Figure 2.1: Three most common sorption isotherms -- linear isotherm, Langmuir isotherm, and Freundlich isotherm. 65

Figure 2.2: Schematic of a soil particle aggregate showing the different diffusion processes (from Pignatello and Xing, 1996). 66

Figure 2.3: Schematic of intra-organic diffusion, illustration diffusion through a rubbery phase A and a condensed phase B (from Pignatello and Xing, 1996). 67

Figure 2.4: Schematic of sorption-retarded pore diffusion, sorption is enhanced in very small pores due to the interaction with more than one surface (from Pignatello and Xing, 1996). 68

Figure 2.5: Schematic illustration of domain types associated with a soil or sediment particle (from Weber and Huang, 1996). 69

Figure 2.6: A pictorial represent of the irreversible sorption model by Kan et al. (1996). 70

Figure 2.7: Breakthrough curves for linear and nonlinear sorption isotherms (from Brusseau and Rao, 1989). 71

Figure 2.8: Plot of the fraction of adsorbed compound, $q^{\text{tot}}$, which is adsorbed in either the reversible or the irreversible compartment as a function of the equilibrium solution phase concentration (from Chen et al., 1998). 72

Figure 3.1: Pictorial representation of the continuous sorption 111
Figure 3.2:  Plot of sediment phase concentrations of 1,4-dichlorobenzene with desorption step in Experiments 3.6 and 3.8.

Figure 3.3:  Plot of the aqueous phase concentrations, with respect to the irreversibly compartment, with varied desorption time in Experiments 3.1 to 3.7.

Figure 3.4:  Plot of observed aqueous phase concentrations of 1,2,3,4-tetrachlorobenzene and hexachlorobenzene with the contact time in continuous sorption experiments -- Experiments 3.3 and 3.4.

Figure 3.5:  Plot of the model predicted vs. experimentally-observed isotherms of 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and hexachlorobenzene in Dickinson sediment.

Figure 3.6:  Plot of the model predicted vs. experimentally-observed isotherms of 1,4-dichlorobenzene in Dickinson, Lake Charles, Lula, and Utica sediments.

Figure 3.7:  Plot of the $K_\infty$ values observed in sorption experiments and the partition coefficients with respect to the irreversible compartment in desorption experiments, with $K_{ow}$ value.

Figure 3.8:  Plot of the irreversible sorption capacities observed in Experiments 3.1 to 3.5 with chemical $K_{ow}$ value and aqueous solubility.
Figure 3.9: The dependency of irreversible sorption capacity (Experiments 3.1 to 3.5) on a combinatory factor of chemical $K_{ow}$ and aqueous solubility.

Figure 3.10: Plot of the irreversible sorption capacities with sediment organic carbon content. Data were obtained from the desorption of 1,4-dichlorobenzene from Dickinson, Lake Charles, Lula, and Utica sediments (Experiments 3.3, and Experiments 3.6 to 3.8).

Figure 4.1: Effect of competitive sorption of naphthalene on the desorption of 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene from Lake Charles sediment.

Figure 4.2: Effect of competitive sorption on the release of 1,4-dichlorobenzene from Dickinson sediment.

Figure 4.3: Effect of caustic treatment on the desorption of 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene from Lake Charles sediment.

Figure 4.4: Illustration of the effect of external mechanic force on the sorption and desorption behaviors of 1,4-dichlorobenzene in Dickinson Sediment.

Figure 5.1: Comparison between model predictions and field observed sediment-porewater distributions of phenanthrene, pyrenen, 2,2',4,5,5'-PCB, and 2,2',3,4,4',5'-PCB in Boston Harbor sediment.
Figure 5.2: Comparison between model predictions and field observed sediment-porewater distributions of 1,2- and 1,4-dichlorobenzenes, 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, hexachlorobenzene, and hexachlorobutadiene in Lake Charles sediment.

Figure 5.3: Illustration of the impact of sorption on solute transport in groundwater. The transport of Compounds a and b are simulated with MODFLOW and MT3D.

Figure 5.4: Illustration of the numerical approximation to the governing solute transport equation.

Figure 5.5: Illustration of the initial conditions (concentration profile at time 0) generated by ISAST.

Figure 5.6: Input sheet of ISAST -- a one dimensional solute transport model simulating the impact of irreversible sorption on solute transport in groundwater.

Figure 5.7: Output graph of ISAST -- breakthrough curves at modeling boundary (x=X) at time T.

Figure 5.8: Output graph of ISAST -- concentration profiles at the end of simulation, t = T.

Figure 5.9: Illustration of the impact of irreversible sorption on the ecological and human-health risks of contaminated sediment.
Chapter 1: Introduction and Overview

This chapter begins with a brief overview of the nature and severity of sediment contamination, introduces the roles of sorption and desorption in contaminant fate and transport and sediment quality, and summarizes the current research stands on the non-ideal sorption and desorption of organic contaminants in natural sediments. The chapter also presents the research objectives and approaches of this thesis.

1.1 Problem Statement

Many organic and inorganic contaminants accumulate in sediment after being discharged to the environment. Subsequently, sediments serve as a contaminant reservoir, from which contaminants may be released into the water column, accumulated by fish and bottom-dwelling organisms, and passed to humans through the food chain. Sediment contamination can pose ecological and human health risks for prolonged period of time, and thus has become a serious national problem. The U.S. EPA estimates that approximately 10 percent -- 1.2 billion cubic yards, of the sediment underlying the nation’s surface water is contaminated with toxic pollutants (U.S. EPA, 1997a). Sediment contamination has caused the loss of recreational sites and revenues, the abandonment of drinking water supplies, and long-term adverse health effects such as cancer and neurological impairment. Sediment-related problems also impose a huge economic impact on the country. For instance, among the 300 million cubic yards of sediment dredged from harbors and shipping channels annually, about 3 to 12 million
cubic yards are so contaminated that they require special handling and disposal (U.S. EPA, 1997a).

Sediment is a very important component of aquatic ecosystems. It provides habitat, feeding, spawning, and rearing areas for many aquatic organisms. Thus, sediment contamination may damage bottom-dwelling organisms, other sediment-associated organisms, as well as both the organisms that feed on sediment-associated organisms and human beings. Contaminated sediments affect aquatic organisms in many different ways, such as direct contact, ingestion of sediment particles, or uptake of dissolved contaminants in pore water. While serious sediment contamination may cause the extinction of some species in aquatic ecosystems, even low-level contamination can cause long-term deleterious effects to benthic organisms. Sediment contamination is also responsible for some human-related diseases, such as liver tumors and skin lesions (Myers et al., 1994).

The occurrence of sediment contamination is a result of various human activities. Numerous nonpoint and point pollution sources contribute a wide variety of contaminants to sediment. These sediment contaminants include highly persistent and toxic chemicals, such as PCBs and chlordane, heavy metals, PAHs, some pesticides, and other existing and new industrial chemicals. Point sources, such as spillage, dumping, municipal and industrial waste discharges, leakage from underground storage tanks and landfills, and addition of herbicides to lakes and reservoirs, often cause elevated local sediment pollution. Depending on local land use activities, nonpoint pollution sources can also cause serious sediment contamination. The typical nonpoint sources include atmospheric deposition, land drainage, and urban and agricultural runoff.
As the national awareness of sediment contamination increases, significant progress has substantially reduced the discharge of toxic and persistent chemicals during the past 10 to 15 years. However, significant amounts of many organic and inorganic pollutants are still being discharged into the environment. In a recent EPA report (U.S. EPA, 1997b) -- National Sediment Contaminant Point Source Inventory -- the annual release of 168 common pollutants found in sediments were summarized. According to the report, the annual release of polychlorinated biphenyls is still as high as 1611 pounds. The release of PAHs is 36,419 pounds per year, and as much as 15,176,965 pounds of divalent metals are released each year.

For many years, both government bureaus and researchers have tried to streamline a strategy to prevent and control sediment pollution, and to improve sediment quality. Recently, four goals have been established in EPA's Contaminated Sediment Management Strategy (U.S. EPA, 1998) to manage the problem of contaminated sediments: 1) prevent the volume of contaminated sediments from increasing; 2) reduce the volume of existing contaminated sediments; 3) ensure that sediment dredging and dredged material disposal are managed in an environmentally sound manner; and 4) develop scientifically sound sediment management tools for use in pollution prevention, source control, remediation, and dredged material management. The implementation of these goals, however, requires extensive knowledge and thorough understanding of the physical, chemical, and biological processes that contaminants undergo in aquatic systems.

Unfortunately, our understanding of the uptake, release, mobility, toxicity, availability, and biodegradability of contaminants in aquatic systems is very limited. To date, little is known about the extent and severity of sediment contamination, the fate
and transport of hazardous contaminants in aquatic ecosystems is poorly modeled, and most sediment management, pollution control, and clean-up practices are expensive but inefficient. There is no common agreement on many fundamental questions, such as, “At what concentrations and under what circumstances should a sediment be considered contaminated?” and “What should be done with contaminated sediments?” Many experts suggest that the best strategy for dealing with many contaminated sediment sites is to leave them alone, because many contaminants stay trapped within undisturbed sediments, while remediation processes may cause even more environmental problems. However, the encapsulation of contaminants may also be broken by sudden environmental changes, by bottom-dwelling organisms (such as worms), and by anthropogenic activities (such as dredging), to mention a few. The unexpected release may cause severe risks to aquatic environments and human health.

Among the numerous physical, chemical, and biological processes controlling the interaction between organic contaminants and sediments, sorption (uptake of contaminants by sediment) and desorption (release of contaminants from sediment) are the most important and probably also the most poorly understood processes. Sorption and desorption of organic compounds in natural sediments is critical for contaminant transport in aquatic systems. Sorption causes contaminants to move more slowly than the flowing ground water -- an effect referred to as “retardation”. Sorption and desorption processes also have significant effects on the efficiency of contaminant remediation and biodegradation. It was found that only desorbed organic compounds are readily available to bacteria. Also, the mechanisms that govern sorption and desorption have to be thoroughly understood to enact realistic sediment quality criteria and regulations.
Since sorption and desorption processes in natural systems are extremely complicated, for many years they were simplified as an equilibrium process, i.e., sorption and desorption were assumed to be instantaneous, linear, and reversible. However, numerous researches, investigations, and cleaning-up practices have demonstrated that this over-simplified model often fails to explain the observed sorption-desorption behaviors. For instance, chemicals with high volatility and reactivity are found to persist in sediment at significant concentrations, after being banned or restricted for dozens of years; a small fraction of sorbed contaminants often resists release, even with the most advanced remediation technologies; while elevated concentrations of hydrophobic organic contaminants are measured in sediments, the concentrations in the water columns are much lower than expected. These observations indicate that sorption and desorption of organic contaminants in sediments are by no means simple equilibrium processes, but rather slow, resistant, or even irreversible processes.

The understanding of non-ideal sorption and desorption phenomena could significantly affect environmental policies and decision making, and could have large economic impact. The potential toxicity of sediment-associated nonionic organic chemicals and divalent metals is indicated by the amount of contaminant that is noncomplex or freely available in the interstitial (pore) water (U.S. EPA, 1998). Thus, the basis of sediment quality criteria (SQCs) is to ensure that the pore water concentration of a certain compound does not exceed the final chronic water quality criteria. The currently adopted equilibrium partitioning approach, however, often significantly over-estimates the actual aqueous phase concentrations. This might imply that many contaminated sediment sites need only moderate treatment, or even can be left alone without causing any significant environmental concern.
Thus far, numerous mechanisms have been proposed to interpret the sorption and
desorption processes. For hydrophobic organic compounds and natural sediments, most of
the mechanisms fall into one of the following categories: 1) slow first-order kinetics
in either the sorption or the desorption direction (Karickhoff, 1984; Connaughton et al.,
1993; and Predit and Miller, 1994); 2) slow diffusion within organic and inorganic
domains (Wu and Gschwend, 1986; Ball and Roberts, 1991; Carroll et al., 1994; and
Young and Weber, 1995); 3) heterogeneous sorption properties exhibited by various
components of natural sorbents (Weber et al., 1992; Weber and Huang, 1996; Burgos et
al., 1996; and Xing and Pignatello, 1996); 4) specific interactions between organic
compounds and high-energy (low solubility) sites in sediment (Burgos et al., 1996; Xing
and Pignatello, 1996; Gustafsson et al., 1997; and Chiou and Kile, 1998); and 5)
physical entrapment of organic compounds within sediment matrix (DiToro and
Horzempe, 1982; Flanagan et al., 1987; Vaccari, 1988; Brusseau and Rao, 1989;
Adamson, 1990; Kan et al., 1994; Burgos et al., 1996; White et al., 1997; Kan et al.,
1998; Burgess et al., 1998; and Devitt and Wiesner, 1998). It is necessary to notice that
each model may well explain some individual observations, but none of these models
can be applied to all the cases.

Recent research at Rice University (Kan et al., 1997; Chen, 1997; and Kan et al.,
1998) has shown that most chemical-sediment combinations exhibit an irreversible
sorption compartment with fixed size; although this fixed size varies among different
compounds and sediments, the apparent $K_{oc}$ value associated with this fraction is nearly
constant for compounds whose $K_{ow}$ values differ by orders of magnitude. These studies
also suggest that the observed biphasic field and laboratory data can be modeled once
the characteristics of the irreversible compartment are incorporated into the conventional
sorption model. Preliminary work (Chen, 1997) also indicated that several factors, such
as pH, ionic strength, temperature, and competitive sorption may affect the desorption behavior of hydrophobic organic compounds in the irreversible compartment. Some recent studies (Xing et al., 1996; Chiou and Kile, 1998; and Xing and Pignatello, 1998) further support the argument that competitive sorption may significantly affect sorption and desorption behaviors, depending on the specific mechanism controlling these two processes.

It appears that for sediment-associated hydrophobic organic contaminants, the irreversibly sorbed fraction is of the greatest concern and uncertainty. Nevertheless, the important characteristics of the irreversible fraction, such as the size of the fraction and its dependency on chemical and sediment properties, as well as natural and anthropogenic factors affecting the release from this fraction, have not been studied. Thus, the unique behavior of hydrophobic organic contaminants associated with this irreversibly sorbed fraction should be an important research direction and is the focus of this thesis.

1.2 Research Objectives and Summary of Approach

The objective of this research was to further understand the characteristics of the irreversible sorption of hydrophobic organic contaminants in natural sediments, as well as the mechanism(s) controlling this process. Specifically, the research has focused on the study of the irreversible sorption capacity, the aqueous phase concentration corresponding to the irreversible fraction, the apparent partitioning coefficients of the irreversible compartment, as well as the factors affecting the magnitude of these three unique properties. The research was also dedicated to developing a simple solute
transport model that can be used to predict the long-term resistant release and the fate and transport of organic contaminants in the environment, and can be used as guidance for clean-up strategies and sediment quality management.

Natural sediments, both clean and contaminated, were used to conduct sorption and desorption experiments. The release of aged contaminates was studied with Lake Charles sediment. This sediment has been impacted by chemical and petroleum industries for over forty years and therefore, reflects the long-term interaction between sorbates and sorbents. The sorption and desorption experiments were also conducted with several other sediments with different properties, including Dickinson sediment, Lula sediment, and Utica sediment.

Sorption experiments were conducted similar to pollution occurrence, such as accidental spillage, leakage from hazardous waste sites and landfills, and the presence of NAPLS. In all these cases, contaminants exist as a non-aqueous phase, either in solid or liquid form and therefore, continuously dissolve in water and then sorb to sediment. A new batch continuous sorption approach was developed for this purpose. It is modified from the conventional batch sorption approach -- in addition to the sediment and electrolyte solution the batch reactor contains a dialysis membrane bag, which holds pure sorbate chemicals. Dissolved chemicals can freely diffuse through the dialysis bag, and the aqueous phase concentration of the chemical can be kept at the maximum during sorption. Therefore, sorption is essentially the equilibrium among three phases -- sediment, aqueous solution, and pure compound, and given sufficient equilibration time, sediment can be saturated with a compound. This approach also greatly shortens the time and simplifies the procedures required to prepare sediment samples.
After a sediment was saturated with a certain contaminant, it was washed extensively with an electrolyte solution simulating the condition of surface or ground water. In this research, desorption was conducted in two manners -- successive desorption with electrolyte solution and Tenax™ desorption. In Tenax desorption, aqueous phase contaminants were continuously removed with Tenax. This was designed to accelerate desorption so that the readily desorbable fraction could be removed within several days.

The desorption of five chlorinated benzenes -- 1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and hexachlorobenzene -- from Dickinson sediment were studied to understand the dependency of the irreversible sorption compartment on chemical properties. Each sediment sample was initially saturated with one of these five compounds, and then extensive desorption was conducted with both Tenax and electrolyte solution. For each chemical-sediment combination, the irreversible sorption capacity, the apparent partitioning coefficient of the irreversible compartment, and the aqueous phase concentration corresponding to the irreversibly sorbed fraction were examined. Similar experiments were conducted using 1,4-dichlorobenzene and four different sediments to study the dependency of the irreversible sorption compartment on sediment properties.

The effect of competitive sorption, caustic treatment of sediment, and external mechanic forces on the release of sorbed compounds was studied. Experiments were conducted with both historically-sorbed compounds (in Lake Charles sediment) and freshly-sorbed compounds (in Dickinson sediment). To study the effect of competitive sorption on the release from the reversible compartment, Lake Charles sediment was saturated with naphthalene, and the release of sorbed chlorinated hydrocarbons was
compared with the release without competition. Also, a highly concentrated trans-cinnamic acid solution was applied to two sediment samples containing naphthalene and 1,4-dichlorobenzene, respectively, to examine the effect of competitive sorption on the release from the irreversible compartment. The effect of caustic treatment was studied by treating sediment samples with NaOH solutions of different concentrations. The effect of external forces was tested by comparing desorption results obtained with different mixing modes -- shaking versus tumbling. The implications of these experimental observations on the mechanism controlling the irreversible sorption of organic contaminants in natural sediments were examined. These experiments were also designed to address some common environmental concerns involved in sediment-related practices, such as the response of contaminant desorption to sudden changes in environmental conditions and the impact of the presence or discharge of other contaminants on the release of a sorbed compound. The implications of these experimental results are discussed.

It would be beneficial to almost every aspect of sediment management practices if a simple model could be applied universally to chemical-sediment combinations. Thus, the conceptual and mathematical models developed from this and previous research (Chen, 1997; Kan et al., 1998) were tested with observations from field studies conducted by independent research groups. The impact of irreversible sorption on fate and transport modeling, contaminant bioavailability, and risk assessment is discussed both qualitatively and quantitatively. A one-dimensional solute transport model was developed to account for the impact of irreversible sorption on solute transport in subsurface environments. Finally, the possibility of re-establishing risk-based sediment quality standards and its impact on site remediation and sediment management are discussed.
Chapter 2: Background and Literature Review

2.1 Adsorption and Desorption

2.1.1 Concept of Adsorption and Desorption

The first observed and widely studied adsorption phenomenon was the adsorption of gases and vapors on solid surface. For the adsorption of nonelectrolytes from solution, as discussed by Adamson (1990), a logical division should be made according to whether the adsorbate solution is dilute or concentrated. For dilute solutions, the treatment is very similar to that for gas adsorption, whereas for concentrated solutions, the role of solvent becomes more explicit. However, in either case, the adsorption and desorption processes are greatly dependent on the physical and chemical properties of the solution-solid interfaces.

It is customary to divide adsorption into two broad classes -- physical adsorption (physi-sorption) and chemical adsorption (chemi-sorption), as discussed by many authors (e.g. Moore, 1972; Parfitt and Rochester, 1983; and Adamson, 1990). Physical adsorption is due to the operation of some undirected and non-specific forces between the solid surface and sorbate molecules similar to the van der Waals force between molecules. Physical adsorption is very rapid and is generally reversible. The heat of adsorption is low. In contrast with physical adsorption, chemical adsorption is the result of much stronger binding forces, comparable with those leading to the formation of chemical compounds. Chemical adsorption may be slow, indicating the presence of high activation energy. Since chemical adsorption may be regarded as the formation of some
sort of surface compounds, it is seldom reversible. Chemical adsorption is completed when a surface is covered by an adsorbed monolayer.

For neutral organic compounds, adsorption to natural sediment occurs predominantly through physical adsorption mechanisms. However, the adsorption is generally not a single process, but the combination of several individual interactions (Schwarzenbach et al., 1993). The dominant interaction governing adsorption is the penetration of a hydrophobic organic compound into the macromolecules of natural organic matter in sediment. This is because neutral organic molecules are very dissimilar to water molecules in shape, size and polarity, and therefore, are hydrophobic ("water-hating"). It is thermodynamically unfavorable for these compounds to remain in solution due to a combination of enthalpy and entropy changes of the system when a compound dissolves (Tanford, 1973). On the contrary, natural organic matter provides a relatively nonpolar environment in which the penetration of neutral organic chemicals does not require the change in their overall H-bonding to the surroundings, and therefore is thermodynamically favorable. This mechanism is similar to the partitioning of organic compounds from aqueous solution to organic solvents. Some other mechanisms also account for the overall adsorption of organic compounds in sediment. For example, sorbate molecules can also be associated with the mineral surface via some weak intermolecular forces, such as van der Waals (dispersion), dipole-dipole, dipole-induced dipole, and hydrogen bonding (Schwarzenbach, 1993). All of these mechanisms operate simultaneously, but a specific interaction may dominate the adsorption depending on the structural properties of the chemicals and solid medium.

2.1.2 Adsorption Equilibrium
In a water-sediment system, the sorption and desorption of an organic compound is essentially the reversible transfer of this compound between the aqueous and solid phases. The distribution of a specific compound between the aqueous phase and the solid phase is controlled by the energy status, described by the chemical potential, $\mu$, of the compound in each phase of the system.

At a given temperature (T) and pressure (P), the energy status of a specific compound A in the solid and aqueous phases are expressed by the corresponding chemical potentials:

\[
\left( \frac{\partial G_{\text{solid phase}}^{\text{total}}}{\partial n_{A, \text{solid phase}}} \right)_{T, P, \text{ and composition } (n_j \neq n_A)} \equiv \mu_s = \mu_{\text{A, liquid}}^0 + RT \ln x_s y_s \tag{2.1}
\]

\[
\left( \frac{\partial G_{\text{aqueous phase}}^{\text{total}}}{\partial n_{A, \text{aqueous phase}}} \right)_{T, P, \text{ and composition } (n_j \neq n_A)} \equiv \mu_a = \mu_{\text{A, liquid}}^0 + RT \ln x_a y_a \tag{2.2}
\]

where $G_{\text{solid phase}}^{\text{total}}$ and $G_{\text{aqueous phase}}^{\text{total}}$ are the total Gibbs free energy (kJ) of the respective solid and aqueous phases; $n_{A, \text{solid phase}}$ and $n_{A, \text{aqueous phase}}$ are moles of A added to the respective phases; the subscripts "composition (n_j \neq n_A)" refers to holding the composition of that phase constant while evaluating the partial derivatives; $\mu$, and $\mu_a$ are the chemical potentials of A in the respective phases (kJ/mole). $\mu_{\text{A, liquid}}^0$ is the standard state chemical potential of compound A (note that the pure liquid A is chosen as the reference state); R is the gas constant (8.31 J/mole K); T is the temperature in degrees Kelvin; $x_s$
and $x_s$ are the mole fractions of compound A in the solid and aqueous phases, respectively; and $\gamma_s$ and $\gamma_a$ are the activity coefficients of compound A in the solid and aqueous phases, respectively.

As with any other chemical equilibrium, when adsorption equilibrium is reached, there is no net flux of compound A from one phase to another, i.e., the chemical potentials of these two phases are equal:

$$\mu_s = \mu_a$$  \hspace{1cm} (2.3)

so,

$$RT \ln x_s \gamma_s = RT \ln x_a \gamma_a$$  \hspace{1cm} (2.4)

Rearrangement of 2.4 yields:

$$RT \ln \left( \frac{x_s}{x_a} \right) = - (RT \ln \gamma_s - RT \ln \gamma_a)$$  \hspace{1cm} (2.5)
Since the mole fractions, \( x_i \) and \( x_j \), are generally small compared to their respective phases, the corresponding activity coefficients, \( \gamma_i \) and \( \gamma_j \), are approximately constant, i.e., independent of concentration. Therefore, \( K' = x_i / x_j \), the relative abundance of compound \( A \) between the solid and aqueous phases at equilibrium, is commonly referred to as the partitioning constant. The right hand side of Equation 2.5 represents the energy difference due to the nonideality of the system relative to pure liquid \( A \).

In environmental chemistry, the abundance of a compound in aqueous and solid phases is commonly expressed as mass per unit volume and mass per unit mass, respectively. Mole fraction can be converted to such units by:

\[
C \left( \frac{\text{mg}}{\text{L}} \right) = \frac{x_3 \left( \frac{\text{moles of } A}{\text{total moles in aqueous phase}} \right) \text{MW}_A \left( \frac{\text{mg of } A}{\text{moles of } A} \right)}{V_{\text{mixture}} \left( \frac{\text{L}}{\text{total mole}} \right)}
\]

\[
\equiv \frac{x_3 \left( \frac{\text{mole}}{\text{total mole}} \right) \text{MW}_A \left( \frac{\text{mg}}{\text{mole}} \right)}{V_{\text{solvent}} \left( \frac{\text{L}}{\text{total mole}} \right)}
\]

(2.6)
\[ q \left( \frac{mg}{kg} \right) = \frac{x_s \left( \frac{\text{mole}}{\text{total mole}} \right) \cdot MW_A \left( \frac{\text{mg of \ A}}{\text{mole of \ A}} \right)}{M_{\text{mixture}} \left( \frac{\text{kg}}{\text{total mole}} \right)} \]

\[ \equiv \frac{x_s \left( \frac{\text{mole}}{\text{total mole}} \right) \cdot MW_A \left( \frac{\text{mg}}{\text{mole}} \right)}{M_{\text{solid}} \left( \frac{\text{kg}}{\text{total mole}} \right)} \]

where \( C \) and \( q \) are the aqueous and solid phase concentrations, respectively; \( V_{\text{mixture}} \) is the molar volume of the mixture of solution; \( V_{\text{solvent}} \) is the molar volume of solvent (for water, \( V_{\text{solvent}} = 0.018 \text{ L/mole} \)); \( M_{\text{mixture}} \) is the molar weight of the mixture of sorbate and sorbent; \( M_{\text{solid}} \) is the molar weight of sorbent; and \( MW \) is the molecular weight of sorbate. If \( x_w \) and \( x_s \) are small, \( V_{\text{mixture}} \) and \( M_{\text{mixture}} \) are approximately equal to \( V_{\text{solvent}} \) and \( M_{\text{solid}} \), respectively. Therefore, the partitioning constant of an organic compound between the bulk water and the solid phase is redefined as:

\[ K_p = \frac{q}{C} \equiv \frac{x_s \cdot V_{\text{sol}}}{x_s \cdot M_{\text{solid}}} = \frac{1}{r_{sw}} K' \]

in which \( r_{sw} \) is the solid to solution ratio. It should be noted that if the above activity coefficients change with the concentration of \( A \), then the resultant isotherm may be non-linear (Morel and Herring, 1993).
2.1.3 Adsorption and Desorption Isotherms

Adsorption isotherms are used to describe the relationship between the total sorbate concentration associated with the sorbent \( q \) and the total sorbate concentration in solution \( C \). The term isotherm indicates that adsorption or desorption occurs at a constant temperature. Isotherms are considered one of the most useful tools for studying adsorption and desorption equilibrium.

Isotherms may exhibit a variety of different shapes, as classified by Giles et al. (1960), depending on the dominant mechanisms. Typically, three types of isotherms -- the linear isotherm, the Langmuir isotherm, and the Freundlich isotherm -- are widely used to study the adsorption and desorption of organic compounds in natural systems. Figure 2.1 is a pictorial representation of these three types of isotherms.

The Langmuir isotherm is the most basic and theoretically straightforward adsorption model, in terms of adsorption kinetics and statistical thermodynamics (Adamson, 1990). The Langmuir model assumes the adsorption energy of a molecule is constant and independent of surface coverage; adsorption only occurs on localized sites; no interaction between sorbate molecules occurs; and the maximum adsorption possible is fixed at a complete monolayer.

The model can be easily derived from mass balance and chemical equilibrium, as described by Morel and Hering (1993). The adsorption process can be represented as a coordination reaction with 1:1 stoichiometry:

\[
\equiv X + C = \equiv X C
\]

(2.9)
where \( \equiv X \) and \( \equiv X^C \) are the unoccupied and occupied adsorptive sites on the solid surface, respectively, and \( C \) is a certain sorbate. The amount of occupied adsorptive sites on the solid surface is conventionally quantified by an adsorption density parameter \( \Gamma \), which is essentially the number of moles of sorbate adsorbed per unit mass of sorbent.

Similarly, the maximum adsorption density \( \Gamma_{\text{max}} \) is the number of moles of sorbate that covers the monolayer of sorbent surface i.e., the total amount of adsorptive sites, including both occupied and unoccupied sites, on the solid surface. Therefore, the adsorption equilibrium described in Equation 2.9 is expressed as:

\[
\frac{\Gamma}{(\Gamma_{\text{max}} - \Gamma) [C]} = K_{\text{ads}} = \exp \left[ -\frac{\Delta G^0_{\text{ads}}}{R T} \right]
\]  \hspace{1cm} (2.10)

where \([C]\) is the sorbate aqueous concentration; \( K_{\text{ads}} \) is the adsorption equilibrium constant; \( \Delta G^0_{\text{ads}} \) is the free energy of adsorption; \( R \) is the gas constant; and \( T \) is temperature in Kelvin. Rearrangement of Equation 2.10 yields:

\[
\Gamma = \Gamma_{\text{max}} \frac{K_{\text{ads}} [C]}{1 + K_{\text{ads}} [C]}
\]  \hspace{1cm} (2.11)
which is the well-known expression of the Langmuir isotherm.

In environmental chemistry, the commonly adopted expression of the Langmuir isotherm is:

\[
q = \frac{Q^0 b C}{1 + b C}
\]  \hspace{1cm} (2.12)

or the following linearized form:

\[
\frac{1}{q} = \frac{1}{Q^0} + \frac{1}{b Q^0 C}
\]  \hspace{1cm} (2.13)

where \(q\) is the mass of solute adsorbed per unit mass of solid at equilibrium, i.e., the solid phase concentration; \(Q^0\) is the maximum adsorption capacity (the sorbed solute concentration for complete monolayer coverage); and \(b\) is a factor related to the affinity of solute surface.

Although many adsorption data exhibit a decrease in incremental adsorption at increasing solute concentrations, not all show the clear maximum of the Langmuir isotherm. Such adsorption data, therefore, are often better described by the Freundlich model, which was first developed to describe monolayer adsorption of gases on heterogeneous solid surfaces. There are many different approaches to derive the
Freundlich isotherm. For example, Morel and Hering (1993) derived the isotherm by assuming that the increased free energy of adsorption is linearly related to the logarithm of the concentration of adsorbate. Adamson (1990) derived the Freundlich isotherm from the Langmuir isotherm by adopting a distribution function $f(b)$, which accounts for the variation of the term $b$ in the Langmuir equation with the heterogeneous adsorption sites on solid surface. Gavels and Christ (1965) derived the Freundlich isotherm by assuming that the activity coefficients of $A$ in the solid was a function of solid concentration. All of these different approaches give a similar expression of the isotherm, as:

$$q = \alpha C^n$$  \hspace{1cm} (2.14)

where $q$ is the weight of solute adsorbed per unit weight of solid; $c$ is the concentration of solute in solution at equilibrium; and $\alpha$ and $n$ are constants. The most commonly accepted form of the Freundlich isotherm is:

$$q = K_r C^n$$  \hspace{1cm} (2.15)

in which $K_r$ is the Freundlich unit-capacity coefficient, and $n$ is a joint measurement of the relative magnitude and diversity of energy associated with a particular adsorption
process. For adsorption and desorption processes occurring in natural systems, n is commonly less than 1.

The linear isotherm is also widely used to study the adsorption and desorption of hydrophobic organic compounds in natural systems. In this model, the solid phase concentration of a specific chemical is directly proportional to its aqueous phase concentration, and can be represented by the following equation:

\[ q = K_p C \]  \hspace{1cm} (2.16)

The linear isotherm is the special case of the Langmuir and Freundlich models. In the Langmuir equation, if the solution concentration is low enough, the denominator is nearly equal to 1. This means that if the solution concentration is very low, only a very small fraction of the adsorptive sites is covered, so the adsorption depends linearly on the concentration in the solution. In the Freundlich equation, if the exponent is 1, the adsorption is linearly proportional to the solution concentration.

The linear isotherm requires only one parameter, the partition coefficient, to predict adsorption and desorption behavior. There are many different equations to estimate the partition coefficient, \( K_p \), using well-known physical-chemical parameters of both sorbate and sorbent. Since hydrophobic organic contaminants are assumed to partition predominantly to natural organic matter in sediment, most equations relate \( K_p \) to the mass fraction of organic carbon (\( f_{oc} \)) in sorbent and the octanol-water partitioning coefficient (\( K_{ow} \)) of the solute, which represents the hydrophobicity of a solute.
Karickhoff (1979) proposed that the partitioning coefficient $K_p$ can be estimated from the following equation:

$$\log(K_p/f_{oc}) = \log K_{oc} = a \log K_{ow} + b$$  \hspace{1cm} (2.17)

where $K_{oc}$ is the organic carbon normalized partition coefficient, i.e., mass of solute adsorbed per unit mass of natural organic matter. The two constants $a$ and $b$ are related to sorbent properties. They can be obtained experimentally, or estimated in a number of ways depending on the hydrocarbon type (Lyman et al., 1982). Karickhoff (1979) reported that the $K_p$ value of a compound can be estimated from its $K_{ow}$ value as:

$$K_p = K_{oc} f_{oc} = 0.63 K_{ow} f_{oc}$$  \hspace{1cm} (2.18)

Schwarzenbach et al. (1993) proposed that for neutral nonpolar sorbate, adsorption to natural organic matter is very similar to the partitioning of an organic chemical between octanol and water. Therefore, the free energy driving this adsorption is determined largely by the excess free energy of aqueous solution. Thus, the partitioning coefficient is strongly related to the solubility or $K_{ow}$ values of a nonpolar compound. They proposed the following two correlations to estimate $K_{oc}$ values:
\[
\log K_{\infty} \equiv -0.75 \log C_{\text{sat}} + 0.44
\]  

(2.19)

\[
\log K_{\infty} \equiv 0.82 \log K_{\text{ow}} + 0.14
\]  

(2.20)

Note that the unit of \( C_{\text{sat}} \) is mol/L in Equation 2.19. Finally, since adsorption to sediment is positively correlated to organic carbon content, \( K_{\infty} \) is more nearly constant among sediments than \( K_p \), and is a more useful measurement.

