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A Rapid, Simple Method to Measure the Desorption Resistant Fraction of Sediment Sorbed Contaminants

by

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ABSTRACT

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Resistant desorption has been widely observed for hydrophobic organic contaminants. It is an important process that impacts sediment quality and contaminated sediment management. Conventional approaches to measure the desorption resistant fraction of sorbed contaminants are by conducting repetitive water desorption, in which the desorption resistant fraction is determined by measuring the solid phase concentration after extended desorption times. This method is time-consuming and impractical for widespread applications. In addition, the final measurement of the solid phase concentration is subject to considerable error, because there is always a fraction of water associated with the solid due to the incomplete separation of the liquid phase from the solid. In this research, a new experimental protocol was developed to rapidly and accurately measure the desorption resistant fraction based on the study of desorption of phenanthrene from Utica sediment.
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Chapter 1: Introduction

1.1 Problem Statement

Many organic and inorganic contaminants accumulate in sediments after being discharged to the environment. These contaminated sediments serve as contaminated reservoirs and therefore pose ecological and human health risks for prolonged periods of time through various pathways, of which the release of contaminants from sediment to groundwater (desorption) is often the most important and also the most poorly understood process.

For many years, desorption of contaminants from natural soil and sediment has been presented as a simple reversible partitioning process in most transport, risk and remediation models. However, this oversimplified model often fails to explain the observed desorption behaviors. Numerous studies have shown that in regions of low contaminant concentrations, desorption is very difficult and contaminants persist much longer than would be expected from the reversible model. Even with the most advanced remediation technologies (physical, chemical, and biologically enhanced), a small fraction of sorbed contaminant is often observed to remain in the soil or sediment.

Thus far, numerous mechanisms have been proposed to account for the existence of this desorption resistant fraction. For hydrophobic organic compounds and natural sediments, most of the mechanisms fall into the following four groups: 1) slow diffusion (Wu and Gschwend, 1986; Ball and Roberts, 1991; Carroll et al., 1994; Young and Weber, 1995); 2) heterogeneous sorption (Weber et al., 1992; Burgoes et al., 1996; Xing
and Pignatello, 1996; Huang and Weber, 1998; Pignatello, 1998); 3) specific interactions between organic compounds and high energy sites in sediments (Burgos et al., 1996; Gustafsson et al., 1997; Chiou and Kile, 1998); 4) physical entrapment of organic compounds within sediment matrix (DiToro and Horzempe, 1982; Adamson, 1990; Kan et al., 1994; Burgos et al., 1996; White et al., 1997; Kan et al., 1998). Unfortunately, these mechanisms require extensive experimentation for every soil/compound combination, which is impractical. However, all of these theories have proposed two distinct desorption processes, one process related to desorption at high contaminant concentration and the second process at low concentration.

Researchers at Rice University (Fu et al., 1994; Hunter et al., 1996; Kan et al., 1997; Kan et al., 1998; Chen et al., 1999; Chen et al., 2000) have shown that the desorption resistant fraction is a general characteristic of the soil-hydrocarbon interaction. Other researchers’ work (Loehr and Webster, 1996; Linz and Nakeles, 1997) also indicates that contaminants associated with the desorption resistant fraction are not bioavailable and therefore pose no significant risk to the environment. If these assumptions are true, then it might be possible to reestablish acceptable remediation endpoints that will result in enormous cost savings but little or no increase in ecological or human health risks.

Currently, many studies are being conducted to evaluate the bioavailability of contaminants in the resistant fraction with micrograms, benthic invertebrates, and plant uptake by researchers at Rice University and Louisiana State University. It is desirable to rapidly access and measure the desorption resistant fraction. Thus far, in most laboratory studies to quantify the desorption resistant fraction of sorbed contaminants, desorption
experiments have been conducted by washing the soil or sediment extensively with an electrolyte solution simulating the condition of surface or ground water. However, this approach is found to be time-consuming. Developing a rapid and simple method to measure the desorption resistant fraction is needed.

1.2 Research Objectives and Summary of Approach

The primary objective of this research was to develop a rapid, effective method to measure the desorption resistant fraction of sorbed hydrophobic organic contaminants. The mechanisms responsible for this resistant fraction were also studied.

Previous work of two other people in the author’s group (summarized in Chapter 3) indicated the high efficiency of isopropanol/electrolyte solution mixed solvent in accelerating the desorption of hydrophobic organic compounds from sediments. Unfortunately, the accurate measurement of the desorption resistant fraction was not possible due to the lack of effective separation methods.

This study built on previous work using isopropanol/electrolyte solution mixed solvent to conduct accelerated desorption experiments. Historically contaminated Utica sediment was used as the sorbent, while phenanthrene was used as the model contaminant. Before conducting the desorption experiments, sorption experiments were performed to contaminate the sediment with freshly added contaminant similar to pollution occurrence, such as accidental spillage, leakage from hazardous waste sites and landfills, and the presence of non-aqueous phase liquids (NAPLs.) The desorption experiments were conducted to measure the desorption resistant fraction. A new separation method was developed and used in the desorption experiments to completely
separate the solution phase from the solid phase after each desorption step. As a result, the contaminant concentrations in both the solid phase and the liquid phase could be accurately measured, and the desorption resistant fraction of sorbed contaminant could be easily determined using a simple approach.
Chapter 2: Background and Literature Review

2.1 Sorption

The association of chemicals with a soil phase is generally referred to as “sorption.” The sorbed chemical is called the sorbate, while the solid material with which the sorbate associates is called the sorbent. Two broad categories of sorption phenomena, adsorption and absorption, can be differentiated by the degree to which the sorbate molecule interacts with and is free to migrate within the sorbent phase. In adsorption, the sorbate accumulation is generally restricted to a surface or interface between the solution and the sorbent. In absorption the sorbate is transferred from the solution to interpenetrate the sorbent phase by at least several nanometers. Since the adsorption process generally yields high surface concentration of the sorbate, an additional precipitation or association can occur, which is different from both adsorption and absorption because it forms a new and distinct three-dimensional phase.

Several interaction mechanisms may be responsible for sorption (Schwarzenbach, 1993). For example, hydrophobic organic molecules may escape the water by penetration into natural organic matter because of the unfavorable free-energy costs of remaining in aqueous solution. This is called the hydrophobic effect, which is the dominant force governing the sorption of nonpolar hydrophobic organic compounds (Tanford, 1980). Molecules may also be associated with the mineral surface of a solid via van der Waals, dipole-dipole, and hydrogen bonding (Schwarzenbach, 1993). For an ionizable sorbate, sorption can also occur via ionic interactions with charged surface
sites. Sorption can also occur via chemical reaction. All of these mechanisms operate simultaneously, but a specific interaction may dominate the sorption process depending on the structural properties of the chemicals and the solid medium. Further understanding of the mechanisms of sorption can be obtained by studying the shape of sorption isotherms at equilibrium.

2.1.1 Equilibrium

In a two-phase system (i.e., water and organic phase), the distribution of an organic compound is the reversible transfer of the compound between the two phases:

\[ A \text{ (phase 1)} \Leftrightarrow A \text{ (phase 2)} \quad (2.1) \]

The ability of a compound to transfer from one phase to another is controlled by the energy status of the compound relative to the system. The energy status of a specific compound at a given temperature (T) and pressure (P) is represented by the chemical potential in each phase:

\[ \mu_1 = \mu_{\text{pure liquid A}}^0 + RT\ln x_1 \gamma_1 \quad (2.2, 2.3) \]

\[ \mu_2 = \mu_{\text{pure liquid A}}^0 + RT\ln x_2 \gamma_2 \]

where \( \mu_{\text{pure liquid A}}^0 \) is the standard state chemical potential of compound A (note here the pure liquid A is chosen as the reference state), \( T \) is the temperature in degrees Kelvin, \( R \)
is the gas constant (8.312 J/mole K), \(x_1\) and \(x_2\) are the mole fractions of compound A in phases 1 and 2, and \(\gamma_1\) and \(\gamma_2\) are the activity coefficients of compound A in phases 1 and 2.

Compound A will transfer from the phase of higher potential to the phase of lower potential until the equilibrium is reached:

\[
\mu_1 = \mu_2 \tag{2.4}
\]

then

\[
RT\ln x_1\gamma_1 = RT\ln x_2\gamma_2 \tag{2.5}
\]

Rearrangement of Equation 2.5 yields:

\[
RT\ln(x_1/x_2) = -(RT\ln\gamma_1 - RT\ln\gamma_2) \tag{2.6}
\]

The left side of Equation 2.6 represents the partition coefficient, \(K' = x_1/x_2\) of A between the two phases at equilibrium, and the right side represents the difference in the excess Gibbs free energy due to the nonideality of the system as compared to pure liquid A. In environmental chemistry, the most common way to express concentrations is related to number of molecules per unit volume. Mole fractions \((x_1 \text{ and } x_2)\) can be converted to such units using the following equations:
\[ C_1 \left( \frac{\text{mole}}{L} \right) = \frac{x_1 \left( \frac{\text{moles of A in phase 1}}{\text{total moles in phase 1}} \right) }{V_{\text{mixture}}^1 \left( \frac{L}{\text{total moles in phase 1}} \right) } \]  

(2.7)

and

\[ C_2 \left( \frac{\text{mole}}{L} \right) = \frac{x_2 \left( \frac{\text{mole of A in phase 2}}{\text{total moles in phase 2}} \right) }{V_{\text{mixture}}^2 \left( \frac{L}{\text{total moles in phase 2}} \right) } \]  

(2.8)

where \( C_1 \) and \( C_2 \) are the molar concentrations in phases 1 and 2, respectively; \( V_{\text{mixture}}^1 \) and \( V_{\text{mixture}}^2 \) are the molar volumes of phases 1 and 2, respectively. The partition constant of an organic compound can be redefined using the molar concentrations:

\[ K_p = \frac{C_1}{C_2} = \frac{x_1 V_{\text{mixture}}^1}{x_2 V_{\text{mixture}}^2} = \frac{V_{\text{mixture}}^1}{V_{\text{mixture}}^2} K' \]  

(2.9)

2.1.2 Sorption Isotherms

Sorption isotherms are used to describe the dependence of the sorbate concentration associated with the sorbent to the total sorbate concentration in the
solution under the assumption of equilibrium conditions. The term isotherm indicates that the sorption is considered at a constant temperature. It is generally agreed that the best way to study the sorption and desorption mechanisms is by measuring the isotherm.

Depending on the dominant mechanism, sorption isotherms may exhibit different shapes (Giles et al., 1960). Three types of isotherms are most commonly used to study the sorption or desorption of organic compounds in natural systems and will be discussed in this thesis. Figure 2.1 (Figures are located at the end of each chapter) is a pictorial representation of these three types of isotherms: the linear isotherm, the Langmuir isotherm, and the Freundlich isotherm.

The linear model is the simplest. In this model, the solute accumulates on the sorbent in direct proportion to the solution concentration:

\[ q = K_p C \]  \hspace{1cm} (2.10)

where \( q \) is the solid phase concentration (\( \mu g/g \)), \( K_p \) is the solid/water partition coefficient (\( ml/g \)), and \( C \) is the solution phase concentration (\( \mu g/ml \)). The linear isotherm can be used in cases when the energy of sorption is uniform with increasing concentrations of sorbate and the loading of sorbate on the sorbent is low.

In the linear model, only one parameter, the partition coefficient, is required to predict the sorption behavior. There are many equations to estimate the partition coefficient. Since soil organic matter is considered to be the predominant sorbent of hydrophobic organic compounds, most equations relate \( K_p \) to the mass fraction of
organic carbon of the solid (foc) and the octanol-water partition coefficient (K\text{ow}) of the solute, which represents the hydrophobicity of a solute.

Karickhoff (1979) reported that the K\text{p} value of a compound could be estimated from its K\text{ow} value by this equation:

\[
K_p = K_{oc} f_{oc} = 0.63 \cdot K_{ow} f_{oc}
\]  
(2.11)

where K\text{oc} is the organic carbon normalized partition coefficient (ml/g OC), f\text{oc} is the organic carbon content of the sorbent (g OC/g sorbent), K\text{ow} is the octanol-water partition coefficient (ml of water/ml of octanol).

Schwarzenbach et al. (1993) proposed that for neutral nonpolar sorbates, the partition coefficient is strongly related to the aqueous solubility or K\text{ow} value. They proposed two correlations to estimate K\text{oc} value:

\[
\log K_{oc} \approx -0.75 \log C_{w}^{sat} + 0.44
\]  
(2.12)

\[
\log K_{oc} \approx 0.82 \log K_{ow} + 0.14
\]  
(2.13)

In Equation 2.12, C_{w}^{sat} is the solubility in terms of molar concentrations (mole/L). Table 2.1 (Tables are located at the end of each chapter) lists more equations to estimate K\text{oc} values. Since sorption to sediment is positively correlated to organic carbon content, K\text{oc} is more constant among sediments than K\text{p} and therefore is a more useful measurement.
In natural subsurface soil and sediment systems, isotherm nonlinearity is exhibited especially for sorption extended over wide solution concentration ranges. The Langmuir and the Freundlich isotherms are the two most commonly adopted non-linear models.

The Langmuir isotherm can be derived from mass action, kinetic or statistical thermodynamic approaches based on the following assumptions: the sorption energy of a molecule is constant and independent of surface coverage; sorption only occurs on localized sites; there are no interactions between sorbate molecules; and the maximum adsorption possibility is fixed at a complete monolayer. In environmental chemistry, the commonly adopted expression of the Langmuir isotherm is:

\[ q = \frac{q_{\text{max}} bC}{1 + bC} \]  

(2.14)

or the linearized form:

\[ \frac{1}{q} = \frac{1}{q_{\text{max}}} + \frac{1}{bq_{\text{max}}C} \]  

(2.15)

Where \( q_{\text{max}} \) is the maximum sorption capacity (\( \mu \text{g/g} \)) and \( b \) is a sorption coefficient (\( \text{ml/g} \)) related to the affinity of the solute for the sorbate surface. Since soils and
sediments have complicated structures, the assumptions required by Langmuir isotherm are frequently not valid.

The Freundlich isotherm is perhaps the most widely used nonlinear sorption equilibrium model. It can be considered as a summation of Langmuir isotherms at different sites in a heterogeneous matrix (Leboeuf and Weber, 1997). The Freundlich model represents varying energetically-favorable sites and can describe most equilibrium data. The Freundlich isotherm can be represented by the following equation:

\[ q = K_f C^n \]  \hspace{1cm} (2.16)

where \( K_f \) is the Freundlich partition coefficient (\( \text{ml}^n \mu \text{g}^{1-n}/\text{g} \)) and \( n \) is a joint measurement of relative magnitude and diversity of energy associated with a particular sorption process. For sorption processes occurring in natural systems, \( n \) is commonly less than 1. According to Graber and Boriover (1998), Freundlich model fits can be exaggerated by using log-log plots, condensed scales and large data points when the data does not actually fit the model.

Both the Langmuir isotherm and the Freundlich isotherm can reduce to the linear isotherm under special conditions. In the Langmuir equation, if the solution concentration is low enough, the denominator is nearly equal to 1. This means only a very small fraction of the absorbing surface is covered, so the sorption depends linearly on the concentration in the solution. In the Freundlich equation, if the exponent is 1, the sorption becomes linear.
Although the Langmuir and Freundlich isotherms are generally better fits for experimental equilibrium data than the linear isotherm, they have the disadvantage that all the parameters used in these two isotherms are empirically derived coefficients that cannot be estimated, which is the reason that these two isotherms are seldom used in standard transport, risk and remediation models to describe sorption processes. Thus far, all of the currently effective environmental standards for sediments, such as the EPA’s sediment quality criteria (SQCs) and sediment quality advisory levels (SQALs) are directly or indirectly derived from the linear sorption model. For instance, the EPA has published SOCs for five contaminants, including acenaphthene, fluoranthene, phenanthrene, dieldrin, and endrin. The purpose of these criteria is to ensure the porewater concentrations do not exceed the final chronic water quality criteria values. The maximum sediment concentration is correlated to the porewater concentration with the partition coefficient between sediment and porewater (U. S. EPA, 1997).

2.2 Sorption of Hydrophobic Organic Compounds (HOCs) to Natural Soil and Sediment

2.2.1 Soil/Sediment Composition

Soil and sediment can be regarded as a mixture of the following constituents: organic and inorganic solids, liquid and gas phases, and living organisms. The solid phase of soil/ sediment can exist as individual particles, colloids or as aggregates of the inorganic and organic phases. Colloids are particles with diameters of less than 10 μm (Stumm, 1977). Aggregates can be further divided into sub-regions with different compositions such as 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 in mineral grains.

