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THERMO AND KINETIC STUDIES ON THE SORPTION AND DESORPTION OF HYDROPHOBIC ORGANIC CONTAMINANTS IN SEDIMENTS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemical Engineering

by

Yunzhou Chai
B.S., Xiamen University, China, 1997
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Abstract

This study investigated the correlation of desorption resistance of hydrophobic organic contaminants (HOCs) in sediment and the heterogeneity of sediment organic matter (SOM). The amorphous and condensed phase organic carbon contents were defined by the method of Gustafsson et al. (1997) using thermal oxidation of sediment under 375°C. The desorption-resistant fraction of contaminants in sediments was operationally defined as the fraction that could not be removed by the adsorbent XAD-2. The correlation of the desorption-resistant fraction with sediment organic carbon characteristics was evaluated for both laboratory-inoculated and field-contaminated sediments.

No strong correlation between the desorption resistant fraction in laboratory-inoculated sediments with their condensed phase organic carbon contents was observed, apparently due to the relatively short period of sorption and desorption. The desorption-resistant fractions of contaminants in field-contaminated sediments, however, were well correlated with the amount of condensed phase organic carbon.

Detailed size and density separation of sediment did not assist in understanding the desorption-resistant phenomena. Large particles could be visually separated, however, and differentiation into woody, charcoal, coal-like and coal-cinder particles provided insight into desorption characteristics and equilibrium partitioning.

A mechanistic model of sorption and desorption including both kinetic and equilibrium effects was developed assuming that sorption and desorption to the amorphous carbon is fast, reversible and characterized by relatively low partition coefficients while sorption and desorption to the condensed phase carbon is slow and characterized by relatively high partition coefficients. The model assumes that sorption to the amorphous carbon is
associated with pore diffusion while sorption to the condensed phase carbon is associated with solid phase diffusion.

Model simulations of sorption and desorption in field-contaminated sediments were more successful than those in laboratory-inoculated sediments. The diffusivity of contaminant and volume to surface area ratio in the condensed phase organic matter were two fitting parameters used in the model. The results were more sensitive to the diffusivity of the condensed phase organic carbon fraction. Changes in diffusivity of an order of magnitude or more were required to significantly impact the correlation between the model and observations.
CHAPTER 1 INTRODUCTION

1.1 Motivation and Relevance of the Problem

Soils and sediments acting as natural sorbents are the ultimate sink for many hydrophobic organic contaminants (HOCs). The extent to which these contaminants subsequently pose a risk to the environment depends upon the availability in phases that are mobile or their availability to organisms. Availability of HOCs has become the focus of more and more researchers in that realistic endpoints for remediation processes depend highly on the availability of HOCs. It might be acceptable to leave the residual contaminants intact in the sediment if the residual fraction of the contaminant exhibits marginal availability.

Availability of contaminants includes physical availability and biological availability. The ability of sediment-bound contaminants to partition or desorb to a mobile phase defines physical availability of contaminants. The biological availability describes the opportunity for exposure, uptake or risk of sediment-bound contaminants to receptor organisms including accumulation in organisms and the ability of organisms to biodegrade sediment-bound contaminants. To a great degree, physical availability of sediment-bound contaminants controls their bioavailability because the partitioning of a contaminant between the solid and water phases is a key indicator of the potential for exposure and risk (Reible and Demnerova, 2001). Thus, sorption and desorption of HOCs in natural sorbents are critical processes determining the transport, fate and bioavailability of HOCs in the environment although enormous uncertainty is involved in the quantification of the risk assessment.
The equilibrium distribution of HOCs between sediment/soil and water has been considered a linear and reversible partitioning process, which suggests that a hundred percent of sediment/soil-associated contaminant is available to partitioning or biological receptors in the environment. The reported desorption resistance or hysteresis, which is not explainable by the conventional linear partitioning theory, suggests that only a fraction of the total contaminants may be available or readily available to partitioning or biological receptors. The fraction that is unavailable or not readily available is often referred to as the desorption-resistant fraction of contaminants or sequestered contaminants. The sequestration of contaminants into organic matter in sediments/soils has been ascribed to the effects of different sorbing nature of various soil/sediment organic matrices and conformational or other changes of the contaminants in the matrices.

Although various research groups have developed models in an attempt to understand the physics and chemistry behind the sequestration of contaminants in natural sorbents, no model is able to predict a priori the contaminant concentration in the aqueous phase in a contaminated sediment system influenced by a desorption resistant fraction of contaminants. In order to establish realistic endpoints for remediation processes, the physical chemical mechanisms that govern sequestration and release of contaminants in sediments/soils must be fully understood. Therefore, the proposed work will focus on understanding the mechanisms for the sequestration of HOCs in natural sorbents and establishment of a predictive model to describe this sorption/desorption behavior in natural sorbents in the environment.
1.2 Background and Literature Review

1.2.1 Sequestration Phenomena of Contaminants in Sediments/Soils

In naturally occurring systems most hydrophobic organic contaminants (HOCs) are associated with sediment or soil, sorbed primarily to the sediment/soil organic matter (Karickhoff et al., 1979; Hassett et al., 1980; Means et al., 1980; Huang et al., 1996). Sorption and desorption of HOCs affect contaminant fate, toxicology and the efficiency of most remediation technologies. In fate, risk, and remediation models, sorption and desorption are commonly described as a linear and reversible partitioning process by the following equation (Karickhoff et al., 1979).

\[ C_S = K_P \cdot C_W \]  

(1.1)

Where \( C_S \) (mg/kg) is the contaminant concentration associated with the soil or sediment phase, \( C_W \) (mg/L) is the aqueous concentration, and \( K_P \) (L/kg) is the equilibrium sediment/soil-water partition coefficient. Since most HOCs are believed to reside in soil/sediment organic matter (SOM) in natural sorbents (Karickhoff, 1981; Di Toro et al., 1991), the organic carbon normalized sediment-water partition coefficient, \( K_{OC} \), is more frequently used, which is related to \( K_P \) by Equation 1.2,

\[ K_P = K_{OC} f_{oc} \]  

(1.2)

Where \( f_{oc} \) is the mass fraction of organic carbon in a sediment/soil and assumed to be the single media-specific factor defining sorption capacity.

The organic carbon normalized partition coefficient \( (K_{OC}) \) is a measure of hydrophobicity of the contaminant and relates to the octanol-water partition coefficient.
(\text{K}_{\text{OW}}) \text{ or aqueous solubility (Sol) of contaminant. The } K_{\text{OC}} \text{ has been correlated with}
\text{octanol-water partition coefficient or solubility by relationship of the form:}

\[ \log K_{\text{OC}} = a_1 \cdot \log K_{\text{OW}} + b_1 \] \hspace{1cm} (1.3)

or

\[ \log K_{\text{OC}} = a_2 \cdot \log \text{Sol} + b_2 \] \hspace{1cm} (1.4)

Where \( a_1, b_1 \) and \( a_2, b_2 \) are constants (Chiou et al., 1979; Karickhoff et al., 1979; Karickhoff, 1981, 1984; Means et al., 1980, 1982; Schwarzenbach and Westall, 1981; Schellenberg et al., 1984; Chin and Weber, 1989). Selected empirical correlations to estimate \( K_{\text{OC}} \) from \( K_{\text{OW}} \) are summarized in Table 1.1.

<table>
<thead>
<tr>
<th>Compound Class</th>
<th>( a_1 )</th>
<th>( b_1 )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAHs, Chlorinated HOCs</td>
<td>1.0</td>
<td>-0.21</td>
<td>Karickhoff et al., 1979</td>
</tr>
<tr>
<td>PAHs, Amino- and Carboxy-substituted PAHs</td>
<td>1.0</td>
<td>-0.317</td>
<td>Means et al., 1980</td>
</tr>
<tr>
<td>PAHs</td>
<td>0.989</td>
<td>-0.346</td>
<td>Karickhoff, 1981</td>
</tr>
<tr>
<td>PAHs, Chlorinated HOCs</td>
<td>0.72</td>
<td>+0.49</td>
<td>Schwarzenbach and Westall, 1981</td>
</tr>
<tr>
<td>Neutral chlorinated phenols</td>
<td>0.82</td>
<td>+0.02</td>
<td>Schellenberg et al., 1984</td>
</tr>
</tbody>
</table>

Equation 1.1 works well to describe the bulk of contaminant sorption and desorption, especially for natural sorbents contaminated for days to weeks, but it has been proven that Equation 1.1 does not appropriately describe the partitioning of the
desorption-resistant fraction of contaminants. It has been observed that the desorption of contaminants from natural sorbents is biphasic, which suggests a relatively rapid release of organic contaminants from soils and sediments initially followed by a period of slow or very slow change. The desorption-resistant fraction may persist much longer (Karickhoff, 1980; Cornelissen et al., 2001; Hawthorne et al., 2001) and be less available to organisms or other receptors than would be expected by the reversibly sorbed contaminants (White et al., 1998; Lee, 2001; Lu, 2003; Lu et al., 2003). It has been reported that desorption resistance increases and bioavailability decreases with the contaminant-sediment contact time, which is commonly referred to as “aging” effect (Pignatello et al., 1993; Ma et al., 1993; Hatzinger and Alexander, 1995; McGroddy et al., 1996; White et al., 1997; White et al., 1999b; Lee, 2001; Lu, 2003). It also has been observed in the field that polycyclic aromatic hydrocarbons (PAHs) sorbed to sediments more than predicted by the linear model depicted by equation 1.1 and 1.2 using literature \( K_{OC} \) values (McGroddy and Farrington, 1995; Jonker and Smedes, 2000).