2.2 Adsorption to Natural Soil and Sediment

2.2.1 Physical-Chemical Properties of Soil and Sediment Constituents

Soil and sediment can be roughly regarded as a complex mixture of the following constituents: organic and inorganic solids, liquid and gas phases, and living organisms. The solid phase of soil and sediment can exist as individual particles, colloids, or aggregates of the inorganic and organic phases. Aggregates can be further divided into subregions with different compositions, such as the coalescence of many fine mineral grains, parent mineral grains coated with other phases like iron oxides and natural organic matter, and natural organic matter entrapped by mineral grains, to mention a few.

The inorganic portion of soil and sediment can exist as colloids (<2μm) to large gravel and rocks (>2 mm), which are composed of primary and secondary minerals. The
most abundant primary minerals are silicates such as quartz and feldspars. The common secondary minerals are carbonate and sulfur minerals, the layer silicates and various oxides. As described by Schwarzenbach et al. (1993), most major minerals expose a surface which consists of hydroxyls protruding into the exterior from a plane of electron-deficient atoms (e.g., Si, Al, Fe) and electron-rich ligands (e.g., sulfur, oxygen, and carbonate). These surface hydroxyls and ligands prefer to form hydrogen bonds with the molecules adjacent to the mineral surface. While all sorbates are attracted to the surface by van der Waals or dispersive forces, the attractions can be stronger if the functional groups are capable of forming dipole:dipole and H-bonding interactions.

For hydrophobic organic compounds, natural organic matter primarily accounts for the overall adsorption since its constituents provide a nonpolar environment into which a hydrophobic compound may partition, away from water. The content of organic matter in soil and sediment varies considerably. A sandy desert soil may have less than 0.1% organic matter whereas a peat may have nearly 100% organic matter. However, most surface mineral soils and sediments have between 0.5 and 1.5% organic matter.

Natural organic matter (NOM), according to Choudry (1984), is composed of the degradation products of plants and animals, as well as living matter such as microorganisms. The predominant fraction of natural organic matter in sediments is humic substances (HS), which has been shown to be a major factor controlling the physical and chemical properties of sediments (Waksman, 1936). Humic substances do not correspond to a unique chemical entity but are very structurally complex and non-uniform. They are a mixture of molecules with molecular weights ranging from a few hundred to 300,000. Humin, humic acids, and fulvic acids are subclasses of humic substances defined operationally on the basis of solubility and molecular weight. Fulvic
acids are soluble in water under all pH conditions and are generally considered to have molecular weights less than 1000. Humic acids are the major component of humic substances. They are structurally similar to fulvic acids but of higher molecular weight, and are soluble only above pH 2. Humin is the fraction insoluble in water at any pH. These operational definitions represent broad mixtures of components for which the elemental composition and their chemical and physical properties can vary depending on the source.

As anionic macromolecules, humic substances contain both aromatic and aliphatic structural units, a variety of functional groups, and some hydrophobic character. The major functional groups in humic substances have been determined to be carboxyl and phenol (Steinberg and Muenster, 1985). The acid-base behavior of HS is generally similar to that of other organic acids. However, because of their numerous functional groups, humic substances exhibit a continuous distribution of equilibrium constants with respect to protons, as well as other ions. The total acidity of humic substances is typically 8 to 12 meq/g C. In the pH range of natural waters, most of the carboxyl groups (pK 2.5 to 7) are dissociated and most of the phenolic groups (pK 8 to 11) are not.

Substantial experimental evidence has shown that the macromolecular conformations of humic substances may be analogous to those of flexible linear polyelectrolytes (Tiller, 1993). The conformation of humic substances can be quite different -- from rigid to loose -- under different solution conditions such as pH and ionic strength. Ghosh and Schnitzer (1980) proposed that humic substances are densely coiled at low pH or high ionic strength where electrostatic repulsion between neighboring functional groups is minimized, but they behave like flexible linear
polyelectrolytes at neutral pH or low ionic strength. Cornel et al. (1986) also concluded that there is a continuous change in the conformations of humic substances from uncoiled macromolecules at low ionic strength to fully coiled macromolecules at high ionic strength, and they also found a similar, but less dramatic, effect of pH.

Soil organic matter can also exist in the form of colloidal macromolecules, and this issue becomes very important when adsorption kinetics and particle-suspension separation are concerned. Colloids are particles with diameters of less than 10 μm (Stumm, 1977). They are small enough to move primarily by Brownian motion, and are not separable from the water by centrifugation. Thus, chemicals exist in solution both as truly dissolved molecules and as molecules associated with very small particles or with macromolecules. Organic colloids in natural water include humic substances and proteins, and organic coatings on very small inorganic particles. It has been demonstrated that colloidal organic matter may adsorb nonpolar organic chemicals much like the organic material associated with larger soil and sediment particles (Kan et al., 1994; Schwarzenbach et al., 1993).

2.2.2 Complex Adsorption Behavior of HOCs Caused by Sorbent Heterogeneity

The mechanisms controlling the adsorption of hydrophobic organic compounds to natural soil and sediment are very complex because of the heterogeneity of natural sorbents. As discussed earlier, natural sediments are comprised of various organic and inorganic constituents. Since these constituents are very structurally and chemically different, they interact differently with hydrophobic organic compounds in terms of binding energy, adsorption linearity, and rate constants. Even the same sediment
constituent can exhibit different adsorption behavior in different geosorbent domains, and this makes the adsorption mechanisms more complicated. Furthermore, the presence of anthropogenic organic matter, such as oils, combustional residuals, and surfactants, may significantly increase the heterogeneity of natural sediments (Edwards, et. al. 1994; Boyd and Sun, 1990; Gustafsson et al., 1997; and Chiou and Kile. 1998). The heterogeneity of natural soil and sediment may also cause desorption hysteresis or irreversible adsorption; this effect will be discussed in detail later in this chapter.

In terms of adsorption properties, such as maximum adsorption capacity, isotherm linearity, activation energy, and adsorption kinetics, natural sediments can be envisioned as containing the following dominant domains: 1) the mineral domain; 2) the soil organic matter domain; and 3) the adherent or entrapped NAPL domain. The mineral domain is further subclassed as: i) exposed external mineral surfaces; ii) interlayer surfaces of swelling clays; and iii) the surfaces within mesopores (pore diameters 2 - 50 nanometer) and micropores (< 2 nanometer) of inorganic mineral matrices (Gregg and Sing, 1982). Different mineral surfaces exhibit different adsorption affinities to hydrophobic organic compounds. For example, sorbate molecules can get into mesopores via capillary condensation and within micropores, where solid surfaces affect adsorption. In the soil organic matter domain, different components exhibit different adsorption behavior. The variation is due to the compositional and structural diversity of soil organic material with different origin and geologic history. Weber et al. (1992) proposed that there is a gradual transformation of organic matter from the amorphous phase to the condensed phase during the diagenesis process. Other researchers have found that polarity, aromatic carbon content, and the relative amount of oxygen-containing functional groups appear to affect the interaction of organic matter with hydrophobic organic compounds (Garbarini and Lion, 1986; Gauthier et. al., 1987;
Grathwohl, 1990; Kile et al., 1995; Huang and Weber, 1997). The NAPL domain may also comprise organic matter from different sources, such as petroleum residues, creosotes, and coal tars, which may exhibit different adsorption behavior because of the different interfacial chemistry (Lathy et al., 1997).

In a recent review article, Lathy et al. (1997) summarized the various interactions of hydrophobic organic compounds with different constituents in natural soil, sediment, and aquifer material, as observed in recent studies. Generally, the adsorption into amorphous natural organic matter (such as geologically immature material and highly weathered soil organic matter) or NAPL is kinetically fast, the isotherm is linear, and both the activation energy and the heat of adsorption are low. On the contrary, the adsorption into condensed organic polymeric matter (such as unweathered shales) or combustion residues is a slow process with high activation energy and heat of adsorption. The observed isotherm is usually nonlinear. While the isotherm for the adsorption onto wet organic surfaces is nonlinear, it is kinetically fast and both the activation energy and the heat of adsorption are low. The macroscopic observations for the adsorption to mineral surfaces are similar to the adsorption into soft organic matter, i.e., the adsorption is fast and linear and the activation energy and the heat of adsorption are low. Finally, the adsorption into microvoids or microporous minerals with porous surfaces is usually slow, because of the slow diffusion rate and the isotherm is nonlinear if the pore size is variable, and the activation energy and heat of adsorption are both high.

Given the fact that natural geosorbents comprise many chemically and structurally different components, the overall adsorption behavior of hydrophobic organic compounds should be the combination of the adsorption to these various
constituents. For instance, the total adsorbed mass per unit of sorbent may be expressed as: \( q_{\text{total}} = q_{\text{condensed SOM}} + q_{\text{amorphous SOM}} + q_{\text{mineral surface}} + q_{\text{NAPL}} + \ldots + q_{\text{soot}} \). Since these adsorption processes include both linear and nonlinear adsorption, the overall shape of the adsorption isotherm depends on the ratio of each constituent in the sediments as well as the range of the aqueous phase concentration of sorbates. Chiou and Kile (1998) observed that at low aqueous phase concentration to solubility (\( C_e/S_w \)) range, both nonpolar and polar solutes exhibit significant nonlinear adsorption, but the adsorption becomes linear at moderate to high \( C_e/S_w \) ranges. They propose that for most natural sediment, the nonlinear adsorption isotherm observed at lower concentration ranges is due to the adsorption to a small amount of high-surface-area carbonaceous material, which has high affinity for hydrophobic organic sorbates. The adsorption capacity of this small amount of material is quickly saturated as the solution phase concentration increases. Then, the partition of solute into natural organic matter becomes the dominant adsorption mechanism and the overall adsorption isotherm becomes linear.

2.3 Irreversible Adsorption

2.3.1 Evidence of Irreversible Adsorption

An adsorption process is called "reversible" if the desorption isotherm, which is brought about by diluting the equilibrium aqueous solution, is the same as the adsorption isotherm, which is obtained by systematically increasing the solution phase concentration. For many years, the adsorption process has been assumed to be instantaneous (local equilibrium), linear, and reversible (Brusseau and Rao, 1989). This
simplification has been widely used to model contaminant transport in subsurface and to enact environmental quality standards. While these assumptions may be adequate under certain conditions, the use of "true equilibrium" is questionable for most of the natural and laboratory systems. Since the 1970s, numerous cases of irreversible adsorption, or adsorption-desorption hysteresis, between chemicals and soil/sediment have challenged the validity of this equilibrium model (Van Genuchten et al., 1974; Hutchins et al., 1983; McCall and Agin, 1985; Coates and Elzerman, 1986; Vaccari and Kaouris, 1988; Pereira et al., 1988; Weber and Miller, 1988; Brusseau and Rao, 1989; Pignatello, 1990; Ball and Roberts, 1991; Pavlostathis and Jaglal, 1991; McGroddy and Farrington, 1995).

Hutchins et al. (1983) observed that the ground water beneath the infiltration sites contained numerous trace level contaminants that were released at a constant concentration. Steinberg et al. (1987) found that 1,2-dibromoethane persisted in agricultural topsoil up to 19 years after its last known application, even though the compound has high volatility and low affinity for soil, and can be degraded rapidly under both aerobic and anaerobic conditions. Pereira et al. (1988) found that the concentrations of halogenated organic compounds in water, suspended sediments, and biota were far below the values predicted on the basis of the assumption of phase equilibrium with respect to concentrations in bottom sediments. McGroddy and Farrington (1995) measured high concentrations of PAHs in sediment cores collected from Boston Harbor. The porewater concentrations of these compounds were significantly lower than the predicted equilibrium values using the partitioning coefficients measured in adsorption experiments with the same sediment. They concluded that a fraction of PAH in the sediment was not available for desorption.

Most studies have shown that the desorption of hydrophobic organic
contaminants is typically a biphasic process -- a fraction of contaminants desorbs within a short period of time (several hours to several days) and for the remaining fraction, the desorption rate is very slow (Gschwend and Wu, 1985; Steinberg et al., 1987; Pignatello, 1989; Brusseau et al., 1990; Ball and Roberts, 1991; Pavlostathis and Jaglal, 1991; Pignatello et al., 1993; Kan et al., 1994; and Chen, 1996). Pignatello et al. (1993) observed that herbicides showed great resistance to release from a historically-contaminated soil, and freshly-spiked compounds behaved similarly. The resistant fraction was from 82 to 92% in this study. Ball and Roberts (1991) observed that the slow release fraction of 1,2,4,5-tetrachlorobenzene in an aquifer sand material was as high as 90%. Kan et al. (1994) found the resistant fraction of freshly added naphthalene was 62% after 10 successive washing for as much as 178 days, despite the relatively low $K_{ow}$ value and high volatility of this compound. Previous work in this research group (Chen et al., 1997) has shown that a significant amount of chlorinated benzenes are bound to Lake Charles sediment -- the resistant fraction is from 48% to 82% even after three Tenax desorption for 151 days. In a recent review article, Pignatello (1996) summarized the observations about the resistant fraction in many freshly- and aged-contaminated soil, sediment and aquifer material. The resistant fraction was found to vary from 10% to as much as 96%, depending on individual chemical-sediment combination. Thus far, the deviation from equilibrium and reversible adsorption and desorption behavior has been reported for many classes of compounds, including polycyclic aromatic hydrocarbons, chlorinated benzenes, pesticides, phenols, surfactants, halogenated aliphatic hydrocarbons, and PCBs (Di Toro and Horzempa, 1982; Coates and Elzerman, 1986; Zawadzki et. 1987; Siracusa and Somasundaran, 1987; Readman and Mantoura, 1987; Pignatello, 1990; and Pavlostathis and Jaglal, 1991).
2.3.2 Proposed Mechanisms for Irreversible Adsorption

Irreversible adsorption processes have been studied for many years. Although dozens of mechanisms have been proposed to interpret the deviation of desorption behavior from equilibrium assumptions, there is no general agreement on the mechanistic origin of the resistant desorption. One reason is that currently there is no direct observation revealing the molecular-scale locations of hydrophobic organic compounds in soil and sediment (Luthy et al., 1997). Macroscopic observations are commonly used to infer adsorption mechanisms, but these observations are often contradictory. Nonetheless, the observed non-ideal adsorption and desorption are often attributed to one or more of the following mechanisms:

1. Slow first-order kinetics in both adsorption and desorption directions (Oddson et al., 1970; Karickhoff, 1981; Connaughton et al., 1993; and Pedit and Miller, 1994)

2. Slow diffusion in solid matrix, either the diffusion within interparticle micropores or the diffusion through the organic matter phase (Wu and Gschwend, 1986; Miller and Weber, 1988; Ball and Roberts, 1991; Carroll et al., 1994; and Young and Weber, 1995)

3. Complex combination of heterogeneous adsorption properties exhibited by various components in the solid matrix (Weber et al., 1992; Weber and Huang, 1996; Burgos et al., 1996; and Xing and Pignatello, 1996)

4. Specific chemical interactions between organic compounds and high-energy sites in sediment (Burgos et al., 1996; Xing and Pignatello, 1996; Gustafsson et al., 1997; and Chiou and Kile, 1998)
5. Physical entrapment of organic compounds within sediment matrix (DiToro and Horzempe, 1982; Flanagan et al., 1987; Vaccari, 1988; Brusseau and Rao, 1989; Burgess et al., 1989; Adamson, 1990; Kan et al., 1994; Burgos et al., 1996; White et al., 1997; Kan et al., 1997; and Devitt and Wiesner, 1998)

Other mechanisms, such as chemisorption of the pollutants to various components of the soil and sediments matrix (Brusseau and Rao, 1989) and either biotic or abiotic degradation of the pollutant being studied (Hermsin et al., 1987; and Miller and Pedit, 1992), may also cause apparently irreversible adsorption. The apparent irreversibility caused by biotic or abiotic degradation can be eliminated using strict experimental procedures, such as requiring close to 100% mass balance. While chemisorption may exert a significant effect on the adsorption and desorption behavior of some reactive chemicals, such as phenols and some substituted phenols (Isaacson and Frink, 1984), it is not very important to hydrophobic organic compounds which are nonreactive and nonpolar. Therefore, these two mechanisms will not be discussed here.

Simple first-order kinetic models require no parameters that are dependent on sorbent geometry, thus, they have been used to simulate adsorption and desorption kinetics and have been incorporated into fate and transport models. These models conceptualize adsorption as either a single first-order reaction or a series of first-order reactions with different kinetic constants. The simplest model -- a one-box model -- contains only two single rate constant, and can be described as (Karickhoff, 1984):

$$
C \overset{k_1}{\leftrightarrow} S
$$

(2.21)
where \( k_i (T^{-1}) \) and \( k_{ij} (\frac{M}{L^3 \cdot T}) \) are the first-order rate constants in the adsorption and desorption direction, respectively, and \( S \) is the solid phase concentration. The two constants are related by the partition coefficient as: \( k_{ij} = k_i / K_p \). For this simple model, the kinetic approach to equilibrium is:

\[
f = f_0 \exp - (k_i - k_{ij}) t \tag{2.22}
\]

where, in adsorption experiments, \( f \) and \( f_0 \) are the fraction of the total adsorbed mass at equilibrium adsorbed up through time \( t \) and time zero, respectively; and in desorption experiments, \( f \) and \( f_0 \) are the fraction of initially adsorbed mass released up through time \( t \) and time zero, respectively. In Karickhoff (1984), \( f \) and \( f_0 \) are defined as:

\[
f = \frac{C - C_e}{C_e} \tag{2.23}
\]

and

\[
f_0 = \frac{C_0 - C_e}{C_e} \tag{2.24}
\]

where \( C, C_0, \) and \( C_e \) are the concentrations at time \( t \), time 0, and equilibrium,
respectively. This single-rate-constant model cannot fit most adsorption and desorption kinetic data characterized by the biphasic pattern.

Karickhoff (1981) developed a two-box model, which includes one more parameter than the one-box model but fits kinetic data better. This model subdivides the overall adsorption or desorption into two fractions -- a rapid fraction, for which equilibrium can be assumed, and a slowly exchanging fraction, which is characterized by a rate constant. The model can be expressed as:

\[
C \xleftarrow{x_t K_p} S_1 \xrightarrow{k} S_2
\]  \hspace{1cm} (2.25)

where \(X_t\) is the fraction of total adsorption capacity associated with Box 1; \(K_p\) is the partition coefficient; and \(S_1\) and \(S_2\) are the solid phase concentrations in Boxes 1 and 2, respectively. The analytical solution for the two-box model is:

\[
f = \frac{(1 - X_t) r_{sw} K_p}{1 + X_t r_{sw} K_p} \exp \left[ - \frac{1 + r_{sw} K_p}{1 + X_t r_{sw} K_p} k (t - t_i) \right]
\]  \hspace{1cm} (2.26)

where \(r_{sw}\) is the sediment to water ratio, and \(t_i\) is the time required for the adsorption (desorption) equilibrium between \(S_1\) and \(C\). Ongley (1993) studied the long term slow release of naphthalene from Lula sediments in column experiments. The breakthrough data was modeled with a two-site model assuming the existence of an instantaneous
equilibrium adsorption site and a time dependent adsorption site. A more common approach is to characterize both the rapid fraction and the slow fraction with kinetic rate constants (Brusseau et al., 1991; and Spurlock and Biggar, 1990).

Upon consideration of the inter- and intra-particle heterogeneity of soil and sediment, some researchers have proposed that only a few rate constants often do not apply over the entire kinetic part of the adsorption or desorption process (Pignatello et al., 1993; Connaughton et al., 1993; Farrel and Reinhard, 1994; and Harmon and Roberts, 1994). Hence, adsorption and desorption in natural sorbents seem to be a continuum (Pignatello and Xing, 1996).

Connaughton et al. (1993) modeled the increasing desorption resistance of naphthalene by assuming that the rate constant \( k \) is distributed according to a statistical gamma (\( \Gamma \)) density function, i.e., the probability density function \( f(k) \) for each rate constant \( k \) is generated by the gamma density function as:

\[
f(k) = \frac{\beta^\alpha k^{\alpha-1} \exp(-\beta k)}{\Gamma(\alpha)}
\]  

(2.27)

where \( \alpha (> 0) \) and \( \beta (> 0) \) are two adjustable parameters. \( \alpha/\beta \) represents the statistical mean of desorption rates, while \( \alpha/\beta \) represents the standard deviation of the desorption rates. \( \Gamma(\alpha) \) is the normalization factor and is defined as:
\[ \Gamma(\alpha) = \int_0^\infty x^{\alpha-1} \exp(-x) \, dx \] (2.28)

The sediment matrix is conceptualized as a series of one-box kinetic compartments each characterized by a different rate constant. Thus, for each compartment, the fraction remaining after time \( t \) is simply \( \exp(-kt) \). For total initial mass \( M \), the mass remaining after time \( t \) is:

\[ M(t) = \int_0^\infty M f(k) \exp(-kt) \, dk = M \left( \frac{\beta}{\beta + t} \right)^\alpha \] (2.29)

Thus, the fraction of the initial mass released up through time \( t \) is:

\[ F(t) = 1 - \frac{M(t)}{M} = 1 - \left( \frac{\beta}{\beta + t} \right)^\alpha \] (2.30)

or,

\[ \ln[1 - F(t)] = -\alpha \ln(1 + t/\beta) \] (2.31)
This function can be fit as a nonlinear regression problem and used to test against experimental data. Since only two parameters -- $\alpha$ and $\beta$ -- are involved, the use of this model entails no loss of degrees of freedom in data fitting.

A more viable approach was developed by Pedit and Miller (1994). They proposed a stochastic model that assumes linear equilibrium and first-order mass transfer apply throughout the bulk sample. But both the linear adsorption partitioning coefficient $K_p$ and the first-order rate constant parameter $k$ are treated as continuously distributed random variables in this model. The partitioning coefficient $K_p$ and rate constant $k$ can be generated by several probability density functions, including a bivariate lognormal distribution, an univariate lognormal distribution, and a $\Gamma$ distribution function similar to that used by Connaughton et al.

Considering the porous nature of soil and sediment particles, most researchers attribute resistant desorption to some sort of diffusion limitation. For hydrophobic organic compounds in natural aquatic systems, the possible diffusion processes, as summarized by Pignatello and Xing (1996), include diffusion in bulk fluid, diffusion in the thin layer covering the surface, diffusion in mesopores (> 2 nm), diffusion in micropores (< 2 nm), and diffusion in organic matter (Figure 2.2). Under the conditions of most experiments, the pore diffusion (diffusion within intra-particle pores) and matrix diffusion (diffusion through penetrable solid phases) are likely to be the rate-limiting steps. Two types of models have been proposed -- adsorption-retarded pore diffusion model and organic matter diffusion model. In both pore diffusion and organic matter diffusion models, the predicted equilibrium partitioning coefficients are often 10 to 100
times higher than that predicted by the octanol/water partition theory.

Wu and Gschwend (1986) developed a radial diffusive penetration model (Figure 2.3) to describe the adsorption and desorption kinetics of hydrophobic organic chemicals in suspended sediment and soil particles. Envisioning sediment and soil particles as aggregates of fine mineral grains and natural organic matter, the model describes adsorption kinetics as sorbate molecules diffusing through the pore fluids held in the interstices of natural silt aggregates; their penetration is "retarded" by microscale partitioning of the compound between essentially mobile (i.e., dissolved in intraparticle pore fluids) and immobile (i.e., in/on intraparticle solids) states of the organic matter. The model assumes that: 1) local adsorption is instantaneous; 2) particles are uniform porous spheres; and 3) the partition coefficient $K_p$ and effective diffusivity $D_{eff}$ are constant in a pore. Therefore, the adsorption or desorption kinetics is quantified by an effective diffusivity parameter, $D_{eff}$, which is defined to be:

$$D_{eff} = \frac{D_m n}{(1 - n) \rho_s K_p} \quad (2.32)$$

where $D_m$ is the pore fluid diffusivity of the sorbate (cm$^2$/s); $n$ is the porosity of the sorbent (cm$^3$ of fluid/cm$^3$ total volume); and $\rho_s$ is the specific gravity of the sorbent (g/cm$^3$). According to Fick's second law of diffusion, for diffusion within a spherical porous particle:
\[
\frac{\partial S(r)}{\partial t} = D_{\text{eff}} \left[ \frac{\partial^2 S(r)}{\partial r^2} + \frac{2}{r} \frac{\partial S(r)}{\partial r} \right]
\] (2.33)

where \( S(r) \) is the local total volumetric concentration in the porous sorbent (mol/cm\(^3\)), and \( r \) is the radial distance (cm). Once proper boundary conditions are set and the particle geometry is known, the differential equation can be solved. Evidence supporting this model includes faster adsorption and desorption rates after particle pulverization and after acidification. Pulverizing particles reduces pore path length (Steinberg et al., 1987; Ball and Roberts, 1991; and Pignatello, 1990), and acidification is supposed to disaggregate grains by dissolving the inorganic oxide cements that hold the aggregates together (Pignatello, 1990). However, the increase in adsorption rate was less than expected (Ball and Roberts, 1991) and weakly dependent on particle size (Steinberg et al., 1987). Also, this model consistently underestimates desorption rates at early times and overestimates rates at later times (Harmon and Roberts, 1994).

Carroll et al. (1994) proposed a permeant-polymer diffusional model to interpret the biphasic desorption kinetics of nonionic organic compounds from soils and sediments (Figure 2.4). In this model, humic material are assumed to be partially swollen and partially condensed. The diffusion from the swollen phase is relatively fast, while the diffusion from the condensed phase is orders of magnitude slower. The model gives the following equation to express the desorption kinetics:

\[
\frac{M_t}{M_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left[ x_i \exp\left(\frac{-4n^2\pi^2 D_i t}{d_i^3}\right) + (1 - x_i) \exp\left(\frac{-4n^2\pi^2 D_2 t}{d_2^3}\right)\right]
\] (2.34)
where $M_t$ is the amount of organic contaminant remaining at time $t$; $M_0$ is the initial amount of the organic contaminant; $x_i$ is the fraction of the contaminant associated with the rubbery phase; $D_1$ and $D_2$ are diffusion coefficients in rubbery and glassy phases, respectively; and $d_1$ and $d_2$ are the sphere equivalent diameters for the rubbery and glassy phases, respectively. In this study, they found that pulverization had no effect on the release of PCBs from Hudson River sediments, however, heat treatment enhanced desorption rates and significantly decreased the resistant fraction.

Studies on rubbery and glassy polymers have shown similar adsorption and desorption patterns (Reynolds et al., 1990; Vieth, 1991; and Koenig, 1993). Pignatello et al. (1993) also reported that a two-compartment diffusion model is better than the two-site first-order kinetic model in fitting the desorption data of atrazine and metolachlor from an aged contaminated soil. Other evidence also supports the intraorganic diffusion model. For example, it was observed that linear adsorption can be restored when the glassy state polymer is converted to the rubbery state polymer, by increasing the temperature above the glass transition point ($T_g$) or by softening with organic solvents. However, this model cannot be used to explain the slow desorption of soil, sediment, or aquifer material with extremely low organic carbon content (Ball and Roberts, 1991; and Farrell and Reinhard, 1994).

Many studies have addressed the non-ideal adsorption and desorption behavior caused by the heterogeneity of soil and sediment particles (Weber et al., 1992; Weber and Huang, 1996; and Xing and Pignatello, 1996). Besides the kinetic mathematical
models, discussed earlier in this section, many conceptual models have been proposed. These models attribute the observed non-ideal adsorption and desorption to variation of the reactivity of the heterogeneous components within solid particles. The basic idea is that different organic and inorganic components of bulk sorbent may exhibit different affinities for sorbate molecules and thus, exhibit their own adsorption properties, such as adsorption energy and isotherm linearity and reversibility. The overall adsorption (desorption) is the combination of local adsorption (desorption) contributed by the various active components in particles.

These conceptual models can be represented by a distributed reactivity model (DRM) proposed by Weber et al. (1992). The DRM model assumes that each component in the bulk solid phase exhibits either a nonlinear (e.g., Freundlich or Langmuir) or a linear isotherm with respect to a particular solute; the contribution of each component to the overall isotherm depends on its mass fraction in the bulk solid. The composite isotherm can be developed from a mass balance on the sorbed solute as:

\[ q_t = q_{\text{linear}} + q_{\text{non-linear}} \]  \hspace{1cm} (2.35)

where \( q_t \) is the total solute mass adsorbed per unit mass of bulk solid, i.e., the total solid phase concentration, and \( q_{\text{linear}} \) and \( q_{\text{non-linear}} \) are the solid phase concentrations contributed by linear components and non-linear components, respectively. \( q_{\text{linear}} \) and \( q_{\text{non-linear}} \) can be developed as:
\[ q_{\text{linear}} = \sum_{i=1}^{m} x_i K_{p,i} C_e \]  

\[ q_{\text{non-linear}} = \sum_{j=1}^{n} x_j K_{F,j} C_e^{a_j} \]  

(2.36)  
(2.37)

where \( x_i \) (\( x_j \)) is the mass fraction of the \( i \)th (\( j \)th) reaction component in the sorbent; \( K_{p,i} \) is the partition coefficient of the \( i \)th linear component; and \( K_{F,j} \) is the Freundlich coefficient of component \( j \).

In their recent study, Weber and Huang (1996) greatly simplified the distributed reactivity model by defining soil and sediment as three domains -- an inorganic mineral domain, an amorphous soil organic matter (SOM) domain, and a condensed soil organic matter domain (Figure 2.5). The adsorption associated with mineral surfaces and amorphous SOM domain is linear and relatively fast, and may dominate the early near-linear isotherm observed. Adsorption by the condensed SOM domain appears to be energetically more favorable and more nonlinear than that by the amorphous SOM domain. Considering the release of aged hydrophobic organic compounds from soil and sediment, the initial fast release is probably from the inorganic mineral and the amorphous organic domains, because of the relatively unstable adsorption. Since organic compounds are strongly associated with the condensed domain, the release is more difficult and slow. They also suggested that soil and sediment humic material may gradually transform from amorphous to microcrystalline structure during diagenesis; hence, this kind of transformation may be used to account for the increase of irreversibility with increased aging time. Ongley (1993) also proposed that sediment humic substances may be dynamic and undergo a conformational rearrangement and
thereby retard the contaminant release.

Xing and Pignatello (1996) proposed a dual-mode adsorption mechanism, on the basis of observed competitive adsorption effects between atrazine and prometon, and between atrazine and trichloroethylene (TCE). They proposed that the overall adsorption was controlled by two mechanisms -- a dissolution (partition) mechanism in the amorphous (rubbery) domain and a hole-filling mechanism in the rigid (glassy) domain, and that these two mechanisms occur concurrently. The holes are a population of isolated “sites” dispersed in solid matrix where specific adsorption occurs according to the Langmuir isotherm. The total isotherm can be written as:

\[
S = K_p C + \sum_{i=1}^{n} \frac{S_i^0 b_i C}{1 + b_i C}
\]  

(2.38)

where \(K_p\) is the partition coefficient in the dissolution domain, and \(b_i\) and \(S_i^0\) are the affinity constant and maximum capacity, respectively, for the \(i\)th unique holes.

Recently, Graber and Borisover (1998) evaluated the validity of the rubbery (amorphous) and glassy (condensed) models. They reconstructed the experimental results of adsorption of phenanthrene in a highly structured and repeating polymer (PBMA) reported by LeBoeuf and Weber (1997a) and found that the Freundlich exponents exhibited by the glassy and rubbery phases were similar and were nearly equal to 1. Thus, they proposed that a glassy phase does not necessarily exhibit nonlinear adsorption. Similarly, they found that the adsorption enthalpies for the
rubbery and glassy phases were indistinguishable and that the adsorption capacities of the rubbery phases were greater than those of the glassy phases (Xing and Pignatello, 1997; LeBoeuf and Weber, 1997a; LeBoeuf and Weber, 1997b). They concluded that such experimental results were in contrast with the argument that glassy phase exhibits higher energy and greater adsorption capacity to organic sorbates. Graber and Borisover (1998) also discussed whether increased contact time could increase the extent of adsorption, as proposed in other studies (Xing and Pignatello, 1996; Weber and Huang, 1996; Xing and Pignatello, 1997). They reanalyzed the data reported by Weber and Huang (1996) with the standard method for evaluating the rate of attaining equilibrium (Crank, 1975) and found that there was no trend of increasing uptake with contact time.

In several recent studies, the non-ideal adsorption and desorption was attributed to the specific interactions between sorbates and high-energy sites in soil and sediment. Burgos et al. (1996) proposed that the irreversible binding of naphthalene and α-naphthol in two sandy soils was due to the oxidative coupling of molecules to soil organic matter. Socha and Carpenter (1987) reported the strong association of PAHs with soot. Gustafsson et al. (1997) developed an experimental procedure to separate non-soot organic carbon, inorganic carbonates, and residual soot carbon in dilute and complex sedimentary matrices. They suggested that the hydrophobic partitioning framework should be expanded to include the partition with anthropogenic soot phase as:

\[ K_p = f_o K_{oc} + f_s K_{sc} \]  \hspace{1cm} (2.39)
where $f_{\infty}$ is the soot carbon fraction of the solid matrix (g of soot carbon/g of solid), and $K_{\infty}$ is the soot-carbon-normalized partitioning coefficient [$((\text{mol/g of soot})/(\text{mol/ml of solution}))$. They reported that the observed in situ sediment-porewater distribution of PAHs are better fitted by the extended soot-partitioning model.

Chiou and Kile (1998) studied the single-solute and binary-solute adsorption of seven nonpolar and polar organic compounds on a peat soil and a mineral soil. They reported that for all the compounds studied, nonlinear adsorption was observed at relatively low solute concentrations, however, the adsorption became linear at moderate and high concentration ranges. They also proposed that more than a single mechanism is required to account for the nonlinear adsorption of both nonpolar and polar compounds. They suggested that the nonideality is probably caused by the adsorption to a small amount of high-surface-area carbonaceous material (HSACM), such as charcoal; HSACM exhibits nonlinear adsorption and a much greater affinity for organic compounds than does soil organic matter; the adsorption capacities of these high-affinity sites are quickly saturated as concentration increases, then, the partition to soil organic matter dominates the overall adsorption and gives the linear shape isotherms. They also reported that the unique observations in this study cannot be explained by the rubbery-glassy organic phase mechanism, nor by the hole-filling mechanism.