According to Choudry (1984), soil organic matter is composed of the degradation products of plants and animals, as well as living matter such as microorganisms and small animals. The content of organic matter in soils varies considerably. A sandy desert soil may have less than 0.1% organic matter, whereas a peat may have nearly 100% organic matter. Most surface mineral soils and sediments have around 0.5 to 5% organic matter.

The predominant fraction of natural organic matter in soil and sediment is humic substances (humus), which is a major factor in controlling the physical and chemical properties of soil and sediment (Waksman, 1936). Humic substances can be divided into three categories depending on the solubility and the molecular weight. Humic acid is the fraction that is insoluble at low pH and becomes soluble as the pH increases. Fulvic acid is the fraction that is soluble under all pH conditions. Humin is the fraction that is not soluble under any pH conditions, and it constitutes the main fraction of humus.

The inorganic portion of soil and sediment can exist as colloids (<2 μm) 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. Most major minerals expose a external surface which consists of hydroxyls protruding into the medium from a plane of electron–deficient atoms (e.g., Si, Fe, Al) and electron–rich ligands (e.g., oxygen, carbonate). These surface hydroxyls and ligands will form hydrogen bonds with the molecules adjacent to the mineral surface.
(Schwarzenbach, 1993). This kind of association becomes significant especially when the sediment does no include a significant amount of natural organic matter.

2.2.2 Sorption to Soil Organic Matter – Hydrophobic Effect

Natural organic matter primarily accounts for the overall sorption of hydrophobic organic compounds, since its constituents provide a nonpolar environment into which a hydrophobic compound may partition away from water phase, which is called the hydrophobic effect. The basis of the hydrophobic effect can be understood by the molecular interactions of the dissolution of organic solutes in water as described by Schwarzenbach (1993). Dissimilarities between an organic compound and water in shape, size and polarity result in various enthalpy and entropic contributions to the excess free energy. Figure 2.2 is a simple representation of the enthalpies involved in dissolving a neutral organic molecule in water. The entropic contributions are from (1) formation of cavity; (2) formation of ice around the solute; and (3) an enhanced randomness due to mixing dissimilar molecules.

2.2.3 Complex Sorption Behavior of HOCs Due to Soil/ Sediment Heterogeneity

As mentioned before, natural soils and sediments are composed of different organic and inorganic constituents. The presence of anthropogenic organic matter, such as oils, surfactants, and combustion residues, may also greatly increase the heterogeneity of natural soils and sediments. These constituents may interact differently with hydrophobic organic compounds in terms of binding energy, sorption rate and linearity. With respect to the sorption properties of neutral organic compounds, natural sediments
can be deemed as containing the following dominant domains: 1) the organic domain, 2) the mineral domain, 3) the entrapped or adherent NAPL domain (Weber and Huang, 1996). In the soil organic matter domain, the variation of sorption behavior is due to the compositional and structural diversity of soil organic matter with different origin and geologic history. According to Weber et al. (1992), there is a gradual transformation of organic matter from the amorphous phase to the condensed phase during the diagenesis process. Other researchers (Garbarini and Lion, 1986; Gauthier et al., 1987; Grathwohl, 1990; Kile et al., 1995; Huang and Weber, 1997) have found that the aromatic carbon content, polarity, and the relative amount of oxygen-containing functional groups affected the interaction of organic matter with hydrophobic organic compounds. In the mineral domain, different mineral surfaces cause different sorption affinities. The NAPL domain comprises organic matter from different sources, such as petroleum residues, creosotes, and coal tars, which exhibit different sorption behavior because of different interfacial chemistry (Luthy et al., 1997).

The total sorption behavior of a hydrophobic organic compound can be characterized as the combination of the sorption to various constituents of soil and sediment. Generally, the sorption to amorphous natural organic matter, mineral surfaces, and NAPL is kinetically fast and linear, while the sorption into condensed organic polymeric matter or combustion residues is slow and nonlinear. The sorption onto wet organic surfaces is found to be kinetically fast but nonlinear. The overall sorption isotherm depends on the fraction of each constituent in the sediment.

2.3 Desorption of HOCs from Soil and Sediment
Once a hydrophobic organic compound has sorbed to a soil or sediment, the desorption process of the chemical is of more concern to environmental scientists, as it is the solution phase concentration of the contaminant that drives risk assessment, regulation and remediation. For many years, the desorption process has been simplified as a reversible process of sorption in risk and remediation models. However, numerous researches, investigations, and clean-up practices have demonstrated that this over-simplified model often fails to explain the observed desorption behaviors.

2.3.1 Observations of Resistant Fraction in the Desorption Process

Most recent studies have shown that the desorption process of hydrophobic organic compounds is typically biphasic, with a rapid desorption (several hours to several days) followed by a lengthy period of slow desorption (Karickhoff, 1980; Steinberg et al., 1987; Pignatello, 1989; Brussau et al., 1991; Ball and Roberts, 1991; Scribner et al., 1992; Pignatello et al., 1993; Fu et al.; 1994; Chen, 1997; Cornelissen et al., 1998; Chen et al., 1999; Chen et al., 2002). Even after extended desorption times, a small fraction of the sorbed compound still remains resistant to desorption. Ball and Roberts (1991) found the desorption resistant fraction of 1, 2, 4, 5-tetrachlorobenzene in an aquifer was 90%. Pignatello et al. (1993) studied the desorption behavior of herbicide from a historically contaminated soil and found the resistant fraction ranged from 82% to 92%. Kan et al. (1994) observed that 62% of freshly added naphthalene resisted desorption after ten successive washings over 178 days. Chen et al. (1997) found the resistant fraction of chlorinated benzenes in Lake Charles sediment fell between 48% to 62% after 151 days of Tenax accelerated desorption. Thus far, the resistant fraction in
desorption process has been reported for many classes of organic compounds, including polycyclic aromatic hydrocarbons (PAHs), chlorinated benzenes, pesticides, phenols, PCBs, and halogenated aliphatic hydrocarbons.

2.3.2 Proposed Mechanisms for Resistant Fraction in Desorption

Currently, many theories have been proposed to interpret the deviation of desorption behavior from equilibrium assumptions, including chemical adsorption, slow diffusion process, soil heterogeneity, specific interactions between sorbates and high energy-sites in soil/sediment, and irreversible adsorption.

One mechanism to explain the resistant fraction is chemical sorption, which results from the formation of chemical bonds between the sorbate and the sorbent. While chemical sorption may have great effect on the sorption and desorption behavior of some reactive chemicals, such as phenols and some substituted phenols (Issascon and Frink, 1984), it is generally thought to be unimportant to non-reactive and nonpolar contaminants.

Many researchers attribute the resistant fraction in desorption to some sort of diffusion limitation (Wu and Gschwend, 1986; Brusseau et al., 1991; McGinley et al., 1993; Carroll et al., 1994; Farrell and Reinhard, 1994; Pignatello and Xing, 1996; Huang and Weber, 1997; Pignatello and Xing, 1999; Huang and Weber, 2001) considering the porous nature of soil and sediment particles. Two types of diffusion models (Figure 2.3) – sorption retarded pore diffusion model (SRPD) and intraorganic diffusion model (OMD) – have been proposed. As summarized by Pignatello and Xing (1996), the OMD may predominate in soils that are high in organic matter content and low in aggregation,
while the SRPD may predominate in soils where the opposite conditions exist. In both the OMD and SRPD models, the predicted equilibrium partition coefficients are often 10 to 100 times higher than those predicted from the octanol/water partition coefficients.

Weber et al. (1992) asserted that the heterogeneity among the sediment and soil particles may lead to sites with varying affinities for the sorbate, which is the origin of many observed sorption nonlinearities. According to Huang and Weber (1996), soil and sediment can be divided into three domains: a mineral domain, an amorphous soil organic matter domain and a condensed soil organic domain (Figure 2.4). The sorption to the mineral domain and the amorphous soil organic matter domain is linear and relatively fast, while the sorption to the condensed soil organic domain is nonlinear and slow. They also suggested that soil or sediment humic material may gradually transform from amorphous to condensed microcrystalline structure during the diagenesis process, and the microcrystalline organic matter adsorbs hydrophobic organic compounds more strongly, which accounts for the increase of resistant fraction with increasing aging time. Xing and Pignatello (1996) proposed that the overall adsorption is controlled by two mechanism – a partition mechanism in the amorphous domain and a hole filling mechanism in the rigid domain – based on the study of competitive sorption between atrazine and prometon, and between atrazine and trichloroethylene.

Some researchers (Socha and Charpenter, 1987; Burgos, 1996; Gustafsson et al., 1997; Chiou and Kile, 1998) suggested the resistant fraction is the result of specific interactions between sorbates and high-energy sites in soil and sediment. Burgos (1996) proposed that the oxidative coupling of naphthalene and α-naphthol molecules to soil organic matter results in the binding of these two compounds in two sandy soils. Chiou
and Kile (1998) studied the single-solute and binary-solute sorption of several nonpolar and polar organic compounds on a mineral soil and a peat soil. They proposed that more than one mechanism accounts for the nonlinear sorption/desorption behavior of both polar and nonpolar compounds, and the nonlinearity is caused by the sorption to a small amount of high-surface-area carbonaceous material such as charcoal which exhibits much greater affinity for organic compounds than does soil organic matter.

The concept of true irreversible adsorption has also been proposed by many researchers (Everett, 1967; West et al., 1985; Brusseau and Rao, 1991; Adamson, 1990; Burgoes et al., 1996; White et al., 1997; Devitt and Wiesner, 1997; Kan et al., 1998; Schludien et al., 1999; Chen et al., 2000) to explain the existence of the desorption resistant fraction in natural soil and sediment. Everett (1967) suggested that irreversible binding could happen through the mechanical and structural rearrangement of the sorbent. Brusseau and Rao (1989) summarized that sorbate molecules could be physically bound within sorbent through the “sieve effect,” where the sorbate molecule is entrapped in porous organic matter (e.g., Burchill et al., 1981; Schweich and Sardin, 1981), internal structure of mineral particles (e.g., McCloskey and Bayer, 1987), and restricted micropores of sorbent aggregates (e.g., Steinberg et al., 1987). Burgoes et al. (1996) developed an experimental procedure to distinguish the contribution of physical binding and oxidative coupling to the irreversible adsorption of naphthalene and naphthol. They found that binding through oxidative coupling alone could not account for the total irreversibly adsorbed amount. Kan et al. (1997) suggested that a small fraction of the sediment organic matter undergoes a conformational or physical rearrangement, trapping some of the contaminant and resulting in desorption resistant
fraction. White et al. (1997) proposed that the sequestration of phenanthrene in soil is due to the partition into soil organic matter and the entrapment of the molecules within soil micropores following sorption. Schlebaum et al. (1998) observed biphasic desorption behavior of pentachlorobenzene and postulated that the resistant fraction is due to a conformation change in the humic acid after binding of the compound.

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 did not increase the release of contaminants from the residual fraction, indicating the observed phenomenon was probably not a simple kinetic or diffusion-limited process. Second, resistant desorption was also found in a non-porous and homogeneous surrogate material – TiO₂, which could not be explained by the intraparticle diffusion mechanism. Third, a finite and fixed compartment size was observed for the resistant fraction. Fourth, the apparent Kₐc values for the resistant fraction seemed to be independent of their Kₐw values. Compounds from different classes exhibited similar Kₐc values – from 5.0 to 5.5, even though their Kₐw values differed by several orders of magnitude. Kan et al. (1998) proposed a conceptual biphasic sorption model (Figure 2.5) to interpret these observations. This model suggests that during the sorption process of hydrophobic organic compounds to natural soil organic matter, some cooperative conformational changes or physical rearrangement of the soil organic matter occur, which causes a portion of the sorbed compound to be irreversibly bound to soil organic matter. Sorbates associated with the reversible compartment follow the linear sorption model, and the size of the irreversible compartment depends on different
chemical-sediment combinations. The biphasic model can be expressed by the following equations:

\[ q = q_{\text{rev}} + q_{\text{irr}} \] \hspace{1cm} (2.17)

where

\[ q_{\text{rev}} = K_{d} C = K_{oc} f_{oc} C \] \hspace{1cm} (2.18)

and

\[ q_{\text{irr}} = \frac{K_{oc}^{\text{irr}} f_{oc} q_{\text{max}}^{\text{irr}} fC}{q_{\text{max}}^{\text{irr}} f + K_{oc}^{\text{irr}} f_{oc} C} \] \hspace{1cm} (2.19)

where \( q \) is the total solid phase concentration of the sorbate (\( \mu g/g \)), \( q_{\text{rev}} \) is the solid phase concentration (\( \mu g/g \)) in the reversible compartment, \( q_{\text{irr}} \) is the solid phase concentration (\( \mu g/g \)) in the irreversible compartment, \( K_{oc} \) and \( K_{oc}^{\text{irr}} \) are the organic carbon content normalized partition coefficients for the reversible and irreversible fractions respectively, \( f_{oc} \) is the organic carbon content of the soil, \( q_{\text{max}}^{\text{irr}} \) is the irreversible sorption capacity (\( \mu g/g \) soil), and \( f \) is the fraction of the irreversible compartment that is filled at the time of exposure and can be assumed to be equal to one when the exposure concentration is
greater than one-third to one-half the aqueous solubility. The whole sorption isotherm can be represented as:

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

(2.20)

2.3.3 Bioavailability of Desorption Resistant Fraction and Its Impact on Remediation

As mentioned earlier, it is often observed that a small fraction of sorbed contaminant remains resistant to desorption even after extended desorption times. The existence of this desorption resistant fraction of sorbed contaminant in sediment has greatly hindered the efficiency of biodegradation and many other sediment clean up practices. In a review paper, Loehr and Webster (1996) presented the results from a number of studies which addressed the impact of resistant desorption on biodegradation. They concluded that for biodegradation of sorbed chemicals in sediment to occur, they must be available to the microorganisms. Therefore, chemicals associated with the desorption resistant fraction will not be available for bioremediation since microorganisms cannot access them. Kan et al. (1998) compared the pore volumes required to clean up a particular contaminated site, based on the predictions on the equilibrium linear sorption model and the irreversible sorption model. The equilibrium linear model predicted that less than 22 pore volumes would be needed to clean up the site, while the irreversible model, which considered the existence of desorption resistant fraction, predicted that more than 3300 pore volumes would be required. They suggested
that the conventional pump and treat method to remediate the resistant fraction was not economically feasible; even with surfactant and cosolvent flushing, the clean up of this resistant fraction would be difficult. It is generally accepted that a contaminated area may never be returned to their original pristine state even after applying the most advanced remediation technologies.

Considering the fact that 100% clean up is an ideal that cannot be reached, the best that can be accomplished is to reduce the contaminants to a level that is no longer harmful to human and ecosystem health (Linz and Nakles, 1997). To environmental scientists, bioavailability represents the accessibility of a chemical for assimilation and possible toxicity. Therefore, it is reasonable to use bioavailability to determine the required endpoints of remediation operations. Once a contaminant is no longer considered bioavailable, it is not a hazard to the environment nor the creatures that live in it and can be safely left in place. According to Loehr and Webster (1996), sediment-sorbed contaminants in the desorption resistant fraction are not bioavailable. If this is true, the remediation of the resistant fraction is not necessary. Currently, the bioavailability of contaminants in the resistant fraction is being evaluated with micrograms, benthic invertebrates, and plant uptake by researchers in Rice University and Louisiana State University. Beckles at Rice University (2000) studied the bioavailability of several PAHs and found that desorption resistant PAHs are bioavailable, despite the fact that initial aqueous phase concentrations were very low. More studies on the bioavailability of desorption resistant fraction are still needed.

2.3.4 Current Method to Measure the Desorption Resistant Fraction
In most laboratory studies to quantify the desorption resistant fraction of sorbed contaminant, the desorption experiments were conducted by washing the soil or sediment extensively with an electrolyte solution simulating the condition of surface or ground water (Brussau et al., 1991; Ball and Roberts, 1991; Scribner et al., 1992; Pignatello et al., 1993; Fu et al., 1994; Kan et al., 1997; Cornelissen et al., 1998; Chen et al., 1999). In this method, successive desorption experiments with electrolyte solution were conducted until no obvious change was found in the sediment phase concentration of the contaminant of interest, and this remaining fraction was measured as desorption resistant. Unfortunately, it usually took a long time (months to years) to reach the resistant fraction using this repetitive electrolyte solution desorption method. For example, Fu et al. (1994) conducted successive desorption experiments of naphthalene and phenanthrene with electrolyte solution, and it took 137 days to reach the desorption resistant fraction. Xing and Pignatello (1989) and Chen et al. (1999) conducted Tenax accelerated desorption experiments, in which continuously desorbed contaminants were continuously removed from the solution phase with Tenax. Still, this method is very time-consuming. Developing an easy, rapid method to measure the resistant fraction is needed and is the primary focus of this research.