Phenomenologically, the biphasic desorption kinetics can be modeled using a two-compartment first-order kinetic model as shown in Equation 1.5 (Karickhoff, 1980; Hawthorne et al., 2001),

\[
\frac{S_t}{S_0} = 1 - Fe^{-k_f t} - (1 - F)e^{-k_s t}
\]

(1.5)

Where \( t \) is time (days), \( S_t \) is the mass of contaminant removed by sorbent at time \( t \), and \( S_0 \) is the total initial mass of contaminant in sediment; \( S_t/S_0 \) is the fraction of contaminant released after time \( t \). \( F \) is the fraction of contaminant released quickly; \( (1-F) \) is the fraction of contaminant released slowly. \( k_f \) and \( k_s \) are the first-order rate constants
describing the fast and slowly releasing fractions respectively (day⁻¹). Similarly, Cornelissen et al. (2001) proposed a three compartment first-order desorption kinetic model to fit their data. These empirical kinetic models are able to fit the experimental data successfully, however, they do not provide information on the mechanisms behind this biphasic desorption behavior.

Various models and interpretations have been proposed to explain the biphasic desorption behavior of HOCs in natural sorbents. Although they take various mathematical forms and different ways of interpretation, they all assume that the sediment organic matter is heterogeneous and composed of a desorption-resistant fraction and a reversibly sorbed fraction. A summary of the basic characteristics and implications of these interpretations is given below.

1.2.2 Different Interpretations of the Sequestration Behavior

Ghosh et al. (2000) applied microscopic direct observation on Milwaukee harbor sediment particles with the aid of infrared spectrophotometry and scanning electron microscopy (SEM). They found “black” particles as the second most abundant particles after “silica” in their sediment. They described the “black” particles containing high organic carbon content as coal or coal/wood-derived component in the sediment by petrography analysis (Ghosh et al., 2000). Ghosh et al. (2000) separated the sediment into two broad categories, “light” and “heavy” fractions, by wet sieving and density separation using a cesium chloride solution with a specific gravity of 1.8. The light fraction, basically black particles, was comprised primarily of coal- and wood-derived particles. After further separation, it turned out that the light fraction was comprised predominantly of coal-derived particles (Ghosh et al., 2001). A cryomicrotome technique
and microprobe two-step laser desorption/laser ionization mass spectrometry (µL²MS) were utilized to investigate the cross sectional distribution of PAHs in these coal-derived particles by Gillette et al. (1999). Results suggested that most PAHs are concentrated in the near surface regions of these coal-derived particles. Given that the presence of PAHs was likely due to historical contamination over decades, slow diffusion of the contaminants was proposed to explain and model the desorption of contaminants from those coal-derived particles. The “rind” model, with an initial PAH concentration in the outer regions of the particle, predicted a very slow long-term release with 40% PAH remaining even after 100 years (Ghosh et al., 2001). Thus Ghosh et al. (2001) would suggest that desorption resistance is associated with slow diffusion from coal-derived particles.

Weber et al. (1992) classified the organic carbon that could be oxidized by low-temperature persulfate oxidation as “soft carbon”, and by high-temperature combustion with pure oxygen as “hard carbon”. They observed that the “hard carbon” fraction increases with the geological age of the organic matter. Elemental analysis and solid-state 13C-NMR spectra revealed that the O/C atomic ratio of the sediment organic matter decreases with increased geological age of the sediment (Huang and Weber, 1997a). They also observed that the sorption affinities of these materials for phenanthrene as well as their respective isotherm nonlinearity and hysteresis correlate inversely with the O/C atomic ratio. They found that samples containing more physically condensed and chemically reduced sediment organic matter matrices exhibited greater solute affinity, more nonlinear sorption equilibria, and more pronounced hysteresis (Huang and Weber, 1997a). Weber et al. (1992) proposed a composite model--Distributed Reactivity Model
(DRM), which describes sorption isotherm as a combination of a series near-linear absorption reactions and nonlinear adsorption reactions. The sorption isotherm is expressed by the following equation,

\[
q_s = x_i K_{Dr} C_w + \sum_{i=1}^{m} (x_{ni})_i K_F C_w^n
\]  

(1.6)

Where, \(q_s\) is the contaminant concentration in sediment, \(C_w\) is the contaminant concentration in aqueous phase, \(x_i\) is the summed mass fraction of solid phase exhibiting linear sorption, \(K_{Dr}\) is the mass averaged partition coefficient for linear portion, \((x_{ni})_i\) is the mass fraction of the \(i^{th}\) nonlinearly sorbing component, and \(m\) is usually 1 or 2. \(K_F\) is the Freundlich sorption constant for nonlinear portion. They believed that the entrapment of sorbing molecules within the condensed phase sediment organic matter matrices contributes to desorption resistance (Huang and Weber, 1997a).

Xing et al. (1996) proposed Dual Mode Model (DMM) to interpret their experimental data by introducing polymer theory in which the sediment organic matter was classified into two categories--“glassy” and “rubbery” phases. They postulated that contaminants are sorbed in rubbery SOM by linear partitioning and in glassy SOM by partitioning and hole-filling processes. The model was expressed by the following equation:

\[
q_s = k_p C_w + \sum_{i=1}^{n} \frac{s_i^0 b_i c_w}{1 + b_i c_w}
\]  

(1.7)

Where \(k_p\) is linear partition coefficient, \(b_i\) is affinity constant, \(s_i^0\) is maximum capacity, and \(n\) denotes \(n\) unique holes. Similar to DRM, sorption hysteresis is ascribed to
the hole-filling process in the “glassy” phase (Xing and Pignatello, 1997). The difference between DRM and DMM is that the Freundlich isotherm was used in DRM to describe the nonlinear contribution while Langmuiran isotherm was used in DMM. Essentially, it does not make any difference in that the Freundlich isotherm can be expressed as the sum of a series Langmuiran isotherms. Pignatello et al. (1993) investigated elution of aged and freshly added herbicides from a soil and they found that the mobility of the added herbicide was much greater than the native herbicide. They argued that the diffusion of herbicide in the slow sorption compartment in soil is probably the cause of the aging effect (Pignatello et al., 1993). Particle scale direct observation by Ghosh et al. (2001) revealed that PAHs distribute mostly in the outer region of the coal-derived particles which indicate that it takes a long time for contaminants to migrate into the condensed phase particles through diffusion and directly support the argument that the aging effect might result from diffusion of contaminants in a certain fraction of the organic matter in sediment.

Rockne et al. (2002) investigated desorption of PAHs from whole and fractionated sediments. One domain and two domain diffusion models were utilized to fit their experimental data for more hydrophobic and less hydrophobic PAHs respectively (Rockne et al., 2002; Shor et al., 2003). Although model fitting was successful for their desorption data, the assumption that PAHs were initially uniformly distributed throughout sediment aggregates was not appropriate in that microscopic observations showed that PAHs only resided in a thin layer near external surface of the coal-derived particles in the sediment (Ghosh et al., 2001).
Kan et al. utilized successive batch sorption/desorption experiments to investigate the desorption reversibility of hydrophobic organic contaminants from natural sorbents (Kan et al., 1994; Kan et al., 1997; Kan et al., 1998; Chen et al., 2000). A maximum “irreversible” concentration, $q^{\text{irr}}_{\text{max}}$, was observed for certain contaminant/sediment systems. Before $q^{\text{irr}}_{\text{max}}$ is reached, 30-50% of the sorbed contaminants resides in the “irreversibly” sorbed compartment and the rest resides in the labile and reversible compartment. The “irreversibly” sorbed amount varied with the initial concentration available for sorption and the amount in the “irreversibly” sorbed compartment increases linearly with the number of adsorption steps. After $q^{\text{irr}}_{\text{max}}$ is reached, adsorption/desorption becomes “reversible”. If the “reversible” portion is removed, the “irreversible” portion is at equilibrium with aqueous phase, but equilibrium concentration in aqueous phase is much lower than would be predicted with conventional partitioning theory. They found that, for most compounds, $q^{\text{irr}}_{\text{max}}$ is approximately $10^{3.8}$ multiplied by the organic carbon content of the sediment, and that organic carbon normalized partition coefficient for the irreversible compartment, $K^{\text{irr}}_{\text{OC}}$, is a single constant for all compounds and all sediments studied; it is $10^{5.53\pm0.48}$ (Kan et al., 1998). The following biphasic isotherm model was proposed to fit the experimental data,

$$q_s = K_{\text{OC}} f_{oc} C_W + \frac{K_{\text{OC}} f_{oc} q^{\text{irr}}_{\text{max}} C_W f}{q_{\text{max}} f + K_{\text{OC}} f_{oc} C_W} \tag{1.8}$$

Where $K_{\text{OC}}$ is the organic carbon normalized partition coefficient for “reversibly” sorbed fraction, $K_{\text{OC}}^{\text{irr}}$ is the organic carbon normalized partition coefficient for “irreversibly” sorbed fraction, $f_{oc}$ is the organic carbon content in sediment, $C_W$ is the
contaminant concentration in aqueous phase, $q_{\text{max}}^{\text{irr}}$ is the maximum “irreversibly” sorbed concentration of contaminant in sediment, and $f$ is the fraction of the irreversible compartment that is filled at the time of exposure. $f$ varies from 0 to 1. $f$ is 1 when the initial aqueous concentration is greater than a half of the solubility of the compound in water. The isotherm consists of two terms, a linear term to represent “reversible” sorption and a Langmuirian-type term to represent “irreversible” sorption. After about 1-3 days of contact time, all laboratory sorption and desorption data could be modeled using the above isotherm equation (Equation 1.8). They postulated that the observed phenomenon might be due to the occlusion of desorption resistant contaminants from desorption by cooperative conformational changes of the organic phase during the sorption process (Kan et al., 1997). The conformational rearrangement of the soil/sediment organic matter in the presence of adsorbed contaminants could cause the chemical environment of the adsorbate to be different and hence be the source of the desorption resistance. The biphasic model fitted their experimental data successfully and explained the biphasic desorption phenomena. However, no evidence was provided to defend the hypothesis of rearrangement of organic matter in sediment.