The concept of true irreversible adsorption has also been discussed by many researchers (Everett, 1967; West et al., 1985; Brusseau and Rao, 1989; Adamson, 1990; Burgess et al., 1989; Flanagan et al., 1987; Burgos et al., 1996; White et al., 1997; Devitt and Wiesner, 1998; and Kan et al., 1998). They proposed that for the adsorption of hydrophobic organic compounds to natural sediment, physical binding seems to be a reasonable mechanism for the observed irreversibility. Brusseau and Rao (1989)
summarized that sorbate molecules could physically be bound within the sorbent through the "sieve effect", where the sorbate molecule is trapped within porous organic matter (e.g., Schweich and Sardin, 1981; and Burchill et al., 1981), internal structure of mineral particles (e.g., McCloskey and Bayer, 1987), and restricted micropores of sorbent aggregates (e.g., Steinberg et al., 1987). Irreversible adsorption could be the result of some sort of cooperative conformational change of the organic matter during the adsorption process. It could also occur through a post-adsorption alteration of the sorbent structure, such as collapse, which results in capture or "lock-in" of the sorbate. Everett (1967) and Winslow (1978) suggested that irreversible binding could happen through mechanical or structural rearrangement of the sorbent, i.e., the solid from which desorption takes place is different from that during adsorption, such as the ink-bottle shaped pores that are formed. From these references, irreversible adsorption is generally associated with some rather permanent change in the sorbent-sorbate system.

White et al. (1997) cited the observations from several recent studies and proposed that the sequestration of phenanthrene in soil is due to the partition into solid organic matter and entrapment of the molecules within soil micropores following adsorption. They proposed that the significance of sequestration should be related to the organic matter content. Hatzinger and Alexander (1995) also observed greater sequestration of aged phenanthrene (measured by availability to bacteria and extractability) in an organic soil than in a mineral soil. Burgos et al. (1996) developed an experimental procedure to distinguish the contribution of both oxidative coupling and physical binding to the irreversible adsorption of naphthalene and naphtnol. They concluded that binding of the contaminants to soil organic matter through oxidative coupling alone could not account for the total amount that was irreversibly adsorbed. A
fraction of adsorbed compounds was not extractable with solvents and alkali, and was believed to be entrapped by physical binding within the interstitial sites in the soil.

Devitt and Wiesner (1998) found that dissolved atrazine was not retained by a dialysis bag with molecular mass cutoffs (MWCO) from 0.1 to 50 Kda, but significant retention was observed in solutions containing natural organic matter (NOM) or tannic acid. However, when NOM or tannic acid was replaced with salicylic acid, which is smaller, simpler, and unable to undergo conformational change, no retention was observed with atrazine. They therefore proposed that the interaction between organic matter and atrazine is not simply the chemical bonding to functional groups in organic matter. They also observed that naphthalene was not retained in the presence of tannic acid, indicating that physical entrapment alone was not the controlling mechanism. The results suggested a model in which atrazine-NOM interactions are governed by a sequence of chemical associations between atrazine and NOM followed by a physical entrapment of atrazine within NOM molecules.

In a recent paper, Kan et al. (1997) summarized several unique features of resistant desorption of hydrophobic organic compounds from natural and surrogate soil and sediment. First, extended desorption time does not increase the release from the residual fraction substantially, indicating that the observed phenomenon is probably not a simple kinetic or diffusion-limited process. Studies of the time dependence of desorption (Chen, 1997) showed that the resistant desorption of aged chlorinated benzenes changed little when desorption time was increased from 30 to 150 days. Second, irreversible adsorption was also observed in a non-porous and homogeneous surrogate material (surfactant coated anatase, TiO₂), therefore, the irreversibility cannot be explained by intra-particle diffusion mechanism (Hunter, 1996). Third, a finite and
fixed compartment size was observed for the irreversible fraction. Fourth, the apparent $K_{oc}$ values for the resistant fraction seem to be independent of their $K_{ow}$ values; different classes of compounds exhibited similar apparent $K_{oc}$ values -- from 5.0 to 5.5, though their $K_{ow}$ values differ by several orders of magnitude. Other researchers also reported that there is a poor correlation between the field-observed partition coefficient and the predicted equilibrium partitioning coefficient $K_p$, derived from conventional $K_{oc}/K_{ow}$ relationships (Pearson et al., 1996; Thibodeaux et al., 1993; Burgess et al., 1996; and Baker et al., 1986).

Kan et al. (1997) proposed a conceptual biphasic irreversible adsorption model (Figure 2.6) to interpret these observations. The model suggests that hydrophobic organic compounds partition into soil organic matter through hydrophobic interactions; during the adsorption process, some cooperative conformational changes or physical rearrangement of the organic matter occur, so that a portion of the adsorbed mass becomes irreversibly bound; the adsorbed mass associated in the "labile" compartment follows the linear adsorption model, i.e., $q = K_p C$; and the size of the irreversible compartment depends on different chemical-sediment combinations. The biphasic model can be expressed by the following equations:

$$q_i = q_{rev} + q_{irr}$$  \hspace{1cm} (2.40)

where $q_i$ is the total solid phase concentration of the sorbate ($\mu g/g$); $q_{rev}$ is the solid phase concentration ($\mu g/g$) in the labile compartment; and $q_{irr}$ is the solid phase concentration ($\mu g/g$) in the irreversible compartment.
Recently, Kan et al. (1998) proposed that since the irreversibly adsorbed fraction has a well-delineated maximum for each compound-sediment combination, it can be represented by a Langmuir-type adsorption isotherm. Substituting the linear and Langmuirian portions to Equation 2.40, the overall adsorption isotherm is given as:

\[
q = K_{oc} f_{oc} C + \frac{K_{oc}^{irr} f_{oc} q_{max}^{irr} f C}{q_{max}^{irr} f + K_{oc}^{irr} f_{oc} C}
\]

(2.41)

where \(K_{oc}\) and \(K_{oc}^{irr}\) are the organic carbon content normalized partitioning coefficients for the reversible and irreversible fractions, respectively; \(f_{oc}\) is the organic carbon content; \(q_{max}^{irr}\) is the irreversible adsorption capacity; and \(f (0 \leq f \leq 1)\) is the fraction of the irreversible compartment that is filled at the time of exposure and can be assumed equal to 1 when the exposure concentration is greater than about one-half the aqueous solubility. Also, the value of \(f\) in the numerator and denominator cancel when \(q_{max}^{irr} \times f > K_{oc}^{irr} \times f_{oc} \times C\), i.e., at low \(C\) value wherein the predominant source of contaminant is from the irreversible compartment. They also proposed a semi-empirical model to predict \(q_{max}^{irr}\) wherein the value of \(q_{max}^{irr}\) is proportional to the product of the aqueous solubility \(C_{sol}^{irr}\) and the exponential of the interaction energy:
\[ q_{\text{max}}^{\text{irr}} = a \times f_\infty C_{\text{aq}}^{\text{sat}} \exp \left( \frac{-\Delta G_{\text{ads}}^{\text{irr}} \text{HSA}}{RT / N_A} \right) \]

\[ = 0.044 f_\infty C_{\text{aq}}^{\text{sat}} \exp (0.048 \text{HSA}) \] (2.42)

where \( \Delta G_{\text{ads}}^{\text{irr}} \) represents the free energy of adsorption per unit area of molecule, and can be determined by curve fitting; HSA is the hydrophobic surface area (\( \text{A}^2/\text{molecule} \)) and can be related to \( K_{\text{ow}} \); \( R \) is the gas constant (\( \text{j mole}^{-1} \text{K}^{-1} \)); \( T \) is temperature (K); \( N_A \) is Avogadro's number; \( C_{\text{aq}}^{\text{sat}} \) (\( \mu\text{g/mL} \)) is the aqueous concentration at saturation; and \( a \) is a constant. Since HSA is proportional to \(-\log C_{\text{aq}}^{\text{sat}}\), the value of \( q_{\text{max}}^{\text{irr}} \) in Equation 2.42 is only weakly dependent on \( C_{\text{aq}}^{\text{sat}} \).

2.3.3 Factors Affecting Adsorption and Desorption in Natural Sediment

A number of factors, including sediment organic carbon content, contaminant aqueous solubility, contaminant \( K_{\text{ow}} \), sediment particle size and geometry, and contamination history, have been shown to influence adsorption and desorption. Some external mechanical forces, such as sediment perturbation and dredging, may have an effect on desorption by changing the intraparticle structure and organic matrix. Natural environmental factors, such as pH, pE, ionic strength, and temperature can affect the desorption process by interacting with both organic sorbates and sediment. Recently, competitive adsorption has drawn much attention because it is an indication that site-specific adsorption may take place in organic matter (Xing et al., 1996; and Chiou and Kile, 1998). However, whether a natural environmental factor or a competitive sorbate
affects the adsorption and desorption of a certain chemical-sediment combination depends on the mechanisms controlling the adsorption and desorption processes.

The same sorbate may exhibit quite different adsorption and desorption behavior under different pHs, because hydrogen or hydroxide ions can interact with either sorbate molecules or sorbent components, or both. Acids and bases exist in two forms, the ion or the neutral molecule, depending on the pH. The sorbability of these two forms can be very different. For polar material pH may affect the sorbability by forming hydrogen bonds. Also, varying solution pH could change the intrinsic structures of organic and inorganic matrices in sediment. For hydrophobic organic compounds, which are neutral, non-polar, and non-ionizable, the interactions between acid or caustic ions and sorbate molecules are not significant. Therefore, the effect of pH is mainly due to the interactions between acid or caustic ions and sediment matrix.

Studies which compare the acid form with the basic form for soil, clay, and sediment generally show the acid form to be a better sorbent for many material (Bailey et al., 1968; Hayes et al., 1968; MacNamara and Toth. 1970; and Nearpass, 1969). Therefore, increasing solution pH should have a positive effect on desorption. On the contrary, Pignatello (1990) found increased release of trichloroethane and tetrachloroethane when acidifying soil to pH below 3. He proposed that the acidification caused the dissolution of metal oxides and thus the partial disaggregation of particles, thereby exposing the sorbate in more remote regions of the solid matrix. However, this increase is restricted to only one-fourth to one half, or less, of the total resistant fraction.

The natural organic matter in sediment can have different conformations at different pH values. Humin, humic acids and fulvic acids, which comprise the dominant fraction of natural organic matter -- humic substances, can be soluble or insoluble under
different pHs. Some kinds of acid-base reactions may happen between hydroxide ion and humic material, and these reactions may cause either a partial breakdown of organic material or a swelling effect in the humic polymer matrix (Carroll et al., 1994). Other researchers also found that humic and fulvic acids in sediment can be solubilized with dilute (0.1 to 0.5 N) caustic solutions (e.g., Mortensen, 1965). Also, evidence has shown that the macromolecular conformation of humic substances may be analogous to that of flexible linear polyelectrolytes whose structures can be quite different, either rigid or loose, under different pH values. It has been found that humic substances are densely coiled at low pH but relatively loose and flexible at neutral or high pHs (Ghosh and Schnitzer, 1980; and Cornel et al., 1986). Therefore, raising solution pH should result in more contaminant being released. Mortensen, however, (1965) found that humin is unaffected by the caustic treatment. Carroll et al. (1994) also found that caustic treatment of PCB contaminated sediment had no effect on the resistant fraction.

Similar to the pH effect, for hydrophobic organic compounds, ions in solution also affect adsorption and desorption behavior by interacting with natural organic matter in soil and sediment. Ghosh and Schnitzer (1980) proposed that humic substances behave like flexible linear polyelectrolytes at low ionic strength, but they tend to coil up at higher ionic strengths. At high ionic strengths, repulsion between functional groups on natural organic matter may be reduced due to charge shielding and neutralization. This results in the shrinking of individual molecules of organic matter while increasing their hydrophobicity, making them more likely to form aggregates. Cornel et al. (1986) also concluded that there is a continuous change in the conformations of humic substances from uncoiled macromolecules at low ionic strength to fully coiled macromolecules at high ionic strength. Demas and Demcheck (1998) observed that mixing bottom material collected from Bayou d’Inde, Louisiana with brackish water
resulted in no remobilization of organic compounds into the water column, though the bottom material is heavily contaminated with chlorinated hydrocarbons. However, mixing bottom material with low ionic-strength water, represented by water in Calcasieu River, Louisiana, resulted in the remobilization of 1,2-dichlorobenzene and hexachlorobutadiene. However, the overall effect of ionic strength on adsorption and desorption behavior cannot always be explained by the conformational change in the organic matter alone. While some cations in solution reduce the charge of the organic matter, they may also reduce the number of potential interaction sites available to the sorbate in solution. Devitt and Wiesner (1998) found that at higher ionic strength, the retention of NOM by dialysis membrane was significantly increased due to the formation of aggregates. However, the retention of atrazine (in the presence of NOM) decreased in this study. They proposed that this decrease in retention is due to the closure of some adsorption sites by calcium ions.

Since adsorption is an exothermic process, increasing temperature decreases the degree of adsorption and thus has a positive effect on desorption equilibrium. In terms of kinetics, increasing temperature accelerates both adsorption and desorption rates. Piatt et al. (1997) studied the temperature-dependent adsorption of naphthalene, phenanthrene, and pyrene to a low organic carbon aquifer sediment. They reported that for all three compounds, the partitioning coefficients and rate constants increased as temperature decreased from 26 to 4 °C. In addition, the intrinsic structure of natural organic matter may be different at various temperatures, and this can affect adsorption and desorption. Carroll et al. (1994) found that high-temperature pretreatment of the sediment substantially increased the fraction of PCBs released from the sediment. They proposed that heat treatment was able to solubilize, swell, or destabilize the organic polymer matrix, or cause the redistribution of contaminants from the resistant to the
labile phase, and therefore, enhanced desorption. Other studies have shown that polymers can be converted from the glassy to the rubbery state by heating (Vieth, 1991; and Berens, 1989). These results show that as the glass transition temperature, $T_g$, is approached, there is a gradual elimination of high-energy adsorption sites accompanied by a shift to a dissolution mechanism.

The effect of competitive adsorption is mainly due to the competition on the specific sites in both the inorganic and organic domains in sorbents. Competitive adsorption is often a highly selective process, dependent upon the mechanism controlling the adsorption (Xing et al., 1996; Xing and Pignatello, 1998; Chiou and Kile, 1998). A sorbate may compete strongly with one compound, causing a significant reduction of the Freundlich constant and an increase in linearity of the compound, but it might have no effect on a different compound. The significance of competitive adsorption depends on the physical-chemical properties of both the solute and the cosolute, such as the size, structure, and polarity of the molecules. The competitive effect also depends on the properties of a sorbent, such as structure and functional groups. For example, adsorption to rubbery polymer phase is often non-competitive, because adsorption occurs through the partition (solid phase dissolution) mechanism. Another possibility is that, the partitioning of a competitive compound into sediment may change the intrinsic structure of sediment organic matter, i.e., an effect similar to swelling. Consequently, either more adsorption sites are exposed to adsorption, or a fraction of the entrapped contaminants becomes available for desorption.

Xing et al. (1996) observed no competition between atrazine and prometon, and between atrazine and trichloroethylene (TCE), in rubbery polymer. In peat soil, humic acid, Tenax, and silica, atrazine and prometon competed strongly, but atrazine and TCE
still exhibited no competition. These observations are very likely due to the similarity in molecular structure between atrazine and prometon. According to the duel-mode adsorption mechanism (Xing and Pignatello, 1996) adsorption to organic matter occurs simultaneously via both the solid-phase dissolution and the hole-filling processes (the holes are internal nanovoids in soil organic matter), but the competition takes place only in the hole-filling domain. Structurally different compounds do not adsorb to the same kind of holes, and thus, exhibit no competition. Recently, Xing and Pignatello (1998) reported the competitive effects of 5 natural aromatic acids on the adsorption of 1,3-dichlorobenzene and 2,4-dichlorophenol. The adsorption of these two compounds was suppressed by up to 40% in a peat and a mineral soil, containing 93% and 3% organic carbon, respectively. They argued that the similarity in the competitive effects between these two soils further supported that competitive adsorption occurs only in the hole-filling domain of soil organic matter.

Chiou and Kile (1998) also studied the adsorption of a series of polar and nonpolar compounds on a peat (49.3% OC) and a mineral (1.26% OC) soils. They reported that in the presence of a competitive solute, the non-linearity observed in single-solute systems was greatly reduced, while the slopes for the linear portions were similar. They also observed that both polar and nonpolar co-solutes greatly decreased the nonlinear adsorption of nonpolar compounds. However, the reduction effect on polar solutes varied significantly with co-solute type, but generally, a large reduction occurred if the co-solute was of high polarity. They proposed that for nonpolar compounds, a specific high-energy interaction exists between a solute and the trace amount of high-surface-area carbonaceous material (HSACM), while for polar compounds, specific interactions also occur in the highly active sites of soil organic matter. Therefore, a polar co-solute can compete for both the HSACM and for the active
sites in SOM, but a nonpolar co-solute can only compete for the trace amount of HSACM. They disagreed with the hole-filling mechanism because it cannot explain the low competition of nonpolar solutes (their dissolution in SOM should have equal access to the holes), and it cannot explain the nonspecific reduction of nonpolar solutes.

2.4 Impact of Irreversible Adsorption

As discussed earlier, the mechanisms controlling the distribution of hydrophobic organic contaminants between sediment and water are critical for their fate and transport in the environment, and it is also very important in improving clean-up technologies and in making reasonable environmental management decisions. Because of the widely recognized concept of resistant desorption, it appears that the total concentration of a certain contaminant detected in sediment does not adequately indicate the availability of this chemical for volatilization, for desorption, and for biodegradation. Resistant desorption reduces the availability of a chemical for transport, and therefore increases the difficulty of remediation. However, the same effect also reduces the potential risk (e.g. toxicity) of a contaminant. Therefore, the resistant desorption process has an impact on the way that contaminated sediment should be managed, and on the appropriate remediation technologies and cleanup standards that should be applied to the sediment.

The impact of non-ideal adsorption on contaminant transport modeling has been discussed by Brusseau and Rao (1989). The conventional model used to describe the one-dimensional adsorption-retarded advective-dispersive transport of a solute is given by:
\[
\frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}
\] (2.43)

where \(C (M/L^3)\) and \(S (M/M)\) are solution-phase and solid-phase concentrations, respectively, of a chemical; \(\rho\) is the bulk density of solid \((M/L^3)\); \(\theta\) is the volumetric water content (dimensionless); \(D\) is the hydrodynamic dispersion coefficient \((L^2/T)\); \(v\) is the average pore-water velocity \((L/T)\); \(x\) is the distance \((L)\); and \(t\) is the time \((T)\). The effect of adsorption-desorption process on the transport of a chemical is reflected through the \(\partial S/\partial t\) term. Conventionally, the ideal conditions of instantaneous equilibrium, isotherm linearity, and adsorption reversibility were assumed, i.e., \(S\) and \(C\) are simply related by \(S = K_p C\). Thus, Equation 2.43 becomes:

\[
\left(1 + \frac{\rho}{\theta} K_p\right) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}
\] (2.44)

or,

\[
R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}
\] (2.45)
where \( R = 1 + \frac{\rho}{\theta} K_p \) is commonly referred to as a retardation factor. This model often fails to reproduce the observed transport data (e.g., breakthrough curves), because the assumptions of ideal adsorption used to derive Equation 2.44 are rarely met.

To make the advective-dispersive model better represent the real transport phenomenon, Equation 2.44 can be modified by incorporating certain non-ideal adsorption mechanisms. For example, if nonlinear adsorption is described by a Freundlich equation, i.e., \( S = K_F C^n \), the differential equation describing \( \frac{\partial S}{\partial t} \) is:

\[
\frac{\partial S}{\partial t} = K_F n C^{n-1} \frac{\partial C}{\partial t} \tag{2.46}
\]

and the modified retardation factor \( R \) is:

\[
R = 1 + \frac{\rho}{\theta} K_F n C^{n-1} \tag{2.47}
\]

Figure 2.7 is a pictorial representation of the effect of adsorption nonlinearity on the shape of breakthrough curves (Brusseau and Rao, 1989).
The advective-dispersive equation can also be modified by including a kinetic or a slow diffusion factor in the retardation factor R. For example, when the one-box first-order rate constant is incorporated, the differential equation becomes:

\[
\frac{\partial S}{\partial t} = k_s \frac{\theta}{\rho} C - k_d S
\]  

(2.48)

where \(k_s\) and \(k_d\) are rate coefficients (T\(^{-1}\)) in adsorption and desorption direction, respectively. Similarly, when a pore diffusion model is used to describe the non-ideal adsorption or desorption, the differential term \(\frac{\partial S}{\partial t}\) takes the form:

\[
\frac{\partial S}{\partial t} = D_m \frac{1}{\pi^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial S}{\partial r} \right]
\]  

(2.49)

An additional model was proposed by Kan et al. (1998). They considered the typical observed biphasic adsorption and desorption pattern, and suggested that the differential equation of \(\partial S/\partial t\) should include both the partitioning coefficient of the labile fraction and that of the resistant fraction. By incorporating both \(K_p\) and \(K_{oc}\), the differential equation becomes:
\[
\frac{\partial q}{\partial t} = \left( K_{oc} f_{oc} + \frac{K_{oc}^{irr} f_{oc} \left(q_{max}^{irr} f\right)^2}{\left(q_{max}^{irr} f + K_{oc}^{irr} f_{oc} C\right)^2} \right) \frac{\partial C}{\partial t}
\]  
(2.50)

In this case, the retardation factor $R$ is:

\[
R = 1 + \frac{\rho}{\theta} \left( K_{oc} f_{oc} + \frac{K_{oc}^{irr} f_{oc} \left(q_{max}^{irr} f\right)^2}{\left(q_{max}^{irr} f + K_{oc}^{irr} f_{oc} C\right)^2} \right)
\]  
(2.51)

The resistant desorption of hydrophobic organic contaminants in sediment also greatly hinders the efficiency of biodegradation and other sediment cleaning-up practices. In a recent review paper, Loehr and Webster (1996) presented the results from a number of studies which address the impact of resistant desorption on bioavailability. They concluded that for biological degradation of chemicals in sediment to occur, they must be available to the microorganisms. Thus, chemicals tightly bound within the soil matrix will not be available for biodegradation, because microorganisms cannot access them. Kan et al. (1998) compared the pore volumes required to clean-up a particular contaminated site, predicted with the equilibrium adsorption model and with the irreversible adsorption model. The reversible model predicts that less than 22 pore volumes would be required, while the irreversible model predicts that over 3300 pore volumes would be necessary. Apparently, in the presence of resistant desorption, the conventional pump and treat method cannot economically clean up contaminated
sediment. They also suggested that the remediation of resistantly adsorbed contaminants is very difficult even with surfactants and cosolvent flushing.

A recent paper by Chen et al. (1998), in this work, illustrated how irreversible adsorption enhanced the difficulty of biodegradation and remediation practices. In this paper, the fractions of a sorbate associated with the reversible compartment, \( f_{\text{rev}} \), and that with the irreversible compartments, \( f_{\text{irr}} \), were expressed as:

\[
f_{\text{rev}} = 1 - f_{\text{irr}} = 1 - \frac{q_{\text{irr}}}{q_t}
\]  
(2.52)

After substituting Equation 2.41 into this equation, the mass fraction of an adsorbed compound in both compartments can be plotted versus the equilibrium aqueous concentration of this compound, as in Figure 2.8. The concentration at which half of the adsorbed concentration is in the reversible compartment and half is in the irreversible compartment is given approximately by:

\[
C \left( q_{\text{rev}} = q_{\text{irr}} \right) \approx \frac{q_{\text{irr}}^{\text{max}}}{K_{\text{oc}} \cdot \text{OC}}
\]  
(2.53)

Such a plot clearly shows the fraction of an adsorbed contaminant that can be readily removed by flushing. For example, the authors proposed that for a flowing stream, it is unlikely that the aqueous concentration will exceed the value in Equation 2.53 for an
extended time, since most of the mass is associated with the reversible fraction. Similarly, it will be difficult to remove the compound from the sediment to a concentration much below about one-tenth of the value in Equation 2.53, because at such a low concentration, the contaminant is primarily bound in the irreversible compartment.

Thus far, all of the currently effective environmental standards, such as EPA's sediment quality criteria (SQCs), sediment quality advisory levels (SQALs), hazardous organic contaminant toxicity index, and chemical-specific fate scores, are directly or indirectly derived on the basis of the equilibrium adsorption model. For instance, EPA has developed and published a draft freshwater sediment quality criteria (SQCs) for five contaminants, including acenaphthene, dieldrin, endrin, fluoranthene, and phenanthrene. The purpose of these criteria is to ensure that the porewater concentration does not exceed the final chronic water quality criteria values (FCVs). The maximum sediment phase concentration is correlated to the porewater concentration with the partitioning coefficient between sediment and pore water, i.e. (U.S. EPA, 1997a):

\[
\text{SQC (\mu g/g)} = K_p (L/kg) \times \text{FCV (\mu g/L)} \times 10^{-3} (kg/g) \quad (2.54)
\]

The SQC based on the reversible partitioning model has the potential to overestimate the desorption and the associated risk to the environment. Kan et al. (1998) reported that by adopting an irreversible adsorption model, about one hundred times more 1,4-dichlorobenzene could be left in the sediment without increasing adverse health or
environmental effects. In that case, the economic impact would be enormous. Other researchers have also suggested that more realistic adsorption and desorption mechanisms should be taken into account in the establishment of sediment quality criteria. For example, Gustafsson et al. (1997) proposed that since the soot phase in sediment may be dominating the environmental PAH speciation, the SQC needs to be redefined as:

\[
\text{SQC} (\text{PAH}_i) = (f_{oc}K_{oc} + f_{sc}K_{sc}) \times \text{FCV(\text{PAH}_i)}
\] (2.55)

Finally, although the resistant desorption has become a focus of environmental researches, our understanding of the impacts of this process is still very limited. Particularly, we are unable to predict the significance of resistance, if there is any, of a specific chemical-sediment combination, because of the complexity and diversity of natural sediment and the effects of many natural and anthropogenic factors. Therefore, as concluded by the EPA's contaminated sediment management strategy (U.S. EPA, 1998), a comprehensive, coordinated program of research is required to identify relationships between sediment contaminants and the viability and sustainability of benthic ecosystems, and ultimately to clarify how such information can be used to direct source control and pollution prevention strategies.
Figure 2.1: Three most common sorption isotherms: linear isotherm, Langmuir isotherm, and Freundlich isotherm (from left to right).

Freundlich Isotherm
\[ q_e = K_f C_e^n \]  \[ (n < 1) \]

Langmuir Isotherm
\[ q_e = \frac{Q^0 b C_e}{1 + b C_e} \]

Linear Isotherm
\[ q_e = K_L C_e \]
Figure 2.2: Schematic of a soil particle aggregate showing the different diffusion processes (from Pignatello and Xing, 1996).
Figure 2.3: Schematic of intra-organic diffusion, illustration diffusion through a rubbery phase A and a condensed phase B (from Pignatello and Xing, 1996).
Figure 2.4: Schematic of sorption-retarded pore diffusion, sorption is enhanced in very small pores due to the interaction with more than one surface (from Pignatello and Xing, 1996).
Figure 2.5: Schematic illustration of domain types associated with a soil or sediment particle (from Weber and Huang, 1996).
Figure 2.6: A pictorial represent of the irreversible sorption model by Kan et al. (1997).
Figure 2.7: Breakthrough curves for linear and nonlinear sorption isotherms (from Brusseau and Rao, 1989).
Figure 2.8: Plot of the fraction of adsorbed compound, $q^{\text{tot}}$, which is adsorbed in either the reversible (dashed line) or the irreversible (solid line) compartment (equation 4) as a function of the equilibrium solution phase concentration, $C$ (µg/ml). Plot was constructed using equation 1 with $K_{OC}^{irr} = 10^{5.53}$ ml/g, $K_{OC} = 10^3$ ml/g, OC = 0.041, $q_{max}^{irr}$ (µg/g-sediment) = $10^{18}$OC, and $f = 1$ (from Chen et al., 1998).
Chapter 3: Characteristics of Irreversible Sorption in Natural Sediments

3.1 Introduction

In the previous chapter the general characteristics of sorption and desorption were reviewed. While numerous researchers have studied the sorption and desorption behavior of hydrophobic organic contaminants in soils and sediments, few have systematically characterized the irreversible compartment. Nonetheless, knowing these unique characteristics is the basis of knowing the mechanism controlling the irreversible process and thus, is of tremendous value for every aspect of sediment quality management. Thus, the primary focus of this thesis is on the irreversible compartment and its impact on sediment quality. In this chapter, the characteristics of irreversible sorption were further characterized using five chlorinated benzenes and four natural sediments. The compounds were intentionally chosen from the same chemical class and include 1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and hexachlorobenzene. These compounds cover a relatively wide range of solubility and $K_{ow}$ values. The four sediments used in this study included Dickinson, Lake Charles, Lula, and Utica sediments. These sediments vary significantly in physical and chemical properties, such as particle size and organic carbon content.

Experiments were designed so that a number of properties of the irreversible sorption compartment could be examined. These properties include the irreversible sorption capacity (the maximum size of the irreversible fraction), the aqueous phase concentration corresponding to the irreversible compartment, and the apparent partition coefficient of the irreversible compartment. In each experiment, the sediment was
initially saturated with one of the five chlorinated benzenes, by equilibrating sediment either repetitively or continuously with an electrolyte solution containing high concentration of this compound. Then, the sediment was stripped extensively with electrolyte solution and Tenax resin until the irreversible fraction was reached. After that, repetitive desorption was conducted to study the unique properties of the irreversible compartment.

The properties of the irreversible sorption compartment of each chemical-sediment combination are compared. The dependency of the irreversible sorption capacity on chemical \( K_{ow} \) value and sediment organic carbon content are also studied. The observed data in this study covered wide solid and aqueous phase concentration ranges and therefore, served as a systematic test case for the proposed sorption and desorption models and mechanisms. An irreversible sorption-desorption model was used to fit the experimentally observed sorption and desorption data, with the objective of seeking a quantitative tool which can accurately predict the resistant release of hydrophobic organic contaminants from soils and sediments. Also described in this chapter is a new experimental approach which greatly simplifies and facilitates the conventional procedures to saturate a sediment with chemicals.

3.2 Experimental

3.2.1 Sorbates and Chemicals

The chemicals, 1,4-dichlorobenzene (Matheson Coleman & Bell, Los Angeles, CA), 1,2,3,4-tetrachlorobenzene, and hexachlorobenzene (Ultra Scientific, North Kingstown, RI) were used upon receipt. Stock solutions of 1,2-dichlorobenzene and
1,2,4-trichlorobenzene (Ultra Scientific, North Kingstown, RI) were prepared by dissolving a certain amount of liquid compound in methanol.

Chlorinated Hydrocarbons Mix™ 8120 Solution (99% in hexane) (Supelco, Inc., Bellefonte, PA) was diluted and used as GC/ECD calibration standard. The mixture contained 2000 µg/mL each of the following compounds: 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, hexachloroethane, 1,2,4-trichlorobenzene, hexachlorobutadiene, 1,2,4,5-tetrachlorobenzene, hexachlorocyclopentadiene, 2-chloronaphthalene, and hexachlorobenzene. Upon receipt, the mixture solution was diluted in isoctane and acetone, respectively, to make two stock solutions. More stock solutions of different concentrations were prepared by further diluting these two solutions in isoctane, acetone, and methanol. 2,5-Dibromotoluene (98%, Aldrich Chemical Company, Inc., Milwaukee, WI) was used as the internal standard in GC/ECD analysis. Stock solutions of 2,5-dibromotoluene with different concentrations were prepared in isoctane, acetone, and methanol.

An electrolyte solution was prepared in D.I. water with sodium chloride, with a purity of > 99.995% (EM Science, A Division of EM Industries, Inc., Gibbstown, NJ), calcium chloride, with a purity of 98.8% (Fisher Scientific, Fair Lawn, NJ), and sodium azide, with a purity of > 98% (Eastman Kodak Company, Rochester, NY). Sodium azide was used as an inhibitor for bacterial growth.

Several solvents were used for solution preparation, extraction, and cleaning purpose. These solvents included acetone (spectranaalyzed, Fisher Scientific, Fair Lawn, NJ), methanol (spectranaalyzed, Fisher Scientific, Fair Lawn, NJ), hexane (Optima,

3.2.2 Tenax TA Resin

Tenax TA resin (20/35 mesh, Alltech Associates, Inc., Deerfield, IL) was used in selective desorption steps to facilitate the release of sorbed compounds from sediments. Tenax resin is the polymeric adsorbent beads of 2,6-diphenyl-p-phenylene oxide. The advantages of Tenax-desorption approach and the development of experimental procedures were discussed in details in a previous study (Chen, 1997). Upon receipt, Tenax was Soxhlet-extracted successively with acetone, acetone/hexane (1:1 by volume), methanol, and acetone, respectively, 48 hours for each extraction step. After extensive cleaning, 1 g resin was mixed with 10 mL of clean acetone and shaken overnight. The acetone extract was then analyzed by GC/ECD to check the cleanness. Clean Tenax resin was baked at 200 °C overnight and stored in methanol. Tenax resin was reused and could be regenerated using the same procedures as described above. To use Tenax resin in desorption experiments, it was withdrawn from methanol, and baked at 200 °C for at least 4 hours in a clean 25 mL glass vial. The vial was then sealed and allowed to cool to room temperature. Tenax resin was transferred immediately to reactors after cooling.

3.2.3 Sediments
The properties of the sediments used in this thesis are summarized in Table 3.1. According to Chandra et al. (1996), Dickinson sediment was collected from Dickinson Bayou in Galveston County, Texas. The uppermost section, typically 5 to 25 cm of unconsolidated, fine-grain sediment, was recovered and chilled to 4 °C for shipping and further study. Upon receipt, the sediment was air dried, ground, and sieved (53 μm). The sediment contains 1.5% of organic carbon. No detectable amount of hydrocarbon contaminants were found in the sediment.

Lake Charles sediment was collected from the lower Calcasieu River at Lake Charles, Louisiana, by Dr. Charles R. Demas of U.S. Geological Survey. The sediment was collected with a stainless-steel sampler, stored in clean plastic zipper bags, and chilled to 4 °C immediately after collection. Upon receipt, sediment samples from two plastic bags were combined, mixed, and centrifuged at a low temperature. After centrifugation, the supernatant was removed from the sediment. Both the sediment and supernatant were stored in a refrigerator. Several sediment properties, including pH, moisture content, inorganic fraction, organic carbon content, and initial contaminant concentrations were measured in a previous study (Chen, 1997). The sediment contains 31.2% of moisture; the pH of the sediment and pore water is 6 to 7; the inorganic fraction is mainly quartz; and organic carbon content of the sediment is 4.1% on the dry-weight basis. Lake Charles sediment is contaminated with various compounds including petroleum hydrocarbons, PAHs, as well as polychlorinated aromatic and aliphatic organic compounds.