2.4 Desorption of HOCs with Cosolvent

2.4.1. Cosolvent Effect

Numerous studies have shown that completely water miscible organic solvents, such as methanol and acetone, will enhance the apparent aqueous solubilities of less soluble hydrophobic organic compounds (Yalkowsky et al., 1972; Rao et al., 1985; Fu
and Luthy, 1986; Woodburn et al., 1986; Pinal et al., 1990; Rao et al., 1990; Kan et al., 1990; Dickhut et al., 1991; Chen et al., 1997; Kan et al., 1997, Taylor et al., 2000). The effect of enhanced solubility typically occurs when the solvent concentration is higher than 10% by volume, where the dissolved solvent molecules influence the aqueous cavity surrounding the solute, and in so doing, change the energetic costs of forming such a cavity (Schwarzenbach, 1993). In this case, the solvent is called a cosolvent (see Figure 2.6).

Yalkowsky et al. (1976) have shown that for nonpolar organic chemicals, the solubility in a mixed solvent (water and cosolvent) is related to the water solubility by the following equation:

\[
\log x_{\text{mix}}^{\text{sat}} = \log x_{w}^{\text{sat}} + \frac{f_c N (\sigma_{h:w} - \sigma_{h:c}) \text{HSA}}{2.303RT} \tag{2.21}
\]

where \(x_{\text{mix}}^{\text{sat}}\) is the mole fraction solubility in the mixed solvent, \(x_{w}^{\text{sat}}\) is the mole fraction solubility in the water, and \(f_c\) is the volume fraction of cosolvent in the solution. \(N\) is Avogadro’s number (6.02×10^{23} molecules/mol) used to convert everything on a per mole basis, \(\sigma_{h:w}\) is the interfacial energy (J/cm^2) where the hydrophobic solute contacts water, \(\sigma_{h:c}\) is the interfacial energy (J/cm^2) where the hydrophobic solute contacts pure cosolvent. HSA is the solute’s hydrophobic surface area (cm^2/molecule), \(R\) is the gas constant (8.312 J/mole K), and \(T\) is the temperature in degrees Kelvin.
Morris et al. (1988) developed another approach to predict the influence of a cosolvent on the solubility of hydrophobic organic chemicals based on the knowledge of octanol-water partition coefficients:

$$\log(C^{\text{sat}}_{\text{mix}}/C^{\text{sat}}_{w}) = (a \log K_{\text{ow}} + b)(f_c) \quad (2.22)$$

where $a$ and $b$ are coefficients unique to a particular solvent, $K_{\text{ow}}$ is the solute's octanol-water partition coefficient, and $f_c$ is the volume fraction of the cosolvent.

Another approach to estimate the magnitude of enhanced solubility by a cosolvent is from activity coefficients by the following equation:

$$F_{Rs} = \frac{\gamma_w V_{Mw}}{\gamma_s V_{Ms}} \quad (2.23)$$

where $F_{Rs}$ is the solubility enhancement factor, $\gamma_w$ and $\gamma_s$ are the activity coefficients of the solute in water and mixed solvent, and $V_{Mw}$ and $V_{Ms}$ are the molar volumes of water and mixed solvent. The activity coefficients of the solute in water and mixed solvent can be predicted with several algorithms, such as UNIFAC.

Universal quasichemical functional group activity coefficient (UNIFAC) is a group contribution method that can be used to predict activity coefficients of nonelectrolytes in liquid mixtures. The fundamental basis of this model is that compounds may be structurally decomposed into functional groups, each functional group making a unique contribution to the activity coefficient of a compound. Originally,
UNIFAC was used to predict the activity coefficients of hydrocarbons in other hydrocarbon solvents, but it has been extended to include water as a solute and as a solvent. The main advantage of using the UNIFAC method to predict the activity coefficient is that it is possible to calculate the activity coefficient using only pure component data. Many people (Fredenslund et al., 1977; Gupte and Danner, 1987; Pina et al., 1990; Li and Andren, 1994; Kan and Tomson, 1996; Kan et al., 1997) checked the accuracy of the UNIFAC method in predicting the solubilities of HOCs in water and mixed solvent and found a strong correlation between the predicted solubilities with the literature reported and laboratory determined solubilities (Figure 2.7). According to these studies, the UNIFAC method can successfully predict the solubilities of HOCs in both water and mixed solvents.

2.4.2 Cosolvent Effect on Desorption of HOCs

It is generally assumed that the impact of a cosolvent on sorption and desorption of hydrophobic organic compounds is only to alter the effective aqueous phase activities of the compounds without changing the solid phase activities. Therefore, the cosolvent effect on sorption and desorption can be predicted. Considering the enhanced solubilities of HOCs by cosolvent, desorption of HOCs from soil and sediment can be accelerated with the presence of a cosolvent.
Table 2.1: Regression equations for the estimation of $K_{oc}$ (Lyman et al. 1982).

<table>
<thead>
<tr>
<th>Eq. No.</th>
<th>Equation(^a)</th>
<th>No.(^b)</th>
<th>$r^2$(^c)</th>
<th>Chemical Classes Represented</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-5</td>
<td>$\log K_{oc} = -0.56 \log S + 3.64$ (S in mg/L)</td>
<td>106</td>
<td>0.71</td>
<td>Wide variety, mostly pesticides</td>
<td>[26]</td>
</tr>
<tr>
<td>4-6</td>
<td>$\log K_{oc} = -0.54 \log S + 0.44$ (S in mole fraction)</td>
<td>10</td>
<td>0.94</td>
<td>Mostly aromatic or polynuclear aromatics; two chlorinated</td>
<td>[25]</td>
</tr>
<tr>
<td>4-7(^d)</td>
<td>$\log K_{oc} = -0.567 \log S + 4.277$ (S in µ moles/L)</td>
<td>15</td>
<td>0.99</td>
<td>Chlorinated hydrocarbons</td>
<td>[11]</td>
</tr>
<tr>
<td>4-8</td>
<td>$\log K_{oc} = 0.544 \log K_{ow} + 1.377$</td>
<td>45</td>
<td>0.74</td>
<td>Wide variety, mostly pesticides</td>
<td>[26]</td>
</tr>
<tr>
<td>4-9</td>
<td>$\log K_{oc} = 0.937 \log K_{ow} - 0.006$</td>
<td>19</td>
<td>0.95</td>
<td>Aromatics, polynuclear aromatics, triazines and dinitroaniline herbicides</td>
<td>[9]</td>
</tr>
<tr>
<td>4-10</td>
<td>$\log K_{oc} = 1.00 \log K_{ow} - 0.21$</td>
<td>10</td>
<td>1.00</td>
<td>Mostly aromatic or polynuclear aromatics; two chlorinated</td>
<td>[26]</td>
</tr>
<tr>
<td>4-11</td>
<td>$\log K_{oc} = 0.94 \log K_{ow} - 0.02$</td>
<td>9</td>
<td>$e$</td>
<td>$s$-Triazines and dinitroaniline herbicides</td>
<td>[7]</td>
</tr>
<tr>
<td>4-12</td>
<td>$\log K_{oc} = 1.029 \log K_{ow} - 0.18$</td>
<td>13</td>
<td>0.91</td>
<td>Variety of insecticides, herbicides and fungicides</td>
<td>[36]</td>
</tr>
<tr>
<td>4-13(^d)</td>
<td>$\log K_{oc} = 0.524 \log K_{ow} + 0.855$</td>
<td>30</td>
<td>0.84</td>
<td>Substituted phenylureas and alkyl-N-phenylcarbamates</td>
<td>[5]</td>
</tr>
<tr>
<td>4-14(^d,f)</td>
<td>$\log K_{oc} = 0.0067 (P - 45N) + 0.237$</td>
<td>29</td>
<td>0.69</td>
<td>Aromatic compounds: ureas, 1,3,5-triazines, carbamates, and uracils</td>
<td>[18]</td>
</tr>
<tr>
<td>4-15</td>
<td>$\log K_{oc} = 0.681 \log BCF(t) + 1.963$</td>
<td>13</td>
<td>0.76</td>
<td>Wide variety, mostly pesticides</td>
<td>[26]</td>
</tr>
<tr>
<td>4-16</td>
<td>$\log K_{oc} = 0.681 \log BCF(t) + 1.886$</td>
<td>22</td>
<td>0.83</td>
<td>Wide variety, mostly pesticides</td>
<td>[26]</td>
</tr>
</tbody>
</table>

\(^a\) $K_{oc}$ = soil (or sediment) adsorption coefficient; $S$ = water solubility; $K_{ow}$ = octanol-water partition coefficient; BCF(t) = bioconcentration factor from flowing-water tests; BCF(t) = bioconcentration factor from model ecosystems; P = parachor; N = number of sites in molecule which can participate in the formation of a hydrogen bond.

\(^b\) No. = number of chemicals used to obtain regression equation.

\(^c\) $r^2$ = correlation coefficient for regression equation.

\(^d\) Equation originally given in terms of $K_{om}$. The relationship $K_{om} = K_{oc}/1.724$ was used to rewrite the equation in terms of $K_{oc}$.

\(^e\) Not available.

\(^f\) Specific chemicals used to obtain regression equation not specified.
Linear Isotherm

$$q_e = K_s C_e$$

Langmuir Isotherm

$$q_e = \frac{Q^\circ b C_e}{1 + b C_e}$$

Freundlich Isotherm

$$q_e = K_f C_e^n \ (n<1)$$

Figure 2.1: Three most commonly used sorption isotherms – Linear isotherm, Langmuir isotherm and Freundlich isotherm.
Figure 2.2: Schematic representation of the various enthalpies involved in dissolving a neutral organic molecule in water (from Schwarzenbach, 1993).
Figure 2.3: Schematic of two diffusion models for slow sorption. (a) Intraorganic Diffusion, illustrating diffusion from a rubbery phase A and a condensed glassy phase B. (b) Sorption Retardation Pore Diffusion, sorption is enhanced in very small pores due to interaction with more than one surface (from Pignatello and Xing, 1996).
Figure 2.4: Schematic illustration of domain types associated with a soil/sediment particle (from Weber and Huang, 1996).
Figure 2.5: A pictorial representation of the biphasic irreversible sorption model by Kan et al. (1998).
Figure 2.6: Illustrations of how dissolved organic substances affect the water molecules surrounding an organic compound of interest (from Schwarzenbach, 1993).
Figure 2.7: Plot of the observed versus UNIFAC predicted solubilities of 11 groups of organic compounds (from Kan et al., 1997). The compounds include Alkanes, Alkenes/Cycloalkane, Alkylbenzenes, Anilines, Chlorinated Benzenes, PAH, Chlorinated Alkanes, Chlorinated Alkenes, Phenols, PCBs and Organohalide insecticides.
Chapter 3: Previous Attempt to Measure the Desorption Resistant Fraction

3.1 Introduction

As discussed in chapter 2, there exists a fraction of sorbed hydrophobic organic compounds which resists desorption and has been observed in both laboratory and field conditions (Karickhoff, 1980; Pignatello, 1989; Brussau et al., 1991; Ball and Roberts, 1991; Scribner et al., 1992; Pignatello et al., 1993; Fu et al., 1994; Chen, 1996; Cornelissen et al., 1998; Kan et al., 1998; Chen et al., 2000). According to Loehr and Webster (1996), contaminants associated with the desorption resistant fraction were not bioavailable. If that is the case, the desorption resistant fraction can be deemed as the endpoint of remediation practice and left alone without causing significant environmental concern. Currently, the bioavailability of contaminants in the desorption resistant compartment is being evaluated with micrograms, benthic invertebrates, and plant uptake by many researchers. It is desirable to have a standard experimental protocol to measure the desorption resistant fraction. The conventional experimental approach to measure this desorption resistant fraction is by conducting multi-step desorption with electrolyte solution which simulates the condition of surface or groundwater. However, this method is time-consuming and therefore impractical for widespread applications.

This chapter summarizes the research done by Wei Liu and Chuanyue Wang in the author’s laboratory. The overall objective of this research was to develop a novel protocol that would expedite the desorption of the readily desorbable fraction so that the desorption resistant fraction could be reached and measured within a short desorption
period. In this research, naphthalene and phenanthrene were used as the model contaminants, while two different sediments – Lake Charles sediment and Bayou Manchac sediment – were used as the sorbents. Eight sorption/desorption experimental protocols were tested. In each experiment, the sediment was initially saturated with either naphthalene or phenanthrene by the sorption experiment. Isopropanol/electrolyte solution mixed solvent was chosen to conduct most of the desorption experiments considering the enhanced solubilities of naphthalene and phenanthrene in the mixed solvent phase. As a result, the release of these two compounds from the sediments was accelerated, and the desorption resistant fraction could be measured within a short desorption period. XAD-2 accelerated desorption was also conducted in a selected experiment and compared with the isopropanol accelerated desorption.

The main problem with conducting the isopropanol accelerated desorption experiments was the re-adsorption of contaminants, which was caused by the residual isopropanol in the sediment pore water due to incomplete separation. As a result, an accurate measurement of the desorption resistant fraction could not be obtained.

3.2 Description of Experiments
3.2.1 Sorbates and Sediments

Radiolabeled $^{14}$C phenanthrene (specific activity of 13.3 mCi/mmol) and naphthalene (specific activity of 10.1 mCi/mmol), were used as the sorbates because of their well-defined physical-chemical properties.

Two sediments were used as the sorbents in these experiments. The Lake Charles sediment was collected from the lower Calcasieu River at Lake Charles, Louisiana and
was contaminated with various compounds including petroleum hydrocarbons, PAHs, as well as polychlorinated aromatic and aliphatic organic compounds. The Bayou Manchac sediment was uncontaminated sediment collected from Baton Rouge, Louisiana. The organic carbon contents of the Lake Charles sediment and the Bayou Manchac sediment were 4.1% and 1.4%, respectively.

3.2.2 Sorption Experiments

Table 3.1 lists the experimental protocols for the eight sorption and desorption experiments. The sorption experiments were conducted in 65-ml glass vials. To begin a sorption experiment, about 16 g of wet soil (with ~31% moisture content) was added into the vial before adding the stirring bar (4.30 g or 6.40 g), and 60 ml of electrolyte solution (0.01 M NaCl, 0.01 M CaCl₂, and 0.01 M NaN₃ in D. I. water). Then the vial was sealed containing approximately 1 ml of headspace. Furthermore, 1 ml of stock solution of radiolabeled compound was injected into the vial using a syringe infusion pump at a rate of 694 μl/min. Afterwards, the glass vial was tumbled at 3 rpm for 30 days to reach sorption equilibrium. The vial was then centrifuged at 3000 rpm for 30 minutes, 90% of the supernatant was removed and analyzed for the solution phase concentration by scintillation counting.

3.2.3 Desorption Experiments

In these studies, the desorption experiments were performed primarily using isopropanol/electrolyte solution mixed solvent. XAD-2 accelerated desorption was also conducted in a selected desorption experiment for comparison.
Upon the completion of a sorption experiment, the reaction vial was hand shaken vigorously to give a uniform distribution of the sediment. Then, a portion of the sediment slurry was immediately withdrawn with a glass syringe and transferred to another vial to measure the solid phase concentration. Similarly, about 2 g of sediment slurry was transferred from the sorption vial to another 43-ml glass vial to conduct the desorption experiment. In these studies, the desorption experiment was conducted with two approaches. In Experiments 3.1-3.7, isopropanol/electrolyte solution mixed solvent with a typical concentration (wt of isopropanol/wt of mixed solvent) was added into the vial to initiate a desorption experiment. Then, the vial was sealed and tumbled at 3 rpm for 2-3 days. Afterwards, the vial was centrifuged and most of the mixed solvent was removed. To remove the residual isopropanol in the pore water, two methods were used: Liu washed the sediment twice with contaminant free electrolyte solution; while in Wang’s method, the sediment was first washed with several isopropanol/electrolyte solution mixed solvents with lower isopropanol concentrations, then the sediment was washed twice with electrolyte solution. A third batch of newly made electrolyte solution was added to the vial, and the vial was tumbled at 3 rpm for 3 days. At the end of this water desorption, the vial was centrifuged to separate the solid from the aqueous solution. The supernatant was then withdrawn, extracted to measure the aqueous phase concentration. A portion of the remaining sediment was withdrawn with a glass syringe and was transferred to another vial to measure the solid phase concentration. If another desorption was needed, fresh isopropanol/electrolyte solution mixed solvent was added to the remaining sediment to initiate another desorption. The operation was identical to the procedure described above. In Experiment 3.8, amberlite XAD-2 was used to
accelerate the release of sorbed compound. A pictorial representation of this desorption system was drawn in Figure 3.1. In this system, the desorption was initiated with XAD-2 resin in a dialysis membrane bag with a molecular weight cutoff of 1000. Fifteen XAD-2 accelerated desorption steps were conducted in Experiment 3.8. At the end of each desorption step, the XAD-2 was changed and the contaminant concentrations in both the solution phase and the sediment phase were measured.