Elevated partition coefficients other than predicted from organic carbon normalized partition coefficients for PAHs have been observed in field sediments. Gustafsson et al. (1997) quantified the “black carbon” (e.g. soot and chars etc.) content in the sediment by thermal oxidation (“black carbon” content is the organic carbon content remaining in the sediment sample after combustion under 375°C). They included the contribution of “black carbon” to understand the elevated partition coefficient and the following isotherm was proposed.
\[ C_s = f_{OC} K_{OC} C_w + f_{BC} K_{BC} C_w^n \]  

where \( C_s \) is the concentration in sediment, \( K_{OC} \) is the “natural organic carbon” normalized partition coefficient, \( K_{BC} \) is the “black carbon” normalized partition coefficient, which is much higher than that of ordinary sediment organic matter. \( f_{oc} \) is the natural organic carbon content, \( f_{BC} \) is the “black carbon” content of sediment. In this way, it is easy to understand the elevated partition coefficient, but no explanation was provided to explain aging effects. The use of this temperature treatment has proven to be a convenient and generally only successful measure of separating the condensed phase organic carbon from the amorphous organic carbon.

Other researchers have also reported that sediment organic carbon particles such as coal, coke, and soot have extremely high partition coefficients. Ghosh et al. (2003) collected organic carbon normalized partition coefficients values for various particles from literature (Karapanagioti, et al., 2000; Walters and Luthy, 1984; Gustafsson and Gschwend, 1997; Gaboriau and Saada, 2001; Chiou et al., 1998; Karickhoff et al., 1979; Salloum et al., 2002) spanning about 3 logarithmic units from 4 to 7. Jonker and Koelmans (2002) reported that sorption of PAHs to different soot and soot-like materials was over 1000 times as strong as the sorption to amorphous sediment organic matter as indicated by elevated partition coefficients.

1.2.3 Summary

The following ideas can be extracted from the above-mentioned models and interpretations:

1. Biphasic desorption phenomenon results from organic carbon heterogeneity.

   Sediment/soil organic matter can be classified into two general categories as
1. Amorphous and condensed phase organic matter. Denotations like “coal-derived” particle, “soot carbon”, “black carbon” and “condensed phase carbon” have been used to refer to condensed phase organic carbon, while natural organic matter has been used to refer to amorphous organic carbon.

2. Condensed phase organic carbon exhibits elevated organic carbon normalized partition coefficient, which indicates greater sorption capacity and slower sorption/desorption rates.

3. Desorption resistance of organic contaminants and aging effect result from the slow diffusion of contaminants in the condensed phase organic carbon.

Although these basic ideas are widely acknowledged to explain the biphasic sorption and desorption behaviors of hydrophobic organic contaminants in sediments and soils, nobody has ever utilized these basic ideas and mathematical models to predict quantitatively the availability of sequestered contaminants in sediments including the desorption resistance, apparent partition coefficients and aging effects. The goal of this work is to develop a predictive model so that the model can be used to estimate a priori the availability of sequestered contaminants in soils and sediments when developing realistic regulations and remediation endpoints for contaminated soils and sediments.

1.3 Objectives of Present Study

1.3.1 Overall Objectives

The proposed research is directed toward confirming this understanding regarding the mechanisms for the desorption resistance of hydrophobic organic contaminants (HOCs) in natural sorbents and establishing a predictive model of sorption/desorption behavior of hydrophobic organic contaminants onto/from natural sorbents in the
environment. The proposed studies will utilize both lab-inoculated and field-contaminated sediments as test media. These studies will focus on polynuclear aromatic hydrocarbons (PAHs) in that they are common sediment contaminants and present a wide range of hydrophobicities and toxic characteristics.

1.3.2 Specific Objectives and Approaches

1.3.2.1 Development of a Predictive Model to Address Sorption/Desorption Behavior of HOCs onto/from Soils and Sediments

A model can be used to link the concepts presented above and provide a tool for testing the mechanisms that have been proposed for desorption resistance. Consistent with the current understanding of these mechanisms, a model is proposed with the following fundamental hypotheses:

**Hypotheses:**
1. Variations in desorption rate and extent from contaminated sediments are associated with soil organic matter heterogeneity. Greater sorption capacity (more limited desorption) and reduced rates of sorption and desorption are associated with condensed phase carbon formed from natural processes over long periods of time or by combustion processes over shorter time periods. 
2. Although there exists a continuum of organic matter quality and resulting sorption capacities and rates, the sorption and desorption phenomena can be described by considering only two broad classes, an amorphous phase in which sorption and desorption is relatively fast and reversible and a condensed phase in which sorption and desorption is relatively slow and for which phase exhibits greater capacity than the amorphous phase.
3. The condensed phase is approximately described by each of the characterizations found in the literature, that is as condensed phase carbon, as glassy polymer, as diagenetically aged carbon, as soot carbon, as coal-derived particle, and
black carbon, etc; and these phases are roughly equivalent. (4) The sorption and desorption to the amorphous carbon can be described by diffusion in a porous matrix with equilibrium partitioning described by the organic carbon based partition coefficient as measured in short-term sorption experiments. (5) The sorption and desorption to the condensed phase carbon can be described by much slower solid phase diffusion and with equilibrium partitioning measured experimentally to be higher than the organic carbon based partition coefficient.

1.3.2.2 Validation of the Model

The hypotheses defined above will be tested through the work described in this dissertation. This hypothesis testing will be conducted via the following approaches.

a. Determination of the relationship between desorption resistance of freshly inoculated contaminants and the heterogeneity of organic matter in soils and sediments, testing the model to determine whether the model is able to predict the biphasic desorption kinetics and the relationship between desorption resistance and heterogeneity of sediment organic matter.

**Expectation:** Contaminants residing in sediment with higher condensed phase organic carbon content ($f_{oc}/f_{oc}$) exhibits greater desorption resistance, and the model is able to predict this relationship and the biphasic desorption kinetics.

b. Determination of relationship between desorption resistance of “aged” inoculated contaminants (aging effect) and the heterogeneity of organic matter in soils and sediments, and testing the ability of the model to predict the aging effect.

**Expectation:** Aging effect for sediment with higher condensed phase organic carbon content is more significant than that of sediment with less condensed phase organic
carbon content, and the model is able to predict aging effect of contaminant in sediments with different condensed phase organic carbon contents.

c. Evaluation of the effects of slow kinetics of contaminants in condensed phase organic carbon on measured apparent partition coefficient of contaminants in sediments, testing the ability of the model to predict the elevated apparent partition coefficient for the desorption-resistant contaminant.

**Expectation:** Relatively short equilibration time for partition coefficient measurement is not long enough to reach real equilibrium; the model is able to predict the elevated apparent partition coefficient for the desorption-resistant contaminant.

d. Determination of the effects of organic matter heterogeneity on contaminants distribution and availability in fractionated sediments

**Expectation:** Distribution and availability of contaminants in different sediment fractions is related to the characteristics of organic carbon matrices in those fractions.

**1.4 Overview**

This dissertation consists of seven chapters. The main contents of each chapter are briefed below. Chapter 1 summarizes the current understanding of the fundamental aspects of sorption and desorption processes involved in the sequestration and release of HOCs by soils/sediments. Chapter 2 covers the availability of HOCs in laboratory-inoculated sediments and field-contaminated sediments. Correlation of desorption resistance and condensed phase carbon content will be discussed. Chapter 3 describes the size and density separation for sediments, including contaminant distribution and sediment mass distribution in sediment fractions, and the availability of contaminant in different sediment fractions. Chapter 4 characterizes the observations obtained on coarse
particles from field-contaminated sediments. Chapter 5 contains the modeling activities. Processes including desorption, partition and aging of contaminants in sediment will be modeled and discussed. Chapter 6 summarizes major conclusions in this study and recommendations for future work.
CHAPTER 2 AVAILABILITY OF CONTAMINANTS IN SEDIMENTS WITH DIFFERENT CONDENSED PHASE ORGANIC CARBON CONTENTS

2.1 Introduction

Recent research has revealed that the availability of sediment-associated hydrophobic organic contaminants and not the total sediment-associated contaminants is critical in defining exposure, uptake or risk of contaminants to receptor organisms in the environment. Availability of contaminants includes physical availability and biological availability. To a great degree, physical availability of sediment-bound contaminants controls its bioavailability because the partitioning of a contaminant between the solid and water phases is a key indicator of the potential for exposure and risk (Reible and Demnerova, 2001; Lu et al., 2003; Kraaij et al., 2003; Lu et al., 2004).

In evaluating contaminant fate, risk, and endpoints for remediation, the total solid phase concentration has often been used and linear partitioning assumed (Karickhoff et al., 1979). This suggests that all of the sediment-associated contaminant is available to partition into mobile phase. There is increasing evidence, however, that a fraction of the sediment-bound contaminant is not easily desorbed, which results in reduced availability of the desorption-resistant fraction of contaminant (Robinson et al., 1990; Alexander, 1994; Loonen et al., 1994; Opdyke and Loehr, 1999, Lu et al., 2003). Thus, the linear, reversible partitioning model (Karickhoff et al., 1979) is no longer appropriate to describe desorption of the resistant compartment, and biphasic empirical models (Karickhoff, 1980; Hawthorne et al., 2001) have been proposed to describe the biphasic desorption phenomenon which exhibits a rapid release of a reversible labile fraction followed by a slow release of the resistant fraction.
The desorption-resistance has been ascribed to the heterogeneity of organic matter present in sediments. In addition to the amorphous natural organic matter, condensed phase carbon, similar names as hard carbon, soot, black carbon, glassy polymer, coal-derived particle etc., has been widely found in field-contaminated sediments and been postulated to be responsible for the desorption resistance of contaminants in sediments (Weber et al., 1992; Huang and Weber, 1997a; Gustafsson, et al., 1997; Ghosh, et al., 2001; Kan et al., 1998; Xing et al., 1996; Xing and Pignatello, 1997; Rockne et al., 2002). The condensed phase carbon has been considered to be the source of desorption resistance in that it exhibits extremely high sorption capacity as indicated by an elevated partition coefficient (Gustafsson and Gschwend, 1997; Ghosh et al., 2003), and it is highly reduced and condensed in form so that the diffusion rate of contaminants in this phase is extremely slow (Ghosh et al., 2001). The condensed phase carbon has been operationally defined by the fraction of organic carbon remaining after sediment was combusted under 375°C (Gustafsson et al., 1997).