Lula sediment was collected from Johnson Ranch, Oklahoma (near the margin of the floodplain of a small river). The properties of this sediment are described in details in Fu, et al. (1994). The sediment was air dried, sieved through cheese-cloth to remove
vegetative matter and pebbles, and stored in a refrigerator. The sediment consists of 92% sand, 6% silt, and 2% clay. Fine sand grains with diameter between 0.11 to 0.5 mm account for about 75% (by weight) of the sediment, and the weighted average diameter of the sediment is 0.23 mm. The organic carbon content of the sediment, determined with a combustion method corrected for inorganic carbonates (Galbraith Laboratories, Knoxville, TN), is 0.27%. The Brunauer Emmett Teller (BET) surface area is 1.24 m²/g and was determined with nitrogen as an absorbing gas (Micromeritics, Inc., Norcross, GA). Lula sediment does not contain a detectable quantity of hydrocarbon pollutants.

Utica sediment was the bottom sediment collected from Utica Harbor near a gas manufacturing plant. The sediment has an organic carbon content of 2.8% and is contaminated with a number of polycyclic aromatic hydrocarbons (PAHs).

3.2.4 Analytical Methods

Gas chromatography with electron capture detector (GC/ECD) (Hewlett-Packard Co., Palo Alto, CA) was used to analyze the concentrations of sorbates and standards. The capillary column of the gas chromatography is the Ultra 2 silicone column, crosslinked with 5% phenyl methyl siloxane phases (Hewlett-Packard Company, Wilmington, DE). The column is 25-m long, and has an internal diameter of 0.32 mm and a film thickness of 0.52 μm. Ultra high purity helium and ultra high purity nitrogen (Trigas Industrial Gases, Irving, TX) were used as the carrier and auxiliary gases, respectively. The column head pressure was set at 15 psi, which gave a column flow rate of about 5 mL/min. The injector and the detector temperatures were set at 275 °C and 390 °C, respectively. The temperature program designed for chlorinated
hydrocarbon analysis was: starting from 50 °C, holding for 4 minutes, increasing
temperature by 8 °C per minute to 220 °C, and holding for 4 minutes.

A stock solution containing the same concentration for each of the 10 chlorinated
hydrocarbons was used to prepare standard solutions. The standard solutions were
analyzed by GC/ECD using the same temperature program as with the sample analysis.
To ensure the accuracy of standard curves, at least six standard solutions with different
concentration levels for each compound were prepared. One of the standard solutions
was at a concentration near but above the method detection limit, while others
corresponded to the expected range of the concentrations in real samples. The
compound, 2,5-dibromotoluene was used as the internal standard, with a concentration
of 25 μg/L in each solution. To minimize the artifact caused by instrumental
fluctuations, standard solutions were analyzed either immediately before or after sample
analysis. Standard curves were made every time samples were analyzed.

Since different solvents, including isooctane, acetone, methanol/water (85%:15%
by volume) were used in this study, chlorinated hydrocarbon standard solutions were
also prepared in these different solvents accordingly. This is because the same
compound may have very different GC/ECD responses with respect to different solvent
matrices. For example, every chlorinated benzene of interest in this study had larger
GC/ECD response in isooctane than they had in acetone.

To analyze the chlorinated hydrocarbon concentrations in each sample, organic
solvents were used to extract these compounds from sediment, Tenax, or electrolyte
solution. The organic solvent extracts containing these compounds were then
concentrated or diluted to a proper concentration, and 2,5-dibromotoluene solution was
added as the internal standard. Finally, samples were analyzed with GC/ECD and the concentration of each compound was obtained using the standard curves.

3.2.5 Sorption and Desorption Experiments

Sorption and desorption experiments were performed in batch reactors, in which sediments were suspended in a well-mixed aqueous solution. A typical reactor consisted of a clear glass vial (Fisher Scientific, Fair Lawn, NJ) of approximately 43 mL total volume and a cap with a Teflon-faced silicone septum (Pierce Chemical Co., Rockford, IL).

All glassware was thoroughly cleaned before being used in experiments. The cleaning procedures described by Hunter et al. (1996) were modified and used in this study. At first, glassware was soaked in a warm cleaning solution overnight. Two types of cleaning solutions were used in this study. One was prepared by diluting a RBS 35 detergent solution (Pierce Chemical Co., Rockford, IL) to 2% (by volume) in tap water, and heated to 60 °C to improve the cleaning capability. The other was made by dissolving 30 g Alconox detergent powder (Alconox Inc., NY) in 4 L of hot water. Then, glassware was brushed, rinsed with tap and D.I. water, and oven-dried (Precision Scientific Co., Chicago, IL) at 200 °C. Finally, glassware was rinsed with acetone 3 times and oven baked at 200 °C for at least 4 hours.

3.2.5.1 Sorption Experiments
In Table 3.2 are listed the experimental protocols for the eight sorption and desorption experiments. In Experiments 3.1 and 3.2, the sediments were saturated with 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, respectively, using the conventional repetitive batch sorption approach (e.g., Kan et al., 1994). Before starting a repetitive sorption experiment, an aqueous solution of a certain compound was prepared using a methanol stock solution of this compound and an electrolyte solution containing 0.01 M of NaCl, CaCl₂, and NaN₃, respectively. About 100 mL of electrolyte solution (exact volume measured by weight) and a Teflon-coated magnetic stir bar was added in a 100 mL volumetric flask. While the solution was stirred, a certain amount of methanol stock solution of a compound was delivered into the solution with a small syringe. The concentration of the stock solution was selected so that the volume of methanol added to the aqueous solution would not exceed 50 μL (0.05% of the total volume). The amount of stock solution added was calculated so that the resulting aqueous solution concentration was about 60% of the solubility of the compound. Then, the aqueous solution was stirred for 2 to 3 hours. Since both compounds have relatively high solubility, this time period should have given a uniform distribution of the compounds in solution. At the end of solution preparation, a portion of the solution was taken to check the aqueous phase concentration.

To begin a repetitive sorption experiment, about 42 mL of freshly prepared solution was placed to a 43 mL glass vial, containing 2 g of sediment. Then, the vial was sealed with a Teflon-septum cap (Fisher Scientific, Fair Lawn, NJ) to leave no head space, and was tumbled at 1 rpm at room temperature for 3 to 4 days. Afterwards, the vial was centrifuged (IEC Centra MP4 Centrifuge, International Equipment Company, MA) at 3000 g for 1 hour. 90% of the supernatant was removed and a portion of the removed supernatant was used to measure the equilibrium aqueous phase concentration.
Finally, the vial was filled with freshly prepared 1,2-dichlorobenzene or 1,2,4-
trichlorobenzene solution to conduct another sorption. Six repetitive sorptions were
completed in Experiment 3.1, and 11 sorptions were completed in Experiment 3.2.

In Experiments 3.3 to 3.8, the sediments were saturated with one of the
chlorinated benzenes using a newly developed continuous sorption approach --
continuous sorption with dialysis membrane bag. A pictorial representation of this
system is drawn in Figure 3.1. This reaction system contained a 43 mL glass vial, a cap
with Teflon-coated liner, electrolyte solution, 10 g of sediment, a Spectra/Por® 6
membrane tube (Spectrum, Houston, TX) with molecular weight cut out (MWCO) of
1000, and a certain amount of solid form chlorinated benzene sealed in the dialysis
membrane bag. The amount of chemical inside the dialysis bag was calculated so that
after the maximum sorption capacity was reached, the pure compound phase would still
exist inside the dialysis bag. The experimental system was designed to simplify and
facilitate the sorption process -- instead of using repetitive sorption to saturate a
sediment, a sediment can be saturated in one step, given enough contact time. This
advantage becomes more significant for compounds with lower solubility and higher \( K_{ow} \)
values, such as hexachlorobenzene, because with repetitive sorption, it is very difficult
to saturate a sediment with such compounds. In the dialysis sorption approach, an
equilibrium exists among three phases -- the pure chemical phase, its dissolved phase,
and its sorbed phase. Ideally, a chlorinated benzene would continuously dissolve into
the aqueous solution and then partition to the sediment until the maximum sorption
capacity was reached. At this stage, the aqueous phase concentration in the system
should also reach the solubility of this compound. After setting up the system, the
reaction vial was immediately filled with electrolyte solution to leave no head space and
was tumbled at 1 rpm for 2 to 4 months, depending on the specific chemical-sediment combination. Aqueous phase concentration in each system was spot-checked during the sorption period.

3.2.5.2 Desorption Experiments

In this study, desorption experiments were conducted primarily using the repetitive desorption with electrolyte solution, but Tenax desorption was also used in selected steps to accelerate the release of sorbed compounds. The procedures of Tenax desorption have been discussed in details in a previous study (Chen, 1997). Tenax-desorption approach is theoretically similar to the gas purge approach -- both facilitate desorption by continuously removing desorbed compounds from the solution phase. With the conventional desorption approach, the concentration of a desorbed compound builds up gradually in aqueous phase solution, and desorption becomes increasingly slower. By removing desorbed compounds from the solution, Tenax desorption creates the maximum concentration gradient between the solid-liquid interface and bulk solution -- the driving force for desorption, throughout the desorption process. Moreover, Tenax-desorption has several advantages. It allows for free tumbling during the experiment, while gas purge results in abrasive disintegration of particles (Wu and Gschwend, 1986). Tenax desorption can also avoid the experimental artifact caused by failure to completely separating the solid and aqueous phases. This is because when phase separation is incomplete, non-centrifugable micro-particles or organic macromolecules remain in the aqueous phase after centrifugation. Therefore, the compounds associated with these micro-particles or macromolecules will also be measured as the compounds desorbed, thus the observed partition coefficient will be smaller than the true value.
Upon the completion of a continuous sorption experiment, the reaction vial containing sediment and solution was hand-shaken vigorously to give a uniform distribution of the sludge. Then, 0.5 mL of the sediment slurry was immediately withdrawn by a glass syringe and transferred to a 20 mL glass auto-sampler vial to measure the solid phase concentration. Similarly, about 9 mL slurry was withdrawn from the vial and transferred to a 43 mL glass vial to conduct the desorption experiment. The amount of sludge withdrawn was weighed and the mass of sediment (on a dry-weight basis) transferred was calculated on the basis of the sediment/solution ratio used in the sorption experiment. After that, the glass vial was filled with an electrolyte solution containing 0.01 M of NaCl, CaCl$_2$, and NaN$_3$, to leave no headspace. Then, it was tightly sealed with a Teflon-septum cap and tumbled (1 rpm) at room temperature for a designed time period. At the end of each time period, the vial was centrifuged at 3000 g for 45 minutes to separate sediment and aqueous solution. The supernatant was then withdrawn, extracted, and analyzed with GC/ECD. If another desorption step was needed, 90% of the supernatant was removed and fresh electrolyte solution was added to the vial to initiate another desorption.

When a Tenax desorption was conducted, about 0.3 to 0.5 g of Tenax was added to the vial containing sediment and electrolyte solution. The vial was sealed and tumbled at 1 rpm for a designed period of time. At the end of each desorption period, the reaction vial was centrifuged at 2500 g for 30 minutes. This resulted in a well separated three-phase system consisting of sediment on the bottom and Tenax beads floating on the top of the aqueous solution. Tenax beads were then taken out with a clean stainless steel spoon and transferred to a pre-weighed 25-mL glass vial; some water was also transferred into the vial. About 0.6 g of water was left with the Tenax beads after excess aqueous solution was removed with a small syringe. Tenax was then
extracted with acetone to determine the amount of desorbed compound. If another
desorption step was needed, fresh Tenax beads were added to the vial. The vial was
again filled with electrolyte solution to leave little head space, and the same procedures
described above were repeated.

3.2.6 Solution and Solid Phase Concentrations

To determine solution phase concentrations, compounds in an aqueous solution
were extracted with isooctane. At the end of each sorption or desorption step, the
reaction vials were centrifuged to separate sediment and solution. Then, a certain
amount of supernatant, depending on the estimated solution phase concentration, was
decanted directly from the reactor to a pre-weighed 43-mL clean glass vial, to minimize
the loss of organic compounds from transferring. The vial was weighed to calculate the
volume of the solution transferred. Either 1,2-dichlorobenzene or 1,2,4-trichlorobenzene
solution was added as a surrogate standard, and 5 to 30 mL of isooctane, again,
depending on the estimated solution phase concentration, was immediately added to the
vial. The vial was weighed to measure the volume of isooctane added. Then, the vial
was tightly sealed, hand-shaken vigorously for 5 minutes, and left undisturbed until the
organic and aqueous phases separated. After apparent separation was complete, the vial
was centrifuged at 2500 g for 15 minutes to get a better separation. The isooctane phase
was then taken out by a clean glass pipet and transferred to a 7-mL clean glass vial
(Fisher Scientific, Fair Lawn, NJ) and sealed with a Teflon-septum cap. The isooctane
extract was either diluted or concentrated to the optimum analytical range for GC
analysis. Finally, the sample was analyzed with GC/ECD along with the standard
solutions. The recovery of the surrogate standard and the concentration of a chlorinated benzene were then calculated using a calibration curve.

In each experiment sediment phase concentration of a chlorinated benzene was checked at the end of sorption and selected desorption steps. Sediment phase concentration was also checked upon the completion of each experiment to determine the amount of compounds remaining in the sediments. Sediment phase concentration was determined by a method similar to that reported by Huang and Pignatello (1990). At the end of a sorption or desorption step, the reaction vial was hand-shaken vigorously for 1 minute, and a certain amount of sludge was withdrawn immediately with a glass syringe and was transferred to a 20 mL glass auto-sampler vial (Wheaton, Millville, NJ). The amount of sludge transferred was calculated so that it contained about 0.2 g of sediment on the dry weight basis. A certain amount of 1,2-dichlorobenzene or 1,2,4-trichlorobenzene stock solution (in methanol) was added as the surrogate standard. Then, methanol/water solution (85%:15% by volume) was added to the vial to leave about 0.5 mL of head space. The vial was sealed with an aluminum seal with Teflon-coated septum (Wheaton, Millville, NJ), sonicated for 30 minutes, and horizontally shaken in a water batch (Yamato, model # 1290, Japan) at 70 °C for 16 hours. Finally, the vial was centrifuged at 3000 g for 30 minutes, and the supernatant was taken and was analyzed with GC/ECD. As mentioned above, since the extract was in methanol/water solution, the standard solutions were also prepared in methanol/water solution.

Chlorinated benzene sorbed by Tenax was extracted with about 6 mL acetone in a 25 mL glass vial, so that the mass of the compound could be determined with GC/ECD. To check the extraction efficiency, either 1,2-dichlorobenzene or 1,2,4-trichlorobenzene solution (in methanol) was added to Tenax as the surrogate standard
before adding acetone. Then, the 25 mL vial was capped with a Teflon-coated septum and left on a shaker overnight. Afterwards, the vial was centrifuged at 1000 g for 20 minutes, and the extract containing both acetone and water was transferred to a clean 7-mL clear glass vial with a clean glass pipet. Fresh acetone was added to the Tenax to perform the next extraction.

3.2.7 Quality Control

The effectiveness of the newly developed continuous-sorption approach using a dialysis bag was checked before being used to conduct sorption experiments. The purpose of this testing was to determine the kinetics of the dissolution and sorption of solid compounds. This is because to maintain the maximum driving force for sorption, it is necessary to maintain the maximum solution phase concentration. Thus, the rate of dissolution should be at least similar to that of sorption to make this approach practical. Two control experiments were conducted using 1,4-dichlorobenzene. In each experiment, about 0.2 g of solid 1,4-dichlorobenzene was encapsulated within a dialysis membrane bag. The two ends of the bag were tightly tied with nylon thread. Then, the bag was added to a 43 mL glass vial, which was immediately filled with an electrolyte solution containing 0.01 M NaCl, CaCl₂, and NaN₃. The vial was then tumbled at 1 rpm for a designed period of time. The aqueous solution was extracted with isoctane after 2, 4, and 7 days, to determine the aqueous phase concentrations of 1,4-dichlorobenzene.

3.3 Results
3.3.1 Sorption and Resistant Desorption

Sorption and desorption experiments were conducted with five chlorinated benzenes and four different sediments. The four sediments were chosen to cover a wide range of organic carbon content -- from 0.27% to 4.1% OC. The five sorbates were selected to span a relatively wide range of solubility and \( K_{ow} \) values. The solubility of these five compounds range from 5.8 \( \mu g/L \) to 120 mg/L, and their \( K_{ow} \) values range from \( 10^{3.38} \) to \( 10^{5.50} \). These compounds were intentionally chosen from a same chemical class. Therefore, for the sorption and desorption of these five compounds in the same sediment, any difference in sorption and desorption behaviors would primarily be due to the differences in their solubility or \( K_{ow} \) values, but not the deviations in their chemical properties. These compounds were also chosen because they were identified in the Lake Charles sediment used in this study. Some physical and chemical properties of these compounds are summarized in Table 3.3.

The results of the sorption experiments are summarized in Table 3.4. In Experiments 3.1 and 3.2, sorption was initiated with solutions containing high concentrations of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, respectively. In each individual sorption step, the initial concentration of the sorbate in solution was higher than one half of its solubility. Repetitive sorption was continued until there was no significant uptake of sorbate from the solution applied to the sediment. The sorption of these two compounds was linear, as indicated by the fact that for both compounds, the organic carbon normalized partition coefficients, \( K_{oc} (\mu g/g\ OC) \) of individual sorption steps were similar. The average Log \( K_{oc} \) value of 1,2-dichlorobenzene was 3.05 in six successive sorptions, with a small standard deviation of 0.05. The average Log \( K_{oc} \) value of 1,2,4-trichlorobenzene during 11 successive sorptions was 3.42 \( \pm \) 0.06. These
values are reasonable comparing to their $K_{ow}$ values — $10^{3.38}$ and $10^{4.00}$, respectively (Schwarzenbach et al., 1992). They are also similar to the values observed previously using Lake Charles sediment and solutions containing much lower aqueous concentrations of these two compounds (Chen, 1997; Chen et al., 1999a). In Experiments 3.3 to 3.8, the chlorinated benzenes were continuously loaded to the sediments until the maximum sorption capacity was reached. Both the aqueous and solid phase concentrations were measured at the end of sorption. The $K_\infty$ value of each sorption experiment was calculated as the ratio of the organic carbon normalized solid phase concentration ($\mu$g/g OC) to the equilibrium aqueous phase concentration. The observed $K_\infty$ values of 1,2,3,4-tetrachlorobenzene (Experiment 3.4) and hexachlorobenzene (Experiment 3.5) were $10^{3.87}$ and $10^{4.93}$, respectively, and were also comparable to their $K_{ow}$ values — $10^{4.55}$ and $10^{5.50}$, respectively. The $K_\infty$ values of 1,4-dichlorobenzene observed among 4 different sediments were similar. They were $10^{2.78}$ in Dickinson sediment, $10^{2.97}$ in Lake Charles sediment, $10^{2.86}$ in Lula sediment, and $10^{3.18}$ in Utica sediment.

The desorption of these compounds deviated significantly from sorption after a few desorption steps. For example, in Experiment 3.3, the observed $K_\infty$ value of 1,4-dichlorobenzene was $10^{2.78}$ at the end of sorption. The value increased to $10^{3.84}$ after 5 repetitive desorptions. Similarly, in both Experiments 3.6 and 3.8, the $K_\infty$ values of 1,4-dichlorobenzene increased by a factor of 10 in 8 desorption steps. It appears that the variation in the resistance to desorption among different chemical-sediment combinations is related to both the organic carbon content ($f_\infty$) of the sediment and the $K_{ow}$ value of the chemical. For the desorption of low-$K_{ow}$ compound from low-$f_\infty$ sediment, sediment phase concentration could drop significantly in a few desorption steps, thus, the fraction of the chemical associated with the irreversible compartment
increases rapidly. Therefore, the low-$K_{ow}$ and low-$f_{oc}$ chemical-sediment combination shows greater resistance. This effect can be well modeled by the irreversible sorption isotherm and will be discussed in details later.

The resistant desorption of these compounds clearly exhibited a bi-phasic desorption pattern. This can be understood by examining the change of solid phase concentration with desorption step. During the desorption, solid phase concentrations dropped exponentially in the first several repetitive desorptions, then they tended to decline to a much slower rate, unless Tenax resin was added to the system to accelerate the release. After 10 to 15 desorption steps, solid phase concentrations dropped to a relatively low range and remained nearly unchanged at a certain value. At this stage, even Tenax could not sufficiently remove the sorbed compounds from sediments. The solid phase concentrations of 1,4-dichlorobenzene in Experiments 3.6 and 3.8 are plotted versus desorption step number in Figure 3.2 as an example for the bi-phasic pattern. As in Experiment 3.6, solid phase concentration of 1,4-dichlorobenzene was as high as 2,330 $\mu$g/g at the end of sorption experiment. The concentration dropped quickly to about 920 $\mu$g/g after only 4 repetitive desorptions with electrolyte solution. Then, the declining rate slowed down, and at the end of the desorption Step 8, 702 $\mu$g/g of 1,4-dichlorobenzene still remained in the sediment. However, more than 90% of the remaining compounds was removed with 3 Tenax desorptions (Steps 9 to 11), and the solid phase concentration dropped to 64.9 $\mu$g/g. The concentration remained nearly the same since thereafter. Even though two more Tenax desorptions were conducted in Steps 18 and 19, only 5% of the remaining sorbed compounds was removed. The sediment phase concentration was 58.7 $\mu$g/g at the end of desorption Step 27. In Experiment 3.8, the same pattern was observed for the change of solid phase concentration with desorption step.
The five compounds used in this study cover a wide range of solubility. 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene have moderate solubility -- 130, 60, and 41 mg/L, respectively. The solubility of 1,2,3,4-tetrachlorobenzene is much lower -- 8.2 mg/L, while the solubility of hexachlorobenzene is only 5.8 µg/L. Thus, the equilibrium aqueous phase concentrations of these compounds at the end of sorption differed quite a bit, from 62.2 mg/L for 1,4-dichlorobenzene to $6.12 \times 10^{-3}$ mg/L for hexachlorobenzene. With the proceeding of repetitive desorption, aqueous phase concentrations of these compounds dropped exponentially in the first several desorption steps and then declined at a much slower rate, until Tenax was added to accelerate desorption. The aqueous concentrations of these five compounds finally leveled off to relatively constant values after extensive desorption. The near constant concentration observed in each experiment was probably due to the small solution to solid ratio applied in this study, i.e., since the solid phase concentration barely changed with repetitive desorption, the aqueous phase concentration was expected to remain constant in a number of desorption steps. The impact of this reduced desorption on clean-up of soils and sediments will be discussed later. Interestingly, except for hexachlorobenzene, the near constant concentrations of different compounds all fell into a similar range -- about several µg per liter (Column 8, Table 3.4). These observations agreed well with the experimental results from a previous study (Chen, 1997), in which concentrations of freshly sorbed 1,2-dichlorobenzene and 1,2,4-trichlorobenzene in Lake Charles sediment dropped quickly during the first several desorption steps and then leveled off to 1.2 and 2.6 µg/L, respectively, after 18 repetitive desorptions with electrolyte solution. The low solution
phase concentration of hexachlorobenzene observed at the end of repetitive desorption experiment was probably due to its low solubility.

Similar to the previous observations (Kan et al., 1994; Chen, 1997; Kan et al., 1998; Chen et al., 1999a), the near constant concentrations observed in this study appeared to be independent on the desorption time applied. Varied desorption time -- from 3 hours to 24 days -- was applied to the last several desorption steps in all of the eight experiments (desorption time of each step was chosen randomly and was not necessarily increased or decreased from one step to the next step). In Figure 3.3 were plotted the aqueous phase concentrations versus the desorption time applied for each of the last few desorption steps in Experiments 3.1 to 3.5 and Experiment 3.7. Relatively short desorption time was applied in individual desorption steps in Experiments 3.6 and 3.8. Thus, even though data in these two experiments are very consistent with those in the other experiments, they are not included in the figure. Among the eight different chemical-sediment combinations, only the desorption of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene from Dickinson sediment (Experiment 3.2) showed very weak time-dependence. For example, the aqueous phase concentration of 1,2,4-trichlorobenzene at the end of a one-day desorption was 0.8 µg/L, while a concentration of 1.3 µg/L was observed in a two-day desorption. However, the concentration did not change appreciably when desorption time was increased to 7 days in another desorption step. In Experiment 3.4, the aqueous concentrations of 1,2,3,4-tetrachlorobenzene were nearly identical among six repetitive desorptions, of which the desorption time varied from 18 hours to 4 days. The concentration increased slightly when the desorption time was increased to 13 days. In the other five experiments, the aqueous phase concentrations of 1,4-dichlorobenzene, and hexachlorobenzene did not show statistically significant
variation with desorption time, even when desorption time of as long as 24 days (Experiment 3.5) was used. These data indicate that the desorption from the irreversible compartment reached equilibrium at these low concentrations.

3.3.2 Irreversible Partition Coefficient, $K_{oc}^{irr}$ and Irreversible Sorption Capacity, $q_{max}^{irr}$

$K_{oc}^{irr}$ and $q_{max}^{irr}$ are the most important parameters characterizing the irreversible compartment. In Table 3.4 are summarized the observed $K_{oc}^{irr}$ and $q_{max}^{irr}$ values of the five chlorinated benzenes with respect to four sediments. The irreversible partition coefficient, $K_{oc}^{irr}$ (μg/g OC), is defined similarly to the organic carbon normalized partition coefficient of sorption, $K_{oc}$, as discussed earlier. $K_{oc}^{irr}$ is the ratio of the organic carbon normalized solid-phase concentration to the solution-phase concentration after extensive desorption, i.e., when the aqueous phase concentration reaches a low, but constant value. The $K_{oc}^{irr}$ value of each compound listed in Table 3.4 is the average $K_{oc}^{irr}$ values observed in the last 5 to 9 desorption steps of each experiment. Since in each experiment, both the solid and the aqueous concentrations were relatively constant during the last few desorption steps, the $K_{oc}^{irr}$ values in these steps were very close. This is indicated by the small standard deviations of each average $K_{oc}^{irr}$ value. Interestingly, the $K_{oc}^{irr}$ values observed in all the eight experiments were very close. The $K_{oc}^{irr}$ values of 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and hexachlorobenzene were $10^{3.44}$, $10^{3.46}$, $10^{5.33}$ and $10^{5.31}$, respectively, even though their $K_{oc}$ values in sorption differed by more than two orders of magnitude. The $K_{oc}^{irr}$ values of 1,4-dichlorobenzene with respect to the four different sediments were also similar.
(Experiment 3.3, and 3.6 to 3.8). The observed values were $10^{5.38}$, $10^{5.32}$, and $10^{5.26}$ and $10^{5.81}$ for Dickinson, Lake Charles, Lula, and Utica sediments, respectively. The eight experiments gave an average $K_{oc}^{irr}$ value of $10^{5.42}$ $\pm$ 0.17. This is in agreement with previous studies by the author, in which an average $K_{oc}^{irr}$ value of $10^{5.53}$ $\pm$ 0.48 was reported (Kan et al., 1998) for compounds with $K_{oc}$ values from $10^{5.3}$ to $10^{6.3}$ and sediments with organic carbon contents from 0.27% to 4.1%. These observations further support the notion that the $K_{oc}^{irr}$ value is independent of either chemical or sediment properties.

Among the parameters describing the properties of the irreversible sorption compartment, $q_{max}^{irr}$ is probably the most difficult one to measure. Under the experimental protocols of this study, it was infeasible to measure $q_{max}^{irr}$ value directly. Thus, the $q_{max}^{irr}$ values listed in Table 3.4 were obtained by curve-fitting the experimental data using the irreversible sorption isotherm -- Equation 2.41. The least square fitting method was used to fit the data of each experiment, with $q_{max}^{irr}$ as the only fitting parameter. Initially, a number of solid phase concentrations, $q$, were calculated using Equation 2.41 and the experimentally observed aqueous phase concentrations. The value of $K_{oc}$ used in the equation was that observed in sorption experiment (Table 3.4). The value of $K_{oc}^{irr}$ used was $10^{5.42}$ (the average value of the eight experiments). A value of 10 $\mu$g/g was assigned to $q_{max}^{irr}$ as the initial guess. Then, the differences between the calculated ($q_{cal}$) and experimentally observed ($q_{exp}$) values were calculated, squared, and summed up as $\Sigma (q_{cal} - q_{exp})^2$. The optimum value of $q_{max}^{irr}$ was obtained by adjusting the value so that $\Sigma (q_{cal} - q_{exp})^2$ could be minimized. Since the five chemicals differ significantly in their solubility and the four sediments covered a wide range of organic
carbon content, the observed \( q_{\text{irr}}^{\text{max}} \) values in the eight experiments varied from 0.450 to 271 \( \mu g/g \), depending on the specific chemical-sediment combination.

3.4 Discussion

3.4.1 Justification of Experimental Protocols

A main concern with regard to the effectiveness of the dialysis-sorption approach was that the dissolution of the solid form of a chemical, which was enclosed within a dialysis bag, could be extremely slow, because of the relatively limited surface area of the solid compound. If that were true, this dissolution process would be the rate-limit step for the equilibrium among the pure compound, its dissolved phase, and its sorbed phase. Thus, even though this approach is theoretically sound and very simple, it could not be applied practically, because the reaction time required would be too long. However, experimental observations showed that chemicals could dissolve easily into the solution within the bag and then diffuse into the bulk solution in the reaction vial. The kinetics of these processes were very fast for compounds with high solubility, such as dichlorobenzenes, and were reasonably fast for compounds with medium and low solubility, such as tetrachlorobenzenes and hexachlorobenzene.

Results from the quality control experiments showed that the equilibrium between a pure compound and its dissolved phase could be established within a short period of time. It was observed that by tumbling (1 rpm) about 42 mL electrolyte solution and solid phase 1,4-dichlorobenzene (encapsulated in a dialysis bag), the aqueous phase concentration of 1,4-dichlorobenzene reached 48 mg/L within two days.
This concentration was only slightly lower than its solubility -- 60 mg/L. After 4 days, the aqueous phase concentration increased to 56 mg/L, and the concentration at the end of the 1-week equilibration was 58 mg/L.

The aqueous phase concentrations of 1,4-dichlorobenzene, 1,2,3,4-tetrachlorobenzene, and hexachlorobenzene during the sorption experiments were also checked at selected times. Similar to the observations in the control experiment, the maximum aqueous phase concentration of 1,4-dichlorobenzene could be reached within a short period of time. In the sorption experiment of 1,4-dichlorobenzene in Dickinson sediment -- Experiment 3.3, aqueous phase concentration was measured after 14, 23, and 27 days. The observed concentration was 58.4 mg/L after 14 days, and it remained essentially constant -- 58.0 mg/L after 23 days, and 58.9 mg/L after 27 days. It was relatively more difficult to saturate a solution with 1,2,3,4-tetrachlorobenzene and hexachlorobenzene. The aqueous phase concentration of 1,2,3,4-tetrachlorobenzene was measured after 23, 37, 69, and 92 days, while the concentration of hexachlorobenzene was measured after 23, 37, and 92 days. The aqueous phase concentrations of these two compounds as a function of equilibration time were plotted in Figure 3.4. As can be seen in the figure, the concentrations of both compounds increased with sorption time. For example, the concentration of hexachlorobenzene was 1.3 at the end of 23 days, and it increased gradually to 2.3 and 5.8 µg/L after 37 and 92 days, respectively. The slow kinetics was probably due to the relatively low solubility of these two compounds, comparing with that of 1,4-dichlorobenzene. Nevertheless, it appears that given enough equilibration time -- about 3 months for 1,2,3,4-tetrachlorobenzene, and 4 months for hexachlorobenzene, aqueous phase concentrations of these two compounds could eventually reach the values close to their solubilities.
The sorption time applied in each of the eight experiments was selected based on the sediment organic carbon content and the solid compound dissolution rate, as mentioned above. In continuous sorption experiments (Experiments 3.3 to 3.8), the applied sorption time for 1,4-dichlorobenzene was from 1 month (Experiment 3.3) to 2 months (Experiments 3.6 to 3.8), while in Experiments 3.4 and 3.5, sediments were equilibrated with 1,2,3,4-tetrachlorobenzene and hexachlorobenzene, respectively, for as long as 4 months. For the repetitive sorption of 1,2-dichlorobenzene (Experiment 3.1) and 1,2,4-trichlorobenzene (Experiment 3.2), the time for each sorption step was from 3 to 4 days, in consideration of the relatively high solubility of these two compounds. Kan et al. (1998) estimated that the equilibrium time was from 1 day to 1 week for compounds with $K_{ow}$ values from $10^{2.7}$ to $10^{6.3}$. Therefore, under the protocols of this research, it is reasonable to assume that sorption reached equilibrium in all the experiments. Previous experiments have also shown that if the equilibrium solution phase concentration is greater than about one-third to one-half of the aqueous solubility, the irreversible compartment can be filled in one step (Kan et al., 1998; Chen et al., 1999a). This was satisfied in all the experiments conducted in this study. In Experiments 3.1 and 3.2, the equilibrium concentrations of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene at the end of repetitive sorption were both higher than one-half of their solubility. In the continuous sorption experiments (Experiments 3.3 to 3.8), the aqueous concentrations were observed to be significantly higher than one-half of the solubility during the sorption. Thus, the irreversible compartments in all the experiments should have been filled after sorption.

3.4.2 Sorption and Desorption Isotherms
An irreversible sorption isotherm has been proposed (Kan et al., 1998) to describe the biphasic sorption and desorption of both laboratory and field observations. It was proposed that compounds associated with the labile fraction follow the linear isotherm, while compounds associated with the irreversible fraction typically exhibit nonlinear behavior. Also, this nonlinear behavior of the irreversible fraction can be described by a Langmurian type of isotherm, considering that the irreversible compartment has a well-delineated maximum sorption capacity, \( q_{\text{max}}^{\text{irr}} \) (similar to the mono-layer sorption capacity in the classical Langmuir isotherm). Thus, the overall isotherm is the combination of the isotherms contributed by both the labile and resistant fractions, as in Equations 2.37 and 2.38. As discussed earlier, since the irreversible compartments were filled during sorption in all the experiments, \( f \) in Equation 2.41 can be assumed to be 1. Thus, for all the chemical-sediment combinations in this study, Equation 2.41 can be simplified as:

\[
q = K_{\text{oc}} f_{\text{oc}} C + \frac{K_{\text{oc}}^{\text{irr}} f_{\text{oc}} q_{\text{max}}^{\text{irr}} C}{q_{\text{max}}^{\text{irr}} + K_{\text{oc}}^{\text{irr}} f_{\text{oc}} C}
\]  

(3.1)

In Figures 3.5 and 3.6, the experimentally observed sorption and desorption data in Experiments 3.1 to 3.8 are fitted with both the linear reversible isotherm and the irreversible sorption isotherm. The solid lines in the two figures are the fitted isotherms using Equation 3.1 and the observed \( K_{\text{oc}} \) and \( K_{\text{oc}}^{\text{irr}} \) values from the sorption and desorption batch experiments (summarized in Table 3.4), and \( q_{\text{max}}^{\text{irr}} \) value was taken as the only fitting parameter. The dotted lines are the linear isotherms plotted with the \( K_{\text{oc}} \)
values observed in sorption experiments (in Table 3.4). The data points are experimental observations. As in these two figures, the irreversible sorption isotherm and the linear isotherm overlap in high aqueous and solid phase concentration ranges. As the aqueous and solid phase concentrations decrease, the irreversible sorption isotherm deviates increasingly from the linear model, and eventually becomes parallel to the linear isotherm. This can be illustrated using Equation 3.1. At high aqueous phase concentration $C$, $K_{oc}^{irr} \times f_{oc} \times C$ dominates the denominator of the Langmurian term.