3.2.4 Solution and Solid Phase Concentrations

In these studies, the solution phase (electrolyte solution) concentrations were determined directly by scintillation counting. To determine the sediment phase concentrations, compounds in the sediment were extracted with acetone. At the end of each sorption and desorption experiment, the reaction vial was hand shaken vigorously for 1 minute, and a certain amount of slurry was withdrawn and transferred to another vial. Acetone was added to the vial to leave no headspace. The vial was sealed and shaken in a water bath at 70°C for 24 hours. Then the vial was centrifuged at 3000 rpm for 30 minutes, and the supernatant was removed and analyzed by scintillation counting.

3.3 Results

3.3.1 Sorption and Resistant Desorption

The results of the sorption experiments are summarized in Table 3.2. The $K_{oc}$ 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 $K_{oc}$ values of naphthalene were similar under different
sorption conditions. They were found to be $10^{2.94}$, $10^{2.89}$, $10^{3.08}$ in the Lake Charles sediment, $10^{2.73}$ in the Bayou Manchac sediment. The $K_{oc}$ values of phenanthrene were also found to be similar in the Lake Charles sediment and the Bayou Manchac sediment, which were $10^{4.05}$ and $10^{4.09}$, respectively.

The desorption of these two compounds deviated significantly from sorption. In Experiment 3.1, the observed $K_{oc}$ value of naphthalene was $10^{2.94}$ at the end of the sorption experiment. The value increased to $10^{5.07}$ after four desorption steps with isopropanol/electrolyte solution mixed solvent. Similarly, in Experiments 3.2, 3.3, 3.5, and 3.6, the $K_{oc}$ values of naphthalene increased by a factor of 100 after three or four desorption steps. For phenanthrene, the $K_{oc}$ value in the Lake Charles sediment (Experiment 3.4) increased by a factor of 10 after three desorption steps, the same phenomenon was found in Experiments 3.7 and 3.8, where the desorption experiments of phenanthrene from the Bayou Manchac sediment were conducted with mixed solvent and XAD-2, respectively.

3.3.2 Isopropanol and XAD-2 Accelerated Desorption

In these studies, two methods were used to accelerate the release of contaminants from sediments. In Experiments 3.1 to 3.7, accelerated desorption experiments were conducted using isopropanol/electrolyte solution mixed solvent; while in Experiment 3.8, XAD-2 resin was used to accelerate the desorption of contaminant. The effect of these two methods in accelerating the desorption of contaminant could be checked by examining the change of solid phase concentration with desorption step, as plotted in Figure 3.2. In Experiments 3.1 to 3.7, with three or four desorption steps using
isopropanol/electrolyte mixed solvent, most of the sorbed contaminant was removed from the sediment. For example, in Experiment 3.7, the solid phase phenanthrene concentration was 95.4 µg/g at the end of the sorption experiment. The concentration dropped quickly to 2.29 µg/g after only three two-day mixed solvent desorption steps. In contrast, the desorption of phenanthrene with XAD-2 was very time-consuming. In Experiment 3.8, the sediment phase phenanthrene concentration decreased from 116 µg/g to 2.29 µg/g after ten XAD-2 desorption steps which took over 70 days.

3.3.3 Determination of Maximum Desorption Resistant Capacity-- $q_{\text{max}}^{\text{irr}}$

Using the experimental protocols of these studies, it was not possible to measure the desorption resistant fraction directly. However, the maximum desorption resistant capacity ($q_{\text{max}}^{\text{irr}}$) could be obtained by curve fitting the experimental data using the irreversible sorption isotherm proposed by Kan et al. (1998) – Equation 2.20. The least square fitting method was used to fit the data of each compound/sediment combination, with $q_{\text{max}}^{\text{irr}}$ as the only fitting parameter. Initially, a number of solid phase concentrations, q, were calculated using Equation 2.20 and the experimentally observed aqueous phase concentrations. The value of $K_{oc}$ used in the equation was that observed in the sorption experiment (Table 3.2). The value of $K_{oc}^{\text{irr}}$ used was $10^{5.47}$ as determined by previous studies. A value of 20 µg/g was initially assigned to $q_{\text{max}}^{\text{irr}}$, then, the difference between the calculated $q_{\text{cal}}$ and experimental determined $q_{\exp}$ values was calculated, squared, and summed as $\Sigma (q_{\text{cal}}-q_{\exp})^2$. The optimum value of $q_{\text{max}}^{\text{irr}}$ was obtained by adjusting the value so that $\Sigma (q_{\text{cal}}-q_{\exp})^2$ could be minimized. Using this method, the $q_{\text{max}}^{\text{irr}}$ values were found
to be 23.5 µg/g and 4.79 µg/g for naphthalene in the Lake Charles sediment and the Bayou Manchac sediment, 53.4 µg/g and 7.65 µg/g for phenanthrene in the Lake Charles sediment and the Bayou Manchac sediment.

3.4 Discussion

3.4.1 Sorption and Desorption isotherm

An irreversible sorption isotherm has been proposed (Kan et al., 1998) to describe the biphasic sorption and desorption of both laboratory and field observations. The overall isotherm is the combination of the isotherms contributed by both the reversible and irreversible fractions, as in Equations 2.18 and 2.19. Previous studies have 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., 1999). In this case, f in Equation 2.19 can be assumed to be 1. This was satisfied in all the experiments conducted in these studies. Thus, for all the chemical-sediment combinations in these studies, the whole sorption isotherm could be simplified as:

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

(3.1)

In Figures 3.3 and 3.4, the experimentally observed sorption and desorption data in Experiments 3.1 to 3.8 were fitted with the irreversible sorption isotherm. The solid lines in the figures were the fitted isotherms using Equation 3.1 and the observed \( K_{oc} \) and
$K_{oc}^{irr}$ values from the sorption experiments. The $q_{max}^{irr}$ value was taken to be the only fitting parameter. The data points were experimental observations. As in these figures, the experimental observed data were well fitted by the irreversible model prediction. The $q_{max}^{irr}$ values obtained from these isotherms vary among the different chemical-sediment combinations, depending on the solubility of the chemical and the organic compound content of the sediment. For example, the highest $q_{max}^{irr}$ value (53.4 µg/g) was obtained for the chemical with larger $K_{ow}$ value (phenanthrene, $K_{ow} =10^{3.36}$), and the sediment with more organic carbon content (Lake Charles sediment, $f_{oc} = 0.041$); while the lowest $q_{max}^{irr}$ (4.79 µg/g) value was observed for the chemical with smaller $K_{ow}$ value (naphthalene, $K_{ow} =10^{3.36}$) and the sediment with less organic carbon content (Bayou Manchac sediment, $f_{oc} = 0.0138$).

3.4.2 Re-adsorption Effect

According to these studies, the isopropanol/electrolyte solution mixed solvent desorption demonstrated much higher efficiency than that of XAD-2 resin. After three or four consecutive mixed solvent desorption steps, with each step taking two or three days, most of the contaminants were removed from the sediment. In contrast, XAD desorption required approximately ten desorption steps and over 70 days to reach the same level of desorption. Isopropanol/electrolyte solution mixed solvent desorption was recommended. However, with this desorption approach, the measurement of the solid phase contaminant concentration after each desorption step was subject to considerable error due to the re-adsorption of the contaminant.
The re-adsorption effect on the measurement of the solid phase contaminant concentration can be better understood with Figure 3.5. At the end of each mixed solvent desorption, the vial containing the sediment and mixed solvent was centrifuged to separate the solution phase from the sediment phase and most of the solution was removed. However, there was still a portion of isopropanol/electrolyte solution mixed solvent remaining in the sediment after separation, and this portion contained a high concentration of contaminant. Direct measurement of the solid phase concentration at this stage is not possible due to the presence of this residual solution with a high contaminant concentration. In these studies, two methods were used to remove this residual solution from the sediment: washing with contaminant free electrolyte solution or washing with contaminant free mixed solvent followed by electrolyte solution. However, when contaminant free mixed solvent (with lower isopropanol concentration) or electrolyte solution was added into the system for washing, the residual solution mixed with the added solution and formed a solution environment with a relatively high contaminant concentration. To reach sorption equilibrium, a portion of the contaminant in the solution must re-adsorb to the sediment. Therefore, the subsequent measured value of the solid phase contaminant concentration included the contribution of the re-adsorbed mass and did not represent the true value. For example, considering phenanthrene desorption with 60% (wt/wt) isopropanol/electrolyte solution mixed solvent from the Lake Charles sediment, the $K_{oc}$ (water) of phenanthrene was found to be $10^{4.05}$ ml/g OC; the $f_{oc}$ of the sediment was 0.041. Assume after separation, 4 ml of mixed solvent (with phenanthrene concentration of 4.5 μg/ml) remained with the sediment (2 g, assuming true phenanthrene concentration is 10 μg/g in the sediment after desorption) by using the
traditional separation method. When contaminant free electrolyte solution (for example, 40 ml) was added to the sediment for washing, the mass of phenanthrene re-adsorbed to the sediment \( q_{\text{re-adsorb}} \) (\( \mu g/g \) soil) can be calculated:

\[
(10 \mu g/g + q_{\text{re-adsorb}}) = 10^{4.05} \mu g/g \cdot 0.04 \left( \frac{4ml \times 4.5 \mu g/ml - q_{\text{re-adsorb}} \times 2g}{40 \text{ ml} + 4 \text{ ml}} \right)
\]

\[ q_{\text{re-adsorb}} = 8.95 \mu g/g \]

therefore, the measured sediment phase phenanthrene concentration was almost twice of the real value. It was also found that during the re-adsorption process, contaminant in the sediment phase would re-distribute between the reversible fraction and desorption resistant fraction. As a result, the \( q_{\text{max}}^{\text{irr}} \) values determined by these studies were also not the true values.

3.5. Summary

The desorption results indicated that isopropanol was more efficient than XAD-2 in accelerating the desorption of contaminants from sediment and was recommended to conduct accelerated desorption experiments for the measurement of desorption resistant fraction. However, when conducting mixed solvent desorption, the re-adsorption of contaminant occurred in each desorption step due to the ineffective separation method, which affected the accurate measurement of solid phase contaminant concentration. The direct measurement of desorption resistant fraction was also not possible.
The desorption results were also compared to an irreversible sorption model, which accounted for the contributions of both the reversible and resistant desorption fractions. The desorption results were well fitted with the model, and the maximum desorption resistant fraction values could be obtained from curve fitting.
Table 3.1: Experimental protocols $^a$

1. Lake Charles sediment

Exp 3.1: naphthalene
1 sorption (18d) – 4 mixed solvent desorption steps (10%, 45%, 45%, 45% wt/wt)

Exp 3.2: naphthalene
1 sorption (25d) – 3 mixed solvent desorption steps (40%, 40%, 40%, wt/wt)

Exp 3.3: naphthalene
1 sorption (17d) – 3 mixed solvent desorption steps (40%, 40%, 40%, wt/wt)

Exp 3.4: phenanthrene
1 sorption (18d) – 3 mixed solvent desorption steps (60%, 60%, 60%, wt/wt)

2. Bayou Manchac sediment

Exp 3.5: naphthalene
1 sorption (15d) – 4 mixed solvent desorption steps (40%, 40%, 40%, 40%, wt/wt)

Exp 3.6: naphthalene
1 sorption (15d) – 3 mixed solvent desorption steps (40%, 20%, 20%, wt/wt)

Exp 3.7: phenanthrene
1 sorption (38d) – 3 mixed solvent desorption steps (45%, 35%, 35%, wt/wt)

Exp 3.8: phenanthrene
1 sorption (38d) – 15 XAD-2 desorption steps. XAD-2/sediment ratio: 0.2.

$^a$ electrolyte solution matrix: 0.01M NaCl, 0.01M CaCl$_2$, and 0.01M NaN$_3$. Solid/solution ratio: 10-16g sediment, 60 ml solution (in sorption), 2 g sediment, 42 ml solution (in desorption).

Mixed solvent desorption: isopropanol/electrolyte solution mixed solvent replaced with freshly prepared mixed solvent. 90% supernatant removed with centrifugation, the residual mixed solvent removed with several mixed solvent or electrolyte solution washings.

XAD-2 desorption: XAD-2 replaced with clean XAD-2, each step took 7 days.
Table 3.2: Summary of the results of the sorption and desorption experiments, including the solid phase concentrations at the end of sorption; the observed partition coefficients in sorption and desorption; and the maximum resistant desorption capacities.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Sediment</th>
<th>Compound</th>
<th>Sorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$q_0^a$</td>
<td>$\log K_{oc}^e$</td>
</tr>
<tr>
<td>3.1</td>
<td>Lake Charles</td>
<td>Naph.</td>
<td>373</td>
<td>2.94</td>
</tr>
<tr>
<td>3.2</td>
<td>Lake Charles</td>
<td>Naph</td>
<td>296</td>
<td>2.89</td>
</tr>
<tr>
<td>3.3</td>
<td>Lake Charles</td>
<td>Naph.</td>
<td>316</td>
<td>3.08</td>
</tr>
<tr>
<td>3.4</td>
<td>Lake Charles</td>
<td>Phen.</td>
<td>423</td>
<td>4.05</td>
</tr>
<tr>
<td>3.5</td>
<td>Bayou Manchac</td>
<td>Naph.</td>
<td>81.7</td>
<td>2.73</td>
</tr>
<tr>
<td>3.6</td>
<td>Bayou Manchac</td>
<td>Naph.</td>
<td>75.4</td>
<td>2.73</td>
</tr>
<tr>
<td>3.7</td>
<td>Bayou Manchac</td>
<td>Phen.</td>
<td>95.4</td>
<td>4.09</td>
</tr>
<tr>
<td>3.8</td>
<td>Bayou Manchac</td>
<td>Phen.</td>
<td>116</td>
<td>4.09</td>
</tr>
</tbody>
</table>

$a$ Measured by solid extraction.

$b$ Fitted with the least square method, using the irreversible sorption isotherm and experimental sorption and desorption data.

$c$ Log $K_{oc}$ values at the end of the last desorption step.
Figure 3.1: Pictorial representation of the XAD-2 accelerated desorption approach. XAD-2 was encapsulated in a dialysis membrane bag (MWCO 1000), and placed in the soil/electrolyte solution mixture to conduct the desorption experiment. Each desorption step took 7 days. Spent XAD-2 was replaced with clean XAD-2 after each desorption step.
Figure 3.2.a: Plot of the sediment phase concentrations of naphthalene with desorption step in Experiments 3.1 (diamond symbols), 3.2 (square symbols) and 3.3 (triangle symbols). In these three experiments, the initial sediment phase naphthalene concentrations were about 300 µg/g. In each experiment, after three or four desorption steps with isopropanol/electrolyte solution mixed solvent (each took 2-3 days), most of naphthalene was removed from the sediment.
Figure 3.2.b: Plot of the sediment phase concentrations of naphthalene with desorption step in Experiments 3.5 (diamond symbols) and 3.6 (square symbols). The initial sediment phase concentrations in these two experiments were about 100 μg/g. In each experiment, after three isopropanol/electrolyte solution mixed solvent desorption steps, most of naphthalene was removed from the sediment.
Figure 3.2.c: Plot of the sediment phase concentrations of phenanthrene with desorption step in Experiment 3.4. The initial sediment phase phenanthrene concentration was 423 μg/g. After three desorptions with isopropanol/electrolyte solution mixed solvent, the sediment phase phenanthrene concentration dropped to less than 10 μg/g.
Figure 3.2.d: Plot of the sediment phase concentrations of phenanthrene with desorption step in Experiments 3.7 and 3.8. The initial sediment phase phenanthrene concentrations were about 100 µg/g. In Experiment 3.7 (square symbols), with three isopropanol/electrolyte solution mixed solvent desorptions (each took 2-3 days), the sediment phase phenanthrene concentration dropped to 2.29 µg/g; while in Experiment 3.8 (diamond symbols), the sediment phase phenanthrene dropped to the same value after 11 XAD-2 desorptions (7 days a step).
Figure 3.3.a: Plot of the model predicted vs. experimentally observed isotherms of naphthalene in Lake Charles sediment. The solid line is the predicted isotherm using the irreversible sorption isotherm. The diamond symbols are experimental observations.
Figure 3.3.b: Plot of the model predicted vs. experimentally observed isotherms of phenanthrene in Lake Charles sediment. The solid line is the predicted isotherm using the irreversible sorption isotherm. The diamond symbols are experimental observations.
Figure 3.4.a: Plot of the model predicted vs. experimentally observed isotherms of naphthalene in Bayou Manchac sediment. The solid line is the predicted isotherm using the irreversible sorption isotherm. The diamond symbols are experimental observations.
Table 3.4.b: Plot of the model predicted vs. experimentally observed isotherms of phenanthrene in Bayou Manchac sediment. The solid line is the predicted isotherm using the irreversible sorption isotherm. The diamond symbols are experimental observations.
Figure 3.5: Pictorial representation of the re-adsorption effect caused by the residual isopropanol remaining in the separated sediment by the conventional separation method. (A) At the end of each mixed solvent desorption, the conventional separation method was used to remove most of the solution from the sediment. A portion of isopropanol/electrolyte solution mixed solvent which contained a high concentration of contaminant remained with the sediment. (B) When contaminant free mixed solvent solution or electrolyte solution was added to the system for the purpose of washing, the contaminant in the solution phase would re-adsorb to the sediment due to the existence of high concentration residual solution. Therefore, the measurement of the sediment phase concentration contained a large error.
Chapter 4: New Method to Measure the Desorption Resistant Fraction

4.1 Introduction

Many studies have been conducted to characterize the desorption resistant fraction of sorbed organic compounds in soil and sediment. The most common approach is by conducting repetitive water desorption, in which the desorption resistant fraction is determined by measuring the solid phase concentration after extended desorption times. This method is time-consuming and impractical, because many desorption steps, each taking days to weeks to complete, must be conducted. In addition, the final measurement of the solid phase concentration is not quite accurate, because there is always a fraction of water associated with the solid, as will be discussed below.