This chapter is directed toward characterizing the relationship between the desorption-resistant phenomena and sediment organic matter quality, specifically the condensed phase organic carbon content as defined by the method of Gustafsson et al. (1997). Two laboratory-inoculated sediments, Bayou Manchac sediment and University Lake sediment, were inoculated with phenanthrene, a hydrophobic polycyclic aromatic hydrocarbon as well as a significant pollutant in contaminated sediments, to conduct the study. The desorption kinetics were determined using XAD-2, a nonpolar sorbent, as an essentially infinite sink to remove rapidly desorbing phenanthrene from the inoculated sediment. The desorption isotherms of phenanthrene were established based on the
measured sediment concentration and pore water concentration at the completion of measurement of apparent sediment–water partition coefficients for a series of partially desorbed sediments prepared according to the procedure stated in Lu (2003). That is, they were prepared by washing the laboratory-inoculated sediment with the relatively weak solvent of an isopropanol/electrolyte solution (v/v 1:1) to remove reversibly sorbed contaminant. The desorbed sediments possess various proportions of contaminants associated with desorption-resistant compartment to the contaminants associated with reversible compartment.

Two field-contaminated sediments, Utica Harbor sediment and Rouge River sediment, were also used in this study. The fast desorbing fraction, as characterized by the fraction removed by XAD-2 in 20 hours, of a number of PAHs in the sediments were determined. The apparent sediment–water partition coefficients of these PAHs in the sediments before and after the sediments were subjected to XAD-2 treatment were determined.

2.2 Materials and Methods

2.2.1 Chemical

Phenanthrene (PHE, 98% purity), used as a tracer contaminant in this study to inoculate Bayou Manchac and University Lake sediments, was purchased from Aldrich Chemical Corporation (Milwaukee, WI, USA).

2.2.2 Sediments

Two clean sediments, Bayou Manchac sediment and University Lake sediment, were used in these experiments to inoculate phenanthrene as a tracer contaminant. Bayou Manchac sediment was collected from Bayou Manchac, a fresh water bayou in Baton
Rouge, Louisiana, in 1998 and University Lake sediment was collected from University Lake, Baton Rouge, Louisiana, in 1999. Contaminants in these sediments were analyzed according to the procedure described in section 2.2.6 and results showed that these sediments were originally free of phenanthrene. After collection, these sediments were coarsely sieved to remove twigs, leaves, etc., and then they were passed through a 2 mm sieve to remove debris and large particles.

Two field-contaminated sediments, Utica Harbor sediment and Rouge River sediment, were also used in this research. Utica Harbor sediment was collected from Utica Harbor, Utica, NY and the sediment was contaminated over many decades ago during the operation of a coal gasification plant. Rouge River sediment was collected from Rouge River, MI and the sediment was contaminated in early 20th century by both sewer pipe and industrial waste discharges.

All sediments were sieved through 2 mm sieves before used for the experiment and were stored at room temperature in tightly sealed barrels with overlying water to avoid air-drying.

2.2.3 Moisture Content

About 1-2 g sediment in a pre-weighed 25 ml glass vial was placed in an oven at 105 °C for 24 hours. The difference in weights represented the moisture content of the sediment sample and was usually represented as a ratio of the moisture mass to the original weight of the wet sediment. Moisture content throughout this dissertation is presented on a wet basis.
2.2.4 Organic Carbon Content

The total organic carbon content (TOC) of sediment was analyzed on a Perkin Elmer 2400 Series II CHN elemental analyzer (Perkin Elmer Corporation, Norwalk, CT, USA) in the Coastal Ecology Institute at LSU. First, sediment was dried at approximately 105°C overnight to remove moisture from sediment. Then the dried sediment was pulverized, treated with 1N HCl to remove carbonates and re-dried before it was analyzed. For each sediment sample, at least three replicates were used, and 5-15 mg sediment was taken for each replicate. The organic carbon content was usually presented as a mass fraction \( f_{oc} \), which is defined as the ratio of the mass of organic carbon in sediment to the total mass of dry sediment.

The total carbon fraction of each sediment treated with 1N HCl was compared to that of the same sediment without acidification. The measured carbon content of the sediment after acidification was not significantly different from the carbon content of the same sediment without acidification. This demonstrated that the inorganic carbonate fractions in sediments used in the study were negligible. Therefore, the total organic carbon content was equivalent to the total carbon content for sediments used in this study, which is consistent with previous results in our group by Lu (2003).

The condensed phase organic carbon content of sediment was measured utilizing the thermal oxidation method as stated in Gustafsson et al. (1997). Operationally, organic carbon content was measured after the sediment was combusted overnight at 375°C with plenty of air. The fraction of oxidizable organic carbon under 375°C was considered to be amorphous organic carbon fraction. The amorphous organic carbon content \( f_{oc}^{A} \) and the condensed phase organic carbon content \( f_{oc}^{C} \) of the sediment were calculated from the
measured total organic carbon content of the sediment \( (f_{oc}) \) and the measured total organic carbon content of the sediment after combustion under 375°C \( (f_{oc}^{375}) \) by the following two equations (Equation 2.1 and 2.2).

\[
\frac{f_{oc}^C}{1 - f_{oc}^A} = f_{oc}^{375} \tag{2.1}
\]

\[
f_{oc}^C + f_{oc}^A = f_{oc} \tag{2.2}
\]

In this study, amorphous organic matter was used to represent the oxidizable organic matter in sediments under 375°C. This could possibly include the “soft carbon” (Weber et al., 1992), “natural organic matter” (Gustafsson et al., 1997) or “rubbery phase” organic matter (Xing et al., 1996), which exhibits no desorption resistance and consistent partition coefficient to the literature value. Condensed phase organic matter was used to denote the organic matter not oxidizable under 375°C. This could possibly include “hard carbon” (Weber et al., 1992), “black carbon” or “soot carbon” (Gustafsson et al., 1997) or “glass phase” organic matter ((Xing et al., 1996), “coal-derived” particles (Ghosh et al., 2001), which are in a reduced and condensed form, and exhibits much stronger association of contaminants in sediment.

2.2.5 Chemical Analysis

Glassware used in any aspect of an experiment was cleaned thoroughly with at least 24 hours soaking in a 10% chromium acid bath. Then the glassware was flushed with tap water, rinsed with deionized water, dried at approximately 300° C except for volumetric glassware, and stored in a clean cabinet. Volumetric glassware was dried at less than 70°C to avoid the invalidation of the calibration caused by expansion/contraction. Reagent grade or better quality was used for all solvents and
chemicals. The frequently used solvents such as hexane and acetone were tested once a month for purity by comparing the chromatography of the current solvent with that of the solvent before first use. Metal-free deionized water from the Corning Mega-pure system was used in all solutions.

For solid samples, ultrasonic extraction method (Lu, 2003) was used to extract PAHs from the sediment matrix. A Hewlett Packard 1100 Series high performance liquid chromatography (HPLC, Hewlett Packard, Palo Alto, CA, USA) with UV-Diode array detector and fluorescence detector was used to measure the concentration of contaminant in the extraction solvent (EPA method 8310, 1986). The concentration of contaminant in sediment was calculated from the concentration of the extraction solvent. The extraction procedures used in this study followed Lu (2003) and involved the following steps: 1) Weighing—Put 1 to 2 g sediment samples (wet) in an extraction vessel (240 ml glass jar). 2) Drying—Mix about 20 g of anhydrous sodium sulfate into the sediment to dehydrate the sediment. 3) Extraction—Add 60 ml 50/50 hexane/acetone mixture. 4) Sonicating—Sonicate for about 20 minutes in a water-bath, then the extraction vessel was placed on lab-bench overnight. 5) Blow down—A 2 ml subsample was put into a 2 ml tube and concentrated under nitrogen flow to approximately 0.2 ml. 6) Solvent Exchange—Add 1.8 ml acetonitrile to the tube and mix thoroughly by vortex machine. Finally, 0.5 ml to 1 ml sample after solvent exchange was transferred to a 1.5 ml glass HPLC sampling vial and analyzed immediately or stored in the refrigerator at 4°C for later analysis. Results in Lu (2003) and results in this study showed that the solvent loss during step four is approximately 0.4 g per sample, less than 1% of the total solvent used. The small solvent loss did not impact our results for the solid phase concentration because the calculation
were based on the final solvent mass at the completion of the step four to eliminate bias due to the solvent loss.

The concentration of contaminant in aqueous phase was measured directly by HPLC (EPA method 8310; SW-846 3rd edition, 1986).

2.2.6 Sediment Inoculation

Two clean sediments, Bayou Manchac sediment and University Lake sediment, after sieving were inoculated with the tracer chemical as model contaminant using the shell-coating procedure employed by Thoma (1994). These sediments were inoculated at saturation concentrations of phenanthrene (PHE), which were estimated from the linear correlation as shown by Equation 1.1 and 1.2 by substituting the \( C_w \) in Equation 1.1 with the water solubility of phenanthrene. The saturation concentration of phenanthrene in Bayou Manchac sediment and University Lake sediment were estimated to be 380 mg and 1600 mg PHE per kilogram dry sediment.