Thus, the denominator is reduced to $K_{oc}^{irr} \times f_{oc} \times C$, and the Langmurian term is reduced to $q_{max}^{irr}$. Since at high concentration range, $q_{max}^{irr}$ is considerably smaller than the solid phase concentration in the labile fraction (the first term of the right hand side of Equation 3.1), the total sediment phase concentration is dominated by the contribution of the linear fraction. Thus, the overall isotherm is reduced to the conventional linear isotherm as:

$$q = K_{oc} \times f_{oc} \times C$$  \hspace{1cm} (3.2)

At very low concentration, $K_{oc}^{irr} \times f_{oc} \times C$ becomes insignificant comparing with $q_{max}^{irr}$, and the denominator of the Langmuirian term is reduced to $q_{max}^{irr}$. Thus, the right-hand side of Equation 3.1 becomes to $(K_{oc} + K_{oc}^{irr}) \times f_{oc} \times C$. Since $K_{oc}$ is typically much smaller than $K_{oc}^{irr}$, the irreversible sorption isotherm is reduced to:
Equation 3.3 is similar to the linear model, except that $K_{oc}$ is substituted with $K_{oc}^{ir}$. At moderate concentrations, neither the contribution of the linear fraction nor that of the irreversible fraction is negligible, and the overall sorption needs to be described with Equation 3.1.

As in Figures 3.5 and 3.6, the experimentally observed desorption results were well fitted by the irreversible isotherm. Most data points fall on the predicted isotherms. In Figure 3.5 are plotted the desorption isotherms of 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and hexachlorobenzene in Dickinson sediment. These compounds differ significantly in both $K_{ow}$ value and aqueous solubility, however, the shape of these isotherms are similar. The resistance of different compounds to desorption is also clearly illustrated with these isotherms -- for the desorption of different chemicals in the same sediment, the resistance to desorption decreases as the hydrophobicity increases. For compounds with small $K_{ow}$ values, such as dichlorobenzenes, the difference between the reversible and irreversible model predictions is more significant -- as indicated by the fact that the irreversible sorption isotherm deviates more significantly from the linear reversible isotherm. For compounds with large $K_{ow}$ values, such as hexachlorobenzene, the irreversible isotherm comes closer to the linear isotherm. Previous research also found that for compounds with $K_{oc}$ values greater than the constant $K_{oc}^{ir}$ value of $10^{5.5}$, the predicted effect of $K_{oc}^{ir}$
on the net sorption is negligible. Other researchers (Schwarzenbach et al., 1992) reported that compounds with larger $K_{\infty}$ values were difficult to study quantitatively. In Figure 3.6 are plotted the isotherms of 1,4-dichlorobenzene in the four different sediments. Again, the irreversible isotherms have a similar shape, while the plateaus shift among different experiments. This is because the organic carbon content of these four sediments are very different -- from 0.27% of Lula sediment to as high as 4.1% of Lake Charles sediment. This difference in organic carbon content results in the huge difference among the irreversible sorption capacities, $q_{\text{irr}}$ (as in Table 3.4).

It is important to notice that although the irreversible sorption model was developed with experimental data covering narrow and low concentration range, it is equally effective for the data obtained in this study, which cover a wide range of both solid and solution-phase concentrations. For example, in Experiment 3.6 (Figure 3.6.a), the solution phase concentration of 1,4-dichlorobenzene at the end of sorption was 59 mg/L, near the solubility of this compound. After extensive desorption, the concentration dropped to less than 1.0 µg/L -- about five orders of magnitude lower. The solid phase concentrations in this experiment also cover a range of more than two orders of magnitude. The experimental results, even though spanning such a wide concentration range, are well represented by the single irreversible sorption isotherm.

3.4.3 Dependency of $K_{\infty}$ and $K_{\text{irr}}^{\infty}$ on $K_{\text{ow}}$

It has been documented that for the sorption of hydrophobic organic compounds in soils and sediments, the partition coefficient $K_{\infty}$ is strongly dependent on the
hydrophobicity of the chemicals -- indicated by the $K_{oc}$ values (discussed in Chapter 2). The eight sorption experiments in this study further support this argument. In Figure 3.7, the observed partitioning coefficients $K_{oc}$ in sorption experiments (upper plot) and the $K_{oc}^{irr}$ values in desorption experiments (lower plot) are plotted with the $K_{ow}$ values of the five compounds used in this study. As in the figure, the observed $K_{oc}$ values of all the eight chemical-sediment combinations show a near linear-dependency on the $K_{ow}$ values of these compounds. The observed $K_{oc}$ values of 1,2-dichlorobenzene in Dickinson sediment and 1,4-dichlorobenzene in four different sediments were almost identical (these 5 data points overlap in the figure). This evidence indicates that sorption is driven by the hydrophobic interaction between organic molecules and sediment organic matters, and is probably independent of the type and amount of organic carbon in a specific sediment. In the lower plot, however, the partition coefficients $K_{oc}^{irr}$ observed in the desorption experiments are independent of the chemical $K_{ow}$ values. All of the eight chemical-sediment combinations exhibited a similar partition coefficient -- about $10^{5.42}$. This might indicate that desorption from the irreversible compartment was not controlled by the hydrophobic interaction between organic molecules and sediment organic matters, as indicated by the $K_{ow}$ values. This kind of behavior is in agreement with the conceptual model of irreversible sorption proposed by Kan et al. (1998), i.e., irreversible sorption might be due to some kind of physical binding of organic molecules in sediment organic matrix. Also, some kind of complex might have been formed between the sorbed chemicals and sediment organic matters, or between the sorbed chemicals and some highly insoluble and hydrophobic materials. Thus, desorption from the irreversible compartment might have reflected the desorption properties of these complexes rather than the properties of the sorbed compounds. Some preliminary
experiments designed to test the nature of this irreversible compartment will be
discussed in Chapter 4.

3.4.4 Dependency of $q_{\text{max}}^{\text{irr}}$ on $K_{ow}$ and $f_{oc}$

In previous studies, it was proposed that irreversible sorption is a consequence of
the interaction between hydrocarbon molecules and organic matters in sediments.
Therefore, for the sorption and desorption of different compounds in a specific sediment,
the $q_{\text{max}}^{\text{irr}}$ value should be dependent on the properties of the organic sorbates. Since the
partition coefficient, which indicates the affinity of an organic compound to natural
organic matters in sediment, is closely related to the $K_{ow}$ value of a certain compound,
there might be some kind of correlation existing between $q_{\text{max}}^{\text{irr}}$ and compound $K_{ow}$ value.
Nevertheless, the observed $q_{\text{max}}^{\text{irr}}$ values seemed to be poorly related to $K_{ow}$ values in this
study (Figure 3.8). In Experiments 3.1 to 3.5, the observed $q_{\text{max}}^{\text{irr}}$ values with respect to
Dickinson sediment were 6.37, 14.5, 13.6, 15.3, and 0.453 μg/g for 1,2-dichlorobenzene,
1,4-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and
hexachlorobenzene, respectively. These values are similar except for that of
hexachlorobenzene. Kan et al. (1998) also found that the organic carbon normalized
$q_{\text{max}}^{\text{irr}}$ value -- $q_{\text{max}}^{\text{irr}}/f_{oc}$ -- varied less than 1 order of magnitude when $K_{ow}$ value increased
from $10^{2-4}$ to $10^{6-4}$. The dependency of $q_{\text{max}}^{\text{irr}}$ value on chemical solubility was also
examined (Figure 3.8). Again, the observed $q_{\text{max}}^{\text{irr}}$ values exhibited a poor correlation
with the solubility of the five compounds. The $q_{\text{max}}^{\text{irr}}$ of hexachlorobenzene observed in
this study was much lower than those of the other four compounds. This might be due to
the small maximum sorption capacity of hexachlorobenzene in the sediment -- only about 17.3 μg hexachlorobenzene can sorb per gram of Dickinson sediment (Table 3.4, Column 7). To put it another way, even though hexachlorobenzene has a high affinity for sediment organic matter, as indicated by its high $K_{ow}$ value, its solubility is very low. Thus, its $q_{max}^{ir}$ value is low. Thus, the observed $q_{max}^{ir}$ values of these compounds might be dependent on a combined effect of both $K_{ow}$ and solubility. The $q_{max}^{ir}$ values observed in the five experiments were plotted with a combined term -- $K_{ow} \times C_s$ in Figure 3.9. As in the figure, $q_{max}^{ir}$ values seem to be more strongly related to this combined term.

For sorption of the same compound to different sediments (again, assuming sorption is primarily to sediment organic matter), it seems that the irreversible sorption capacities of these compounds in different sediments should be proportional to the organic carbon content of these sediments. The $q_{max}^{ir}$ values of 1,4-dichlorobenzene with respect to four different sediments are plotted in Figure 3.10 with the organic carbon contents of these four sediments (Experiment 3.3 and Experiments 3.6 to 3.8). A correlation of $q_{max}^{ir} = 10^{3.80} \times f_{oc}$ was obtained by linear curve fitting of these data. This equation is in agreement with a previous study (Kan et al., 1998), in which the authors summarized the experimental data in many field and laboratory studies, and proposed that for most neutral hydrophobic organic compounds, $q_{max}^{ir} = 10^{3.8} \times f_{oc}$. However, this correlation seems to over-estimate the $q_{max}^{ir}$ value observed for Dickinson sediment, and may suggest $q_{max}^{ir}$ value depends on some other properties of the sediment. One possibility is, again, the association of sorbate molecules with some highly insoluble and
hydrophobic materials in the sediment. Such highly insoluble and hydrophobic materials could be DNAPL type of petroleum product deposits, or wax, which is a common product of many natural and anthropogenic processes. If this were true, it would be reasonable that Lake Charles and Utica sediments exhibit stronger entrapment of sorbed compounds. This is because both sediments have been affected by petroleum chemicals for dozens of years and thus, may contain more DNAPLs or waxy materials than clean sediments such as Lula and Dickinson sediments. More research is needed, however, before any conclusion can be drawn.

3.5 Summary

In this chapter, experiments were designed to further understand the unique characteristics of the irreversible compartment, particularly, the dependency of these unique characteristics on the physical and chemical properties of both chemicals and sediments. The eight experiments in this study fell into two divisions -- first, the resistant desorption of closely related compounds in the same sediment (Experiments 3.1 to 3.5); and second, the resistant desorption of the same compound in different sediments (Experiments 3.3, and 3.6 to 3.8). Also, most experiments conducted previously covered a relatively low range of both solid and aqueous phase concentrations. In this study, the sediments were saturated with sorbates, so that both the maximum sorption capacity and the irreversible sorption capacity were filled after sorption, and the desorption results covered a wide concentration range -- more than 5 orders of magnitude. The observed sorption and desorption behaviors in this study were consistent with previous observations. First, sorption odd linear, even when aqueous concentrations approach chemical solubility. Second, a maximum irreversible sorption
capacity exists for all the chemical-sediment combinations. Third, after about one or two days, the aqueous phase concentration, in equilibrium with the irreversible compartment, is not time-dependent, indicating that the observed phenomenon is probably not a simple kinetic or diffusion-limited process as has been suggested by numerous other researchers. Fourth, $K_{oc}^{ir}$ is constant among different chemical-sediment combinations. These observations suggest that sorption and desorption are not controlled by the same mechanism(s). The sorption and desorption results are well modeled with an irreversible sorption model, which accounts for the contributions of both the reversible and irreversible compartments. Thus, the model can be used as a reliable model to predict the resistant release of hydrophobic organic contaminants from natural soils and sediments. One parameter of the irreversible compartment, $q_{max}^{ir}$, however, has greater uncertainty. The $q_{max}^{ir}$ values observed in this study exhibited poor correlation with the $K_{ow}$ values and the solubility of the five chlorinated benzenes, however, the magnitude of $q_{max}^{ir}$ might be affected by a combined effect of these two chemical properties. For sorption of the same compound in different sediments, $q_{max}^{ir}$ might be estimated as $q_{max}^{ir} = 10^{3.8} \times f_{oc}$. The observed variation in $q_{max}^{ir}$ values might also suggest that the irreversibly sorbed compounds are associated with some highly insoluble and hydrophobic materials, such as high molecular weight NAPLs and waxes.
<table>
<thead>
<tr>
<th>Sediment</th>
<th>Particle size (μm)</th>
<th>Organic carbon content, f_{oc} (%)</th>
<th>Sorbed contaminants</th>
<th>PAHs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dickinson</td>
<td>&lt; 53</td>
<td>1.5</td>
<td>Petroleum hydrocarbons, PAHs, polychlorinated aromatic and aliphatic compounds</td>
<td>-</td>
</tr>
<tr>
<td>Lake Charles</td>
<td>0.11 - 0.50</td>
<td>4.1</td>
<td>-</td>
<td>PAHs</td>
</tr>
<tr>
<td>Lula</td>
<td>0.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Utica</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2: Experimental protocols

I. Dickinson Sediment

Exp. 3.1: 1,2-Dichlorobenzene
1st cycle: 6 repetitive sorption ($C_0 \sim 50$ mg/L, 3 to 5 days per step) -- 15 repetitive desorption (1 to 4 d)
2nd cycle: 1 sorption ($C_0 \sim 50$ mg/L, 5 d) -- 18 repetitive desorption (2 to 10 d) -- 1 Tenax desorption (3 d) -- 5 repetitive desorption (6 hr to 7 d)

Exp. 3.2: 1,2,4-Trichlorobenzene
1st cycle: 10 repetitive sorption ($C_0 \sim 17$ mg/L, 3 to 5 d) -- 12 repetitive desorption (1 to 4 d)
2nd cycle: 1 sorption ($C_0 \sim 17$ mg/L, 5 d) -- 17 repetitive desorption (2 to 10 d) -- 1 Tenax desorption (3 d) -- 5 repetitive desorption (6 hr to 7 d)

Exp. 3.3: 1,4-Dichlorobenzene
1 continuous sorption (4 weeks) -- 5 repetitive desorption (2 to 10 d) -- 3 Tenax desorption (3 to 7 d) -- 21 repetitive desorption (12 h to 10 d)

Exp. 3.4: 1,2,3,4-Tetrachlorobenzene
1 continuous sorption (4 months) -- 3 repetitive desorption (3 to 6 d) -- 3 Tenax desorption (2 to 4 d) -- 13 repetitive desorption (1 to 23 d) -- 3 Tenax desorption (1 to 5 d) -- 7 repetitive desorption (1 to 13 d)

Exp. 3.5: Hexachlorobenzene
1 continuous sorption (4 months) -- 3 repetitive desorption (3 to 6 d) -- 3 Tenax desorption (2 to 4 d) -- 7 repetitive desorption (1 to 23 d)

II. Lula Sediment

Exp. 3.6: 1,4-Dichlorobenzene
1 continuous sorption (65 d) -- 8 repetitive desorption (2 to 6 d) -- 3 Tenax desorption (4 to 6 d) -- 6 repetitive desorption (1 to 8 d)

III. Lake Charles Sediment

Exp. 3.7: 1,4-Dichlorobenzene
1 continuous sorption (65 d) -- 8 repetitive desorption (2 to 6 d) -- 3 Tenax desorption (4 to 6 d) -- 6 repetitive desorption (1 to 8 d) -- 2 Tenax desorption (2 d) -- 7 repetitive desorption (1 to 13 d)

IV. Utica Sediment

Exp. 3.8: 1,4-Dichlorobenzene
1 continuous sorption (65 d) -- 8 repetitive desorption (2 to 6 d) -- 3 Tenax desorption (4 to 6 d) -- 6 repetitive desorption (1 to 8 d) -- 2 Tenax desorption (2 d) -- 7 repetitive desorption (1 to 13 d)

*Solution matrix: 0.01 M NaCl, 0.01 M CaCl₂, 0.01 M NaN₃. Solid/solution ratio: 2 g sediment, 42 mL solution. Mixing: tumbling at 1 rpm. Repetitive sorption: 90% supernatant replaced with freshly prepared sorbate solution. Continuous sorption: 10 g sediment and solid compound (in dialysis bag) equilibrated with 35 mL electrolyte solution. Tenax desorption: Tenax replaced with 0.25 g clean Tenax. Repetitive desorption: 90% supernatant replaced with fresh electrolyte solution.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Formula</th>
<th>Molecular Weight</th>
<th>$T_m$ (°C)</th>
<th>Solubility (mg/L)</th>
<th>Log $K_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dichlorobenzene</td>
<td>C₈H₇Cl₂</td>
<td>147.2</td>
<td>-17.0</td>
<td>93 - 140</td>
<td>3.38</td>
</tr>
<tr>
<td>1,4-dichlorobenzene</td>
<td>C₈H₇Cl₂</td>
<td>147.2</td>
<td>53.1</td>
<td>60</td>
<td>3.38</td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>C₈H₅Cl₃</td>
<td>181.5</td>
<td>16.9</td>
<td>41</td>
<td>4.00</td>
</tr>
<tr>
<td>1,2,3,4-tetrachlorobenzene</td>
<td>C₈H₄Cl₄</td>
<td>215.9</td>
<td>47.5</td>
<td>8.2</td>
<td>4.55</td>
</tr>
<tr>
<td>hexachlorobenzene</td>
<td>C₈H₃Cl₆</td>
<td>284.8</td>
<td>2.9</td>
<td>0.0058</td>
<td>5.50</td>
</tr>
</tbody>
</table>

Table 3.3: Physical and chemical properties of the five chlorinated benzenes used in sorption and desorption experiments. Data were obtained and calculated from Schwarzenbach et al. (1992).
Table 3.4: Summary of the results of sorption and desorption experiments, including solid phase concentrations at the end of sorption and desorption cycles, respectively; observed partition coefficients in sorption; observed apparent partition coefficients associated with the resistant fraction; and the irreversible sorption capacities.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Sediment</th>
<th>Compound</th>
<th>Log $K_{ow}$</th>
<th>$q_0$ $^a$ (μg/g)</th>
<th>Log $K_{ec}$</th>
<th>$q_{max}^{ss}$ (μg/g)</th>
<th>$q_{max}^{rm}$ (μg/g)</th>
<th>$C_{rm}$ (μg/L)</th>
<th>Log $K_{esc}^{rm}$ (L/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Dickinson</td>
<td>1,2-DCB</td>
<td>3.38</td>
<td>960</td>
<td>3.05 ± 0.05 $^b$</td>
<td>2108 - 3174</td>
<td>6.37</td>
<td>0.81 ± 0.19</td>
<td>5.44 ± 0.10</td>
</tr>
<tr>
<td>3.2</td>
<td>Dickinson</td>
<td>1,2,4-TCB</td>
<td>4.00</td>
<td>442</td>
<td>3.42 ± 0.06 $^b$</td>
<td>3875</td>
<td>13.6</td>
<td>1.3 ± 0.29</td>
<td>5.46 ± 0.11</td>
</tr>
<tr>
<td>3.3</td>
<td>Dickinson</td>
<td>1,4-DCB</td>
<td>3.38</td>
<td>562</td>
<td>2.78</td>
<td>1360</td>
<td>14.5</td>
<td>1.4 ± 0.55</td>
<td>5.38 ± 0.17</td>
</tr>
<tr>
<td>3.4</td>
<td>Dickinson</td>
<td>1,2,3,4-TeCB</td>
<td>4.55</td>
<td>688</td>
<td>3.87</td>
<td>2749</td>
<td>15.3</td>
<td>2.0 ± 0.53</td>
<td>5.33 ± 0.10</td>
</tr>
<tr>
<td>3.5</td>
<td>Dickinson</td>
<td>HCB</td>
<td>5.50</td>
<td>6.12</td>
<td>4.93</td>
<td>17.3</td>
<td>0.450</td>
<td>0.15 ± 0.02</td>
<td>5.31 ± 0.05</td>
</tr>
<tr>
<td>3.6</td>
<td>Lake Charles</td>
<td>1,4-DCB</td>
<td>3.38</td>
<td>2330</td>
<td>2.97</td>
<td>3718</td>
<td>271</td>
<td>6.9 ± 1.1</td>
<td>5.32 ± 0.08</td>
</tr>
<tr>
<td>3.7</td>
<td>Lula</td>
<td>1,4-DCB</td>
<td>3.38</td>
<td>116</td>
<td>2.86</td>
<td>245</td>
<td>0.970</td>
<td>0.92 ± 0.16</td>
<td>5.26 ± 0.08</td>
</tr>
<tr>
<td>3.8</td>
<td>Utica</td>
<td>1,4-DCB</td>
<td>3.38</td>
<td>2660</td>
<td>3.18</td>
<td>2539</td>
<td>202</td>
<td>3.28 ± 0.16</td>
<td>5.81 ± 0.02</td>
</tr>
</tbody>
</table>

$^a$ Measured by solid extraction. $^b$ Average values of individual steps in repetitive sorption. $^c$ $q_{max}^{ss}$ estimated as: $q_{max}^{ss} = 0.63 K_{ow} f_{ec} C_i$. $^d$ Fitted with the least square fitting method, using the irreversible sorption isotherm (Equation 3.1) and experimental sorption and desorption data.
Figure 3.1: Pictorial representation of the continuous sorption approach. Solid form compound is encapsulated in a dialysis membrane bag (MWCO 1000), and is in equilibrium with its aqueous phase and sorbed phase.
Figure 3.2: Plot of sediment phase concentrations of 1,4-dichlorobenzene with desorption step in Experiments 3.6 and 3.8. Desorption clearly exhibits a bi-phasic pattern. In both experiments, Tenax desorption was applied in Steps 9 to 11, and Steps 18 and 19. Concentrations dropped significantly during the first set of Tenax desorption (Steps 9 to 11), but remained nearly constant during the second set of Tenax desorption (Steps 18 and 19).
Figure 3.3.a: Plot of the aqueous phase concentrations, with respect to the irreversibly compartment, with varied desorption time in Experiments 3.1 and 3.2. For both graphs, data points are observed aqueous phase concentrations in the last 5 desorption steps. Desorption time in the last 5 desorption steps in each experiment was randomly chosen, and was not necessarily increased from one step to the next step.
Figure 3.3.b: Plot of the aqueous phase concentrations, with respect to the irreversibly compartment, with varied desorption time in Experiments 3.4 and 3.5. For both graphs, data points are observed aqueous phase concentrations in the last 7 (6) desorption steps. Desorption time in the last few desorption steps in each experiment was randomly chosen, and was not necessarily increased from one step to the next step.
Figure 3.3.c: Plot of the aqueous phase concentrations, with respect to the irreversibly compartment, with varied desorption time in Experiments 3.3 and 3.7. For both graphs, data points are observed aqueous phase concentrations in the last 7 desorption steps. Desorption time in the last few desorption steps in each experiment was randomly chosen, and was not necessarily increased from one step to the next step.
Figure 3.4: Plot of observed aqueous phase concentrations of 1,2,3,4-tetrachlorobenzene and hexachlorobenzene with the contact time in continuous sorption experiments -- Experiments 3.3 and 3.4. Dashed lines are aqueous solubility of these two compounds.
Figure 3.5.a: Plot of the model predicted vs. experimentally-observed isotherms of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene in Dickinson sediment. Solid lines are predicted isotherms using the irreversible sorption isotherm (Equation 3.1). Dotted lines are the linear isotherms plotted using the $K_{oc}$ values obtained in sorption experiments. The diamond symbols are experimental observations.
Figure 3.5.b: Plot of the model predicted vs. experimentally-observed isotherms of 1,2,3,4-tetrachlorobenzene and hexachlorobenzene in Dickinson sediment. Solid lines are predicted isotherms using the irreversible sorption isotherm (Equation 3.1). Dotted lines are the linear isotherms plotted using the $K_{oc}$ values obtained in sorption experiments. The diamond symbols are experimental observations.
Figure 3.6.a: Plot of the model predicted vs. experimentally-observed isotherms of 1,4-dichlorobenzene in Dickinson and Lake Charles sediments. Solid lines are predicted isotherms using the irreversible sorption isotherm (Equation 3.1). Dotted lines are the linear isotherms plotted using the $K_{oc}$ values obtained in sorption experiments. The diamond symbols are experimental observations.
Figure 3.6.b: Plot of the model predicted vs. experimentally-observed isotherms of 1,4-dichlorobenzene in Lula and Utica sediments. Solid lines are predicted isotherms using the irreversible sorption isotherm (Equation 3.1). Dotted lines are the linear isotherms plotted using the $K_{oc}$ values obtained in sorption experiments. The diamond symbols are experimental observations.
Figure 3.7: Plot of the $K_{oc}$ values observed in sorption experiments and the partition coefficients with respect to the irreversible compartment in desorption experiments, with $K_{ow}$ value. Data were obtained with five chlorinated benzenes and four sediments in Experiments 3.1 to 3.8.
Figure 3.8: Plot of the irreversible sorption capacities observed in Experiments 3.1 to 3.5 with chemical $K_{ow}$ value (upper plot) and aqueous solubility (lower plot). The irreversible sorption capacities ($\mu g/g$ sediment) were normalized with sediment organic carbon content in the graphs.
Figure 3.9: The dependency of irreversible sorption capacity (Experiments 3.1 to 3.5) on a combinatory factor of chemical $K_{w}$ and aqueous solubility. Irreversible sorption capacities (µg/g sediment) were normalized with sediment organic carbon content. The unit of aqueous solubility is mg/L.
Figure 3.10: Plot of the irreversible sorption capacities with sediment organic carbon content. Data were obtained from the desorption of 1,4-dichlorobenzene from Dickinson, Lake Charles, Lula, and Utica sediments (Experiments 3.3, and Experiments 3.6 to 3.8).
Chapter 4: Mechanistic Aspects of Irreversible Sorption

4.1 Introduction

It is not yet clear what mechanisms control the irreversible sorption of hydrophobic organic contaminants in natural soils and sediments. As discussed in Chapter 2, dozens of mechanisms have been proposed to interpret this unique process. While each mechanism has its own merits, none can be applied universally to any experimental or field observation. Ideally, the mechanism controlling the irreversible sorption process can be understood with microscopic-level studies. However, many macroscopic observations can also give valuable insights to the nature of the process. In this chapter, three sets of experiments were conducted to further understand the mechanism controlling the irreversible sorption of hydrophobic organic contaminants in natural sediments. These three sets of experiments included: the effect of competitive sorption on the release of sorbed compounds; effect of caustic treatment of sediments on the release of sorbed compounds; and effect of external mechanic force on the release of sorbed compounds. Competitive sorption, caustic treatment, and external mechanic force have been observed to significantly affect sorption (Xing and Pignatello, 1998; Carrol et al., 1994; Pereira, et al., 1988). Thus, comparing the effects on sorption and that on desorption may serve to better understand the nature of the irreversible binding. The implications of the experimental results on the mechanism controlling non-ideal sorption and desorption are discussed.

The effect of competitive sorption on the release of both aged and freshly sorbed compounds was studied with Dickinson sediment. The sorbates studied were
naphthalene and 1,4-dichlorobenzene, and the competitive sorbate used was trans-cinnamic acid. Trans-cinnamic acid was selected as the competitive sorbate because it was found that among 11 aromatic acids commonly found in pore water, it exhibited the strongest suppression effect on the sorption of 1,3-dichlorobenzene (Xing and Pignatello, 1998). Before conducting competitive sorption experiments, the sediment samples used in these two experiments were initially saturated with naphthalene and 1,4-dichlorobenzene, respectively. Then, extensive desorption was conducted to remove the reversible compartments from the sediments. Thus, experimental results in this study reflect the effect of competitive sorption on the release from the irreversible compartment only. For both chemical-sediment combinations, sorption and desorption have been studied extensively in previous research (Kan et al., 1994; Fu et al., 1994; Kan et al., 1996; Kan et al., 1998; Chen, 1999b), and thus, these research provide background information for this study. In addition, the competitive effect of naphthalene on the release of aged 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene from Lake Charles sediment has been studied previously (Chen, 1997). The results are reanalyzed in this chapter and are compared with the experimental observations in this study.

The effect of caustic treatment on the desorption from the irreversible fraction was examined using historically-contaminated Lake Charles sediments. Sediment samples in this study were initially treated with NaOH solutions of different concentrations. Then, desorption was conducted with Tenax resin. The release of sorbed 1,3- and 1,4-dichlorobenzenes, hexachlorobenzene, and hexachlorobutadiene from the sediments treated with different NaOH solutions are compared to understand the effect of caustic ions on irreversible binding.
The effect of external mechanic force on the desorption from the reversible and irreversible compartments was studied with 1,4-dichlorobenzene and Dickinson sediment. The two sediment samples in this study were initially saturated with 1,4-dichlorobenzene and then, extensive desorption was performed with both Tenax and electrolyte solution. While one sample was mixed by tumbling as in all the other experiments, the other was mixed by horizontal shaking. Shaking is much milder than tumbling and may better simulate the conditions in natural environments. The experimental results obtained by shaking and tumbling are compared.

4.2 Experimental

4.2.1 Sorbates and Sediments

Both $^{14}$C-radiolabeled naphthalene and non-labeled naphthalene (Sigma Chemical, MO) were used in this study. The specific activity of $^{14}$C-radiolabeled naphthalene was 49.8 mCi/mmol, and the solution was made in methanol. This solution was further diluted in methanol to prepare the stock solutions of $^{14}$C-radiolabeled naphthalene. Stock solutions of non-labeled naphthalene were prepared by dissolving solid naphthalene (>98%) in methanol. Trans-cinnamic acid (Acros Organics, NJ) stock solution was also prepared by dissolving the solid compound in methanol.

The sediments used in these experiments included Dickinson and Lake Charles sediments. The physical and chemical properties of these two sediments are discussed in details in Chapter 3. Organic carbon contents of these two sediments are 1.5% and 4.1%, respectively.
4.2.2 Radio-Active Analysis

Concentrations of $^{14}$C-labeled compounds were determined by the liquid scintillation counting method. To check the concentration in a stock solution, about 10 μL of the solution was added to 10 mL of scintillation cocktail (OrganicSafe™, Beckman Instrument Co., Fullerton, CA) in a pre-weighed scintillation counting vial (Wheaton, Millville, NJ). To measure the concentration in an aqueous solution, about 0.2 to 1 mL of the solution was added in 10 mL of scintillation cocktail (ReadySafe™, Beckman Instrument Co., Fullerton, CA). The amount of aqueous solution used in radio-active analysis was calculated based on the predicted concentration range in the solution. Optimum amount of solution added would give a scintillation counts from 5,000 to 50,000 dpm. Once the solution was added in scintillation cocktail, the scintillation vial was thoroughly shaken by hand and analyzed on a Beckman LS3801 liquid scintillation counter (Beckman Instrument Co., Fullerton, CA) for 10 to 20 minutes. Finally, the scintillation count reading (in dpm) was converted to the concentration of the $^{14}$C-labeled compound. A number of standard solutions, with known concentrations of $^{14}$C-labeled naphthalene were used to produce a standard curve.

4.2.3 Competitive Sorption

Competitive effect on the desorption from the irreversible compartment was studied with two chemical-sediment systems, with trans-cinnamic acid as the competitive sorbate. The two systems included: 1) desorption of naphthalene from the
irreversible compartment in Dickinson sediment (Experiment 4.3); and 2) desorption of 1,4-dichlorobenzene from the irreversible compartment in Dickinson sediment (Experiment 4.4). The protocols of these two experiments are summarized in Table 4.1.

Before starting a competitive sorption experiment, a 100 mg/L trans-cinnamic acid solution was prepared with a trans-cinnamic acid stock solution (53.5 mg/L in methanol) and an electrolyte solution containing 0.01 M of NaCl, CaCl₂, and NaN₃. The trans-cinnamic acid stock solution was prepared by dissolving a certain amount of solid compound in methanol. To prepare aqueous trans-cinnamic acid solution, about 100 mL of the electrolyte solution (volume measured by weighing) and a Teflon-coated magnetic stir bar were added in a 100 mL volumetric flask. The pH of the electrolyte solution was measured with a pH meter (Fisher Scientific, Fair Lawn, NJ) before being used in solution preparation. While the electrolyte solution was stirred, 0.18 mL of trans-cinnamic acid stock solution was delivered into the solution with a small syringe. The volumetric flask was then capped and the solution was stirred for 1 hour to give a uniform concentration. The trans-cinnamic acid solution was then transferred to a 150 mL glass beaker and the pH was measured again. Then, a digital titrator and a 0.16 N NaOH solution cartridge (Hach Company, Loveland, CO) were used to adjust the pH of the aqueous trans-cinnamic acid solution to the same value of the electrolyte solution. The pH control was designed so that the experimental results would only reflect the effect of competitive sorption, but not the effect of pH.

The sediment samples used in these two experiments were obtained from two previous studies. The sample in Experiment 4.3 was the sample used by Fu et al. (1994), with which the sorption and desorption of naphthalene in Dickinson sediment were studied. The sample in Experiment 4.4 was the sample used in Experiment 3.3 (Chapter
3), with which the sorption and desorption of 1,4-dichlorobenzene in Dickinson sediment were studied. For both samples, the sediment was initially saturated with the sorbate and then desorbed extensively until the irreversible compartment was reached. Before being used in this study, 11 repetitive desorption with electrolyte solution were performed for both samples, with the objective to re-establish the equilibrium between the aqueous phase and the irreversible compartment (because the two samples were left undisturbed upon the completion of previous studies). Then, for both samples, two more desorption were conducted using the electrolyte solution containing 100 mg/L of trans-cinnamic acid. To begin a competitive sorption experiment, 90% of the supernatant at the end of desorption Step 11 was removed from the reaction vial. The vial was then filled with 100 mg/L trans-cinnamic acid solution, tightly capped, and tumbled at 1 rpm for 3 days. The aqueous phase concentrations of naphthalene and 1,4-dichlorobenzene were monitored at the end of the two desorptions with competitive sorbate. At the end of the second desorption, the sediments were also extracted so that the solid phase concentrations of naphthalene and 1,4-dichlorobenzene could be measured.