In the previous chapter, two previous attempts to measure the desorption resistant fraction within one or several desorption steps were reviewed. In these works, isopropanol/water mixed solvent was used to accelerate the desorption of sorbed contaminants in sediment, so within one or several desorption steps, the desorption resistant fraction could be reached and measured. Although this method successfully decreased the time needed to reach the desorption resistant phase, it suffered from the same shortcoming related to residual volume in the solid phase and with re-adsorption as was discussed in the previous chapter.

In order to fully understand the problems associated with measuring the amount of contaminant in the resistant phase using previous methods, it is first necessary to
precisely define the “distribution coefficient, $K_d$.” Sediment/water distribution coefficient, $K_d$ is defined as:

$$K_d = \frac{q}{C_w} \quad (4.1)$$

where

$q$ is the sorbate concentration in the sediment phase (µg/g), and

$C_w$ is the solute concentration in the solution phase (µg/ml).

In practice, the true $K_d$ value cannot be measured. In batch sorption and desorption experiments, when people try to separate solution from all particles in a soil or sediment suspension, it is practically impossible not to include some colloids (micro-particles or macromolecules that are small enough to move by Brownian motion rather than gravitational settling) in the aqueous separate, also to some extent a small portion of solution remains with the solid separate. As a result, experimental attempts to measure $K_d$ actually measure colloid-bound molecules along with the dissolved molecules in the aqueous phase. Furthermore, the dissolved molecules in the solution remaining with the solid phase will be measured as if they were sorbate concentration (Schwarzenbach et al, 1993). The apparent $K_d$ measured is:
\[ K_d^{\text{apparent}} = \frac{n_{\text{solid}}/m_{\text{solid}} + \frac{n_{\text{solid pore water}}}{V_{\text{solid pore water}}} \cdot \frac{V_{\text{solid pore water}}}{m_{\text{solid}}}}{n_{\text{aqueous}}/V_{\text{supernate water}} + \frac{n_{\text{colloids}}}{m_{\text{colloids}}} \cdot \frac{m_{\text{colloids}}}{V_{\text{supernate water}}}} \]

\[ K_d^{\text{apparent}} = \frac{q + C_w \cdot V_{w/s}}{C_w + q_{\text{colloid}} r_{cw}} \]

(4.2)

where

\( n_{\text{solid}} \) is the mass of sorbate on the separated sediment (\( \mu g \)),
\( m_{\text{solid}} \) is the mass of separated sediment (g),
\( n_{\text{solid pore water}} \) is the mass of solute in the solution remaining with the sediment separate (\( \mu g \)),
\( V_{\text{solid pore water}} \) is the volume of solution remaining with the solid separate (ml),
\( n_{\text{aqueous}} \) is the mass of solute in the separated solution (\( \mu g \)),
\( V_{\text{supernatant}} \) is the volume of the separated solution (ml),
\( n_{\text{colloids}} \) is the mass of sorbate on the colloids (\( \mu g \)),
\( m_{\text{colloids}} \) is the mass of colloids remaining in the separated solution (g),
\( q \) is the sorbate concentration on the separated sediment (\( \mu g/g \)),
\( C_w \) is the solute concentration in the water (\( \mu g/ml \)),
\( V_{w/s} \) is the volume of solution remaining with the separated particles (ml/g),
\( q_{\text{colloid}} \) is the sorbate concentration on the colloids (\( \mu g/g \)), which equals to \( q \),
\( r_{cw} \) is the colloid mass remaining with the separated solution (g/ml).

This equation can be rewritten as
\[ K_{d \text{ apparent}} = \frac{K_d C_w + C_w V_{w/s}}{C_w + K_d C_w r_{cw}} \]  

(4.3)

or

\[ K_{d \text{ apparent}} = \frac{K_d + V_{w/s}}{1 + K_d r_{cw}} \]  

(4.4)

This expression indicates that the apparent solid/solution distribution coefficient will only equal the true \( K_d \) (solid/solution distribution coefficient) when \( V_{w/s} << K_d \) and \( K_d * r_{cw} << 1 \) (see Figure 4.1). For compounds with low \( K_d \) (do not sorb easily), the experimentally determined \( K_d \) value may be erroneously high because of solution remaining in the solid separate. For compounds with high \( K_d \) (tend to sorb), the observed \( K_d \) will be lower than the true value in situations where colloid phases are substantial (high \( r_{cw} \)).

In this study, a new separation method was developed to completely separate the solution phase from the sediment. Quality control experiments indicated only 0.03-0.05 ml/g solution was remaining with the sediment using this separation method. As a result, the \( V_{w/s} \) term in Equation 4.4 could be neglected. In this separation method, the use of an ultra-filtration membrane also ensured the complete removal of colloids from the liquid phase, so the \( r_{cw} \) value was reduced to 0. Therefore, the true sediment solution distribution coefficient could be measured with this separation method. One or several steps of desorption experiments with isopropanol/electrolyte solution mixed solvent were
then designed using this new separation method so that the desorption resistant fraction could be determined easily and rapidly.

4.2 Materials and Methods

4.2.1 Sorbates and Chemicals

Both $^{14}$C-radiolabeled phenanthrene (Sigma Chemical, MO) and non-labeled phenanthrene (Aldrich Chemical Company, Inc., Milwaukee, WI) were used in this study. The purity of the $^{14}$C-radiolabeled phenanthrene was >98% as determined by GC-MS. The specific activity of $^{14}$C-radiolabeled phenanthrene was 13.3 mCi/mmol. Upon receipt, stock solution of $^{14}$C-radiolabeled phenanthrene (471 μg/ml) was prepared in methanol. Stock solution of non-labeled phenanthrene (366 μg/ml) was prepared by dissolving solid phenanthrene in methanol. The $^{14}$C-radiolabeled phenanthrene stock solution was further diluted with the non-labeled phenanthrene stock solution to make mixture stock solution (376 μg/ml) of $^{14}$C-radiolabeled and non-labeled phenanthrene in methanol.

Polycyclic Aromatic Hydrocarbons Mix (99% in methylene chloride) (Ultra Scientific, North Kingstown, RI) was diluted and used as the GC/FID and GC/MS calibration standard. Upon receipt, the mixture solution was diluted in acetone to make stock solution. More stock solutions of different concentrations were made by further diluting the stock solution in acetone, methanol, and methylene chloride. 2, 5-dibromotoluene (Aldrich Chemical Company, Inc., Milwaukee, WI) was used as the internal standard in GC/FID and GC/MS analysis. 1, 4-dibromobenzene (Ultra Scientific,
North Kingstown, RI) solution (90.94 µg/ml) in acetone was used as the surrogate standard in Soxhlet extraction.

An electrolyte solution was prepared in D. I. water with sodium chloride, with a purity of > 9.995% (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 is used as an inhibitor for bacterial growth.

Isopropanol (spectranalyzed, Fisher Scientific, Fair Lawn, NJ) was used in the desorption experiments. Several other solvents were used for solution preparation, sediment and solution extraction, and cleaning purposes. These solvents include acetone (spectranalyzed, Fisher Scientific, Fair Lawn, NJ), methanol (spectranalyzed, Fisher Scientific, Fair Lawn, NJ), methylene chloride (GC Reslov, Fisher Scientific, Fair Lawn, NJ), isooctane (HPLC, Fisher Scientific, Farir Lawn, NJ), hexane (Optima, Fisher Scientific, Fair Lawn, NJ), and n-pentane (HPLC, Fisher Scientific, Fair Lawn, NJ). All the chemicals used in this research were reagent grade or better.

4.2.2 Sediment

The sediment used in this study is the bottom sediment collected from Utica Harbor, NY, near an old MSP (manufactured synthetic-gas petroleum) plant that made synthetic gasoline and natural gas from coal. The waste from this plant contaminated the sediment with a number of PAHs for several years. Upon receipt, the sediment was air dried, sieved through cheesecloth to remove vegetative matters and pebbles and stored in
the refrigerator at 4°C. The organic carbon content of the sediment was 0.028 by chemical oxygen demand (COD) measurement (Chen, 1996).

4.2.3 Analytical Methods

Several analytical methods were used in this study. Before conducting the sorption experiment, GC/MSD was used to identify the contaminants in the sediment, and GC/FID was used to determine the concentration of each contaminant. At the end of each sorption and desorption experiment, the liquid phase $^{14}$C-radiolabeled phenanthrene concentration was determined by scintillation counting and the liquid phase phenanthrene concentration was then determined from the $^{14}$C-radiolabeled phenanthrene/non-labeled phenanthrene ratio in the system. The accuracy of this calculation was checked with GC/MSD analysis. GC/MSD was also used to check the mass balance after each sorption and desorption experiment.

4.2.3.1 GC/FID

Gas chromatography (HP 5850 Series II, Hewlett-Packard Co., Palo Alto, CA) with flame ionization detector (GC/FID) was used to analyze the concentrations of contaminants in the sediment before conducting the sorption experiment. The capillary column was a HP-5 silicone column (crosslinked, with 5% phenyl methyl siloxane phase) (Hewlett-Packard Company, Wilmington, DE). The column was 30 m in length, with an internal diameter of 0.32 mm and a film thickness of 0.32 μm. Ultra high purity hydrogen and ultra high purity air (zero grade) (Trigas Industrial Gases, Irving, TX) were used as the carrier gases, and both ultra high purity helium and ultra high purity nitrogen
(Trigas Industrial Gases, Irving TX) were used as the makeup gases. The flow rates for helium, nitrogen, hydrogen and air were 5.8, 13, 40 and 260 ml/min, respectively. The injector and the detector temperatures were set at 250°C and 280°C, respectively. The temperature program designed for PAHs was: starting from 50°C, holding for 1 minute, increasing temperature by 10°C per minute to 100°C, holding for 1 minute and then increasing temperature by 6°C per minute to 280°C, holding for 2 minutes.

A PAHs mixture stock solution was used to prepare standard solutions. 2, 5-dibromobenzene was used as the internal standard, and its concentration in each standard solution was 11.73 mg/ L. The standard solutions were analyzed by GC/FID using the same temperature program as well as the sample analysis. To ensure the accuracy of the standard curves, at least 6 standard solutions were prepared. One of the standard solutions was at a concentration near and above the method detection limit, while others corresponded to the expected range of the concentrations in real samples. To minimize the artifact caused by instrumental fluctuations, standard solutions were analyzed immediately before sample analysis.

4.2.3.2 GC/MSD

Gas chromatography (HP 6890 Series, Hewlett-Packard Co., Palo Alto, CA) with a Mass Selective Detector (HP 5973, Hewlett-Packard Co., Palo Alto, CA) was used to analyze the liquid phase phenanthrene concentrations and the sediment phase phenanthrene concentration at the end of each sorption/desorption experiment. 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 30 m in length, and has an internal diameter of 0.25 mm and a film thickness of 0.25 μm. Ultra high purity helium and ultra high purity nitrogen (Trigas Industrial Gases, Irving, TX) were used as the carrier and auxiliary gases. The temperature program was the same as that for GC/FID.

Phenanthrene stock solution (500 μg/ml) in methanol was used to prepare standard solutions. The compound, 2, 5-dibromtoluene, was used as the internal standard, with a concentration of 29.28 μg/ml in each standard solution.

Since different solvents, such as acetone, methylene chloride, were used in this study, phenanthrene standard solutions were prepared in these solvents accordingly.

4.2.3.3 Radioactive Analysis

Concentrations of ¹⁴C-radiolabeled phenanthrene were determined by the liquid scintillation counting method. To analyze the concentration in a stock solution, 10 μl of the stock solution was added to 10 ml of scintillation cocktail (OrganicSafe ™, Beckman Instrument Co., Fullerton, CA) in a pre-weighted scintillation counting vial (Wheaton, Millville, NJ). To measure the concentration in an aqueous solution, about 0.1 to 1 ml of the solution was added to 10 ml of scintillation cocktail (ReadySafe ™, Beckman Instrument Co., Fullerton, CA). The amount of aqueous solution used in each radioactive analysis was calculated based on the predicted concentration range in the solution. Optimum amount of solution added would give a scintillation count from 2000-50,000 dpm. After adding the solution to the scintillation cocktail, the scintillation vial was shaken by hand and analyzed on a Beckman LS3801 liquid scintillation counter (Beckman Instrument Co., Fullerton, CA) for 30 minutes. Finally, the scintillation count
reading in dpm was converted to the concentration of the $^{14}$C-radiolabeled phenanthrene. For example, the average reading of the $^{14}$C-radiolabeled phenanthrene stock solution is 781,420.4 dpm with a blank reading of 50 dpm, the concentration of the $^{14}$C-labeled phenanthrene in the stock solution can be calculated:

$$\text{Conc} = \frac{(781420.4 - 50) \text{dpm} \times 1 \mu\text{mole} \times 178 \mu\text{g}}{2.22 \times 10^5 \text{dpm/} \mu\text{Ci} \times 13.3 \mu\text{Ci} \times 1 \mu\text{mole} \times \frac{1}{0.01 \text{ml}}} = 471 \mu\text{g/ml} \quad (4.5)$$

4.3 Experimental Design

4.3.1 Determination of Initial Solid Phase Phenanthrene Concentration

The initial solid phase concentration of phenanthrene (historically contaminated) in the Utica sediment was determined by Soxhlet extraction before conducting the sorption and desorption experiments. Soxhlet extraction was done following the EPA Method 3540 – a procedure for extracting water insoluble and slightly soluble nonvolatile and semi-volatile organic compounds from soils and sediments. This procedure ensured intimate contact of the sample matrix with the extraction solvent.

Figure 4.2 is the pictorial representation of the Soxhlet extraction. In the Soxhlet extraction, about 10 g of the dry sediment was mixed with 10 g of anhydrous sodium sulfate (baked at 100°C for 24 hours and cooled in a dessicator). The well-mixed sediment and anhydrous sodium was placed in a double thickness extraction thimble (Whatman Laboratory Division, Maidstone, England). The extraction thimble was then placed into a Soxhlet extractor (Kimax *Brand). 1, 4-dibromobenzene stock solution in
methanol was added to the sediment as the surrogate standard. 200 ml of methylene chloride was placed into a 500-ml round-bottom flask (Kimax*Brand), and one or two clean glass beads were also put into the flask. The flask was then attached to the Soxhlet extractor and placed in a 70°C water bath to conduct extraction for 16-24 hours. After extraction, the extract was passed through a 20-mm I. D. drying column (Supelco, Bellefonte, PA) containing 10 cm of anhydrous sodium sulfate. The extraction flask and the drying column were washed four times with 25 ml of methylene chloride to complete the quantitative transfer of PAHs and the surrogate standard. The effluent was then collected and concentrated to 2 ml in a Kuderna-Danish concentrator (Kimax*Brand). The concentrated solution was then changed to cyclohexane by adding 4 ml of cyclohexane into the solution and conducting another concentration in a 100°C water bath for 10-20 minutes. The concentrated solution was then cleaned by passing through a clean 25-mm I. D. chromatographic column (Supelco, Bellefonte, PA) containing 10 g of activated silica gel (baked at 180°C for 24 hours and cooled in a dessicator) (Aldrich Chemical Company, Inc., Milwaukee, WI) and 0.1 g of phosphoric acid treated glass wool (Supelco, Bellefonte, PA) at the bottom of the column. The final extract was analyzed with GC/MS to identify the compounds in the sediment. The extract was also analyzed with GC/FID to accurately determine the phenanthrene concentration in the sediment.