The procedures to inoculate phenanthrene into sediment included the following steps: 1) A certain amount of phenanthrene, determined according to the mass of sediment and the objective phenanthrene concentration to be inoculated, was dissolved in hexane in a pre-cleaned beaker and then transferred into an inoculation vessel (4-L glass jar). 2) Hexane was evaporated under a stream of highly purified nitrogen while the inoculation vessel was being rotating. Solid phenanthrene was uniformly deposited on the internal wall of the inoculation vessel when hexane was completely evaporated. 3) Pre-weighed wet sediment was added into the inoculation vessel. In order to achieve better mixing during tumbling in step 5, water might be added to adjust the moisture content of the sediment to approximately 50% if the original moisture content in the sediment was
less than 50%. 4) Approximately 3000 mg/kg sodium azide was added to the inoculation vessel to inhibit bacterial metabolism of the contaminants during tumbling. This concentration of sodium azide was sufficient to prevent degradation as indicated by the ability to maintain constant sediment concentration after inoculation. 5) The inoculation vessel was tumbled for five weeks at an axial rotation rate of 5-10 rpm on a roller mill.

2.2.7 Desorption Kinetics

Kinetics of desorption for Bayou Manchac sediment and University Lake sediment were measured by mixing sediments with Amberlite XAD-2, a nonpolar polymer resin sorbent. Amberlite XAD-2 was used as an essentially infinite sink to maintain the porewater adjacent to the desorbing solid at effectively zero concentration.

Amberlite XAD-2 was purchased from Supelco Inc, USA. Properties of Amberlite XAD-2 are listed in Table 2.1. XAD-2 sorbent was pre-conditioned to remove residual organics by successive washing with HPLC grade methanol and deionized water. XAD-2 resin was placed in a separatory funnel and methanol was added to maintain about one inch methanol above XAD-2. Methanol was drained slowly after XAD-2 resin was soaked by methanol for at least one hour. Deionized water was then passed through XAD-2 resin three times to remove any residual methanol. XAD-2 was ready to use for the experiment after this pre-conditioning treatment.

A certain amount of sediment, generally 100-200 grams of wet sediment, was placed in a glass jar and mixed homogeneously with 10% (dry mass ratio) pre-conditioned XAD-2. Preliminary studies showed that this level of XAD-2 loading was sufficient to capture all desorbed HOCs during the time frame of the experiment. The
glass jar containing sediment amended with XAD-2 was sealed using aluminum foil lined screw cap and placed into an incubator at 25°C.

Table 2.1 Properties of Amberlite XAD-2

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Styrene/Divinylbenzene co-polymer</td>
</tr>
<tr>
<td>Diameter</td>
<td>20-60 Mesh</td>
</tr>
<tr>
<td>Pore Volume</td>
<td>0.65 ml/g</td>
</tr>
<tr>
<td>Pore Size</td>
<td>90 Å</td>
</tr>
<tr>
<td>Surface Area</td>
<td>300 m²/g</td>
</tr>
<tr>
<td>Density</td>
<td>1.08 g/ml (skeletal)</td>
</tr>
<tr>
<td>Density</td>
<td>1.02 g/ml</td>
</tr>
</tbody>
</table>

At the end of the intended contact time period, sediment and XAD-2 were separated and chemical concentrations in sediment and XAD-2 resin were determined. When the sediment and XAD-2 were being separated, 100 ml of cesium chloride (CsCl) solution with density of 1.1 g/ml was added into 20 grams of the sediment amended with XAD-2 resin and mixed thoroughly using magnetic stirring bar. The system was then allowed to settle for 10-15 minutes until the XAD-2 was floating on the surface and the solution was clear enough to assure no XAD-2 stuck to the interface of sediment and CsCl solution. XAD-2 was then removed via tip-truncated glass pipette onto a sieve. The XAD-2 was then washed with tap water, and set aside to air-dry overnight. The sediment was separated from the cesium chloride solution by centrifugation at relative centrifugal force of 3000 g for 20 minutes (Beckman Model J-6B Centrifuge) and washed with tap
water three times to remove any residual salt. Sediment was then collected to measure chemical concentrations and moisture content.

The advantage of using this procedure to desorb contaminants from sediments was that it limited the destruction of sediment particles to the least extent by mixing XAD-2 into sediment as is without addition of excessive water or shaking.

2.2.8 Preparation of Desorption-resistant Sediment and Determination of Desorption Isotherms

Laboratory-inoculated Bayou Manchac sediment and University Lake sediment were desorbed using an isopropanol and electrolyte solution (0.01M NaCl, 0.01M CaCl₂·2H₂O) with a ratio of 1:1(v/v) in a glass vessel. The weight ratio of sediment to the isopropanol solution was around 1:4. The vessel with sediment slurry was tumbled for different times (2 hours to 96 hours) at the same rotation rate of sediment inoculation. At the end of desorption, the sediment slurry was centrifuged (Beckman Model J-6B Centrifuge) for 20 minutes in a 1-L plastic centrifuge bottle with relative centrifugal force of 3000 g. The sediment was washed 3 to 4 times with electrolyte solution to remove the residual isopropanol. The concentration of contaminant in sediment and proportion of contaminant associated with reversible to desorption-resistant compartment were controlled by the number of desorption batches and the time periods of each desorption.

At the end of each desorption, the concentration of the model contaminant in sediment, total organic carbon content of the sediment, and sediment-water partition coefficients were measured using procedures that will be described later. Desorption isotherms were established using the measured partitioning data for the resulting series of sediments with different proportion of desorption-resistant to reversible contaminant.
Tomson et al. (unpublished) has shown that desorption with this isopropanol solution allows the rapid removal of reversibly sorbed contaminant, and the resulting isotherm closely tracks multiple batch-desorption in water. Isopropanol solution washing is, however, much more efficient than water desorption. One-step isopropanol washing readily removes the bulk of the reversibly sorbed contaminant and the remainder shows indications of desorption resistance (Lu, 2003). Thus, a desorption isotherm covering several order of magnitude in solid phase concentration could be prepared by a small number of batch desorption.

2.2.9 Measurement of Apparent Partition Coefficient

The apparent sediment-water partition coefficients for phenanthrene were measured following the procedures of Kan et al. (1994) and standard procedures of the American Society for Testing and Materials (1998). Two grams of wet sediment (water content of ~ 40%) of known initial concentration was placed into a 45 ml glass bottle with Teflon lined screw cap. The bottle was then filled with electrolyte solution (0.01M NaCl, 0.01M CaCl₂·2H₂O, and 0.01M NaN₃ in deionized water) with minimal headspace. At the end of the equilibration time of 10 days or 60 days, the sediment slurry was centrifuged at relative centrifugal force of 2000 g. Aqueous samples were then taken from each bottle, and the contaminant concentration in water was analyzed by high performance liquid chromatography (HPLC). The contaminant concentration in sediment at completion of equilibration was calculated based on mass balance assuming that no loss of phenanthrene occurred during equilibration. Lu (2003) showed that this was a reasonable assumption as the recovery of phenanthrene was greater than 90% after a 10-day equilibration.
To evaluate the possibility that the observed desorption behavior was an artifact of short equilibration times, the equilibration time was lengthened from 10 days to 60 days. The results are shown in Figure 2.1 and corresponding apparent partition coefficients are presented in Table 2.2.

Figure 2.1 Apparent desorption isotherms of phenanthrene in freshly inoculated Bayou Manchac sediment at different equilibration time.

Note: Diamonds denote measurements obtained at equilibration time of 10 days and squares 60 days. Dashed line is the desorption isotherm predicted by reversible linear partitioning model.

The equilibration time of 10 days was elucidated because desorption isotherms were determined by many researchers at comparable time length scale. For instance, Lu (2003) determined desorption isotherm at 10 days, Kan et al. (1998) at 1-3 days, Huang and Weber (1997a) at 14 days. However, Huang and Weber (1997) reported that apparent equilibria obtained by relatively geologically old materials within 28 days did not approach steady state. Thus, longer equilibration time of 60 days was used to investigate the potential effect of extended equilibration time on the apparent partition coefficient.
Table 2.2 Apparent partition coefficients of phenanthrene in Bayou Manchac sediments with different desorption-resistant phenanthrene concentrations determined at 10 days and 60 days

<table>
<thead>
<tr>
<th>PHE conc. in sediment (mg/kg)</th>
<th>Apparent Log$K_{OC}$ at 10 days</th>
<th>Apparent Log$K_{OC}$ at 60 days</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>380.33±10.09</td>
<td>4.47±0.02</td>
<td>4.40±0.01</td>
<td>0.07</td>
</tr>
<tr>
<td>49.99±1.73</td>
<td>4.51±0.02</td>
<td>4.41±0.01</td>
<td>0.10</td>
</tr>
<tr>
<td>38.97±0.27</td>
<td>4.59±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29.59±0.61</td>
<td>4.63±0.02</td>
<td>4.50±0.01</td>
<td>0.13</td>
</tr>
<tr>
<td>20.94±1.09</td>
<td>4.73±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.51±0.27</td>
<td>4.78±0.01</td>
<td>4.64±0.03</td>
<td>0.14</td>
</tr>
<tr>
<td>13.39±0.78</td>
<td>4.72±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.16±0.14</td>
<td>4.79±0.01</td>
<td>4.62±0.02</td>
<td>0.17</td>
</tr>
<tr>
<td>3.81±0.14</td>
<td>4.92±0.02</td>
<td>4.74±0.02</td>
<td>0.18</td>
</tr>
<tr>
<td>2.99±0.01</td>
<td>4.99±0.03</td>
<td>4.79±0.03</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 2.2 suggested that prolonged equilibration time results in a significantly lower partition coefficient. The difference ranged from 0.07 to 0.20 logarithmic units. The above results indicated that the dynamics of desorption from the desorption-resistant fraction are exceedingly slow. Although results showed that true equilibrium might not be achieved in 10 days, the apparent partition coefficient measured at equilibration time of 10 days was able to provide a valid basis to evaluate the effective partitioning and availability of contaminants associated with sediments.
2.2.10 Determination of Fast Desorbing Fraction of Contaminants in Field-contaminated Sediments

The fast desorbing fractions of the contaminants in two field-contaminated sediments were determined by allowing sediment and Amberlite XAD-2 to contact for 20 hours. Experimental results on laboratory-inoculated sediments showed that the contact time of 20 hours is appropriate to characterize the fast desorbing fraction of contaminant in sediment because the desorption kinetics showed that the contaminant was removed by XAD-2 dramatically in the first 20 hours, then the contaminant concentration leveled off (Figures 2.2, 2.3 and 2.4).