Detailed experimental procedures for the desorption of aged 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene from Lake Charles sediment, with naphthalene as the competitive sorbate, have been reported previously (Chen, 1997). Two experiments (numbered as Experiments 4.1 and 4.2 in Table 4.1) were set up to understand the effect of naphthalene sorption on the release of sorbed compounds. In each of the two experiments, 0.5 mL of 50.0 mg/L $^{14}$C-radiolabeled naphthalene solution (in methanol) and 0.2 mL of $1.21 \times 10^4$ mg/L of non-labeled naphthalene solution (in hexane) were added to a 40 mL glass vial. The vial was held near horizontally and was rotated by hand to evaporate the organic solvents.
Afterwards, about 1.4 g Lake Charles sediment and 42 mL electrolyte solution were introduced to the vial. The vial was tumbled at 1 rpm for 6 days and both solution and sediment phase concentrations were analyzed at the end of the competitive sorption experiments.

4.2.4 Caustic Treatment

The effect of caustic treatment on the release of historically sorbed compounds was studied with four Tenax-desorption experiments using Lake Charles sediment (Experiments 4.5 to 4.8, Table 4.1). The sediment sample in each experiment was pre-treated by a NaOH solution before conducting desorption experiments. The concentration of NaOH solution applied in these experiments were $0, 10^{-4}, 10^{-2}$, and 1M, for Experiments 4.5 to 4.8, respectively. Each solution also contained 0.01 M of NaCl, CaCl$_2$, and NaN$_3$, to control the ionic strength and to inhibit bacterial growth. In each experiment, the sediment was initially mixed with about 40 mL NaOH solution for 3 days. Then, about 0.5 g of Tenex resin was added to the reaction vial. The vial was tumbled again for 3 days, and centrifuged at 3000 g for 30 minutes upon the completion of the experiment. Tenax resin was then transferred to a 25 mL clean glass vial and extracted with about 7 mL of acetone. The vial containing acetone and Tenax resin was left on a horizontal shaker overnight. Afterwards, it was centrifuged at 2500 g for 15 minutes, and acetone extract was taken to determine the concentrations of 1,3- and 1,4-dichlorobenzenes, hexachlorobenzene, and hexachlorobutadiene. Finally, fresh Tenax resin was added to the vial to initiate another desorption. Two desorptions were completed for each experiment.
4.2.5 External Mechanic Force

One experiment of the sorption and desorption of 1,4-dichlorobenzene (Experiment 4.9, Table 1) was conducted to study the effect of external mechanic force on the desorption from the reversible and irreversible compartment in natural sediments. The experimental protocols were nearly identical to those of Experiment 3.3 in Chapter 3. The sediment samples used in Experiments 3.3 and 4.9 were prepared together -- about 10 g Dickinson sediment was saturated with 1,4-dichlorobenzene using the dialysis continuous sorption approach. For both Experiments 3.3 and 4.9, about 2 g of the pre-saturated sediment was extracted extensively with Tenax resin and electrolyte solution, with aqueous phase concentrations being measured at the end of each desorption and solid phase concentrations measured upon the completion of multiple-step desorption. The only difference between these two experiments was that in Experiment 4.9, the reaction system was equilibrated using a horizontal shaker (Yamato, Japan), rather than a tumbler as being used in Experiment 3.3 and all of the other experiments. Aqueous and solid phase concentrations in Experiment 4.9 were monitored in the same way as discussed in Chapter 3.

4.3 Results

4.3.1 Effect of Competitive Sorption

The competitive effect of naphthalene on the release of aged 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene
from Lake Charles sediment was studied in a previous research (Chen, 1997). The results were reanalyzed and are summarized in Table 4.2. Data from the control experiments are summarized in Columns 4 to 6. The aqueous phase concentrations listed in Column 4 were the average values observed in four individual desorption experiments (reported in Chen, 1997). These four desorption experiments all used 1.4 g of sediment and about 42 mL electrolyte solution containing 0.01 M of NaCl, CaCl₂, and NaN₃. The solid phase concentrations (Column 5) were calculated with the initial solid phase concentrations (Column 3) and the average aqueous phase concentrations (Column 4) on the basis of mass balance. The $K_\infty$ values listed in Column 6 are the apparent $K_\infty$ values of these four compounds. The apparent $K_\infty$ value is defined as the ratio of organic carbon normalized solid phase concentration $q$ (mg/kg of OC) to the solution phase concentration $C_w$ (mg/L). The values listed in Column 6 were obtained by dividing the solid phase concentration $q$ (Column 5) with the aqueous phase concentration $C$ (Column 4) and the fractional organic carbon content $f_\infty$ as:

$$K_\infty \text{ (L/kg)} = \frac{q \text{ (mg/kg sediment)}}{f_\infty \text{ (kg OC/kg sediment)}} \frac{1}{C \text{ (mg/L)}}$$  \hspace{1cm} (4.1)

The results of Experiments 4.1 and 4.2 are summarized in Columns 7 to 9. The aqueous phase concentrations summarized in Column 7 are the average values observed in the two competitive sorption experiments -- Experiments 4.1 and 4.2. The solid phase concentrations (Column 8) were calculated from mass balance, and the apparent $K_\infty$ values in Column 9 were calculated using Equation 4.1. In both Experiments 4.1 and
4.2. 2.42 mg of naphthalene was introduced to the reactor to initiate naphthalene sorption. After the single-step sorption, the solid and solution phase concentrations of naphthalene in Experiment 4.1 were 406 μg/g and 22.9 mg/L, corresponding to an apparent $K_{oc}$ value of $10^{2.64}$. Similarly, the observed solution phase concentration in Experiment 4.2 was 24.7 mg/L (Because the same amount of naphthalene was used in these two experiments, it is reasonable to assume that approximately the same amount of naphthalene also sorbed to the sediment in Experiment 4.2.). Since the observed aqueous phase concentrations in these two experiments were close to the solubility of naphthalene -- 31 mg/L, the corresponding solid phase concentrations were close to the maximum sorption capacity of naphthalene in this sediment. Therefore, these two experiments should reflect the maximum possible competitive effect of naphthalene. As in Table 4.2, the initial solid phase concentrations of 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene were 4.70, 16.7, 49.5, and 3.50 μg/g, respectively, before naphthalene sorption. The solid phase concentration of naphthalene is therefore 8.2 to 120 times as high as the initial concentrations of these four compounds.

Comparing the release of the four chlorinated compounds in the control and competitive sorption experiments, it was found that the release of all four compounds was facilitated when the sediment was saturated with naphthalene. The facilitated desorption can be understood with Figure 4.1, which compares the desorption without competition (Column 1 of each compound), desorption with naphthalene competition (Column 2), and estimated equilibrium concentration (Column 3) for each compound. Without competition, the observed concentrations at the end of a single-step desorption were 4.8, 5.9, 0.41, and 0.66 μg/L for 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene, respectively (Column 5 of Table 4.2).
The concentrations of these compounds at the end of the naphthalene sorption experiments were 15, 18, 0.58, and 0.71 μg/L, respectively (Column 8 of Table 4.2). Thus, the aqueous phase concentrations were increased by a factor of 1.1 to 3.1 with the sorption of naphthalene. The apparent $K_{oc}$ values of these compounds at the end of control and competitive sorption experiments are summarized in Columns 7 and 10. As a comparison, the equilibrium partition coefficients of these compounds were estimated using the following equation (Karickhoff, 1984):

$$K_{oc} = 0.63 \times K_{ow}$$

(4.2)

The calculated equilibrium $K_{oc}$ values were $10^{3.30}$ for 1,3-dichlorobenzene, $10^{3.18}$ for 1,4-dichlorobenzene, $10^{3.30}$ for hexachlorobenzene, and $10^{4.70}$ for hexachlorobutadiene. Comparing the $K_{oc}$ values listed in Columns 7 and 10, it was found that the $K_{oc}$ values of these four compounds were decreased in the competitive sorption experiments. For each compound, the ratio of the $K_{oc}$ value in competitive sorption experiment to the $K_{oc}$ value in control experiment is summarized in Column 11. These ratios are similar to those reported by Xing and Pignatello (1998). However, even though smaller $K_{oc}$ values were observed in competitive sorption experiments, these values were still considerably larger than the estimated equilibrium $K_{oc}$ values. Also, experimental results showed that the suppression effect of naphthalene on the $K_{oc}$ value was more significant for 1,3- and 1,4-dichlorobenzenes sorbed to Lake Charles sediments (Rows 1 and 2 of Table 4.2).
The impact of the competitive sorption of trans-cinnamic acid on the desorption of naphthalene and 1,4-dichlorobenzene, from Dickinson sediment are also summarized in Table 4.2. In both Experiments 4.3 and 4.4, the reversible compartments in the sediments were removed before conducting competitive sorption. This was designed so that the experimental results would reflect the effect of competitive sorption on the desorption from the irreversible compartment only. With initial concentration of trans-cinnamic acid as high as 100 mg/L, neither naphthalene nor 1,4-dichlorobenzene exhibited an increase in desorption (The aqueous phase concentration of 1,4-dichlorobenzene with desorption step is plotted in Figure 4.2 as an example.). Before the competitive sorption experiments, the aqueous phase concentration of naphthalene reached a relatively constant value -- 1.50 μg/L in five repetitive desorptions, with a small standard deviation of 0.03 μg/L. The corresponding partition coefficient, $K_{oc}^{irr}$, was $10^{5.92}$, and was within the reported range -- $K_{oc}^{irr} = 10^{5.53 \pm 0.48}$, for compounds with $K_{ow}$ values from $10^{2.3}$ to $10^{6.4}$ (Kan et al., 1998). The average aqueous phase concentration of naphthalene observed in the two trans-cinnamic acid sorptions was $1.48 \pm 0.02 \mu g/L$, and was almost identical to the concentration observed before trans-cinnamic acid sorption. The observed $K_{oc}^{irr}$ values of naphthalene in the two trans-cinnamic acid sorptions were both $10^{5.92}$. Similarly, before the competitive sorption experiments, an average aqueous phase concentration of $1.50 \pm 0.47 \mu g/L$ was observed for 1,4-dichlorobenzene in five repetitive desorptions, with respect to the irreversible compartment. The observed average concentration of 1,4-dichlorobenzene in the two trans-cinnamic acid sorptions was $1.50 \pm 0.84 \mu g/L$, indicating that no significant change in the release of sorbed 1,4-dichlorobenzene occurred. The $K_{oc}^{irr}$ values of 1,4-
dichlorobenzene before and after trans-cinnamic acid sorption were essentially identical -- $10^{3.37}$.

4.3.2 Caustic Effect on Desorption

In Figure 4.3 are summarized some preliminary results of the effect of caustic treatment on the release of aged 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene from Lake Charles sediment. Each column represents the cumulative release of a compound in two successive Tenax desorptions. Column 1 of each compound is the result obtained in the control experiment (Experiment 4.5), in which sediment was not treated with NaOH solution; Columns 2, 3, and 4 represent the results obtained with the sediments which were treated with $10^{-4}$, $10^{-2}$, and 1 M NaOH solutions (Experiments 4.6 to 4.8), respectively. As in the figure, treating sediment with caustic solution had no significant effect on the release of aged chlorinated compounds. Among the four compounds studied, only 1,3-dichlorobenzene exhibited a significant increase when sediment was treated with 1M NaOH. Cumulative desorption percentages of this compound in Experiments 4.5 to 4.7 were similar -- about 35%, and a 15% increase was observed in Experiment 4.8. For 1,4-dichlorobenzene and hexachlorobenzene, the cumulative release from untreated sediment was slightly higher than those from treated sediments. The release of hexachlorobutadiene varied quite a bit among the four experiments. However, the variation was independent of the concentration of NaOH applied.

4.3.3 Effect of External Mechanic Force
In Figure 4.4 is summarized the potential impact of external force on the release of sorbed compounds. The two experiments (Experiments 3.3 and 4.9) were set up similarly -- in both experiments, multiple-step desorption were conducted with about 2 g of Dickinson sediment pre-saturated with 1,4-dichlorobenzene. The two reaction systems, however, were mixed with horizontal shaking and tumbling, respectively. Results included in Figure 4.4 are desorption data, the fitted desorption isotherms with Equation 3.1, and the linear sorption isotherms plotted with data observed in the dialysis sorption experiment (detailed in Table 3.3). As in the figure, alternating mixing protocol had essentially no impact on the desorption of 1,4-dichlorobenzene from Dickinson sediment, especially for the desorption from the irreversible fraction. In fact, sorption and desorption data obtained from shaking and tumbling experiments are very similar, especially at lower concentration range. Particularly, for both $q_{\text{max}}^{\text{irr}}$ and $K_{\text{irr}}^{\infty}$ values (as indicated by the plateau and the intercept of the isotherm), the observed values in Experiments 3.3 and 4.9 are nearly identically. Thus, the fitted isotherms of these two experiments nearly overlap.

4.4 Discussion

Experimental results of the impact of competitive sorption on the release of sorbed compounds fell into two categories -- 1) desorption of chlorinated benzenes and hexachlorobutadiene from Lake Charles sediment (Experiments 4.1 and 4.2) was enhanced by the competitive sorption of naphthalene; and 2) desorption of naphthalene and 1,4-dichlorobenzene from Dickinson sediment (Experiments 4.3 and 4.4) was not affected by the competitive sorption of trans-cinnamic acid. The deviation in the impact of competitive sorption exhibited by these two categories might have been due to the
different experimental protocols applied. According to a previous study (Chen et al., 1999a), a fraction of sorbed chlorinated benzenes and hexachlorobutadiene in Lake Charles sediment was associated with the reversible compartment, and 10 to 15 desorptions with electrolyte solution were required to remove this fraction. Since only two desorptions were conducted in Experiments 4.1 and 4.2, the amount of compounds desorbed should have been primarily from the reversible compartments. In Experiments 4.3 and 4.4, however, most of the reversible fractions in the sediments were removed before the sediments were used in competitive sorption experiments, and thus, desorption should have primarily reflected the contribution of the irreversible fraction. These experimental results, therefore, might imply that while competitive sorption could affect the desorption from the reversible fraction to a certain extent, its effect on the desorption from the irreversible fraction might be minimal. This would be consistent with the results of Xing and Pignatello (1998). Furthermore, the impact of naphthalene sorption on the release of sorbed compounds was more significant for 1,3-dichlorobenzene and 1,4-dichlorobenzene than for hexachlorobenzene and hexachlorobutadiene. As in Column 11 of Table 4.2, naphthalene sorption sufficiently suppressed the apparent $K_{oc}$ values of 1,3- and 1,4-dichlorobenzenes to about 70%. However, it only suppressed the apparent $K_{oc}$ values of hexachlorobenzene and hexachlorobutadiene by 29% and 9%, respectively. The apparent $K_{oc}$ values of 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene in the control experiments were $10^{4.36}$, $10^{4.82}$, $10^{5.37}$, and $10^{5.10}$ (Column 7, Table 4.2), respectively. According to a previous study (Chen et al., 1999a), these $K_{oc}$ values gradually increased as the reversible compartment being removed, until they reached the constant $K_{oc}^{irr}$ values, $10^{5.62}$, $10^{5.73}$, $10^{6.70}$, and $10^{5.44}$, respectively, for these compounds. The consistently high $K_{oc}$ value for hexachlorobenzene sorbed to Lake Charles sediment
may suggest that there is a small amount of pure solid hexachlorobenzene phase in this sediment. Since the $K_{ac}$ values of hexachlorobenzene and hexachlorobutadiene were considerably closer to their $K_{ir}$ values than those of 1,3- and 1,4-dichlorobenzenes, a smaller fraction of these two compounds should have been associated with the reversible compartment. Thus, the fact that naphthalene sorption had more significant effect on the release of 1,3- and 1,4-dichlorobenzenes than on hexachlorobenzene and hexachlorobutadiene further implies that competitive sorption had a more profound impact on the desorption from the reversible compartment only.

The experimental results in this study may have significant implication on the mechanism(s) controlling irreversible sorption of hydrophobic organic compounds in natural sediments. Xing and Pignatello (1998) proposed a dual-mode sorption mechanism to interpret the effect of competitive sorption. According to this mechanism, sorption takes place in both dissolution and hole-filling domains in soil organic matters; sorption to the “holes” -- some specific sites that are postulated as nanometer-size voids -- is characterized by a Langmuir-type isotherm; the competitive effect stems from the competition on the specific sites (holes) within soil organic matters; and a competitive solute (co-solute) functions by competing for the holes that bind the designated solute, causing a suppression in the sorption of the designated compound. Quantitatively, competitive sorption can be described by the following equation, as proposed in a recent publication (Pignatello, 1998):

$$S_i = \frac{S_i^0 b_i C}{1 + b_i C + b_{co} C_{co}}$$

(4.3)
where \( b_{co} \) and \( C_{co} \) are the affinity constant and aqueous concentration, respectively, of the co-solute; \( b_i \), \( S_i^0 \), and \( S_i \) are the affinity constant, capacity constant, and total sorption, respectively, of a specific hole site \( i \) with regard to the designated solute; and \( C \) is the aqueous phase concentration of the designated solute. Pignatello proposed that at sufficiently high co-solute concentration \( C_{co} \), \( S_i \) is reduced to zero, the Langmuir term drops out, and the overall isotherm (refer to Equation 2.38) of the designated solute becomes linear.

If the association with specific sites in natural organic matters were the cause of irreversible sorption, competitive sorption would affect the release of a sorbed compound similarly. This is, if compounds A and B compete for specific sorption sites, a similar competition would be expected to occur if compound A were applied to a sediment in which compound B is sorbed, or vice versa. In Experiments 4.1 and 4.2, the sediments were essentially saturated with naphthalene. That is, if competitive sorption were ever going to be predominant in this system, it should have been so in these experiments when the concentration of the co-solute, naphthalene, was at saturation. According to Equation 4.3, at such a high co-solute concentration \( C_{co} \), the Langmuir sorption of the four chlorinated compounds to the specific sites in soil organic matters would have been eliminated, and the desorption of these compounds would have become linear, i.e., the observed \( K_{oc} \) values would have been close to their equilibrium values. Nonetheless, even though the observed partition coefficients of these four compounds (Column 10, Table 4.2) were suppressed to some extent by competitive sorption, the observed values were much higher than those predicted via linear equilibrium values. These observations, however, are consistent with the irreversible sorption model (Kan et
al., 1998), if it is assumed that a significant fraction of sorbed chlorinated compounds was irreversibly bound to the sediment. Thus, while specific interaction might be a satisfactory explanation for the effect of competitive sorption on the enhanced release from the reversible fraction, it could not account for the irreversible binding of chlorinated benzenes and hexachlorobutadiene in the sediments used in this study.

Results observed in Experiments 4.3 and 4.4 provided more explicit evidence on the nature of irreversible sorption. Since a majority of the reversible fraction in the sediments was removed before competitive sorption experiments, it is reasonable to assume that naphthalene (Experiment 4.3) and 1,4-dichlorobenzene (Experiment 4.4) sorbed in the sediments were primarily associated with the irreversible fraction. If irreversible sorption were due to the specific interactions between sorbate molecules and the specific sites in soil organic matter, the sorbed naphthalene and 1,4-dichlorobenzene should have been bound primarily to these specific sites. Thus, if a co-solute could strongly compete for these sites, the desorption of naphthalene and 1,4-dichlorobenzene would have been greatly facilitated, if not becoming completely reversible. Since trans-cinnamic acid was reported to compete strongly on the sorption of 1,3-dichlorobenzene (Xing and Pignatello, 1998), it probably should also compete strongly with naphthalene and 1,4-dichlorobenzene, which have similar structure and polarity as 1,3-dichlorobenzene. Thus, applying trans-cinnamic acid to the sediments in Experiments 4.3 and 4.4 should have greatly enhanced the desorption of naphthalene and 1,4-dichlorobenzene. Nevertheless, the competitive sorption of trans-cinnamic acid had no effect on the desorption of these two compounds. Thus, these observations again imply that the observed irreversible sorption of these two compounds could not be attributed simply to the sorption to the specific sites in the sediments.
Experimental results in this study seem to be in agreement with the irreversible sorption mechanism proposed previously by Kan et al. (1998). In this mechanism, irreversible sorption is attributed to some kind of post-sorption conformational change or physical rearrangement of soil organic matter, and as a result, a portion of sorbed compounds is entrapped within sediment matrices and becomes unavailable for desorption. Evidence supporting the irreversible mechanism includes the observation that desorption from this irreversible compartment is independent on the physical and chemical properties of sorbates and that after a short equilibration of a few days, long-term slow desorption is not observed (Kan et al., 1998; Devitt and Wiesner, 1998). Devitt and Wiesner (1998) observed that atrazine sorbed to natural organic molecules was significantly retained by a dialysis bag; atrazine sorbed to small organic molecules was not retained; and naphthalene was not retained in either case. They also suggest the retention is due to the sorption of atrazine to natural organic matter followed by a physical entrapment. Using data reported in their paper, a $K_{oc}^{ir}$ value of $10^{5.5}$ can be validated for atrazine, which is in agreement with the irreversible model.

Preliminary results obtained in this study showed that caustic treatment of sediment might not be able to effectively enhance the release of sorbed compounds from the irreversible fraction. For neutral, non-polar, and non-ionizable molecules such as chlorinated hydrocarbons, the caustic effect is mainly due to the interactions between caustic ions and the inorganic and organic components in sediment. For example, it was found that the acid form of soils, clays, and sediments was a far better adsorbent for many materials (Bailey et al., 1968; Hayes et al., 1968; MacNamara and Toth, 1970). Caustic treatment of sediment may have a profound effect on desorption, because organic macromolecules are generally densely coiled at low pH but relatively loose and flexible at neutral or higher pH value (Carroll et al., 1994; Ghosh and Schnitzer, 1980;
Cornel et al., 1986). Therefore, caustic ions may function by “swelling” soil organic matter, and result in an increase in desorption of sorbed hydrocarbons, in addition to desorbing the organic matter. Experiments in this study were designed so that results would reflect the effect of caustic treatment on the release from the irreversible fraction, and thus the nature of the irreversible compartment could be further understood.

According to previous research (Chen, 1997), the reversible fraction in Lake Charles sediment could be removed with 1 or 2 Tenax-desorptions, while the desorption from the irreversible fraction could not be enhanced greatly even with multiple Tenax desorptions. Thus, the cumulative desorption observed in the control experiment, Experiment 4.5, in which sediment was not treated with NaOH, should primarily account for the desorption from the reversible fraction. If caustic treatment of sediment could facilitate the desorption from the irreversible fraction, a gradual increase in the cumulative desorption would have been observed in the order of Experiments 4.5, 4.6, 4.7, and 4.8, because the concentration of NaOH was increased in the same order.

Furthermore, several researchers have demonstrated that natural organic matter becomes much more soluble in 1 M NaOH solution. If this were true, nearly complete release of sorbed compounds from the sediment might have been expected in Experiment 4.8. Nevertheless, data observed in this study did not show systematic evidence of an enhanced desorption of aged chlorinated hydrocarbons, even when sediments were treated with 1 M NaOH. Although under the experimental protocols of this study, it is not clear whether caustic treatment of sediment could affect the desorption from the reversible fraction, it is possible that caustic treatment has little impact on the desorption from the irreversible compartment. This might suggest that either the caustic solution could not access the sites where sorbed molecules were physically entrapped, or sorbed molecules were associated with some kinds of very insoluble or hydrophobic organic
materials (such as waxes) which were insensitive to 1 M NaOH. Similar results were reported in other studies, in which caustic treatment exhibited no effect on the release from the resistant fraction (Carroll et al., 1994; Mortensen, 1965). More data is needed, however, to draw any further conclusions.

Preliminary results from the experiments comparing the mixing effect (shaking vs. tumbling) on desorption showed that external mechanic force may have little effect on the release of sorbed compounds from soils and sediments. While tumbling provides a far better mixing between solution and sediment and may represent some extreme conditions such as sediment dredging, horizontal shaking (with one or two gentle mixing by hand per day) may better represent the relatively tranquil conditions in aquatic systems. Thus, the similarity in desorption behavior between these two sets of experiments (as indicated by the overlapped isotherms in Figure 4.4) implies that laboratory observations may indeed closely represent what happens in the field. More importantly, such experimental observations may provide valuable insights on the nature of the irreversible binding. For a system with a small solid to solution ratio (as in Experiments 3.3 and 4.9), tumbling results in a thoroughly-mixed suspension of the sediment, compared with the same system equilibrated by shaking in which the sediment essentially lays on the bottom of the vial. Thus, more sediment surfaces are exposed to the aqueous solution in the tumbling experiment. Also, the well-mixed system essentially eliminates the thickness of the relatively stagnant solid-liquid interface and thus, greatly reduces the effect of diffusion and increases the concentration gradient between the bulk solution and the region where aqueous solution is in equilibrium with the solid phase. If irreversible sorption were due to some kind of diffusion limitation, desorption would probably have been facilitated in such a well-equilibrated system. Therefore, although Experiments 3.3 and 4.9 alone cannot demonstrate the mechanism
controlling irreversible sorption, they provide additional support for the irreversible sorption model proposed by Kan et al. (1998). These two experiments show that the desorption from the reversible compartment is probably a quick process, and the equilibrium can be reached even in relatively tranquil conditions. These experiments also show that the unique characteristics of the irreversible compartment are not affected by external force.

From the experiments in this chapter, it seems that the irreversible compartment is relatively stable and cannot be affected by a number of factors. Therefore, it is quite possible that this kind of binding is due to (at least partly) the association or entrapment of sorbate molecules with some sort of highly insoluble or hydrophobic materials, such as high molecular weight NAPLs or waxes. If this were true, this kind of entrapment would not be easily broken by factors such as competitive sorption, caustic treatment, or external mechanic force. In addition, the association of organic molecules with such highly insoluble and recalcitrant materials may also explain the observation that most chemical-sediment combinations exhibit a similar $K_{\infty}$ value. This is because once a compound becomes associated with such materials, their own physical and chemical properties are covered by the properties of the highly insoluble materials. Thus, the overall desorption behavior would be that exhibited by the desorption of the highly insoluble or hydrophobic materials. Similarly, this is probably the cause of the extremely slow release kinetics associated with the irreversible compartment.

4.5 Summary
To further understand the nature of the irreversible compartment and the mechanism(s) controlling irreversible sorption, the effects of competitive sorption, caustic treatment, and external mechanic force on the release of sorbed hydrocarbons from natural sediments were studied. While competitive sorption facilitated the release from the reversible fraction, its effect on the release from the irreversible fraction was minimal. Similarly, caustic treatment and external mechanic force could not affect the release of sorbed compounds from the irreversible compartment to any significant extent. These experimental results are in agreement with a previously proposed irreversible sorption mechanism, in which irreversible sorption is attributed to a physical entrapment of organic molecules in sediment matrices. Also, the irreversible binding is relatively stable and may partly be due to the associated of sorbates to some kind of highly insoluble or hydrophobic materials. Thus, once the desorption from the irreversible compartment dominates the overall sorption of a contaminant, the release of this contaminant is not likely to be affected by sudden environmental changes such as varied pH. The release should also be insensitive to the presence or discharge of other contaminants. Furthermore, the similarity exhibited by the two experiments conducted with shaking and tumbling may imply that sediment disturbance, such as dredging will not significantly facilitate the release of sorbed contaminants and cause much environmental concern.
Table 4.1: Experimental protocols

I. Competitive Sorption

Exp. 4.1 & 4.2
- Co-solute: naphthalene
- Sorbates: 1,3-dichlorobenzene 1,4-dichlorobenzene
  hexachlorobenzene  hexachlorobutadiene
- Procedures: - 2.42 mg naphthalene loaded to a 42 mL vial
  - 2 repetitive desorption conducted with 1.4 g Lake
    Charles sediment and 40 mL electrolyte solution

Exp. 4.3 & 4.4
- Co-solute: trans-cinnamic acid
- Sorbates: Exp. 4.3: naphthalene
  Exp. 4.4: 1,4-dichlorobenzene
- Procedures: - samples * initially saturated with sorbate and then
  desorbed extensively
  - 2 desorption conducted with 100 mg/L trans-
    cinnamic acid solution

II. Caustic Effect

- NaOH concentration: Exp. 4.5: 0  Exp. 4.6: \(10^{-4}\) M
  Exp. 4.7: \(10^{-2}\) M  Exp. 4.8: 1 M
- Solid/solution ratio: 1.4 g sediment, 0.5 g Tenax, 40 mL solution
- Procedures: 2 Tenax desorption

III. External Mechanic Force

Exp. 4.9
- multiple-step sorption and desorption with electrolyte solution and Tenax
- sample mixed by horizontal shaking

* Sediment sample of Exp. 4.3 was obtained from a previous study, Fu et al., (1994); and sediment sample of Exp. 4.4 was from Exp. 3.3 (Chapter 3).
Table 4.2: Summary of competitive sorption effect on the release of sorbed compounds, including the effect of naphthalene on the release of 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene from Lake Charles sediment, and the effect of trans-cinnamic acid on the release of naphthalene and 1,4-dichlorobenzene, respectively, from Dickinson sediment.

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Compound</th>
<th>Log $K_{oc}$</th>
<th>$q_0$ (µg/g)</th>
<th>$C_w$ (µg/L)</th>
<th>$q$ (µg/g)</th>
<th>Log $K_{oc,1}$</th>
<th>$C_w$ (µg/L)</th>
<th>$q$ (µg/g)</th>
<th>Log $K_{oc,2}$</th>
<th>$K_{oc,2}/K_{oc,1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Charles</td>
<td>1,3-DCB</td>
<td>3.50</td>
<td>4.70</td>
<td>4.8 ± 1.4 (4)</td>
<td>4.52</td>
<td>4.36</td>
<td>15 ± 1.7 (2)</td>
<td>4.23</td>
<td>3.83</td>
<td>0.30</td>
</tr>
<tr>
<td>Lake Charles</td>
<td>1,4-DCB</td>
<td>3.38</td>
<td>16.7</td>
<td>5.9 ± 1.8 (4)</td>
<td>16.3</td>
<td>4.82</td>
<td>18 ± 1.3 (2)</td>
<td>15.9</td>
<td>4.32</td>
<td>0.33</td>
</tr>
<tr>
<td>Lake Charles</td>
<td>HCB</td>
<td>5.50</td>
<td>49.5</td>
<td>0.41 ± 0.25 (4)</td>
<td>49.4</td>
<td>6.47</td>
<td>0.58 ± 0.07 (2)</td>
<td>49.4</td>
<td>6.32</td>
<td>0.71</td>
</tr>
<tr>
<td>Lake Charles</td>
<td>HBut</td>
<td>4.90</td>
<td>3.50</td>
<td>0.66 ± 0.23 (4)</td>
<td>3.38</td>
<td>5.10</td>
<td>0.71 ± 0.33 (2)</td>
<td>3.38</td>
<td>5.06</td>
<td>0.91</td>
</tr>
<tr>
<td>Dickinson</td>
<td>Naph</td>
<td>3.36</td>
<td>--</td>
<td>1.50 ± 0.03 (3)</td>
<td>17.4</td>
<td>5.92</td>
<td>1.48 ± 0.02 (2)</td>
<td>17.4</td>
<td>5.92</td>
<td>1.0</td>
</tr>
<tr>
<td>Dickinson</td>
<td>1,4-DCB</td>
<td>3.38</td>
<td>--</td>
<td>1.50 ± 0.47 (3)</td>
<td>4.9</td>
<td>5.37</td>
<td>1.50 ± 0.84 (2)</td>
<td>4.9</td>
<td>5.37</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$q_0$ values (Column 4) were measured by Soxhlet extraction (Chen et al., 1999a). $q$ values (Columns 6 and 9) were calculated from mass balance using $q_0$ values and observed $C_w$ values. The numbers in the parentheses in Columns 5 and 8 are the numbers of individual experiments that were used to calculate the average $C_w$ values. $K_{oc}$ values were obtained using $K_{oc} = (q/f_{oc})/C_w$. $f_{oc}$ values of Lake Charles and Dickinson sediments are 4.1% and 1.5%, respectively.
Figure 4.1: Effect of competitive sorption of naphthalene on the desorption of 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene from Lake Charles sediment. Column 1 of each compound is the aqueous phase concentration observed in control experiments, in which desorption was conducted with electrolyte solution; Column 2 is the enhanced desorption with the sorption of naphthalene to the sediment (average of Experiments 4.1 and 4.2); and Column 3 is the estimated concentration under equilibrium assumptions.
Figure 4.2: Effect of competitive sorption on the release of 1,4-dichlorobenzene from Dickinson sediment. Aqueous phase concentration is plotted with desorption step. The 6th desorption was a Tenax desorption. The last two desorptions were conducted with 100 mg/L trans-cinnamic acid solution.
Figure 4.3: Effect of caustic treatment on the desorption of 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, and hexachlorobutadiene from Lake Charles sediment. Column 1 of each compound is the cumulative desorption in two successive Tenax-desorption experiments with untreated sediment. Column 2, 3, 4 are the desorption from the sediments treated with 0.0001 M, 0.01 M, and 1 M of NaOH solutions, respectively.
Figure 4.4: Illustration of the effect of external mechanic force on the sorption and desorption behaviors of 1,4-dichlorobenzene in Dickinson Sediment. The two experiments were set up identically, while the equilibration was achieved by horizontal shaking and tumbling, respectively.
Chapter 5: Impact of Irreversible Sorption on Sediment Quality

5.1 Introduction

Among the numerous physical, chemical, and biological processes controlling the fate, transport, availability, and risk of organic contaminants in surface and subsurface environments, sorption and desorption are possibly the most fundamental and dominant processes. The existence of the irreversible entrapment of sorbed compounds in natural soils and sediments makes it even more complicated to understand and to quantitatively model sorption and desorption processes. Once the desorption from the irreversible compartment dominates the overall release of sorbed compounds, the extent of desorption could be orders of magnitude lower than that predicted with the conventional approach. Thus, irreversible sorption could have a tremendous impact on the accuracy of fate and transport modeling and risk assessment, the efficiency of remediation and biodegradation, and the effectiveness of environmental policies and decision making. In addition, it is of central importance in sediment management and pollution control to establish a quantitative model for the resistant desorption -- a model that can be used to guide regulatory and remediation practices.

In the previous two chapters, the characteristics of irreversible sorption were further defined with systematic laboratory studies. The results from this research and a
series of research conducted by the Rice group (Kan et al., 1998; Chen et al., 1999a; Chen et al., 1999b) have demonstrated that the irreversible sorption model provides not only a sound explanation of the mechanism controlling the resistant release of hydrophobic organic contaminants from natural soils and sediments, but also an accurate approach to quantitatively predict this resistant release. In this chapter, the conceptual and mathematical models are tested with the observations from two comprehensive field studies, to test whether the irreversible model can be applied universally to most chemical-sediment combinations, especially in the field. The two field studies were conducted by independent research groups and thus, provide good test cases for the effectiveness of the irreversible sorption model. The impact of irreversible sorption on contaminant fate and transport modeling, contaminant bioavailability and risk assessment, and environmental regulations is discussed. Also discussed in this chapter is the development of a one-dimensional solute transport model, which takes into account of advection, dispersion, sorption and irreversible sorption, and natural attenuation of organic contaminants in subsurface environments.