4.3.2 Sorption and Desorption Experiments

Sorption and desorption experiments were performed in batch reactors, in which sediment was suspended in a well-mixed aqueous solution. Figure 4.3 is a pictorial
representation of a typical reactor used in the sorption and desorption experiments, which consisted of a clean glass vial of approximately 43-ml total volume (Fisher Scientific, Fair Lawn, NJ) and a cap with Teflon-faced silicone septum (Pierce Chemical Co., Rockford, IL).

All glassware was thoroughly cleaned before using in the experiments. The cleaning procedures described by Hunter et al. (1996) were modified and used in this study. First, glassware was soaked in a warm cleaning solution overnight. Then, glassware was rinsed with tap water and D. I. water, and oven dried at 105°C. Finally, glassware was rinsed with acetone and oven dried at 105°C.

Three sets of sorption and desorption experiments were conducted in this study. Table 4.1 lists the experimental protocols for these three experiments. Experiment 4.1 consisted of one sorption and one mixed solvent desorption; in Experiment 4.2, one sorption and two steps of mixed solvent desorption were conducted; and Experiment 4.3 was composed of one sorption and four steps of mixed solvent desorption.

4.3.2.1 Sorption Experiments

Sorption experiments were conducted to add freshly sorbed phenanthrene onto the sediment. Figure 4.4 is a pictorial representation of the sorption system. To begin a sorption experiment, about 40 ml of freshly prepared electrolyte solution was placed in a 43-ml glass vial, containing 1 g of dry sediment and a Teflon-coated magnetic stir bar (1-2 g). Then, the vial was sealed with a Teflon-septum cap to leave a headspace of 1 ml. Furthermore, 500 μl of phenanthrene mixture stock solution (containing 14C-radiolabeled phenanthrene and nonlabeled phenanthrene) in methanol was injected into the glass via
using a syringe infusion pump (Harvard Apparatus) at a rate of 0.347 μl/min when stirring the solution. After injection, the stir bar was removed from the vial and 1-2 ml of electrolyte solution was added to the vial to leave no headspace. The stir bar was extracted with acetone for 1 day and analyzed to determine the phenanthrene mass loss on it. Then the vial was tumbled at 3 rpm at room temperature for 30 days to reach sorption equilibrium. Afterwards, the vial was centrifuged (IEC Centra MP4 Centrifuge, International Equipment Company, MA) at 3500 rpm for 45 minutes. 90% of the supernatant was removed by pipette and a portion of the removed supernatant was used to measure the equilibrium aqueous phase concentration.

4.3.2.2 Desorption Experiments

In this study, desorption experiments were conducted using isopropanol/electrolyte solution mixed solvent with complete separation of solvent from sediment after each desorption step. This desorption approach had several advantages: (1) Using isopropanol/electrolyte solution mixed solvent could enhance the phenanthrene solubility, which made the measurement of solution phase concentrations easier compared to the conventional repetitive water desorption approach; (2) The use of isopropanol/electrolyte solution mixed solvent in desorption accelerated the release of sorbed phenanthrene due to the enhanced solution phase concentration, which in turn shortened the time to reach the desorption resistant fraction; (3) The newly developed separation method could avoid the experiment artifact caused by failure to completely separating the solid and aqueous phases. When separation was incomplete, colloids (micro particles or macromolecules) remained in the aqueous phase after separation.
Therefore, the compounds associated with the colloids would also be measured as the desorbed mass. Also, with incomplete separation, some solution remained with the solid separates, so the compounds dissolved in this solution would be measured as mass sorbed. As a result, the observed partition coefficient would be quite different from the true value; (4) Complete separation of solvent from sediment also avoided re-adsorption – a phenomenon that happened when conducting mixed solvent desorption. The effect was discussed in detail in chapter 3.

Upon completion of a sorption experiment, about 42 ml of isopropanol/electrolyte solution mixed solvent with a typical concentration (weight of isopropanol/ weight of mixed solvent) was added to the glass vial containing the sediment. The glass vial was then tightly sealed with a Teflon-septum cap and tumbled at 3 rpm at room temperature for 3-4 days. At the end of the desorption period, the vial was centrifuged at 3500 rpm for 45 minutes to separate the sediment from the mixed solvent. Most of the supernatant was removed and analyzed for the mixed solvent phase phenanthrene concentration. A different separation method was used to separate the remaining solvent from the sediment. Figure 4.5 is a pictorial representation of the separation system. To remove the remaining solvent in the system, the sediment solvent slurry was transferred into an ultra-filtration core membrane (Amicon Corp., MA) with a molecular weight cutoff of 10,000, and centrifuged at 20,000 rpm for 25 minutes. After centrifugation, more than 99.99% (this result was determined from quality control experiments) of mixed solvent was removed from the sediment and the sediment was powder dry in appearance. The sediment was then transferred to another vial. Multi-step mixed solvent desorption was induced by successively replacing the mixed solvent with
contaminant free mixed solvent. At the end of desorption, the sediment was mixed with electrolyte solution for 2 or 3 days, the solution was then completely separated from the sediment to analyze the equilibrium aqueous phase phenanthrene concentration. The sediment was extracted following the Soxhlet extraction procedure and analyzed for the solid phase phenanthrene concentration.

To determine the water phase concentrations, C18-Sep-Pak* Plus Environmental Cartridges (Fisher Scientific, Fair Lawn, NJ) was used to extract phenanthrene from water solution. The cartridge contained organic macromolecules, which acted by sorbing hydrophobic organic compounds from the aqueous solution. First, clean Sep-Pak was pre-wetted with 10 ml of D. I. water followed by 10 ml of methanol. Then, about 30 ml of the water solution was pushed through the pre-wetted cartridge with a 30-ml syringe (Perpektum* Brand). The flow rate was controlled at about 5 drops per second to ensure sufficient contact between phenanthrene and the sorbent in the cartridge. Afterwards, about 30 ml of air was pushed through the cartridge to remove the solution remaining in the cartridge. Finally, 5 ml of isoctane was pushed through the cartridge to extract compounds from the sorbent in the cartridge. The effluent was collected and analyzed by scintillation counting to determine the concentration of $^{14}$C-radiolabeled phenanthrene. Total concentration of phenanthrene in the water solution was determined by the ratio of $^{14}$C- radiolabeled phenanthrene and non-labeled phenanthrene in the system.

4.3.3 Quality Control of the New Separation Method

The effectiveness of the newly developed separation method was checked before being used in the desorption experiments. Three control experiments were conducted
with electrolyte solution, 15% isopropanol/electrolyte solution mixed solvent and 50% isopropanol/electrolyte solution mixed solvent. In each experiment, about 1 g of Utica sediment was mixed with 6 ml of liquid in an ultra-filtration core membrane. The core membrane was then put in a plastic core holder and centrifuged at 20,000 rpm for 25 minutes, after centrifugation, sediment was collected from the membrane and weighed to determine how much liquid was remaining in the solid phase.

4.4 Results

4.4.1 Identification of Contaminants and Initial Concentrations

Utica sediment was pretreated before being used in experiments. The sediment was air dried, sieved through cheesecloth to remove vegetative matters and pebbles. The dry sediment containing 3% moisture, was used in this study exclusively. The organic carbon content in the sediment was 2.8%.

To identify the contaminants existing in the sediment and to determine their solid phase concentrations, 9.528 g of sediment was Soxhlet-extracted for 24 hours. The final volume of methylene chloride, the extraction solvent, was 5.37 ml. The methylene chloride was further concentrated and cleaned by activated silica gel, and the final methylene chloride volume was 3.67 ml.

Six major polycyclic aromatic hydrocarbons with significant solid phase concentrations were identified by GC/MS. The six compounds were naphthalene, phenanthrene, pyrene, fluoranthene, bentoanthracene and chryrene. Figure 4.6 includes two typical GC/MS printouts: a GC/MS chromatogram and a derived spectrum of the phenanthrene peak.
The accurate concentrations of these six compounds were determined by GC/FID. Figure 4.7 is the GC/FID chromatogram of the final methylene chloride extract. The recovery of 1, 4-dibromobenzene was 92.1% in this experiment. The initial phase concentrations of the six compounds are summarized in Table 4.2. Several important physical-chemistry constants of these six compounds are also included in this table.

4.4.2 Sorption

Sorption experiments were performed to add freshly sorbed phenanthrene to the sediment. The results of the sorption experiments are summarized in Table 4.3. In each sorption experiment, the aqueous phase concentration was measured at the end of the sorption experiment and the solid phase phenanthrene concentration was calculated by mass balance:

\[ q = q_0 + \frac{M_{\text{added}} - M_{\text{stir}} - CV}{m_{\text{sediment}}} \]  \hspace{1cm} (4.6)

where

- \( q \) is the solid phase phenanthrene concentration after sorption (µg/g),
- \( q_0 \) is the original solid phase concentration of phenanthrene (µg/g) (In this experiment, \( q_0 \) equals to 30.44 µg/g for phenanthrene.),
- \( M_{\text{added}} \) is the mass of phenanthrene added to the system (µg),
- \( M_{\text{stir}} \) is the mass of phenanthrene sorbed onto stir bar (µg) (in this experiment, this value is almost 0 and can be neglected.),
- \( C \) is the equilibrium aqueous phase concentration (µg/ml),
- \( V \) is the volume of the electrolyte solution (ml), and
m_{sediment} is the mass of sediment (g).

After sorption, the sediment concentrations of phenanthrene in Experiments 4.1, 4.2, 4.3 were 189.12 µg/g, 189.88 µg/g, 165.38 µg/g, respectively.

The $K_{oc}$ value of each sorption experiment was calculated as the ratio of the organic carbon normalized solid phase concentration (µg/g OC) to the equilibrium aqueous phase concentration. The observed $K_{oc}$ values in these three sorption experiments were $10^4.19$, $10^4.25$, $10^4.19$, respectively. The average log $K_{oc}$ of phenanthrene was 4.21, with a small standard deviation of 0.03. The observed $K_{oc}$ values were also compared to the $K_{oc}$ value estimated from the $K_{ow}$ of phenanthrene. According to Lyman et al. (1982), for polycyclic aromatics, two equations were most commonly used to estimate the $K_{oc}$ values:

\[ \log K_{oc} = 0.937 \log K_{ow} - 0.006 \quad (4.7) \]

\[ \log K_{oc} = 1.00 \log K_{ow} - 0.21 \quad (4.8) \]

The estimated log $K_{oc}$ values from these two equations were 4.24 and 4.33 using the $K_{ow}$ value of 4.54 for phenanthrene (Schwarzenbach, 1993). The observed $K_{oc}$ values in the three experiments were in excellent agreement with the estimated values.

4.4.3 Desorption with the New Solid/Solution Separation Method

4.4.3.1 Results of Mixed Solvent Desorption
Table 4.4 summarizes the results of the desorption experiments. In Experiment 4.1, one step desorption was initiated with 40 ml of isopropanol/electrolyte solution mixed solvent (60%, wt of isopropanol/wt of mixed solvent); in Experiment 4.2, the same amount of isopropanol was used but divided into two desorption steps – 40 ml of isopropanol/electrolyte solution mixed solvent (35%, wt/wt) in the first desorption step, and 40 ml of isopropanol/electrolyte solution mixed solvent (25%, wt/wt) in the second desorption step; in Experiment 4.3, four steps of mixed solvent desorption were conducted with 40 ml of isopropanol/electrolyte solution mixed solvent (15%, wt/wt) in each desorption step. At the end of each desorption step, the liquid phase was completely separated from the sediment, and the phenanthrene concentration in the liquid phase was measured. The solid phase phenanthrene concentration was then calculated with the following equation:

\[ q = q_{\text{initial}} - \frac{CV}{M} \quad (4.9) \]

where

- \( q \) is the solid phase concentration at the end of a desorption step (µg/g),
- \( q_{\text{initial}} \) is the solid phase concentration before the desorption step (µg/g),
- \( C \) is the phenanthrene concentration in the solution (µg/ml),
- \( V \) is the volume of solution (ml), and
- \( M \) is the mass of sediment (g).

In Experiment 4.1, with one step mixed solvent (60%, wt/wt) desorption, the solid phase phenanthrene concentration decreased from 189.11 µg/g to 3.59 µg/g. More than 98% of
sorbed phenanthrene was removed. In Experiment 4.2, the solid phase phenanthrene concentration decreased from 189.88 μg/g to 10.31 μg/g after two steps of mixed solvent desorption (35%, 25% wt/wt), 94% of sorbed phenanthrene was removed during the desorption. In Experiment 4.3, the solid phase phenanthrene concentration was reduced to 86 μg/g, 45.6 μg/g, 26.36 μg/g and 14.24 μg/g after each desorption step. At the end of the desorption, 91.5% of sorbed phenanthrene was removed from the sediment.

At the end of each desorption experiment, sediment was mixed with electrolyte solution for 2 to 3 days and the equilibrium aqueous phase phenanthrene concentration was measured. The $K_{oc}$ value at the end of each desorption experiment was calculated. The observed $K_{oc}$ values in Experiments 4.1, 4.2 and 4.3 were $10^{4.78}$, $10^{5.10}$, $10^{4.51}$, respectively.

4.4.3.2 Determination of Desorption Resistant Fraction

With the complete separation method, the solid and liquid phases phenanthrene concentrations in each desorption step could be accurately measured, and the resistant fraction in the solid phase concentration could be determined by the following approach:

$$q_{\text{resistant}} = q - q_{\text{reversible}} \quad (4.10)$$

where

$q$ is the solid phase phenanthrene concentration at the end of the desorption (μg/g),

$q_{\text{resistant}}$ is the desorption resistant fraction in q (μg/g),
$q_{\text{reversible}}$ is the desorption reversible fraction in $q_t$ ($\mu g/g$).

In this equation, $q$ was calculated from Equation 4.9, while $q_{\text{reversible}}$ (the reversibly sorbed phenanthrene concentration) could be calculated by the following equation:

$$q_{\text{reversible}} = K_{\text{rev}}^{\text{mixed solvent}} C_{\text{mixed solvent}} \quad (4.11)$$

where

$C_{\text{mixed solvent}}$ is the mixed solvent phase phenanthrene concentration ($\mu g/ml$);

$K_{\text{rev}}^{\text{mixed solvent}}$ is the sediment/mixed solvent partition coefficient of reversible sorbed phenanthrene (ml/g).

$C_{\text{mixed solvent}}$ was directly measured in this experiment, and $K_{\text{rev}}^{\text{mixed solvent}}$ could be estimated from the sediment/water partition coefficient and the activity coefficients by the following equation:

$$K_{\text{rev}}^{\text{mixed solvent}} = K_{\text{rev}} \frac{\gamma_{\text{mixed solvent}}}{\gamma_{\text{water}}} \quad (4.12)$$

where

$K_{\text{rev}}$ is sediment/water partition coefficient of reversible sorbed phenanthrene (ml/g),

$\gamma_{\text{mixed solvent}}$ and $\gamma_{\text{water}}$ are activity coefficients of phenanthrene in mixed solvent and water, respectively.
In this calculation, $K_{rev}$ was determined in the sorption experiment and the value was 433 ml/g, while $\gamma_{\text{mixed solvent}}$ and $\gamma_{\text{water}}$ (activity coefficients of phenanthrene in mixed solvent and water) were predicted from the UNIFAC method, which had been tested by many researchers for its predicting accuracy (Banerjee, 1985; Hansen et al., 1991; Kan and Tomson, 1996; Kan et al., 1997). Table 4.5 lists the UNIFAC predicted $\gamma_{\text{mixed solvent}}$ and $\gamma_{\text{water}}$ values used in this study.