The fast desorbing fraction or called labile fraction of a contaminant, \( F \), was operationally defined by equation 2.3,

\[
F = \frac{C_0 - C_{\text{Des20hr}}}{C_0} \tag{2.3}
\]

where \( C_0 \) (mg/kg) was the initial concentration of contaminant in sediment and \( C_{\text{Des20hr}} \) (mg/kg) was the concentration of contaminant in sediment after treatment with XAD-2 for 20 hours. The proportion of contaminant remaining in sediment after XAD-2 treatment for 20 hours was considered to be desorption resistant fraction in the sediment.

2.3 Results and Discussion

2.3.1 Desorption Kinetics in Laboratory-inoculated Sediments

Organic carbon contents of two lab-inoculated sediments, Bayou Manchac (BM) sediment and University Lake (UL) sediment are presented in Table 2.3.
Table 2.3 Characteristics of laboratory-inoculated sediments

<table>
<thead>
<tr>
<th>Sediment</th>
<th>( f_{oc} )</th>
<th>( f_{oc}^A )</th>
<th>( f_{oc}^C )</th>
<th>( f_{oc}^A/f_{oc} )</th>
<th>( f_{oc}^C/f_{oc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayou Manchac</td>
<td>1.54(±0.02)%</td>
<td>0.80(±0.03)%</td>
<td>0.74(±0.02)%</td>
<td>51.95(±2.01)%</td>
<td>48.05(±1.47)%</td>
</tr>
<tr>
<td>University Lake</td>
<td>6.35(±0.12)%</td>
<td>5.52(±0.12)%</td>
<td>0.83(±0.01)%</td>
<td>86.93(±2.55)%</td>
<td>13.07(±0.54)%</td>
</tr>
</tbody>
</table>

\( f_{oc} \): total organic carbon content of sediment;
\( f_{oc}^A \): amorphous organic carbon content;
\( f_{oc}^C \): condensed phase organic carbon content.

The two sediments exhibited significantly different total organic carbon contents and amorphous/condensed phase organic carbon ratios. Bayou Manchac sediment had a total organic carbon content of 1.54(±0.02)%, 48.05(±1.47)% of which was condensed phase organic carbon, whereas University Lake sediment had a total organic carbon content of 6.35(±0.12)%, 13.07(±0.54)% of which was condensed phase organic carbon.

Desorption kinetics determined using nonpolar sorbent Amberlite XAD-2 for freshly inoculated Bayou Manchac sediment and University Lake sediment are shown in Figure 2.2. The desorption of phenanthrene from the two sediments showed that the two sediments, with various condensed phase carbon content, behaved almost the same. Initial concentrations of phenanthrene at the completion of inoculation were 390 and 1643 mg/Kg for Bayou Manchac sediment and University Lake sediment respectively. Phenanthrene was removed from the sediment dramatically during the first day after XAD-2 was added into sediment, then, the fraction of phenanthrene remaining in two sediments leveled off at approximated 3%.

Desorption kinetics determined using nonpolar sorbent Amberlite XAD-2 for freshly inoculated and aged Bayou Manchac sediment and University Lake sediment are
shown in Fig. 2.3. Aged Bayou Manchac sediment had been aged for three years and aged University Lake sediment had been aged for two years. Aging effects were observed for both Bayou Manchac sediment and University Lake sediments in Fig. 2.3 because greater fractions of phenanthrene remained in the aged sediments than the corresponding freshly inoculated sediments after desorption.

Figure 2.2 Biphasic desorption kinetics of phenanthrene from freshly inoculated Bayou Manchac and University Lake sediments

Note: Data points were experimental data and lines were calculated from biphasic first-order model as described in Equation 1.5.

Desorption kinetics data for freshly-inoculated and aged Bayou Manchac sediment and University Lake sediment were fitted using the empirical biphasic desorption model as described in Equation 1.5:

\[
\frac{S_t}{S_0} = 1 - Fe^{-k_1t} - (1 - F)e^{-k_2t}
\]
Figure 2.3 Desorption kinetics of phenanthrene from freshly inoculated and aged Bayou Manchac and University Lake sediments

Note: Data points were experimental measurements and lines were calculated using biphasic first-order model described in Equation 1.5.
Fitted parameters are listed in Table 2.4. Excellent agreement between the model and data was observed as the R-squared values were 0.99 for both sediments. Fast desorbing fractions for the two sediments were 0.96 and 0.97 respectively. This indicated that about 4% and 3% of phenanthrene in Bayou Manchac sediment and University Lake sediment were desorption resistant as determined by XAD-2 desorption, showing no significant difference for the two sediments. The rate constants for fast fraction were both 0.11 h⁻¹ for the two sediments, and rate constants for slow fraction were 6.1×10⁻⁴ and 6.6×10⁻⁴ h⁻¹ respectively.

Table 2.4 Fitting parameters for desorption kinetics of phenanthrene from freshly inoculated and aged Bayou Manchac and University Lake sediments using simple empirical biphasic model

<table>
<thead>
<tr>
<th>Sediment</th>
<th>F</th>
<th>k_f (h⁻¹)</th>
<th>k_s (h⁻¹)</th>
<th>R-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh BM</td>
<td>0.964</td>
<td>0.108</td>
<td>6.06×10⁻⁴</td>
<td>0.999</td>
</tr>
<tr>
<td>Aged BM</td>
<td>0.915</td>
<td>0.102</td>
<td>6.14×10⁻⁴</td>
<td>0.998</td>
</tr>
<tr>
<td>Fresh UL</td>
<td>0.971</td>
<td>0.114</td>
<td>6.58×10⁻⁴</td>
<td>0.999</td>
</tr>
<tr>
<td>Aged UL</td>
<td>0.915</td>
<td>0.074</td>
<td>1.55×10⁻³</td>
<td>0.999</td>
</tr>
</tbody>
</table>

F: fast desorbing fraction; k_f: rate constant for fast fraction; k_s: rate constant for slow fraction.

No significant difference between sediments was observed for Bayou Manchac sediment and University Lake sediment. The absence of difference between the sediments was unexpected because these two sediments showed great variation on their condensed phase organic carbon contents. The lack of a difference was likely due to the very slow diffusion rate in the condensed phase organic matter particles which is
responsible for the desorption resistance. Even an aging period of three years was apparently insufficient to show a significant aging effect. This was reasonable because Ghosh et al. (2001) utilized cryomicrotome technique and microprobe two-step laser desorption/laser ionization mass spectrometry ($\mu$L $^2$MS) to investigate the cross sectional distribution of PAHs in coal-derived and silica particles. Their results suggested that most PAHs are concentrated in near external surface regions of coal-derived particles. The presumption of slow diffusion of the contaminants in coal-derived particles was supported by their modeling results which showed 40% PAH remaining even after 100 years (Ghosh et al., 2001). In this context, the time length scale of the inoculation time of five weeks and the aging time of two years or three years were too short a time period to cause significant migration into the condensed phase organic matter by diffusion.

### 2.3.2 Desorption Isotherms in Laboratory-inoculated Sediments

Apparent desorption isotherms determined at equilibration time of 10 days of freshly inoculated Bayou Manchac and University Lake sediment are shown in Figure 2.4. Phenanthrene concentrations in sediments were organic carbon content normalized for the ease of comparison between sediments with different organic carbon contents. Desorption isotherms for the two sediments were almost identical. Experimental results were fitted using the biphasic model of Kan et al. (1998) as described in Equation 1.8:

$$q_s = K_{OC} f_{\infty} C_w + \frac{K_{irr} f_{\infty} q_{max}^{irr} C_w f}{q_{max}^{irr} f + K_{OC} f_{\infty} C_w}$$

Fitted maximum irreversible concentrations, $q_{max}^{irr}$, for freshly-inoculated Bayou Manchac sediment and University Lake sediment were 6 and 25 mg/Kg respectively. These consisted of 1.5% of the initial saturated phenanthrene concentrations in both
sediments. The organic carbon normalized maximum irreversible phenanthrene concentrations in the two sediments were 430 and 440 mg/(Kg organic carbon). These results for the two sediments with different condensed phase organic carbon contents showed surprising similarity.

Figure 2.4 Desorption isotherm of phenanthrene in freshly inoculated Bayou Manchac and University Lake sediments

Note: Diamonds denote BM sediment and squares denote UL sediment. Points are experimental measurements, the solid lines are the desorption isotherm of phenanthrene predicted by the biphasic model of Kan et al. (1998), dashed line is the desorption isotherm predicted by reversible linear partitioning model.

Desorption isotherms of phenanthrene in freshly inoculated Bayou Manchac sediment and aged Bayou Manchac sediment are displayed in Figure 2.5 and Figure 2.6. The fitted maximum “irreversible” phenanthrene concentration, $q_{max \text{ irr}}$, for aged Bayou Manchac sediment using the biphasic model of Kan et al. (1998) was 20 mg/Kg and the organic carbon normalized maximum “irreversible” phenanthrene concentration in the sediment was 1430 mg/(Kg organic carbon).
Figure 2.5 Desorption isotherm of phenanthrene in freshly inoculated Bayou Manchac sediment.