5.2 Field Observations and Model Prediction

Field observations from two extensive studies on sediment contamination -- the study on Boston Harbor sediment and the study on Lake Charles sediment -- were used to test the effectiveness of the irreversible sorption model. Boston Harbor sediment is well-
known for being heavily contaminated with PAHs and PCBs. A series of studies have
been conducted to understand the distribution of these two classes of compounds in the
harbor (Shiaris and Jambard-Sweet, 1986; N.O.A.A., 1988; McGroddy and Farrington,
1995; McGroddy et al., 1996). The concentrations of a number of PAHs and PCBs in
both porewater and sediment were measured for three core samples taken from the
Harbor. The in-situ partition coefficients of these compounds were reported. Lake
Charles sediment has also been heavily affected by chemical and petroleum industries for
over forty years. In 1985, the U.S. Geological Survey began a series of studies to
determine the fate and transport of various organic compounds in the lower Calcasieu
River, Louisiana. As part of the study results, Pereira et al. (1988) delineated the
distribution of a numbers of halogenated organic compounds between Lake Charles
sediment and the pore water. In this section, field data from these two studies are
summarized, reconstructed, and compared with the results predicted using the irreversible
sorption model developed herein.

The sediment-porewater distribution of two PAHs and two PCBs in Boston
Harbor is summarized in Table 5.1. The compounds are phenanthrene, pyrene, PCB-101
(2,2',4,5,5'-polychlorobiphenyl), and PCB-138 (2,2',3,4,4',5- polychlorobiphenyl). The
organic carbon contents for the three sediment core samples are 5.19, 5.47, and 3.34%,
respectively. For each core sample, concentrations of these four compounds in sediment
and porewater were measured. The authors also reported the equilibrium $K_{oc}$ values
(Column 2 of Table 5.1) of these compounds that have been observed in laboratory
sorption experiments (Chin and Gschwend, 1992; Gschwend and Wu, 1985), as well as
the predicted equilibrium aqueous phase concentration \( C_{eq} \), from total sediment phase
concentrations of these compounds. The sediment phase concentrations (Column 5 of
Table 5.1) of these compounds were not reported in this paper. Thus, the concentrations
in Column 5 were reconstructed using the equilibrium \( K_{oc} \) values and the reported
equilibrium aqueous concentrations as: \( q = K_{oc} \times C_{eq} \).

The sediment-porewater distribution of these four compounds were simulated
with the following irreversible sorption isotherm (modified from Equation 3.1):

\[
q = K_{oc} C + \frac{K_{oc}^{irr} q_{max}^{irr} C}{q_{max}^{irr} + K_{oc}^{irr} C}
\]  
(5.1)

Note that the units of \( q \) and \( q_{max}^{irr} \) in the equation are \( \mu g/g \) OC, instead of \( \mu g/g \) sediment as
in Equation 3.1. The unit of \( C \) is \( mg/L \). To use this isotherm, the following parameters
of each compound need to be specified:

1) \( K_{ow} \) -- the octanol-water partition coefficient (dimensionless);

2) \( K_{oc} \) -- the organic carbon content normalized partition coefficient for the
   reversible compartment (L/Kg);
3) $K_{oc}^{irr}$ -- the organic carbon content normalized partition coefficient for the irreversible compartment ($L/Kg$); and

4) $q_{max}^{irr}$ -- the irreversible sorption capacity ($\mu g/g$ OC).

The $K_{ow}$, $K_{oc}$, $K_{oc}^{irr}$, $q_{max}^{irr}$ values of the four compounds are summarized in Columns 6 to 9 of Table 5.1. The $K_{oc}$ value of each compound (Column 7 of Table 5.1) is the average of the three $K_{oc}$ values reported for the three sediment cores (Column 3). As discussed in the previous chapters, most compounds exhibit a similar $K_{oc}^{irr}$ value of $10^{5.5}$. Thus, $10^{5.5}$ was assigned as the $K_{oc}^{irr}$ value for all four compounds. The $q_{max}^{irr}$ values of these compounds were calculated using the following equation (modified from the correlation proposed by Kan et al., 1998):

$$q_{max}^{irr} = 37765 \times K_{ow}^{-0.23}$$  \hspace{1cm} (5.2)

The reported sediment and porewater concentrations of these four compounds and the isotherms predicted with the irreversible sorption isotherm (Equation 5.1) are summarized in Figure 5.1. The linear isotherms of these compounds are also included as comparisons. The linear isotherms were estimated with the following equation:

$$q = K_{oc} C$$  \hspace{1cm} (5.3)
with the $K_\infty$ values listed in Column 7 of Table 5.1. Note that similar to Equation 5.1, the unit of $q$ is $\mu g/g$ OC. For both PCBs, the linear isotherm and the irreversible sorption isotherm are similar, because the $K_\infty$ and $K_{irr}^\infty$ values are very close (Columns 7 and 8). Because solid phase concentrations were normalized by $f_\infty$ in this simulation, for each compound, the sediment-porewater distributions in the 3 core samples were plotted on the same graph. For the PAHs, significant deviation exists between the linear and irreversible sorption isotherms. As in Figure 5.1, the desorption data of these four compounds are better modeled by the irreversible sorption isotherms, especially for the two PAHs, for which the linear model failed completely. It is necessary to notice that field data showed even higher resistance to desorption than that predicted with the irreversible sorption model, as indicated in Figure 5.1a. While this may suggest that the laboratory derived $K_{irr}^\infty$ value might systematically underestimate irreversible sorption, it could also be due to some kind of kinetic limitation (Kan et al., 1998). Nevertheless, such experimental results imply that the irreversible sorption isotherm at least provides a much more accurate approach to predict the maximum possible release of sorbed compounds.

The sediment and porewater concentrations of six chlorinated hydrocarbons observed in the filed study on Lake Charles sediment are summarized in Table 5.2. These compounds include 1,2- and 1,4-dichlorobenzenes, 1,2,4-trichlorobenzene, 1,2,3,4-
tetrachlorobenzene, hexachlorobenzene, and hexachlorobutadiene. The parameters used to plot the irreversible sorption isotherms are also summarized in the Table 5.2. The $K_{oc}$ values listed in Column 4 were calculated from the observed aqueous and solid phase concentrations (Columns 2 and 3) in the field. The equilibrium $K_{oc}$ values (Column 6 of Table 5.2) used in the irreversible sorption isotherms were estimated using: $K_{oc} = 0.63 K_{ow}$ (Karickhoff, 1984). The $K_{oc}^{irr}$ values of all six compounds were assumed to be $10^{5.5}$, and the $q_{max}^{irr}$ values were calculated using Equation 5.2. Once again, both $q$ and $q_{max}^{irr}$ are normalized by the sediment organic carbon content and have a unit of $\mu g/g$ OC.

The field observations are compared to the predictions with both the linear and irreversible sorption isotherms in Figure 5.2. The linear isotherms were predicted with Equation 5.3, using the $K_{oc}$ values in Column 6 of Table 5.2. The irreversible isotherms were predicted with Equation 5.1, using the $K_{oc}$, $K_{oc}^{irr}$, and $q_{max}^{irr}$ values listed in Columns 6 to 8. As in Figure 5.2, the sediment-porewater distributions of the six compounds observed in the field cannot be modeled by the conventional linear isotherms. The field data of 1,3-dichlorobenzene, 1,4-dichlorobenzene, and hexachlorobutadiene are well-predicted with the irreversible sorption isotherms -- the sediment-porewater data of these three compounds nearly lie on the predicted isotherms. For 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and hexachlorobenzene, however, the irreversible sorption isotherm underestimated the resistance to desorption. While once again, this might suggest that the laboratory derived irreversible sorption isotherm may systematically underestimate irreversible sorption, it is questionable whether the reported solid phase
concentrations of these three compounds reflect the realistic concentrations in the sediment. According to a previous study (Chen, 1997), the concentration of 1,2,4-trichlorobenzene in Lake Charles sediment is relatively low, and is not uniformly distributed in the sediment samples received. The reported sediment phase concentration of hexachlorobenzene is unreasonably high -- 7544 μg/g OC in this field study. Since the solubility of hexachlorobenzene in water is only about 5.8 μg/L, the maximum sorption capacity of this compound should only be 1157 μg/g OC, if predicted using Equation 5.3 and a $K_{oc}$ value of $10^{5.3}$ (Column 6 of Table 5.2). This indicates that non-sorbed phase hexachlorobenzene probably exists in the sediment. Previous research (Chen, 1997) also showed significant variation in the sediment phase concentration of hexachlorobenzene in Lake Charles sediment.

In summary, the comparison between field observations and model predictions as shown in Figures 5.1 and 5.2 indicate that the irreversible sorption isotherm could quantitatively predict the resistant release of hydrophobic organic contaminants from field contaminated sediments. Along with the laboratory data shown in the previous chapters, it seems that the irreversible sorption isotherm provides thus far the most accurate approach to modeling the resistant release of hydrophobic organic contaminants from natural sediments. Also, since all the parameters used in the isotherm either are readily available or can be easily predicted, the model can be easily adapted in most environmental practices.
5.3 Impact on Contaminant Fate and Transport Modeling

Sorption and desorption of contaminants could significantly affect the fate and transport of contaminants in surface and subsurface environments. Sorption of contaminants to soil particles causes contaminants to move more slowly than the advective movement of groundwater -- an effect typically referred to as "retardation". Thus, retardation must be modeled to predict the movement of contaminants in subsurface. The effect of sorption on the migration of contaminant plume can be illustrated with Figure 5.3. The figure shows the movements of two contaminants from a DNAPL zone (shaded areas in Figures 5.3.a and 5.3.b) 30 years after the pollution occurs in a confined aquifer. The groundwater flow and solute transport were predicted with MODFLOW and MT3D, respectively (McDonald and Harbaugh, 1988; Zheng, 1992). Groundwater flow is basically from the north to the south in the aquifer. All of the hydrogeological parameters (such as hydraulic conductivity, hydraulic gradient, soil bulk density, aquifer effective porosity, and recharge) used in flow and solute transport simulations are identical. The initial concentrations and dispersivity of the two compounds were also assumed to be identical. However, the partition coefficient of Compound A (simulated in Figure 5.3.a) is 0.3 L/kg, and is five times as small as that of Compound B (simulated in Figure 5.3.b) -- 1.5 L/kg. Sorption of these two compounds in the aquifer was assumed to follow the linear isotherm. The two simulations clearly show that when sorption is controlled by a higher partition coefficient, plume migrates much more slowly. The retardation in contaminant transport caused by sorption becomes
even more significant for compounds with higher hydrophobicity and soils with higher organic carbon content.

As discussed in Chapter 2, the effect of sorption on contaminant fate and transport in groundwater is typically incorporated into a "retardation factor" -- $R$, which is equivalent to the ratio of velocity of the sorbing contaminant and the velocity of the ground water seepage flow. The retardation factor $R$ takes different forms according to the isotherm used to describe sorption. For example, when sorption is described as the linear model, $R$ is expressed as:

$$R = 1 + \frac{\rho}{n} K_p$$  \hspace{1cm} (5.4)

When sorption takes the Langmuirian form, $R$ is:

$$R = 1 + \frac{\rho}{n} \frac{b Q^0}{(1 + b C)^2}$$  \hspace{1cm} (5.5)
The symbols in the above two equations have been defined in Chapter 2. In addition, one or more kinetics factors can be incorporated into the retardation factor $R$ (e.g., Equation 2.48), considering that groundwater migration rate may be faster than the equilibrium time required for sorption and desorption processes.

While precisely describing sorption and desorption of organic contaminants is critical to the accuracy of fate and transport modeling, sorption and desorption are very poorly modeled in all the solute transport models currently available. Most simple solute transport models can only simulate linear sorption. More sophisticated models, such as the widely used Bioplume, MT3D, and RT3D, typically incorporate linear, Langmuir, and Freundlich isotherms. Unfortunately, none of these isotherms can accurately predict the resistant release of sorbed contaminants from soils and sediments. This inability becomes even more problematic when the desorption process dominates the interaction between solute and soils, such as in pump and treat. Failure in describing sorption process inevitably forces modelers to vary other modeling parameters, such as hydraulic conductivity and dispersivity, to obtain better calibration results and therefore, introducing more uncertainties and errors in model simulations.

Since the irreversible sorption isotherm is a far better model to describe the resistant release of sorbed compounds, it could significantly improve the modeling accuracy once incorporated into solute transport models. The irreversible sorption model is a relatively simple isotherm that correlates solid and aqueous phase concentrations, and can be fit into most solute transport models currently available. However, unlike the
linear isotherm, when irreversible sorption isotherm is used to describe desorption, the retardation factor $R$ is also a function of the aqueous phase concentration $C$. Thus, it may be difficult to solve the governing equation for solute transport analytically. Fortunately, most sophisticated solute transport models, such as MT3D and RT3D, solve transport equation using numerical approaches, using either finite difference or finite element methods. Thus, the retardation factor derived from the irreversible sorption isotherm can be easily implemented. The following section describes the implementation of the irreversible sorption isotherm in the governing equation for solute transport.

The governing equation for the one-dimensional advective-dispersive transport of a solute in groundwater is given by:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (5.6)$$

where $C$ is the solution-phase concentration ($M/L^3$) of a chemical; $D$ is the hydrodynamic dispersion coefficient ($L^2/T$); $v$ is the seepage velocity ($L/T$); $x$ is the distance ($L$); and $t$ is the time ($T$). When sorption and first order decay of the solute are considered, the governing equation can be modified as:
\[
\frac{\partial C}{\partial t} + \frac{\rho}{n} \frac{\partial q}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C
\] (5.7)

where \( q \) is the solid phase concentration of the solute (M/M); \( \rho \) is the bulk density of aquifer materials (M/L³); \( n \) is the porosity (dimensionless); and \( \lambda \) is the 1st-order decay coefficient (T⁻¹).

When sorption and desorption follow the linear isotherm, the solid and aqueous phase concentrations can be related as:

\[
q = K_p C = K_\infty f_\infty C
\] (5.8)

Thus, the temporal differentiation of the solid phase concentration is:

\[
\frac{\partial q}{\partial t} = K_p \frac{\partial C}{\partial t} = K_\infty f_\infty \frac{\partial C}{\partial t}
\] (5.9)

When Equation 5.9 is plugged into Equation 5.7, the governing equation becomes to:
\[
\left(1 + \frac{p}{n} K_{oc} f_{oc}\right) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} - \lambda C \tag{5.10}
\]

or,

\[
R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} - \lambda C \tag{5.11}
\]

where \( R = 1 + \frac{p}{n} K_{oc} f_{oc} \) is the retardation factor.

When desorption is controlled by the irreversible sorption isotherm, the correlation between the solid and aqueous phase concentrations of a solute becomes:

\[
q = K_{oc} f_{oc} C + \frac{K_{oc} f_{oc} q_{max}^{irr} C}{q_{max}^{irr} + K_{oc} f_{oc} C} \tag{5.12}
\]

The symbols used above have been defined in Chapters 2 and 3. Note that the "f" factor
is not included in the equation because \( f \) is typically equal to 1 in natural environments.

Differentiating the solid phase concentration \( q \) with regard to time yields:

\[
\frac{\partial q}{\partial t} = \partial \left( K_{oc} f_{oc} C + \frac{K_{oc}^{irr} f_{oc} q_{max}^{irr} C}{q_{max}^{irr} + K_{oc}^{irr} f_{oc} C} \right)
\]

\[ (5.13) \]

i.e.,

\[
\frac{\partial q}{\partial t} = \frac{\partial \left( K_{oc} f_{oc} C \right)}{\partial t} + \frac{\partial \left( \frac{K_{oc}^{irr} f_{oc} q_{max}^{irr} C}{q_{max}^{irr} + K_{oc}^{irr} f_{oc} C} \right)}{\partial t}
\]

\[ (5.14) \]

The first term of the right hand side of Equation 5.14 can be simplified as:

\[
\frac{\partial \left( K_{oc} f_{oc} C \right)}{\partial t} = K_{oc} f_{oc} \frac{\partial C}{\partial t}
\]

\[ (5.15) \]
The second term of the right hand side of Equation 5.14 can be expanded as:

\[
\frac{\partial}{\partial t} \left( \frac{K_{oc}^{irr} f_{oc} q_{max}^{irr} C}{q_{max}^{irr} + K_{oc}^{irr} f_{oc} C} \right) = \frac{1}{q_{max}^{irr} + K_{oc}^{irr} f_{oc} C} \frac{\partial}{\partial t} \left( K_{oc}^{irr} f_{oc} q_{max}^{irr} C \right) \\
+ K_{oc}^{irr} f_{oc} q_{max}^{irr} C \frac{\partial}{\partial t} \left( \frac{1}{q_{max}^{irr} + K_{oc}^{irr} f_{oc} C} \right)
\]

(5.16)

The first term of the right hand side of Equation 5.16 then becomes:

\[
\frac{K_{oc}^{irr} f_{oc} q_{max}^{irr}}{q_{max}^{irr} + K_{oc}^{irr} f_{oc} C} \frac{\partial C}{\partial t}
\]

(5.17)

The second term of the right hand side of Equation 5.16 becomes:
\[ K_{oc} f_{oc} q_{max} C \left[ - \left( \frac{1}{q_{max} + K_{oc} f_{oc} C} \right)^2 \frac{\partial}{\partial t} \left( q_{max}^{irr} + K_{oc}^{irr} f_{oc} C \right) \right] \]

(5.18)

and can be rearranged as:

\[ K_{oc}^{irr} f_{oc} q_{max}^{irr} C \left[ \frac{- K_{oc}^{irr} f_{oc}}{(q_{max}^{irr} + K_{oc}^{irr} f_{oc} C)^2} \right] \frac{\partial C}{\partial t} \]

(5.19)

Combining Equations 5.13 to 5.19 yields:

\[ \frac{\partial q}{\partial t} = \left( K_{oc} f_{oc} + \frac{K_{oc}^{irr} f_{oc} \left( q_{max}^{irr} \right)^2}{(q_{max}^{irr} + K_{oc}^{irr} f_{oc} C)^2} \right) \frac{\partial C}{\partial t} \]

(5.20)

When Equation 5.20 is plugged into the governing equation, the retardation factor \( R \) becomes to:
\[ R = 1 + \frac{\rho}{n} \left( K_{oc} f_{oc} + \frac{K_{oc} f_{oc} (q_{max}^{irr})^2}{(q_{max}^{irr}) + K_{oc} f_{oc} C} \right) \] (5.21)

Thus, the governing equation of solute transport in groundwater -- Equation 5.7 can be expressed as:

\[
\left[ 1 + \frac{\rho}{n} \left( K_{oc} f_{oc} + \frac{K_{oc} f_{oc} (q_{max}^{irr})^2}{(q_{max}^{irr}) + K_{oc} f_{oc} C} \right) \right] \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} - \lambda C
\] (5.22)

Equation 5.22 can be solved by many numerical approaches. The simplest numerical integration method is probably the Euler's method, which can be used with any spatial or temporal interpolation scheme. In addition, since Euler's method is extremely simple, Equation 5.22 can be easily implemented in a computer code. The Euler's Forward-Time Center-Space (FTCS) approximation is derived below as an example of the numerical solutions for Equation 5.22.

According to Tyler's series expansion, a function of a variable x can be expressed
as:

\[ f(x + \Delta x) = f(x) + \Delta x \frac{\partial f}{\partial x} + \frac{(\Delta x)^2}{2!} \frac{\partial^2 f}{\partial x^2} + \frac{(\Delta x)^3}{3!} \frac{\partial^3 f}{\partial x^3} \]

\[ + \ldots + \frac{(\Delta x)^{2n}}{(2n)!} \frac{\partial^{2n} f}{\partial x^{2n}} + \frac{(\Delta x)^{2n+1}}{(2n+1)!} \frac{\partial^{2n+1} f}{\partial x^{2n+1}} + \ldots \]

(5.23)

where \( n \) is an integer. Similarly,

\[ f(x - \Delta x) = f(x) - \Delta x \frac{\partial f}{\partial x} + \frac{(\Delta x)^2}{2!} \frac{\partial^2 f}{\partial x^2} - \frac{(\Delta x)^3}{3!} \frac{\partial^3 f}{\partial x^3} \]

\[ + \ldots + \frac{(\Delta x)^{1n}}{(2n)!} \frac{\partial^{2n} f}{\partial x^{2n}} - \frac{(\Delta x)^{2n+1}}{(2n+1)!} \frac{\partial^{2n+1} f}{\partial x^{2n+1}} + \ldots \]

(5.24)

Rearranging Equation 5.23 yields:
\[
\frac{\partial f}{\partial x} = \frac{f(x + \Delta x) - f(x)}{\Delta x} - \frac{\Delta x}{2!} \frac{\partial^2 f}{\partial x^2} - \frac{(\Delta x)^2}{3!} \frac{\partial^3 f}{\partial x^3} - \ldots \\
= \frac{f(x + \Delta x) - f(x)}{\Delta x} + O(\Delta x)
\]

(5.25)

where \(O(\Delta x)\) represents the error term, indicating this approximation is accurate to the first order of \(\Delta x\). Similarly, rearranging Equation 5.24 yields:

\[
\frac{\partial f}{\partial x} = \frac{f(x) - f(x - \Delta x)}{\Delta x} + \frac{\Delta x}{2!} \frac{\partial^2 f}{\partial x^2} - \frac{(\Delta x)^2}{3!} \frac{\partial^3 f}{\partial x^3} + \ldots \\
= \frac{f(x) - f(x - \Delta x)}{\Delta x} + O(\Delta x)
\]

(5.26)

Alternatively, the approximation for \(\frac{\partial f}{\partial x}\) can be derived by combining Equations 5.23 and 5.24, and can be expressed as:
\[
\frac{\partial f}{\partial x} = \frac{f(x + \Delta x) - f(x - \Delta x)}{2\Delta x} - \frac{(\Delta x)^2}{3!} \frac{\partial^3 f}{\partial x^3} - \frac{(\Delta x)^4}{5!} \frac{\partial^4 f}{\partial x^4} - \ldots
\]

\[
= \frac{f(x + \Delta x) - f(x - \Delta x)}{2\Delta x} + O(\Delta x)^2
\]

(5.27)

Comparing to Equations 5.25 and 5.26, Equation 5.27 is a more accurate approximation for \( \frac{\partial f}{\partial x} \) because it involves a smaller error, \( O(\Delta x)^2 \), -- it is accurate to the second order of \( \Delta x \).

Using similar approaches, the second-order differentiation of \( \frac{\partial^2 f}{\partial x^2} \) can be obtained as:

\[
\frac{\partial^2 f}{\partial x^2} = \frac{f(x + 2\Delta x) - 2f(x + \Delta x) + f(x)}{2\Delta x} + O(\Delta x)
\]

(5.28)

or,
\[
\frac{\partial^2 f}{\partial x^2} = \frac{f(x - 2\Delta x) - 2f(x - \Delta x) + f(x)}{2\Delta x} + O(\Delta x) \quad (5.29)
\]

and or,

\[
\frac{\partial^2 f}{\partial x^2} = \frac{f(x + \Delta x) - 2f(x) + f(x - \Delta x)}{(\Delta x)^2} + O(\Delta x)^2 \quad (5.30)
\]

When using Euler's Forward-Time Central-Space approach to solve the governing transport equation (Equations 5.6 and 5.22), the differentiation of concentration with time at a certain location is approximated by a forward differencing scheme with Equation 5.25 as:

\[
\frac{\partial C}{\partial t} = \frac{C_{i+1}^t - C_i^t}{\Delta t} + O(\Delta t) \quad (5.31)
\]

where \( C_i^t \) and \( C_{i+1}^t \) are the concentrations of a solute at location \( x \) at two adjacent time steps -- time step \( t \) and time step \( t+1 \), respectively. The first-order differentiation of
concentration with respect to space is approximated by a central differencing scheme
with Equation 5.27 as:

\[ \frac{\partial C}{\partial x} = \frac{C_x^{i+1} - C_x^{i-1}}{2\Delta x} + O(\Delta x)^2 \] (5.32)

where \( C_x^{i+1} \) and \( C_x^{i-1} \) are the concentrations of a solute at time step \( t \) at location \( x+1 \) and
\( x-1 \), respectively. The second-order differentiation of concentration with space is also
approximated by the central differencing scheme with Equation 5.30, i.e.:

\[ \frac{\partial^2 C}{\partial x^2} = \frac{C_x^{i+1} - 2C_x^i + C_x^{i-1}}{(\Delta x)^2} + O(\Delta x)^2 \] (5.33)

Therefore, the governing equation (Equation 5.6) for the advective-dispersive transport of
a solute can be expressed as:
\[
\frac{C_{s+1}^t - C_s^t}{\Delta t} = D \frac{C_{s+1}^t - 2C_s^t + C_{s-1}^t}{(\Delta x)^2} - \gamma \frac{C_{s+1}^t - C_{s-1}^t}{2\Delta x} \\
(5.34)
\]

Similarly, when irreversible sorption isotherm and first-order decay are considered, the governing equation -- Equation 5.22 -- can be approximated as:

\[
\left[ 1 + \frac{\rho}{n} \left( K_{oc} f_{oc} + \frac{K_{oc}^{irr} f_{oc} \left(q_{max}^{irr}\right)^2}{\left(q_{max}^{irr} + K_{oc}^{irr} f_{oc} C_s^t\right)^2} \right) \right] \frac{C_{s+1}^t - C_s^t}{\Delta t} = D \frac{C_{s+1}^t - 2C_s^t + C_{s-1}^t}{(\Delta x)^2} - \gamma \frac{C_{s+1}^t - C_{s-1}^t}{2\Delta x} - \lambda C_s^t \\
(5.35)
\]

Essentially, Equation 5.35 approximates derivatives (Equation 5.22) with differences by defining both spatial and temporal domains as discrete sections. The concept of this numerical approximation can be illustrated with Figure 5.4. As in the figure, the concentration of a solute at any time \(t\) and space \(x\), \(C_s^t\), can be solved with the concentrations at three adjacent nodes in the previous time step. For example, \(C_1^t\) can be solved by plugging \(C_0^0\), \(C_1^0\), and \(C_2^0\) into Equation 5.35, and \(C_2^t\) can be solved by using...
$C_1^1$, $C_1^1$, and $C_2^1$, and so on. Thus, once the initial conditions ($C_0^0$, $C_1^0$, $C_2^0$, $\ldots$, $C_m^0$) and boundary conditions ($C_0^n$, $C_1^n$, $C_2^n$, $\ldots$, $C_0^n$) are given, the concentration of a solute at any time $t$ and space $x$ can be calculated using Equation 5.35.

A few stability requirements, though, have to be met for Equation 5.35 to be accurate. This is because a difference equation cannot reasonably approximate a differential equation unless the spatial and temporal domains are sufficiently fine-discretized, i.e., $\Delta x$ and $\Delta t$ are sufficiently small. Otherwise, the model simply will not converge. Three parameters -- $d$, $C_r$, and $P_e$ -- are typically used to describe advection and dispersion properties. The definitions of these three parameters are:

$$d = \frac{D \Delta t}{(\Delta x)^2} \quad (5.36)$$

$d$ indicates the significance of dispersion;

$$C_r = \frac{v \Delta t}{\Delta x} \quad (5.37)$$
C; indicates the significance of advection, and is referred to as the Courant Number; and,

\[ P_c = \frac{v \Delta x}{D} \]  \hspace{1cm} (5.38)

\( P_c \) indicates the relative significance of advection to dispersion, and is referred to as the Peclet Number.

Zheng and Bennet (1995) summarized the stability criteria for the numerical approximation of solute transport equations. A stability criterion for one-dimensional transport can be evaluated independently for the advection and dispersion terms. When only dispersion is considered, the stability criterion is:

\[ d = \frac{D \Delta t}{(\Delta x)^2} \leq 0.5, \text{ or } \Delta t \leq \frac{\Delta x^2}{2D} \]  \hspace{1cm} (5.39)

If only advection term is considered, the stability criterion depends on the spatial weighting scheme used, and is:
When dispersion and advection are solved simultaneously, such as in Equation 5.35, the stability criterion is constrained by both terms as:

\[
\frac{2D \Delta t}{(\Delta x)^2} + \frac{v \Delta t}{\Delta x} \leq 1, \text{ or } \Delta t \leq \frac{(\Delta x)^2}{2D + v \Delta x}
\] (5.41)

A simple one-dimensional solute transport model -- "ISAST" -- was developed based on Equation 5.35. The model is programmed in Excel/Visual Basic, and the visual basic codes for this model is included in Appendix 5.1. The model input window of the program is illustrated in Figure 5.5. The required parameters for this model are very simple and include:

hydrogeological parameters:

1) soil bulk density, \( \rho \) (kg/L);

2) aquifer effective porosity, \( n \) (dimensionless);

3) soil organic carbon content, \( f_{oc} \) (dimensionless); and
4) groundwater seepage velocity, \( v \) (ft/day)

solute chemical-biochemical parameters:

5) dispersion coefficient, \( D \) (ft\(^2\)/day);

6) organic carbon normalized partition coefficient, \( K_\infty \) (L/kg); and

7) first-order decay coefficient, \( \lambda \) (day\(^{-1}\))

modeling parameters:

8) inflow concentration, \( C_0 \) (mg/L) (typically \( C_0 = 0 \));

9) spatial dimension, \( X \) (ft); and

10) simulation time, \( T \) (day)

Note that \( v \), \( D \), \( K_\infty \), and \( \lambda \) can either be input directly or estimated by the model using additional input parameters. If the hydraulic conductivity, \( K \) (ft/day), and groundwater hydraulic gradient, \( \frac{dh}{dL} \), are given, groundwater seepage velocity can be calculated as:

\[
    v = -\frac{K}{n} \frac{dh}{dL} \tag{5.42}
\]
Dispersion coefficient, $D$, can be estimated from the longitudinal dispersivity, $\alpha_x$ (ft), with:

$$D = v \alpha_x$$  \hspace{1cm} (5.43)

Note that in Equation 5.43, the contribution of diffusion to solute transport is assumed to be negligible. In this model, the longitudinal dispersivity, $\alpha_x$, is calculated from the estimated plume length, $L_p$ (ft), as proposed by Xu and Eckstein (1995):

$$\alpha_x = 3.28 \times 0.83 \left[ \log_{10} \left( \frac{L_p}{3.28} \right) \right]^{2.414}$$  \hspace{1cm} (5.44)

Thus, once the estimated plume length is given, $D$ is not required by the model. Instead of inputting the $K_{oc}$ value of the solute, a user can input its $K_{ow}$ value instead, and $K_{oc}$ is then calculated automatically with (Karickhoff, 1984):

$$K_{oc} = 0.63 K_{ow}$$  \hspace{1cm} (5.45)
Also, the users have the option of inputting the half life of the solute, $t^{1/2}$ (day), if $\lambda$ is unavailable. In this case, $\lambda$ will be automatically calculated as:

$$\lambda = \frac{\ln 2}{t^{1/2}} \quad (5.46)$$

Other parameters, including $K_{\infty}^{irr}$, $q_{\max}^{irr}$, $\Delta x$, and $\Delta t$ are typically generated by the model. However, a user can also overwrite the default values by manually inputting numbers.

The model can also deal with non-uniformed initial concentration along the spatial domain, which is probably a more realistic case in the field. This situation is illustrated in Figure 5.6, i.e., concentration in the center of the plume is typically higher. Thus, a user has the option of inputting the highest concentration in the modeling domain ($C_{\max}$) and its location ($X_{\max}$), as well as the concentrations at the two ends of the spatial domain -- $C_o$ (at $x = 0$) and $C_x$ (at $x = X$), respectively. The model will then generate the initial concentrations in each node along the spatial domain assuming concentration follows logarithm distribution. If a uniform initial concentration is assumed, the same value should be given to $C_o$, $C_{\max}$, and $C_x$.

The output of the model are two graphs -- the breakthrough curves (e.g., Figure
5.7) and the concentration profiles (e.g., Figure 5.8). Figure 5.7 shows the output breakthrough curves observed in the monitoring well located at the modeling boundary \((x = X)\) in Figure 5.6). The five breakthrough curves simulate the transport as controlled by the following five different schemes:

1) advection and dispersion;

2) advection, dispersion, and linear sorption;

3) advection, dispersion, linear sorption, and natural attenuation;

4) advection, dispersion, and irreversible sorption; and

5) advection, dispersion, irreversible sorption, and natural attenuation.

As in the figure, the concentration observed in the monitoring well drops rapidly when solute transport is controlled by advection and dispersion only. If the compound can sorb to the aquifer materials, concentration at the boundary drops more slowly, because in this case, aquifer materials act as a constant source and continuously release the contaminant to groundwater. When sorption is controlled by the irreversible sorption isotherm, the concentration essentially levels off after dropping to a certain value. This implies that when desorption is controlled by the irreversible isotherm, it could greatly extend the time required to clean up a contaminated site to regulatory standards, such as MCL. Similarly, in Figure 5.8, when sorption is controlled by the irreversible sorption isotherm, the concentration of the contaminant that persists in the soil after extensive treatment can
be orders of magnitude higher than the estimated value using the linear isotherm.

5.4 Impact on Bioavailability and Ecological Risk

Bioavailability is a measure of the potential of a contaminant for entry into ecological or human receptors (Anderson et al., 1999). Numerous researchers have demonstrated that the response of an ecosystem to a contaminant is not controlled by the total concentration of the contaminant, but instead by only the portion which is biologically available (Linz and Nakles, 1996). Thus, bioavailability defines the relationship between chemical levels measured in an absolute sense in the soil or sediment phase and the quantity of the same chemical that can enter into an organism, potentially causing harm (Anderson et al., 1999). The concentration of a chemical in a soil or sediment that is determined by rigorous solvent extraction, therefore, is not an appropriate predictor of bioavailability and hence, of toxicity or risk (Linz and Nakles, 1996). Irreversible sorption of contaminants in soils and sediments may cause a significant portion of the sorbed compounds to persist in the soils and sediments and thus, could greatly reduce the availability of these compounds. Linz and Nakles (1996) compiled a number of field and laboratory observations on the persistence of contaminants in soils and sediments and on the declining of bioavailability. These observations share a common feature -- the initial microbial utilization was reasonably rapid, but the rate slowed subsequently with time (note that the pattern of the declining
degradation is very similar to the pattern of the increasing resistance to desorption). They proposed that since environmental conditions had not changed, it is the bioavailability that diminished with time. Apparently, this is because with more compounds desorbing from the soils and sediments and being degraded, the fraction of sorbed compounds associated with the reversible compartment decreases significantly, i.e., the percentage of desorbable compounds with respect to the total amount of compounds remaining in the sediment becomes increasingly smaller. Moreover, the impact of irreversible sorption on bioavailability is more profound for aged sediments (as illustrated in Chen et al., 1999a), for which a larger fraction of sorbed contaminants resides in the irreversible compartment (compounds associated with the reversible compartment typically has been removed during the long process). For example, previous research by the author (Chen, 1997) demonstrated that up to 70 to 95% of chlorinated hydrocarbons that is sorbed to Lake Charles sediment was not available. Biodegradation has been adopted as a major mechanism for soil and sediment remediation. However, the irreversibly sorbed fraction may take an extremely prolonged period of time to remove. Thus, the irreversible sorption process can greatly reduce the efficiency of biodegradation and hinder the closure of many contaminated sites.