Using this approach, the desorption resistant fraction of sorbed phenanthrene could be determined easily. For example, in Experiment 4.1, after one step isopropanol/water mixed solvent desorption, the mixed solvent phase phenanthrene concentration was measured to be 4.39 $\mu$g/ml, the mixed solvent volume was 42.258 ml which was totally separated from the sediment after the desorption. The sediment phase concentration was calculated from Equation 4.9 and the result was 3.59 $\mu$g/g (this value was also checked by GC/MS analysis). Then the desorption resistant fraction in this sediment phase concentration was:

$$q_{\text{resistant}} = q - K_{rev} \frac{\gamma_{\text{mixed solvent}}}{\gamma_{\text{water}}} C_{\text{mixed solvent}}$$

$$= 3.59 \mu g / g - 433 \text{ml/g} \times 0.00023 \times 4.39 \mu g / \text{ml}$$

$$= 3.51 \mu g / g$$

(4.13)

97% of sediment phase phenanthrene concentration was from the resistant fraction. In Experiment 4.2, the $q_{\text{resistant}}$ value was found to be 8.74 $\mu$g/g at the end of the first
desorption step, and dropped to 8.04 μg/g after the second desorption step. In Experiment 4.3, the $q_{resistant}$ values after each desorption step were 10.55 μg/g, 8.02 μg/g, 7.04 μg/g and 5.65 μg/g, respectively.

4.5 Discussion

4.5.1 Desorption of Historically and Fresh Sorbed Phenanthrene

Aging of contamination was considered to be a factor that may have an effect on the desorption behavior of organic compounds. The decline in bioavailability and extractability with aged organic compounds was observed by some researchers (Hatzinger and Alexander, 1995; Madsen et al., 1996, Chuang and Alexander, 1998). Alexander (2000) proposed that during aging, molecules slowly move into sites in the soil matrix and get entrapped, which causes the difference between desorption of contaminants from historically and freshly contaminated sediments. The three sorption/desorption experiments in this study disagreed with this argument. In this study, Utica sediment was chosen to be the sorbent because this sediment was historically contaminated with several PAHs (dozens of years). The concentration of historically sorbed phenanthrene in this sediment was found to be 30.44 μg/g. A certain amount of phenanthrene was added to the sediment in each sorption experiment. The freshly added phenanthrene (30 days sorption) in the three sorption experiments were 158.68 μg/g, 159.44μg/g, and 135.94 μg/g, respectively. In Experiment 4.1, after one step mixed solvent (60%, wt/wt) desorption and one step water desorption, the sediment phase phenanthrene concentration dropped to 3.35 μg/g, which was determined by GC analysis. This value agreed quite well with the calculated value (3.51 μg/g) based on the
assumption that historically and freshly sorbed phenanthrene had the same desorption behavior, which indicated that both historically and freshly sorbed phenanthrene in the sediment was desorbed by the mixed solvent. The same phenomenon was found in Experiments 4.2 and 4.3, where several mixed solvent desorption steps were conducted. The final sediment phase phenanthrene concentrations in these two experiments were 5.12 µg/g and 9.54 µg/g determined by GC analysis, both were less than the historically sorbed phenanthrene concentrations. These values are reasonable compared to the calculated values assuming no difference existed between the desorption of historically and freshly sorbed phenanthrene. According to this study, both historically and freshly sorbed phenanthrene could be readily desorbed by isopropanol/water mixed solvent.

4.5.2 Consistency of Desorption Results with the Biphasic Model Predictions

Kan et al. (1998) proposed a biphasic irreversible adsorption model to interpret the resistant desorption of hydrophobic organic compounds. It was proposed that during the sorption process, a portion of sorbed mass became irreversibly bound and exhibited desorption resistant behavior; compounds associated with the reversible fraction followed the linear isotherm, while compounds associated with the irreversible fraction typically exhibited nonlinear behavior. The overall isotherm can be described as:

\[
q = K_{oc} f_{oc} C + \frac{K_{oc}^{irr} f_{oc} q_{max} fC}{q_{max} f + K_{oc}^{irr} f_{oc} C}
\]  
(4.14)
Chen et al. (2000) proposed that the cosolvent effect can be included in this equation by correcting $K_{oc}$ and $K_{oc}^{irr}$ to their respective values for mixed solvent instead of water, and this correction can be done by multiplying both constants by the ratio: $\gamma_{\text{mixed solvent}} / \gamma_{\text{water}}$, where $\gamma_{\text{mixed solvent}}$ and $\gamma_{\text{water}}$ represent the contaminant activity coefficients in mixed solvent and water. Therefore, the whole biphasic isotherm is changed to:

$$q = K_{oc} \gamma_{\text{mixed solvent}} f_{oc} C + \frac{K_{oc}^{irr} \gamma_{\text{mixed solvent}} f_{oc} q_{max} f C}{q_{max} f + K_{oc}^{irr} \gamma_{\text{mixed solvent}} C}$$

(4.15)

In this study, the liquid and solid phases phenanthrene concentrations in each desorption step were predicted with the biphasic model with the following approach:

$$qm + CV = n$$

(4.16)

where

- $q$ is the solid phase concentration at the end of a desorption step (µg/g),
- $m$ is the mass of sediment (g),
- $C$ is the liquid phase concentration in equilibrium with $q$ (µg/ml),
- $V$ is the liquid volume (ml), and
- $n$ is the total mass of phenanthrene in the system (µg).
By substituting Equation 4.15 into Equation 4.16, Equation 4.16 becomes:

\[
\left[ K_{oc} \frac{\gamma_{\text{mixed solvent}}}{\gamma_{\text{water}}} f_{oc} C + \frac{K_{irr} \gamma_{\text{mixed solvent}} f_{oc} q_{\text{max}} f C}{q_{\text{max}} f + K_{oc} \frac{\gamma_{\text{mixed solvent}}}{\gamma_{\text{water}}} f_{oc} C} \right] \ast m + CV = n
\]

(4.17)

rearranging:

\[
\left( K_{oc} \frac{\gamma_{\text{mixed solvent}}}{\gamma_{\text{water}}} f_{oc} \left( V + mK_{oc} \frac{\gamma_{\text{mixed solvent}}}{\gamma_{\text{water}}} f_{oc} \right) \right) C^2 + \left( V + mK_{oc} \frac{\gamma_{\text{mixed solvent}}}{\gamma_{\text{water}}} + mK_{irr} \frac{\gamma_{\text{mixed solvent}}}{\gamma_{\text{water}}} f_{oc} \right) q_{\text{max}} f - nK_{oc} \frac{\gamma_{\text{mixed solvent}}}{\gamma_{\text{water}}} f_{oc} \right] C - nq_{\text{max}} f = 0
\]

(4.18)

In this equation:

- $K_{oc}^{irr}$ is the organic carbon content normalized partition coefficient for the reversible fraction (ml/g OC). It is found to be constant for all hydrophobic compounds tested to date (Chen et al., 2000). The value of $10^{5.47}$ is used in this calculation.
- $K_{oc}$ is the organic carbon content normalized partitioning coefficient for the reversible fraction (ml/g OC).
- $f_{oc}$ is the organic carbon content of sediment.
\( \gamma_{\text{mixed solvent}} \) and \( \gamma_{\text{water}} \) are activity coefficients of phenanthrene in mixed and water calculated by UNIFAC. The values are listed in Table 4.5 (also see Figure 4.8). \( q_{\text{max}} \) is the maximum resistant desorption capacity (\( \mu g/g \)), which can be calculated with the following equation proposed by Chen et al. (1999):

\[
q_{\text{max}} = f_{oc} \left\{ K_{\text{ow}} C_{\text{sat}} (\text{mg/l}) \right\}^{0.534} \tag{4.19}
\]

the value of \( q_{\text{max}} \) is 8.02 \( \mu g/g \) for phenanthrene/Utica sediment combination. \( f \) represents the fraction of the desorption resistant compartment that is saturated. It is assumed to be 1 at the beginning of the first step desorption. At the end of the each desorption step, \( f \) can be calculated as the fraction of \( q_{\text{resistant}}/q_{\text{max}} \).

\( m \) and \( V \) are sediment mass (g) and solution volume (ml), respectively.

By solving Equation 4.18, the liquid phase phenanthrene concentration in each desorption step could be predicted. The sediment phase phenanthrene concentration could be determined by substituting the \( C \) value into Equation 4.11 or 4.12. The predicted \( C \) and \( q \) values are listed in Table 4.6. The experimentally determined \( C \) and \( q \) value are also listed in this table. The desorption results in Experiment 4.1 were in excellent agreement with the model prediction. In Experiments 4.2 and 4.3, the desorption results were also consistent with the model predictions even though several desorption steps were conducted. In Figure 4.9 the desorption results are also compared with the biphasic irreversible isotherm prediction. In this figure, the \( f \) (the fraction of the irreversible compartment that is filled at the time of exposure) value in the irreversible isotherm predictions was assumed to be equal to 1 at all concentrations.
4.5.3 Determination of Desorption Resistant Fraction of Sorbed Contaminants Using the New Separation Method – Comparison with Previous Work

As discussed in chapter 2, the desorption process of hydrophobic organic compounds from soils and sediments is found to be typically biphasic, with a rapid desorption (several hours to several days) followed by a lengthy period of slow desorption. Even after extended desorption times, a small fraction of the sorbed compound still remains resistant to desorption. The traditional approach to determine this desorption resistant fraction is by conducting repetitive water desorption, where the solid phase contaminant concentration is measured at the end of each desorption step. The solid phase contaminant concentration will stop decreasing and reach a constant value after extended desorption steps, which is measured as the desorption resistant fraction. Unfortunately, this method is impractical because it is time-consuming. In addition, due to the lack of effective separation methods, there is always a fraction of water remaining with the sediment, which in turn causes inaccurate measurement of the desorption resistant fraction.

Chapter 3 summarized two previous attempts to measure the desorption resistant fraction of sorbed organic contaminants within several desorption steps. In their studies, desorption was successfully accelerated using isopropanol/water mixed solvent. Unfortunately, this method also failed to characterize the desorption resistant fraction directly.

In this study, desorption was also conducted with isopropanol/water mixed solvent. The newly developed separation method ensured complete separation of the mixed solvent from the sediment after each desorption step. The contaminant
concentration in the mixed solvent was then accurately measured. The solid phase concentration could be either calculated or measured. Since complete separation was conducted, the effect of re-adsorption was avoided. The resistant fraction in the solid phase concentration could then be easily determined (Equations 4.10, 4.11 and 4.12).

4.6 Summary

In this chapter, a new separation method was developed and used in the desorption experiments of historically and freshly sorbed phenanthrene from Utica sediment with isopropanol/water mixed solvent. With this separation method, the solution can be completely separated from the sediment after each desorption step, which enabled the accurate measurement of phenanthrene concentrations in these two phases. The desorption resistant fraction in the sorbed phenanthrene was then easily determined using a simple approach.

The results of the desorption experiments indicated no difference between the desorption behavior of historically and freshly sorbed phenanthrene. According to this study, both historically and freshly sorbed phenanthrene could be readily desorbed by isopropanol/water mixed solvent solution.

Sorption and desorption results in this study were also compared with the biphasic irreversible desorption model proposed by Kan et al. (1998). The experimental results were in excellent agreement with the model predictions, which suggested that the model could be used as a reliable model to predict the resistant release of hydrophobic organic contaminants from natural soils and sediments.
Table 4.1: Experimental protocols

Exp. 4.1: 1 sorption (30 days) + 1 step mixed solvent desorption (4 days)* followed by 1 step
electrolyte solution desorption (2 days)
Mixed solvent composition: (60% isopropanol, 40% electrolyte solution, wt/wt)

Exp. 4.2: 1 sorption (30 days) + 2 steps of mixed solvent desorption (3-4 days each step)*.
Mixed solvent composition: 1st desorption step, 35% isopropanol, 65% electrolyte
solution, wt/wt.
2nd desorption step, 25% isopropanol, 75% electrolyte
solution, wt/wt.

Exp. 4.3. 1 sorption (32 days) + 4 steps of mixed solvent desorption* (3-5 days each step).
Mixed solvent composition: 15% isopropanol, 85% electrolyte solution, wt/wt in four
desorption experiments.

Solution matrix in sorption: electrolyte solution (0.01M NaCl, 0.01M CaCl₂, 0.01M NaN₃.)
Solution matrix in desorption: isopropanol + electrolyte solution
Solid/solution ratio: 1g sediment, 42ml solution. Mixing: tumbling at 3 rpm.
* After each desorption step, sediment was completely separated from the solution before
conducting next desorption.
Table 4.2 Summary of the initial solid phase concentrations and physical-chemistry constants of the 6 PAHs in the Utica sediment (2.8% OC).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Initial concentrations in sediment (µg/g)</th>
<th>Physical-Chemistry Constants</th>
<th>Solubility In water (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>8.2</td>
<td>128.2</td>
<td>3.36</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>30.44</td>
<td>178.2</td>
<td>4.54</td>
</tr>
<tr>
<td>Fluoranthrene</td>
<td>30</td>
<td>202.3</td>
<td>5.22</td>
</tr>
<tr>
<td>Pyrene</td>
<td>31.5</td>
<td>202.3</td>
<td>5.13</td>
</tr>
<tr>
<td>Benzoanthracene</td>
<td>24.2</td>
<td>228.3</td>
<td>5.61</td>
</tr>
<tr>
<td>Chrysene</td>
<td>11.8</td>
<td>228.3</td>
<td>5.61</td>
</tr>
</tbody>
</table>

*(from Schwarzenbach, 1993)*
Table 4.3: Summary of the results of sorption experiments.

<table>
<thead>
<tr>
<th>Exp</th>
<th>Compound</th>
<th>Sediment wt (g)</th>
<th>$q_{\text{Initial}}^a$ (μg/g)</th>
<th>$q_{\text{Added}}^b$ (μg/g)</th>
<th>$C_w$ (μg/ml)</th>
<th>LogKoc</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Phen.</td>
<td>1.004</td>
<td>30.44</td>
<td>158.68</td>
<td>0.44</td>
<td>4.19</td>
</tr>
<tr>
<td>4.2</td>
<td>Phen.</td>
<td>0.999</td>
<td>30.44</td>
<td>159.44</td>
<td>0.38</td>
<td>4.25</td>
</tr>
<tr>
<td>4.3</td>
<td>Phen.</td>
<td>1.000</td>
<td>30.44</td>
<td>135.94</td>
<td>0.38</td>
<td>4.19</td>
</tr>
</tbody>
</table>

$^a$ Measured by solid extraction.

$^b$ Calculated by mass balance.
Table 4.4: Summary of the results of desorption experiments, including the solid phase concentrations after each desorption step, the resistant fraction in the solid phase concentration and the observed partition coefficients at the end of desorption.

<table>
<thead>
<tr>
<th>Exp</th>
<th>q_{initial} (^a) (µg/g)</th>
<th>Mixed solvent composition (^b)</th>
<th>C_{mixed solvent} (^c) (µg/g)</th>
<th>q (^d) (µg/g)</th>
<th>q_{resistant in q} (^e) (µg/g)</th>
<th>Log K_{oc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>189.11</td>
<td>60%</td>
<td>4.39</td>
<td>3.59</td>
<td>3.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0%</td>
<td>0.0021</td>
<td>3.51</td>
<td>2.60</td>
<td>4.78</td>
</tr>
<tr>
<td>4.2</td>
<td>189.89</td>
<td>35%</td>
<td>4.078</td>
<td>17.84</td>
<td>8.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25%</td>
<td>0.177</td>
<td>10.31</td>
<td>8.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0%</td>
<td>0.029</td>
<td>9.16</td>
<td>5.10</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>166.38</td>
<td>15%</td>
<td>1.933</td>
<td>86.00</td>
<td>10.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15%</td>
<td>0.988</td>
<td>45.60</td>
<td>8.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15%</td>
<td>0.470</td>
<td>26.36</td>
<td>7.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15%</td>
<td>0.220</td>
<td>14.24</td>
<td>5.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0%</td>
<td>0.015</td>
<td>13.63</td>
<td></td>
<td>4.51</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) q_{initial} contained both aged and freshly added phenanthrene.

\(^b\) Mixed solvent composition described as the percent of isopropanol in the isopropanol/electrolyte solution mixed solvent, wt/wt.

\(^c\) Concentration determined by scintillation counting and \(^{14}\)C/\(^{12}\)C phenanthrene ratio in the system, also checked by GC/MS.

\(^d\) q, the phenanthrene concentration in the sediment after each desorption step calculated from C.

\(^e\) q_{resistant} determined from theoretical approach.
Table 4.5: UNIFAC predicted activity coefficients of phenanthrene in isopropanol/water mixed solvent and water.