Note: Square points are experimental measurements, the solid line is the desorption isotherm of phenanthrene predicted by the biphasic model of Kan et al. (1998), dashed line is the desorption isotherm predicted by reversible linear partitioning model.

Figure 2.6 Desorption isotherm of phenanthrene in aged Bayou Manchac sediment

Note: Square points are experimental measurements, the solid line is the desorption isotherm of phenanthrene predicted by the biphasic model of Kan et al. (1998), dashed line is the desorption isotherm predicted by reversible linear partitioning model. Sediment was aged for 3 years.
This consisted of 4.9% of the initial saturated phenanthrene concentration in aged Bayou Manchac sediment and was roughly three times larger than that in freshly-inoculated Bayou Manchac sediment. It should be noted that the choice of isotherm is somewhat arbitrary. The form of the isotherm was constrained to fit $K_P = f_{oc}K_{OC}$ at high concentrations and then fit to lower concentrations using the Kan et al. (1998) isotherm. Other functional forms for the fitted isotherm could have been selected and the “goodness of fit” would be similar.

### 2.3.3 Fast Desorbing Fraction in Field-contaminated Sediments

Major PAHs identified in the field-contaminated sediments in this study and their selected properties are listed in Table 2.5. Fast desorbing fractions of contaminants in Utica Harbor and Rouge River sediment are presented in Table 2.6 and 2.7. The fast desorbing fractions of PAHs of interest ranged from 0.12 to 0.46 in Utica Harbor sediment and from 0.21 to 0.44 in Rouge River sediment. As expected, the fast desorbing fractions in Rouge River sediment for different compounds generally decreased as the molecular size increased possibly because of the effect of steric hindrance. But this trend was not observed in Utica Harbor sediment. The average of fast desorbing fractions for all compounds in Utica Harbor and Rouge River sediment were $0.28 \pm 0.01$ and $0.35 \pm 0.01$, respectively. Note that the proportion of condensed phase carbon to the total organic carbon ($f_{oc}C/f_{oc}$) in the two sediments were 39.07% and 24.89% as shown in Table 2.8. Thus the desorption resistant fraction of contaminants ($1-F$) was greater for the sediment exhibiting greater condensed phase organic carbon fraction ($f_{oc}C/f_{oc}$).
### Table 2.5 Major PAHs of interest and selected properties

<table>
<thead>
<tr>
<th>Compound</th>
<th>Log$K_{OW}$</th>
<th>Log$K_{OC}$</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHE</td>
<td>4.57</td>
<td>4.36</td>
<td>178</td>
</tr>
<tr>
<td>ANT</td>
<td>4.54</td>
<td>4.33</td>
<td>178</td>
</tr>
<tr>
<td>PYR</td>
<td>5.18</td>
<td>4.97</td>
<td>202</td>
</tr>
<tr>
<td>CHR</td>
<td>5.86</td>
<td>5.65</td>
<td>228</td>
</tr>
<tr>
<td>B$\text{bF}$</td>
<td>5.80</td>
<td>5.59</td>
<td>252</td>
</tr>
<tr>
<td>B$kF$</td>
<td>6.00</td>
<td>5.79</td>
<td>252</td>
</tr>
<tr>
<td>BaP</td>
<td>6.04</td>
<td>5.83</td>
<td>252</td>
</tr>
<tr>
<td>D$\text{BaA}$</td>
<td>6.5</td>
<td>6.29</td>
<td>278</td>
</tr>
<tr>
<td>BghiPER</td>
<td>6.75</td>
<td>6.54</td>
<td>276</td>
</tr>
</tbody>
</table>

Log$K_{OW}$: Mackay et al. (1991), Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Vol. II, Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans;

Log$K_{OC}$: Calculated from Log$K_{OW}$ using correlation reported by Karickhoff et al. (1979) (Equation 2.4: Log$K_{OC}$=1.0×Log$K_{OW}$–0.21).
Table 2.6 Fast desorbing fractions of contaminants in Utica Harbor sediment

<table>
<thead>
<tr>
<th>Compound</th>
<th>C₀ (mg/Kg)</th>
<th>C_{Des20hr} (mg/Kg)</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHE</td>
<td>6.53(±0.22)</td>
<td>5.07(±0.12)</td>
<td>0.22(±0.01)</td>
</tr>
<tr>
<td>ANT</td>
<td>5.80(±0.10)</td>
<td>4.16(±0.14)</td>
<td>0.28(±0.01)</td>
</tr>
<tr>
<td>PYR</td>
<td>23.75(±0.45)</td>
<td>18.25(±0.34)</td>
<td>0.23(±0.01)</td>
</tr>
<tr>
<td>CHR</td>
<td>24.25(±1.03)</td>
<td>17.22(±0.75)</td>
<td>0.29(±0.02)</td>
</tr>
<tr>
<td>BbF</td>
<td>8.91(±0.31)</td>
<td>4.83(±0.19)</td>
<td>0.46(±0.02)</td>
</tr>
<tr>
<td>BkF</td>
<td>4.15(±0.05)</td>
<td>3.68(±0.06)</td>
<td>0.11(±0.01)</td>
</tr>
<tr>
<td>BaP</td>
<td>12.67(±0.36)</td>
<td>9.29(±0.33)</td>
<td>0.27(±0.01)</td>
</tr>
<tr>
<td>DBahA</td>
<td>7.63(±0.08)</td>
<td>5.94(±0.14)</td>
<td>0.22(±0.01)</td>
</tr>
<tr>
<td>BghiPER</td>
<td>5.38(±0.21)</td>
<td>3.24(±0.15)</td>
<td>0.40(±0.02)</td>
</tr>
</tbody>
</table>

C₀: Initial concentration of contaminant in sediment, mg/Kg;
C_{Des20hr}: Concentration of contaminant in sediment after treatment with XAD-2 for 20 hours, mg/Kg;
F is fast desorbing fraction, operationally defined by the (C₀-C_{Des20hr})/C₀.
### Table 2.7 Fast desorbing fractions of contaminants in Rouge River sediment

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_0$(mg/Kg)</th>
<th>$C_{Des20hr}$(mg/Kg)</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHE</td>
<td>22.93(±0.48)</td>
<td>12.77(±0.19)</td>
<td>0.44(±0.01)</td>
</tr>
<tr>
<td>ANT</td>
<td>8.05(±0.23)</td>
<td>4.25(±0.17)</td>
<td>0.47(±0.02)</td>
</tr>
<tr>
<td>PYR</td>
<td>36.51(±1.25)</td>
<td>24.73(±0.88)</td>
<td>0.32(±0.02)</td>
</tr>
<tr>
<td>CHR</td>
<td>22.44(±1.01)</td>
<td>13.94(±0.32)</td>
<td>0.38(±0.02)</td>
</tr>
<tr>
<td>BbF</td>
<td>15.43(±0.54)</td>
<td>9.54(±0.29)</td>
<td>0.38(±0.02)</td>
</tr>
<tr>
<td>BkF</td>
<td>8.75(±0.37)</td>
<td>5.63(±0.16)</td>
<td>0.36(±0.02)</td>
</tr>
<tr>
<td>BaP</td>
<td>11.60(±0.28)</td>
<td>8.81(±0.35)</td>
<td>0.24(±0.01)</td>
</tr>
<tr>
<td>DBahA</td>
<td>21.18(±0.46)</td>
<td>16.67(±0.53)</td>
<td>0.21(±0.01)</td>
</tr>
<tr>
<td>BghiPER</td>
<td>14.50(±0.32)</td>
<td>9.69(±0.14)</td>
<td>0.33(±0.01)</td>
</tr>
</tbody>
</table>

$C_0$: Initial concentration of contaminant in sediment, mg/Kg;  
$C_{Des20hr}$: Concentration of contaminant in sediment after treatment with XAD-2 for 20 hours, mg/Kg;  
$F$ is fast desorbing fraction, operationally defined by the $(C_0 - C_{Des20hr})/C_0$.

### Table 2.8 Characteristics of field-contaminated sediments

<table>
<thead>
<tr>
<th>Sediments</th>
<th>$f_{oc}^*$</th>
<th>$f_{oc}^A$</th>
<th>$f_{oc}^C$</th>
<th>$f_{oc}^A/f_{oc}$</th>
<th>$f_{oc}^C/f_{oc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utica Harbor</td>
<td>2.10±0.02%</td>
<td>1.28±0.03%</td>
<td>0.82±0.02%</td>
<td>60.93±1.47%</td>
<td>39.07±1.02%</td>
</tr>
<tr>
<td>Rouge River</td>
<td>7.90±0.17%</td>
<td>5.93±0.17%</td>
<td>1.97±0.02%</td>
<td>75.11±2.70%</td>
<td>24.89±0.59%</td>
</tr>
</tbody>
</table>

*: Data was obtained after the sediments sieved through 2 mm sieve;  
$f_{oc}$: Total organic carbon content in sediment;  
$f_{oc}^A$: Amorphous organic carbon content;  
$f_{oc}^C$: Condensed phase organic carbon content.
2.3.4 Partition Coefficients of Contaminants in Field-contaminated Sediments

The organic carbon normalized apparent partition coefficients \( (K_{OC}) \) of contaminants measured in bulk sediment \( (K_{OC, bulk}) \) and predicted \( (K_{OC, bulk}) \) for Utica Harbor and Rouge River sediments are presented in Table 2.9 and 2.10, respectively. Literature value of the organic carbon normalized partition coefficient \( (K_{OC, lit.}) \) for each compound was calculated from octanol-water partition coefficient \( (K_{OW}) \) value (Mackay et al., 1991) using the correlation reported by Karickhoff et al. (1979) (Equation 2.4).

\[
\text{Log}K_{OC, lit.} = 1.0 \times \text{Log}K_{OW} - 0.21 \tag{2.4}
\]