A similar concept can be used to address the ecological and human-health risks associated with the exposure to contaminated sediments. The measure of the risk should also depend on the portion of the sorbed compound that is available to the receptors, because a chemical must be released from soils or sediments for the potential exposure to
the receptors to occur (except for direct ingestion). Thus, once again, the magnitude of desorption is the dominant factor controlling the potential ecological risk of a sorbed contaminant. Currently, risk assessment is primarily based on the total concentration in soils or sediments. However, since a significant portion of a chemical may be irreversibly bound, this approach could significantly overestimate the potential ecological risk of contaminated soils and sediments. The impact of irreversible sorption on the potential ecological risk of sorbed compounds is illustrated in Figure 5.9. The figure is constructed with the sorption and desorption data of 1,2,4-trichlorobenzene in Dickinson sediment (1.5% OC). The dotted line is the linear isotherm plotted with the $K_\infty$ value observed in sorption experiments, and the solid line is the fitted irreversible sorption isotherm using desorption data obtained in the experiment. According to the linear model, a 1,2,4-trichlorobenzene concentration of 1 μg/g in sediment could result in a 20 μg/L concentration in water. However, since the release is much more accurately predicted by the irreversible sorption model, the actual concentration in the water would more likely to be 0.2 μg/L -- 100 times lower. To put in another way, the potential risk of the sorbed 1,2,4-trichlorobenzene would be 100 times smaller than that estimated using the conventional approach. Therefore, the same process which reduces the efficiency of bioremediation also reduces the ecological and human-health risks of contaminated sediments. This brings up an interesting question: Why do we need to remove the irreversibly sorbed contaminants which are so difficult to remove and which may not be of any risk to ecological systems and human beings at all?
5.5 Risk Based Sediment Quality Standards

All the currently available sediment-quality-related regulations and standards, such as EPA's sediment quality criteria (SQCs) and sediment quality advisory levels (SQALs), are directly or indirectly related to the potential ecological and human health risks of contaminated soils and sediments (U.S. EPA, 1998). As discussed in Section 5.4, the potential ecological and human-health risks of contaminated soils and sediments depend on the portion of the sorbed compounds that is available to the environment, instead of the total concentration which resides in the soils and sediments. This is because contaminants can only impact ecological systems and human beings when they are available to the environment and the ecological receptors. Thus, the basis of sediment quality standards is to ensure that the pore water concentration of a certain compound does not exceed the final chronic water quality criteria (FCVs), i.e., the sediment quality standards are derived from the water quality criteria. Currently, all the sediment quality standards are established from the water quality standards with the linear sorption model. For example, the sediment quality criteria (SQCs) are derived as (U.S. EPA, 1998):

\[
\text{SQC (µg/g) = } K_p \text{ (L/kg) × FCV (µg/L) × 10}^3 \text{ (kg/g)}
\]  
\[(5.47)\]
This equilibrium partitioning approach often significantly over-estimates the extent of desorption and thus, the associated risk to aquatic environments. Since a chemical may exhibit great resistance to desorption, the real partition coefficient could be orders of magnitude higher than the equilibrium partition coefficient, $K_p$, used in Equation 5.47. This effect is more significant for compounds with lower $K_{ow}$ values. As discussed in Chapter 3, the apparent partition coefficient ($K_{ap}$) and the equilibrium partition coefficient of hexachlorobenzene only differed by a factor of 2.4, but the apparent partition coefficient of 1,4-dichlorobenzene was more than two orders of magnitude higher than its equilibrium partition coefficient. Moreover, the incapability of the linear model in predicting long-term resistant release becomes more problematic in natural environments, where contaminants typically exist in lower concentrations. As illustrated by the irreversible sorption isotherm (e.g., Figure 5.9), the resistance to desorption is more significant at lower concentration ranges. In fact, the sediment quality standards based on this linear correlation are often over-stringent and have greatly hindered the efficiency of remediation processes and delayed the closure of pollution sites. It is often observed that once a contaminated sediment is cleaned to a certain concentration, the remaining fraction cannot be removed with advanced technologies for prolonged time.

Since a fraction of sorbed contaminants is apparently not available for the release to the environment, it is reasonable to re-establish the environmentally acceptable end points for soil contamination -- a risk-based soil and sediment quality standards. This is to better reflect the potential toxicity of sediment-associated chemicals by using more
realistic models that describe the correlation between aqueous and solid phase concentrations. Since the irreversible sorption isotherm can successfully represent the correlation between the solid and aqueous concentrations, the sediment quality criteria might be modified as:

\[
SQC = K_p \cdot FCV \cdot 10^3 + \frac{K_{oc}^{irr} \cdot f_{oc} \cdot q_{max}^{irr} \cdot FCV \cdot 10^3}{q_{max}^{irr} + K_{oc}^{irr} \cdot f_{oc} \cdot FCV \cdot 10^3}
\] (5.48)

The \( K_p \) value in this equation can be estimated with a numbers of equations (e.g., \( K_p = 0.63 K_{ow} f_{oc}, \) Karickhoff, 1984). \( K_{oc}^{irr} \) is relatively constant (\( K_{oc}^{irr} = 10^{5.5} \)), and the range of \( q_{max}^{irr} \) can also be estimated using Equation 5.2 (Kan et al., 1998). It should be noted that the specific value of \( q_{max}^{irr} \) that is used only impacts the isotherm in the narrow plateau region (refer to Figure 5.9). Kan et al. (1998) have shown that the sediment quality criterion of 1,4-dichlorobenzene would be nearly two orders of magnitude less strict when the resistant fraction in sediment is taken into account. Should this risk-based sediment quality criteria be incorporated in environmental management practices, it would increase the allowable soil and sediment clean-up standards. Then, moderate treatment or even no treatment of a contaminated site might provide adequate protection to the receptors, and thus allows for more cost-effective uses of human and financial resources. Furthermore, the risk-based standards could even take natural attenuation into
account, which has been empirically demonstrated as a valuable approach in environmental remediation for a variety of classes of compounds and pollution sites. If so, even less strict sediment quality standards can be adopted without increasing ecological and human-health concerns.

However, it is necessary to realize that if EPA sticks to the current soil and sediment quality standards, the cost for soil and sediment remediation could be skyrocket. As illustrated earlier, it can be extremely difficult to decrease the concentration of a contaminant in sediment to a value below the plateau of the irreversible isotherm. This effect has been clearly shown in Figures 5.7 and 5.8, where after intensive pump and treat for prolonged period of time the sediment phase concentration still persist at a level which is two orders of magnitude higher than the MCL.

5.6 Summary

The irreversible sorption model was tested with results from field studies conducted by independent research groups. For highly hydrophobic compounds such as PCBs, both the linear and the irreversible sorption isotherms could quantify the distribution of contaminants between pore water and sediment. However, for compounds with lower hydrophobicity, the irreversible sorption model provided a more accurate approach in predicting the resistant release of sorbed compounds in the field. The existence of irreversible sorption of organic contaminants in soils and sediments has
significant impact on contaminant transport, bioavailability, and ecological and human-health risks. Sorption causes a contaminant to move more slowly in surface and subsurface environments. Thus, the overall effect of irreversible sorption on the movement of contaminants is probably an accumulation of the contaminants in soils and sediments, which then continuously release these contaminants at low concentrations for prolonged times. Irreversible sorption may greatly reduce the availability of a contaminant sorbed in soils and sediments, since a fraction of sorbed compounds cannot be removed. The impact of irreversible sorption on bioavailability is more profound for aged contaminated sediments, because for such sediments, most of the sorbed compounds are associated with the irreversible fraction. However, irreversible sorption also reduces the ecological and human-health risks of contaminated sediments. Since the fraction of sorbed compounds that is associated with the irreversible compartment is not likely to be released under even extreme conditions, it causes no harm to ecological systems and human beings. Thus, it is necessary to reestablish the environmental quality criteria for contaminated soils and sediments. The new standards should take into account of the availability and ecological risks of sorbed compounds and will be less stringent than the currently available standards for most compounds. Should the risk-based standards be in effect, it will greatly improve the efficiency of environmental management and will make the requirements for the closure of many contaminated sites more realistic. Otherwise, the cost for soil and sediment remediation could skyrocket. Finally, a one-dimensional solute transport model has been developed to simulate the transport of hydrophobic
organic contaminants in groundwater as affected by irreversible sorption. This simple model should provide technical support in site assessment and remediation process design.
Table 5.1: Summary of field observations and modeling input parameters used to construct Figure 5.1. Field data were obtained and reconstructed from McGroddy et al. (1996).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Log $K_{oc}$ a (L/Kg)</th>
<th>$f_{oc}$</th>
<th>$C_w$ (ng/L)</th>
<th>$q$ b (µg/g OC)</th>
<th>Field Observations</th>
<th>Modeling Parameters</th>
<th>Modeling Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenanthrene</td>
<td>4.30</td>
<td>0.0519</td>
<td>17 ± 8.7 (9)</td>
<td>29.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td>0.0547</td>
<td>7.1 ± 2.0 (6)</td>
<td>35.9</td>
<td>4.57</td>
<td>4.30</td>
<td>5.50</td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td>0.0334</td>
<td>8.57 ± 4.66 (6)</td>
<td>34.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pyrene</td>
<td>5.18</td>
<td>0.0519</td>
<td>220 ± 51 (9)</td>
<td>121</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.20</td>
<td>0.0547</td>
<td>84 ± 36 (8)</td>
<td>87</td>
<td>5.13</td>
<td>5.18</td>
<td>5.50</td>
</tr>
<tr>
<td></td>
<td>5.23</td>
<td>0.0334</td>
<td>20.7 ± 9.12 (7)</td>
<td>109</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2',4,5,5'-</td>
<td>5.79, 5.93</td>
<td>0.0519</td>
<td>0.44 ± 0.12 (8)</td>
<td>0.63</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCB</td>
<td>5.79, 5.93</td>
<td>0.0547</td>
<td>1.3 ± 0.56 (8)</td>
<td>2.10</td>
<td>6.36</td>
<td>5.86</td>
<td>5.50</td>
</tr>
<tr>
<td>2,2',3,4,4',5'-</td>
<td>6.16</td>
<td>0.0519</td>
<td>0.43 ± 0.15 (5)</td>
<td>0.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCB</td>
<td>6.16</td>
<td>0.0547</td>
<td>1.0 ± 0.35 (8)</td>
<td>2.46</td>
<td>6.50 c</td>
<td>6.16</td>
<td>5.50</td>
</tr>
</tbody>
</table>

---

a Reported values in Chin et al. (1992) and Wu and Gschwend (1986). b Reconstructed with the reported $K_{oc}$ values (Column 2) and the equilibrium aqueous phase concentrations predicted from the total sediment phase concentrations (data not shown).

Obtained from Schwarzenbach et al. (1992). d Obtained from Mackay et al. (1992). e Obtained by averaging the $K_{oc}$ values of three sediment cores (Column 2). f Calculated using $q_{oc}^{\prime} = 37765 \times f_{oc} \times K_{oc}^{0.23}$ (Kan et al., 1998).
Table 5.2: Summary of field observations and modeling input parameters used to construct Figure 5.2. Field data were obtained and derived from Pereira et al. (1988).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Field Observations</th>
<th>Modeling Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_w$ (ng/L)</td>
<td>$q$ (µg/g OC)</td>
</tr>
<tr>
<td>1,2-dichlorobenzene</td>
<td>9.0</td>
<td>7.1</td>
</tr>
<tr>
<td>1,4-dichlorobenzene</td>
<td>74.0</td>
<td>82.0</td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>40.0</td>
<td>306.0</td>
</tr>
<tr>
<td>1,2,3,4-tetrachlorobenzene</td>
<td>9.0</td>
<td>48.0</td>
</tr>
<tr>
<td>hexachlorobenzene</td>
<td>8.0</td>
<td>7544.0</td>
</tr>
<tr>
<td>hexachlorobutadiene</td>
<td>1298.0</td>
<td>1148.0</td>
</tr>
</tbody>
</table>

$^a$ Calculated with $K_{oc} = q/C_w$, using $q$ and $C_w$ values listed in Columns 2 and 3. $^b$ Obtained from Schwarzenbach et al. (1992). $^c$ Calculated with $K_{oc} = 0.63 K_{mw}$ (Karickhoff, 1984). $^d$ Calculated using $q_{int}^{''} = 37765 \times f_a \times K_{mw}^{-0.21}$ (Kan et al., 1998).
Appendix 5.1: Visual Basic Codes for ISAST Model

'declare sheets, graphs, and parameters
Public s_main, c_graph1, c_graph2
Public s_adv_disp, s_lin_sorp, s_irr_sorp, s_lin_ddecay, s_irr_ddecay
Public r_adv_disp, r_lin_sorp, r_irr_sorp, r_lin_ddecay, r_irr_ddecay
Public v_K, v_n, v_gradient, v_density, v_foc
Public v_plumelength, v_kow
Public v_sim_time, v_sim_dist
Public v_lambda
Public v_c0, v_x1, v_c1, v_c2
Public v_v, v_alphax, v_D
Public v_dx, v_dt
Public v_koc, v_kocirr, v_qmax
Public v_dimX, v_dimT

'define the methods of model simulation
Sub model_contaminant()

determine_parameters

'set up matrices within calculation worksheets
initialize_ranges s_adv_disp, r_adv_disp
initialize_ranges s_lin_sorp, r_lin_sorp
initialize_ranges s_irr_sorp, r_irr_sorp
initialize_ranges s_lin_ddecay, r_lin_ddecay
initialize_ranges s_irr_ddecay, r_irr_ddecay

'determine concentrations at time 0
input_initial_concentrations r_adv_disp
input_initial_concentrations r_lin_sorp
input_initial_concentrations r_irr_sorp
If v_lambda <> 0 Then
    input_initial_concentrations r_lin_ddecay
    input_initial_concentrations r_irr_ddecay
End If

'calculate concentrations for simulation time
calculate_concentrations r_adv_disp, 0, "adv_disp"
calculate_concentrations r_lin_sorp, 0, "lin_sorp"
calculate_concentrations r_irr_sorp, 1, "irr_sorp"
If v_lambda <> 0 Then
    calculate_concentrations r_lin_dcy, 0, "lin_dcy"
    calculate_concentrations r_irr_dcy, 1, "irr_dcy"
End If

'graph breakthrough curves
v_series_count = 5 - Charts(c_graph1).SeriesCollection.Count
If v_series_count > 0 Then
    For i = 1 To v_series_count
        Charts(c_graph1).SeriesCollection.NewSeries
        Next i
End If

'graph concentration profiles
v_series_count = 5 - Charts(c_graph2).SeriesCollection.Count
If v_series_count > 0 Then
    For i = 1 To v_series_count
        Charts(c_graph2).SeriesCollection.NewSeries
        Next i
End If

graph_breakthrough_curve r_adv_disp, 1, "adv_disp"
graph_breakthrough_curve r_lin_sorp, 2, "lin_sorp"
graph_breakthrough_curve r_irr_sorp, 3, "irr_sorp"
graph_breakthrough_curve r_lin_dcy, 4, "lin_dcy"
graph_breakthrough_curve r_irr_dcy, 5, "irr_dcy"

Charts(c_graph1).Activate

End Sub

'define the sheets, graphs, and parameters
Sub determine_parameters()

'define sheet names
s_main = "Parameters"
s_adv Disp = "C_adv Disp"
s_lin_sorp = "C_lin_sorp"
s_irr_sorp = "C_irr_sorp"
s_lin_dcay = "C_lin_dcay"
s_irr_dcay = "C_irr_dcay"
c_graph1 = "Breakthrough Curve"
c_graph2 = "Concentration Profile"

'define input parameters
Sheets(s_main).Select
v_K = Sheets(s_main).Range("K").Value
v_n = Sheets(s_main).Range("n").Value
v_gradient = Sheets(s_main).Range("dh_dl").Value
v_density = Sheets(s_main).Range("density").Value
v_foc = Sheets(s_main).Range("foc").Value
v_plumelength = Sheets(s_main).Range("plume_length").Value
v_kow = Sheets(s_main).Range("kow").Value
v_sim_time = Sheets(s_main).Range("sim_time").Value
v_sim_dist = Sheets(s_main).Range("sim_dist").Value
v_lambda = Sheets(s_main).Range("lambda").Value
v_c0 = Sheets(s_main).Range("c_0").Value
v_x1 = Sheets(s_main).Range("x_max").Value
v_c1 = Sheets(s_main).Range("c_max").Value
v_c2 = Sheets(s_main).Range("c_x").Value
v_v = Sheets(s_main).Range("v").Value
v_alphax = Sheets(s_main).Range("a_x").Value
v_D = Sheets(s_main).Range("D").Value
v_dx = Sheets(s_main).Range("dx").Value
v_dt = Sheets(s_main).Range("dt").Value
v_koc = Sheets(s_main).Range("koc").Value
v_kocirr = Sheets(s_main).Range("koc_irr").Value
v_qmax = Sheets(s_main).Range("qmax").Value
v_dimX = WorksheetFunction.Ceiling(v_sim_dist / WorksheetFunction.Round(v_dx, 0), 1) + 3
v_dimT = WorksheetFunction.Ceiling(v_sim_time / WorksheetFunction.Round(v_dt, 0), 1) + 1

End Sub

'define the method of generating temporal-spatial domains
Sub initialize_ranges(s_name, r_name)

clear calculation worksheets
Sheets(s_name).Cells.ClearContents
Sheets(s_name).Cells.Interior.Pattern = xlPatternNone

'determine and initialize calculation ranges
Sheets(s_name).Range("A1").Value = 0
c_lastcell = Sheets(s_name).Range("A1").Offset(v_dimT, v_dimX).Address
Set r_name = Sheets(s_name).Range("A1", c_lastcell)
r_name.FillRight
r_name.FillDown

'input time frames
r_name = Sheets(s_name).Range("A2").Offset(v_dimT - 1, 0).Address
Set r_name_sub = Sheets(s_name).Range("A2", c_lastcell)
r_name_sub(1).Value = 0
r_name_sub.DataSeries step:=v_dt, rowcol:=xlColumns
With r_name_sub.Interior
  .Color = RGB(200, 200, 200)
  .Pattern = xlSolid
End With

'input spatial frames
r_name = Sheets(s_name).Range("A1").Offset(0, v_dimX - 1).Address
Set r_name_sub = Sheets(s_name).Range("A1", c_lastcell)
r_name_sub(1).Value = 0
r_name_sub.DataSeries step:=v_dx, rowcol:=xlRows
With r_name_sub.Interior
  .Color = RGB(200, 200, 200)
  .Pattern = xlSolid
End With
r_name(1).FormulaR1C1 = ""
r_name(2).FormulaR1C1 = ""
r_name(1).Offset(0, v_dimX).FormulaR1C1 = ""

End Sub

'define the method of generating initial concentrations along the spatial domain
Sub input_initial_concentrations(r_name)

'input initial concentration
r_name(2, 3) = v_c0
'input initial downstream concentrations
v_int_col = 2 + WorksheetFunction.Ceiling(v_x1 / v_dx, 1)
If v_int_col < 4 Then
    v_int_col = 4
End If

c_lastcell = r_name.Range("B2").Offset(0, v_int_col - 2).Address
Set r_name_sub = r_name.Range("D2", c_lastcell)
r_name_sub(1).FormulaR1C1 =
"=10^((log10(c_0)+log10(c_max/c_0))*(dx/x_max)*(column()-3))"
If r_name_sub.Count > 1 Then
    r_name_sub.FillRight
End If

c_startcell = r_name.Range("B2").Offset(0, v_int_col - 1).Address

c_lastcell = r_name.Range("B2").Offset(0, v_dimX - 3).Address
Set r_name_sub = r_name.Range(c_startcell, c_lastcell)
r_name_sub(1).FormulaR1C1 =
"=10^((log10(c_max)+log10(c_x/c_max))*(dx/(sim_dist-x_max))*(column()-" + Str(v_int_col) + ")")"
If r_name_sub.Count > 1 Then
    r_name_sub.FillRight
End If

r_name(2, v_dimX) = v_c2
r_name(2, v_dimX + 1) = v_c2

End Sub

'define the method for calculate the concentrations
Sub calculate_concentrations(r_name, v_irreversible, v_characteristic)
c_lastcell = r_name.Range("B2").Offset(v_dimT - 1, v_dimX - 2).Address
c_lastcol1 = r_name.Range("B2").Offset(1, v_dimX - 1).Address
c_lastcol2 = r_name.Range("B2").Offset(v_dimT - 1, v_dimX - 1).Address
Set r_name_sub = r_name.Range("C3", c_lastcell)
Set r_name_last = r_name.Range(c_lastcol1, c_lastcol2)

v_advection = "((-v/(2*dx))*(R^[1]-R^[0]-C^[1]-C^[0]))"

If v_irreversible = 0 Then
    v_sorption = "((koc*foc)"
Else  
v_sorption = "((koc*foc+ (koc_irr*foc*(qmax^2))/((qmax+koc_irr*foc*R[-1]C)^2))"  
End If  
v_retardation = "((1+density/n*)" + v_sorption + ")"  
v_decay = ":-lambda*R[-1]C"

Select Case v_characteristic
  Case "adv_disp"
    v_formula = "=R[-1]C + dt*"( + v_advection + "+" + v_dispersion + ")"
  Case "lin_sorp"
    v_formula = "=R[-1]C + dt*"( + v_advection + "+" + v_dispersion + ")/" + 
    v_retardation
  Case "irr_sorp"
    v_formula = "=R[-1]C + dt*"( + v_advection + "+" + v_dispersion + ")/" + 
    v_retardation
  Case "lin_decay"
    v_formula = "=R[-1]C + dt*"( + v_advection + "+" + v_dispersion + "+" + 
    v_decay + "")/" + v_retardation
  Case "irr_decay"
    v_formula = "=R[-1]C + dt*"( + v_advection + "+" + v_dispersion + "+" + 
    v_decay + ")/" + v_retardation
End Select

r_name_sub(1).FormulaR1C1 = v_formula
r_name_sub.FillRight
r_name_sub.FillDown

r_name_last(1).FormulaR1C1 = "=RC[-1]"
End Sub

'define the method for plotting output graphs

'plot breakthrough curves and concentration profiles
Sub graph_breakthrough_curve(r_name, v_series_count, v_name)

c_lastcell = r_name.Range("A2").Offset(v_dimT - 1, 0).Address
Set r_time = r_name.Range("A2", c_lastcell)
c_lastcell = r_name.Range("C1").Offset(0, v_dimX - 3).Address
Set r_dist = r_name.Range("C1", c_lastcell)
c_startcell = r_name.Range("A2").Address(0, v_dimX - 2).Address

Set r_time_conc = r_name.Range(c_startcell, c_lastcell)

Charts(c_graph1).SeriesCollection(v_series_count).XValues = r_time
Charts(c_graph1).SeriesCollection(v_series_count).Values = r_time_conc
Charts(c_graph1).SeriesCollection(v_series_count).Name = v_name

Charts(c_graph2).SeriesCollection(v_series_count).XValues = r_dist
Charts(c_graph2).SeriesCollection(v_series_count).Values = r_dist_conc
Charts(c_graph2).SeriesCollection(v_series_count).Name = v_name

End Sub
Figure 5.1.a: Comparison between model predictions and field observed sediment-porewater distributions of phenanthrene and pyrene in Boston Harbor sediment. The solid lines are predicted with the irreversible sorption isotherm (Equation 3.1). The dotted lines are predicted with the linear isotherm (Equation 2.16). Data points were reconstructed from McGrady et al. (1996).
Figure 5.1.b: Comparison between model predictions and field observed sediment-porewater distributions of 2,2',4,5,5'-PCB and 2,2',3,4,4',5'-PCB in Boston Harbor sediment. The solid lines are predicted with the irreversible sorption isotherm (Equation 3.1). The dotted lines are predicted with the linear isotherm (Equation 2.16). Data points were reconstructed from McGroddy et al. (1996).
Figure 5.2.a: Comparison between model predictions and field observed sediment-porewater distributions of 1,2- and 1,4-dichlorobenzenes in Lake Charles sediment. The solid lines are predicted with the irreversible sorption isotherm (Equation 3.1). The dotted lines are predicted with the linear isotherm (Equation 2.16). Data points were reconstructed from Pereira et al. (1988).
Figure 5.2.b: Comparison between model predictions and field observed sediment-porewater distributions of 1,2,4-trichlorobenzene and 1,2,3,4-tetrachlorobenzene in Lake Charles sediment. The solid lines are predicted with the irreversible sorption isotherm (Equation 3.1). The dotted lines are predicted with the linear isotherm (Equation 2.16). Data points were reconstructed from Pereira et al. (1988).
Figure 5.2.c: Comparison between model predictions and field observed sediment-porewater distributions of hexachlorobenzene and hexachlorobutadiene in Lake Charles sediment. The solid lines are predicted with the irreversible sorption isotherm (Equation 3.1). The dotted lines are predicted with the linear isotherm (Equation 2.16). Data points were reconstructed from Pereira et al. (1988).
Figure 5.3: Illustration of the impact of sorption on solute transport in groundwater. The transport of Compounds a and b are simulated with MODFLOW and MT3D. The aquifer is assumed to be confined and with a uniform thickness of 40 ft. Groundwater flow within the aquifer is from the north to the south. The hydrogeological parameters used for the simulation of the two compounds are identical -- hydraulic conductivity is 3.0 ft/day; porosity is 0.3; bulk density is 1.7 kg/L; and recharge is 1 in/yr. Both compounds have a longitudinal dispersivity of 100 ft, a transverse dispersivity of 10 ft, and an initial concentration of 1000 mg/L (shaded areas). The partition coefficients for compounds a and b are 0.3 and 1.5 L/kg, respectively. The simulation time for both compounds is 30 years.
Figure 5.4: Illustration of the numerical approximation to the governing solute transport equation (Equation 5.35). Concentration at any temporal and spatial step can be approximated with the concentrations at three adjacent spatial steps at the previous temporal step. Flow dimension X is discretized into m sections of distance dx, and simulation time T is discretized into n sections of time dt.
Figure 5.5: Illustration of the initial conditions (concentration profile at time 0) generated by ISAST. The user should input $C_0$, $C_{\text{max}}$, and $C_x$, as well as the location where the $C_{\text{max}}$ occurs -- $x_{\text{max}}$. Concentration at any location $x$ can be calculated assuming concentration follows logarithm distribution.
Figure 5.6: Input sheet of ISAST -- a one dimensional solute transport model simulating the impact of irreversible sorption on solute transport in groundwater.
Figure 5.7: Output graph of ISAST -- breakthrough curves at modeling boundary (x=X), at time T.
Figure 5.8: Output graph of ISAST -- concentration profiles at the end of simulation, t = T.
Figure 5.9: Illustration of the impact of irreversible sorption on the ecological and human-health risks of contaminated sediment. Solid line is the irreversible isotherm; dotted line is the linear isotherm; data points are desorption data of 1,2,4-trichlorobenzene in Dickinson sediment.
Chapter 6: Conclusions and Future Work

The mechanism controlling the resistant release of hydrophobic organic contaminants in natural soils and sediments has been a debatable topic for many years. To understand the mechanism, the unique properties of the irreversibly sorbed compartment need to be characterized. Thus, this research was conducted to further characterize the irreversible sorption of hydrophobic organic contaminants in natural sediments, with the objective of exploring the nature of this process and its impact on sediment quality.

In Chapter 3, the sorption and desorption of five chlorinated benzenes in four different sediments were studied. The five compounds were intentionally chosen from the same chemical class, so that the difference in chemical property could be minimized. These compounds, however, span a wide range of hydrophobicity and solubility -- two of the most important properties controlling the sorption and desorption of hydrophobic organic contaminants. In all the experiments, the sediment was initially saturated with one of the five compounds and then extracted extensively until no significant release was observed. The experimental results, thus, covered an aqueous (solid) phase concentration range of up to 5 orders of magnitude and provided solid evidence from which the properties of the irreversible compartment can be better characterized. A few patterns were observed for the sorption and desorption of these compounds in varied sediments:
1. Sorption was linear, even when aqueous phase concentration approached solubility. The observed partition coefficients of these compounds were linearly related to their $K_{ow}$ values, implying sorption was driven by hydrophobic effects.

2. Second, desorption deviated increasingly from sorption as sorbed compounds are removed from the sediments, and a fixed irreversible sorption capacity was observed for each chemical-sediment combination.

3. Third, once desorption reached the irreversible fraction, the aqueous phase concentration showed essentially no dependency on the desorption time applied, implying desorption from this fraction was not controlled simply by slow diffusion.

4. Fourth, all the chemical-sediment combinations exhibited a similar partition coefficient with regard to the irreversible fraction -- $10^{5.42\pm0.17}$.

These sorption and desorption patterns indicate that desorption was controlled by a mechanism different from the mechanism controlling the sorption of these compounds. Furthermore, sorption and desorption results of these experiments were well-modeled by an irreversible sorption isotherm (Kan et al., 1998), even when aqueous concentration spanned more than 5 orders of magnitude. The irreversible sorption capacity, $q_{\text{irr}}^{\text{max}}$, however, is relatively difficult to predict. For the sorption and desorption of different compounds in the same sediment, $q_{\text{irr}}^{\text{max}}$ is controlled by both $K_{ow}$ and solubility. For the sorption and desorption of a same compound in different sediments, $q_{\text{irr}}^{\text{max}}$ depends mainly on sediment organic carbon content but may also be affected by the origin of the sediments. Sediments which are historically affected by petroleum products tend to exhibit a larger irreversible compartment. Thus, this may suggest that the irreversible
binding is due to (at least partially) the association of sorbate molecules to some highly insoluble and hydrophobic materials in the sediments, such as high molecular weight NAPLs and waxes. Once a sorbate molecule is associated with such materials, its desorption properties would be characterized by the properties of these highly insoluble and hydrophobic materials.

Competitive sorption, caustic treatment of sediment, and external mechanic force have been found by others to significantly affect the sorption of hydrophobic organic compounds in soils and sediments. The effect of these factors on the release of sorbed compounds was examined in Chapter 4. This was designed so that any resemblance or difference between the effect on sorption and the effect on desorption should give valuable insights into the nature of irreversible sorption. While competitive sorption may significantly affect the desorption from the reversible compartment, its effect on the desorption from the irreversible compartment was minimal. The release from the irreversible compartment was unaffected by caustic treatment of sediment, even when 1 M NaOH solution was applied. Also, external mechanic force may not be able to affect the sorption and desorption of hydrophobic organic contaminants in any significant extent. All these experimental observations suggest that the irreversible binding is a relatively stable formation, i.e., either such vigorous treatments cannot reach or break this binding, or other factors (besides of the interaction with natural organic matters) are controlling irreversible sorption. Once again, a possible explanation is that sorbate molecules are associated with some highly insoluble and hydrophobic materials in sediments. These experimental results also indicate that once the overall desorption is dominated by the desorption from the irreversible fraction, desorption can hardly be affected by a number of natural environmental factors and external disturbance. In particular, the release of a compound is unlikely to be affected by sudden pH change, or
the presence or discharge of other compounds. Also, sediment perturbation, such as
dredging, may not affect the release of sorbed compounds as expected, once the
sediment phase concentration is in the low range of concentration where irreversible
sorption predominates.

In Chapter 5, the conceptual and mathematical models of irreversible sorption
were tested with field observations obtained by two independent research groups, and
the impact of irreversible sorption on the fate and transport, bioavailability, ecological
and human-health risks of organic contaminants was discussed. Also addressed in this
chapter were the development of a one-dimensional solute transport model (which
incorporates the impact of irreversible sorption and natural attenuation), as well as the
justification for establishing risk-based sediment quality standards. Most field
observations were predicted equally well or better with the irreversible sorption model
than with the presently used linear model. Thus, this model should provide a simple yet
reliable approach to quantitatively predict the resistant release of sorbed contaminants
from natural soils and sediments. Irreversible sorption has a significant impact on the
fate and transport of contaminants in surface and subsurface environments. Because of
irreversible sorption, contaminants can persist in sediments for dozens of years and
continuously release to surface and groundwater at low concentrations -- an effect that
has greatly hindered the efficiency of groundwater remediation. Similarly, irreversible
sorption can greatly reduce the bioavailability of sorbed compounds, and thus, could
significantly increase the time and costs for bioremediation and delay the closure of
contaminated sites. However, since only the readily desorbable compounds are
available to ecological and human receptors, irreversible sorption also causes the
reduction of potential risks of contaminated sediments. Thus, the more reasonable and
practical sediment quality standards should be risk-oriented. Should such risk-based
standards be in effect, many contaminated sites may only need moderate treatment or
can even be left alone without increasing the adverse effect on ecosystems, and the
economic effect should be enormous. Otherwise, it could cost much more then expected
to clean up soil and sediment to the current standard (e.g., MCL). To quantitatively
address the impact of irreversible sorption, the irreversible sorption model was
incorporated into a one-dimensional solute transport model. The model was
programmed in Excel/Visual Basic, and was implemented with numerical solutions.
The model requires only common hydrogeological, chemical, and biochemical
parameters and can provide support for sediment management and remediation design.

Irreversible sorption is an extremely complicated process, especially when
natural soils and sediments are concerned. While this research produced valuable results
that can be used to understand the nature of irreversible sorption, to fully understand this
process is beyond the scope of this study. However, it remains an interesting research
direction and needs more extensive study. Considering the potential future work on this
topic, an important direction is probably to test the possible association of sorbate
molecules with highly insoluble and hydrophobic materials in sediments. Thus far, the
irreversible sorption model has been demonstrated to be a reliable tool to predict the
long-term resistant release of hydrophobic organic contaminants from natural soils and
sediments. However, to use it in regulatory practice, the model needs to be tested
against more diversified systems, i.e., more contaminants of different chemical classes
and more sediments of varied origins. In particular, more data are necessary to derive
empirical equations that can be used to predict the irreversible sorption capacity.
Finally, it would be worthwhile to test the irreversible sorption mechanism on heavy
metals, one other class of contaminants of great environmental concern.
Reference


Chen, W. *Sorption and Desorption of Hydrophobic Organic Compounds to and from Historically Contaminated Lake Charles Sediments*, Rice University, **1997**.


Hermosin, M.C.; Cornejo, J.; Rodrigues, P. Soil Science 1987, 144, 250.


Technol. 1998, 32.


Ongley, L.K. *The Effect of Fluid Ionic Strength and System Temperature on Naphthalene Sorption to and Desorption from Lincoln Fine Sand*, Rice Univeristy, **1993**.