<table>
<thead>
<tr>
<th>Mixed solvent composition</th>
<th>Activity coefficient in mixed solvent ($\gamma_{\text{mixed solvent}}$)</th>
<th>Activity coefficient in water ($\gamma_{\text{water}}$)</th>
<th>Activity coefficients ratio ($\gamma_{\text{mixed solvent}}/\gamma_{\text{water}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropanol (wt%)</td>
<td>Water (wt%)</td>
<td>1730.39</td>
<td>7522168</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>65</td>
<td>39411.92</td>
<td>7522168</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>156781.1</td>
<td>7522168</td>
</tr>
<tr>
<td>15</td>
<td>85</td>
<td>693684.1</td>
<td>7522168</td>
</tr>
</tbody>
</table>
Table 4.6: Comparison of experimentally observed sediment and liquid phases concentrations of phenanthrene versus biphasic irreversible sorption isotherm predictions.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Mixed solvent composition</th>
<th>Experimental measurements</th>
<th>Isotherm Predictions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C (µg/ml)</td>
<td>q (µg/g)</td>
</tr>
<tr>
<td>4.1</td>
<td>60%</td>
<td>4.39</td>
<td>3.59</td>
</tr>
<tr>
<td></td>
<td>0%</td>
<td>0.0021</td>
<td>3.51</td>
</tr>
<tr>
<td>4.2</td>
<td>35%</td>
<td>4.078</td>
<td>17.84</td>
</tr>
<tr>
<td></td>
<td>25%</td>
<td>0.177</td>
<td>10.31</td>
</tr>
<tr>
<td></td>
<td>0%</td>
<td>0.029</td>
<td>9.16</td>
</tr>
<tr>
<td>4.3</td>
<td>15%</td>
<td>1.933</td>
<td>86.00</td>
</tr>
<tr>
<td></td>
<td>15%</td>
<td>0.988</td>
<td>45.60</td>
</tr>
<tr>
<td></td>
<td>15%</td>
<td>0.470</td>
<td>26.36</td>
</tr>
<tr>
<td></td>
<td>15%</td>
<td>0.290</td>
<td>14.24</td>
</tr>
<tr>
<td></td>
<td>0%</td>
<td>0.015</td>
<td>13.63</td>
</tr>
</tbody>
</table>
Figure 4.1: Effects of incomplete phase separations on apparent $K_d$'s of three nonpolar sorbates as a function of solids to water ratio, $r_{sw}$, using sediment from Missouri River. Only the horizontal portions of the curves reflect true $K_d$'s (from Schwarzenbach, 1993).
Figure 4.2: Pictorial representation of Soxhlet extraction: (1) extraction with methylene chloride for 16-24 hours, (2) removing water from extract by running through drying column, (3) concentration with K-D apparatus, (4) cleaning concentrated extract by running through activated silica gel.
Figure 4.3: Typical reactor in the sorption and desorption experiments, which contained a 43-ml glass vial and a cap with Teflon-faced septum.
Figure 4.4: Pictorial representation of the sorption experiment. (1) syringe infusion pump; (2) 500-μl glass syringe containing phenanthrene stock solution; (3) glass vial containing the mixture of sediment and electrolyte solution. In the sorption experiment, phenanthrene stock solution was injected to the mixture of sediment and electrolyte solution when stirring the mixture, after this step, the stir bar was removed, and the glass vial was sealed and tumbled for 30 days to reach sorption equilibrium.
Figure 4.5: Pictorial representation of the new separation system: (1) core membrane, 10,000 MWCO, with sediment solution mixture in it; (2) plastic core holder with a hole at the bottom; (3) centrifuge vial with a volume of 25 ml. The whole system was centrifuged at 20,000 rpm for 25 minutes. After centrifugation, only ~0.03-0.05 ml solution was remaining in the sediment.
Figure 4.6-1: The GC/MS printout of the Soxhlet extraction sample from the Utica sediment – the GC/MS chromatogram of the Soxhlet extraction sample; program: 50°C for 4 minutes, 8°C/min to 280°C for 4 minutes.
Figure 4.6-2: The GC/MS printout of the Soxhlet extraction sample (in methylene chloride) from the Utica sediment – a derived spectrum of phenanthrene peak (20.31 minutes); program: 50°C for 4 minutes, 8°C/min to 280°C for 4 minutes.
Figure 4.7: The GC/FID chromatogram of the Soxhlet extraction sample (in methylene chloride) of the Utica sediment, with 2, 5-dibromobenzene as the internal standard. Column: 30 m long × 0.32 mm internal diameter; program: 50°C for 2 minutes, 8°C/min to 100°C, holding for 2 minutes and then 6°C/min to 280°C; injector: 250°C, detector: 280°C.
Figure 4.8: UNIFAC predicted activity coefficients of phenanthrene in isopropanol/water mixed solvent versus the isopropanol weight percent in the mixed solvent.
Figure 4.9: Plot of the model predicted vs. experimentally observed isotherms of phenanthrene in Utica sediment. In the isotherm prediction, f (the fraction of the irreversible compartment that is filled at the time of exposure) was equal to 1 at all concentrations.
Chapter 5: Summary of the New Method

Chapter 4 describes a new experimental protocol which was developed to rapidly measure the desorption resistant fraction of sorbed hydrophobic organic contaminants in soil or sediment. In this chapter, a summary of the new method is given.

1. General Discussion

This method is applicable to the determination of desorption resistant fraction of hydrophobic organic compounds sorbed in soil or sediment.

Principle: A measured mass of sediment is extracted with methylene chloride. The extract is dried, concentrated and analyzed with gas chromatographic method to determine the sediment phase contaminant concentration. Another measured mass of sediment is desorbed with an isopropanol/electrolyte solution mixed solvent (recommended concentration: 15%-40%, wt/wt) for 3 or 4 days. After desorption, all of the mixed solvent is separated from the sediment. The separated mixed solvent is analyzed using the gas chromatographic method to determine the mixed solvent phase concentration. The sediment phase concentration is then determined by mass balance, and the desorption resistant fraction in this concentration can be calculated with a simple approach.

2. Apparatus

2.1 Soxhlet extractor – 40 mm I. D., with 500-ml round bottom flask.
2.2 Drying column – 20 mm I. D. Pyrex chromatographic column with Pyrex glass wool at bottom.
2.3 Kuderna-Danish (K-D) apparatus
2.3.1 Concentrator tube – 10 ml, graduated. A ground-glass stopper is used to prevent evaporation of extracts.

2.3.2 Evaporation flask – 500 ml. Attach to concentrator tube with springs or clamps.

2.3.3 Three-ball macro Snyder column.

2.3.4 Two-ball macro Snyder column.

2.4 Boiling chips – extracted with methylene chloride in a Soxhlet extractor.

2.5 Water bath – heated, with temperature control to ± 5°C.

2.6 Chromatographic column, 250 mm long × 10 mm I. D. with coarse fit filter disk at bottom and TEE stopcock.

2.7 Glass vials, 43-ml total volume with TFE-lined screw cap.

2.8 Centrifuge, capable of operating at 20,000 rpm.

2.9 Gas Chromatograph:

1) Column: HP-5 silicone column (crosslinked, with 5% phenyl methyl siloxane phase) (Hewlett-Packard Company, Wilmington, DE). The column was 30 m in length, with an internal diameter of 0.32 mm and a film thickness of 0.32 μm.

2) Detector: flame ionization.

3. Reagents

3.1 Organic-free reagent water (D. I. water).

3.2 Sodium sulfate (anhydrous).

3.3 Electrolyte solution, prepared in D. I. water with sodium chloride, calcium chloride and sodium azide.

3.4 Methanol, acetone, methylene chloride, cyclohexane, pentane, pesticide quality or equivalent.

3.5 Silica gel, 100/200 mesh. Before use, activate for at least 16 hours at 130°C.

3.6 Isopropanol, pesticide quality or equivalent.
4. Procedure

4.1 Determine the initial contaminant concentration in the soil sample.

4.1.1 Soxhlet extraction

4.1.1.1 Blend 10 g of soil sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. Add surrogate standard to the soil sample. Place the extraction thimble in a Soxhlet extractor.

4.1.1.2 Place 200 ml of methylene chloride into a 500-ml round bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the soil sample for 16-24 hours at 70°C. After extraction is complete, allow the extract to cool.

4.1.1.3 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a Kuderna-Danish (K-D) concentrator (10-ml concentrator tube attached to a 500-ml evaporation flask). Wash the extractor flask and sodium sulfate column with 100 ml of methylene chloride to complete the quantitative transfer.

4.1.1.4 Attach a three-ball Snyder column to the K-D concentrator. Put the K-D apparatus on a hot water bath (70°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Complete the concentration in 10-20 minutes by adjusting the water bath temperature and the vertical position of the apparatus. When the apparent volume of liquid reaches 1-2 ml, remove the K-D apparatus from the water bath and allow it to drain and cool.

4.1.2 Cleanup and separation

Several procedures are available for cleanup purpose, for PAHs, silica gel cleanup is recommended.
4.1.2.1 Before using the silica gel cleanup technique, exchange extract solvent to cyclohexane. Add 1-10 ml of sample extract (in methylene chloride) and a boiling chip to a K-D concentrator tube. Add 4 ml of cyclohexane and attach a two-ball micro-Snyder column. Place micro-K-D apparatus on a boiling water bath so that concentrator is partially immersed in hot water. Adjust vertical position of apparatus and water temperature so as to complete concentration in 5-10 minutes. When apparent volume of liquid reaches 0.5 ml, remove K-D apparatus and let drain and cool for at least 10 minutes. Remove micro-Snyder column and rinse its lower joint into concentrator tube with a minimum amount of cyclohexane. Adjust extract volume to 2 ml.

4.1.2.2 Make a slurry of 10 g of activated silica gel in methylene chloride and place in a 10 mm I. D. chromatographic column. Add 1-2 g of anhydrous Na$_2$SO$_4$ to top of silica gel. Pre-elute with 40 ml of pentane at a rate of 2 ml/min. discard eluate and just before exposure of Na$_2$SO$_4$ layer to the air, transfer all the cyclohexane sample extract onto column using an additional 2 ml cyclohexane. Just before exposure of Na$_2$SO$_4$ layer to air, add 25 ml of pentane and continue elution. Discard this pentane eluate. Next, elute column with 25 ml of methylene chloride/pentane (4+6) (V/V) into a 500-ml K-D flask equipped with a 10-ml concentrator tube, concentrated collected fraction to less than 10 ml.

4.1.3 Analyze the cleaned concentrate using gas chromatography

Recommended column conditions for PAHs detection: Column temperature held at 100°C for 4 minutes, then programmed at 8°C/min to a final hold at 280°C.

4.2 Conducting one step isopropanol/water mixed solvent desorption to the soil.
4.2.1 Add 1-2 g of soil sample (air dried) to a clean 43-ml glass vial. Then add isopropanol/electrolyte solution mixed solvent with a typical concentration (for example, 40%, wt/wt) to the glass vial containing the soil sample to leave no headspace. Tightly seal the glass vial with a Teflon-septum cap and tumble the vial with 3 rpm at room temperature for 2 or 3 days.

4.2.2 At the end of the desorption period, centrifuge the vial at 3500 rpm for 45 minutes to separate the sediment from the mixed solvent solution. Remove most of supernatant with glass pipette.

4.2.3 To remove the remaining solvent in the system, transfer the remaining soil/solvent slurry from the glass vial into an ultra-filtration core membrane with a molecular weight cutoff (MWCO) of 10,000, put the membrane in a core holder and centrifuge at 20,000 rpm for 25 minutes. With this separation method, sediment can be completely separated from the mixed solvent solution.

4.2.4 Measure the mixed solvent phase contaminant concentration with gas chromatography.

5. Calculation

5.1 The initial solid phase contaminant concentration, \(q_{\text{initial}} (\mu g/g)\).

\[
q_{\text{initial}} = \frac{C_{\text{extract}} V_{\text{extract}}}{m_{\text{soil}}} \quad (5.1)
\]

where \(q_{\text{initial}}\) is the initial concentration in the soil sample (\(\mu g/g\)); \(C_{\text{extract}}\) is the contaminant concentration in the methylene chloride extract (\(\mu g/ml\)), which is measured with GC/FID; \(V_{\text{extract}}\) is the methylene chloride extract volume (ml); and \(m_{\text{soil}}\) is the soil weight used in the extraction (g).

5.2 Solid phase contaminant concentration after desorption, \(q (\mu g/g)\).
\[ q = q_{\text{initial}} - C_{\text{mixed solvent}} \frac{V}{M} \]  \hspace{1cm} (5.2)

where \( V \) is the mixed solvent volume (ml) removed, \( M \) is the mass of solid (g); \( C_{\text{mixed solvent}} \) is the mixed solvent phase concentration (\( \mu g/ml \)) determined by gas chromatograph.

5.3 Desorption resistant fraction, \( q_{\text{resistant}} \):

\[ q_{\text{resistant}} = q - K_p \gamma_{\text{mixed solvent}} C_{\text{mixed solvent}} \gamma_{\text{water}} \]  \hspace{1cm} (5.3)

where \( K_p \) is the partitioning coefficient of the contaminant in water, which can be easily measured or predicted from the octanol-water partition coefficient, \( K_{\text{ow}} \), and the soil organic carbon content (\( f_{\text{oc}} \)):

\[ K_p = K_{\text{oc}} f_{\text{oc}} = 0.63 K_{\text{ow}} f_{\text{oc}} \]  \hspace{1cm} (5.4)

\( \gamma_{\text{mixed solvent}} \) and \( \gamma_{\text{water}} \) are activity coefficients of contaminant in mixed solvent and water, which can be easily predicted from several algorithms. SPARC On-Line Calculator is recommended here for the calculation of activity coefficients. The website address of SPARC On-Line Calculator is http://ibmlc2.chem.uga.edu/sparc/index.cfm.
Chapter 6: Conclusions and Future Work

6.1 Conclusions

This study began with two objectives: 1) to develop a rapid, effective method for the measurement of the desorption resistant fraction of sorbed hydrophobic organic contaminants; and 2) to further understand the mechanisms controlling the desorption resistant desorption.

In chapter 3, the work of Wei Liu and Chuangyue Wang in the author’s group was reviewed. These studies indicated that isopropanol/electrolyte solution mixed solvent greatly accelerated the release of freshly added naphthalene and phenanthrene from two sediments with different properties such as organic carbon content and initial contaminant concentrations. Typically with three or four mixed solvent desorption steps, more than 95% of freshly sorbed contaminant could be removed from the sediment. Sorption and desorption results of these people’s study were well-modeled by an irreversible sorption isotherm (Kan et al., 1998). The irreversible sorption capacity, $q_{\text{irr}}^{\max}$, determined by curve fitting the irreversible sorption isotherm varied among different chemical-sediment combinations, depending on the solubility of chemical and the organic compound content of the sediment. Unfortunately, in these people’s study, due to the lack of an effective separation method, re-adsorption of contaminant was observed at the end of each mixed solvent desorption. Therefore, desorption results obtained in this
study were subject to considerable error and the $q_{\text{irr}}^{\text{max}}$ values determined in this study were not quite correct.

In Chapter 4, a new separation method was developed to completely separate the solution phase from the sediment. Quality control experiments indicated only 0.03-0.05 ml solution was remaining with the sediment using this separation method. The use of an ultra-filtration membrane in separation also ensured the complete removal of colloids from the liquid phase. Therefore, the true sediment and solution phases concentrations can be measured. One or several steps of isopropanol/electrolyte solution mixed solvent desorption experiments were then designed using this separation method. In these experiments, desorption of historically and freshly added phenanthrene from a well-defined sediment – Utica sediment was studied. The conclusions that could be drawn from this study were as follows:

1. With this new separation method, the mixed solvent and sediment phases phenanthrene concentrations could be accurately measured. The desorption resistant fraction in the sediment phase concentration could also be determined using a simple theoretical approach. The only parameters needed were the activity coefficients of phenanthrene in water and mixed solvent, which could be easily predicted by UNIFAC method.

2. No difference was found in the desorption behaviors between historically and freshly added phenanthrene, both historically and freshly sorbed phenanthrene could be readily desorbed with isopropanol/electrolyte solution mixed solvent.
3. Using the same amount of isopropanol, one step mixed solvent desorption worked better than several steps of mixed solvent desorption in desorption efficiency. The best mass balance was also obtained in the one step mixed solvent desorption.

4. The desorption results in this study were in excellent agreement with the irreversible sorption isotherm proposed by Kan et al. (1998), which suggested that the model can be used as a reliable model to predict the resistant release of hydrophobic organic contaminants from natural soils and sediments.

Chapter 5 summarized the detailed procedure for the measurement of desorption resistant fraction. Given a contaminated sediment, the desorption resistant fraction in the sorbed contaminant could be determined following the procedure.

6.2 Future work

Resistant desorption is an extremely complicated process, especially when natural soils and sediments are concerned. While this research produced a useful method that can be used to rapidly access and measure the desorption resistant fraction based on the study of phenanthrene desorption from Utica sediment, the method has not been tested with other contaminant/sediment combinations. Before wide application of this method, more experimental work is needed to test the efficiency and accuracy of this method. 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 still needs to be tested with more diversified systems.
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