The apparent bulk partition coefficient (after 10 day equilibration time) was compared to that expected assuming linear reversible sorption from only the fast desorbing fraction was responsible for the observed water concentrations used to determine the apparent partition coefficient. As will be shown later, the apparent partition coefficient from the desorption resistant fraction is higher (meaning lower water concentrations) and desorption is slow. Thus assuming that the labile, fast desorbing fraction controls the porewater concentration in a short-term equilibrium measurement is likely valid. If only the labile, fast desorbing fraction \( (C_{s,labile}) \) contributed to the porewater concentration, the porewater concentration should be

\[
C_W = \frac{C_{s,labile}}{f_{oc}K_{OC, lit.}} \tag{2.5}
\]

Using Equation 2.5, the predicted apparent bulk \( K_{OC} \) is given by

\[
K_{OC, bulk} = \frac{C_S}{C_W f_{oc}} = \frac{C_S}{f_{oc}K_{OC, lit.}f_{oc}} = \frac{C_S}{C_S F} = \frac{K_{OC, lit.}}{F}
\]

44
\[
\text{Log}K_{OC,\text{bulk}} = \text{Log}K_{OC,\text{lit.}} - \text{Log}F
\] (2.6)

As shown in Table 2.9 and 2.10, the predicted Log\text{K}_{OC,\text{bulk}} are approximately equal to that observed. The primary uncertainty is the literature Koc and there is not a statistically significant difference between the logarithm of the organic carbon normalized apparent partition coefficient for bulk sediment (Apparent log\text{K}_{OC,\text{bulk}}) and the predicted value. These observations suggested that the labile fraction of the contaminants associated with sediment controlled the short-term release.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Literature Log\text{K}_{OC}</th>
<th>Apparent Log\text{K}_{OC,\text{bulk}}</th>
<th>F</th>
<th>Predicted Log\text{K}_{OC,\text{bulk}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHE</td>
<td>4.36</td>
<td>4.78(±0.02)</td>
<td>0.22(±0.01)</td>
<td>5.02</td>
</tr>
<tr>
<td>ANT</td>
<td>4.33</td>
<td>4.96(±0.02)</td>
<td>0.28(±0.01)</td>
<td>4.88</td>
</tr>
<tr>
<td>PYR</td>
<td>4.97</td>
<td>5.40(±0.01)</td>
<td>0.23(±0.01)</td>
<td>5.61</td>
</tr>
<tr>
<td>CHR</td>
<td>5.65</td>
<td>6.32(±0.02)</td>
<td>0.29(±0.02)</td>
<td>6.19</td>
</tr>
<tr>
<td>BbF</td>
<td>5.59</td>
<td>6.58(±0.03)</td>
<td>0.46(±0.02)</td>
<td>5.93</td>
</tr>
<tr>
<td>BkF</td>
<td>5.79</td>
<td>6.65(±0.02)</td>
<td>0.11(±0.01)</td>
<td>6.75</td>
</tr>
<tr>
<td>BaP</td>
<td>5.83</td>
<td>6.70(±0.02)</td>
<td>0.27(±0.01)</td>
<td>6.40</td>
</tr>
</tbody>
</table>

Log\text{K}_{OC} in literature was calculated from Log\text{K}_{OW} (Mackay et al., 1991) using correlation reported by Karickhoff et al. (1979) (\text{Log}K_{OC} = 1.0 \times \text{Log}K_{OW} – 0.21)

2.4 Summary

The desorption resistance of laboratory-inoculated contaminants in Bayou Manchac and University Lake sediment was not observed to be significantly different,
though the two sediments have different condensed phase carbon contents based upon the carbon remaining after combustion at 375°C. Only 3-4% of the original saturated phenanthrene in Bayou Manchac and University Lake sediment were considered to be slow desorbing fraction based on the desorption kinetics. Aged sediment exhibited slightly higher desorption resistance for both Bayou Manchac and University Lake sediment, but no differences between sediments were noted.

Table 2.10 Apparent partition coefficients for bulk Rouge River sediment

<table>
<thead>
<tr>
<th>Compound</th>
<th>Literature Log$K_{OC}$</th>
<th>Apparent Log$K_{OC,\text{bulk}}$</th>
<th>$F$</th>
<th>Predicted Log$K_{OC,\text{bulk}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHE</td>
<td>4.36</td>
<td>4.87(±0.02)</td>
<td>0.44(±0.01)</td>
<td>4.72</td>
</tr>
<tr>
<td>ANT</td>
<td>4.33</td>
<td>4.84(±0.01)</td>
<td>0.47(±0.02)</td>
<td>4.66</td>
</tr>
<tr>
<td>PYR</td>
<td>4.97</td>
<td>5.43(±0.01)</td>
<td>0.32(±0.02)</td>
<td>5.46</td>
</tr>
<tr>
<td>CHR</td>
<td>5.65</td>
<td>6.03(±0.02)</td>
<td>0.38(±0.02)</td>
<td>6.07</td>
</tr>
<tr>
<td>BbF</td>
<td>5.59</td>
<td>6.21(±0.02)</td>
<td>0.38(±0.02)</td>
<td>6.01</td>
</tr>
<tr>
<td>BkF</td>
<td>5.79</td>
<td>6.31(±0.03)</td>
<td>0.36(±0.02)</td>
<td>6.23</td>
</tr>
<tr>
<td>BaP</td>
<td>5.83</td>
<td>6.34(±0.02)</td>
<td>0.24(±0.01)</td>
<td>6.45</td>
</tr>
</tbody>
</table>

Log$K_{OC}$ in literature was calculated from Log$K_{OW}$ (Mackay et al., 1991) using correlation reported by Karickhoff et al. (1979) ($LogK_{OC} = 1.0 \times LogK_{OW} – 0.21$)

The absence of a correlation between desorption resistance and condensed phase organic carbon content in laboratory-inoculated Bayou Manchac and University Lake sediment was most likely due to the extremely slow diffusion rate of contaminant in the condensed phase organic carbon. Prolonged equilibration time for Bayou Manchac sediment exhibited lower apparent partition coefficient. Different apparent partition
coefficients with different equilibration times suggested deviations from equilibration were significant. The time scale of 5 weeks for inoculation and 0-2 or 3 years for aging was apparently not long enough for a considerable amount of contaminant to migrate into the condensed phase organic carbon. Thus any differences in condensed phase capacity for contaminants between the two sediments were not detectable.

This hypothesis was tested with field-contaminated sediments from Utica Harbor and Rouge River that had a lengthy (decades) period of exposure. The field-contaminated sediments showed significantly different desorption resistant behavior. The Utica Harbor sediment exhibited a more pronounced desorption resistant behavior (i.e., greater fractions of contaminants desorbed slowly or not at all over the course of the experiments) consistent with its greater fraction of condensed phase carbon.
CHAPTER 3 SIZE AND DENSITY SEPARATION

3.1 Introduction

Desorption resistance of HOCs in sediment has been widely ascribed to the heterogeneity of organic matter in sediments and soils. Condensed phase organic carbon has been considered to be responsible for the sequestration of HOCs in sediments. Ghosh et al. (2001) suggested that desorption resistance is associated with slow diffusion for “coal-derived” particles. Huang and Weber (1997a) believed that the entrapment of sorbing molecules within the “hard” carbon, i.e., condensed phase sediment organic matter matrices, contributes to desorption resistance. Xing and Pignatello (1997) attributed the desorption resistance to be associated with the “glassy” phase organic matter.

Because desorption-resistance was apparently correlated with the condensed phase organic carbon, size and density separation was undertaken in an attempt to isolate the condensed phase and/or desorption-resistant fraction. This chapter is focused on size and density separation of the sediments with the objective of isolating the amorphous and condensed phase organic carbon and understanding the availability of HOCs in each category of organic matter.

Separation of the sediment into different fractions has been attempted previously (Ghosh et al., 2000; Ghosh et al., 2001; Rockne et al., 2002). But complete separation of what we have termed amorphous and condensed phase carbon has not been attempted. This effort was undertaken with one of the laboratory-inoculated sediments, Bayou Manchac sediment, in the hope that separation of amorphous and condensed carbon
phases could sharpen the contrast in sorption behavior of these two carbon types in the sediment.

3.2 Materials and Methods

3.2.1 Sediments

Bayou Manchac sediment was used for this study. The desorption-resistant sediments were prepared using the procedures described in chapter 2 after the sediment was inoculated with phenanthrene. Five sediment concentration levels were evaluated. Each sediment level was created by sequential washing of the sediment with dilute isopropanol solutions. These are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Level</th>
<th>Sediment/isopropanol solution mass ratio (g/g)</th>
<th>Washing steps</th>
<th>Washing time (hr)</th>
<th>Loading (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1:4.0</td>
<td>1</td>
<td>24</td>
<td>49.99(±1.73)</td>
</tr>
<tr>
<td>II</td>
<td>1:4.2</td>
<td>1</td>
<td>24</td>
<td>38.97(±0.27)</td>
</tr>
<tr>
<td>III</td>
<td>1:4.2</td>
<td>1</td>
<td>38</td>
<td>13.39(±0.78)</td>
</tr>
<tr>
<td>IV</td>
<td>1:4.0</td>
<td>1</td>
<td>48</td>
<td>10.16(±0.14)</td>
</tr>
<tr>
<td>V</td>
<td>1:3.6</td>
<td>1</td>
<td>58</td>
<td>3.81(±0.14)</td>
</tr>
</tbody>
</table>

Note: sediment weight was based on dry weight.

3.2.2 Separation of Sediments

Separation of sediments using wet sieving and high-density solution was similar to the procedures described by Mayer et al. (1993) and Ghosh et al. (2000) with minor modification. One hundred grams of wet sediment and 200 ml of water were added into a
500 ml glass jar and mixed thoroughly using spatula. After settling for three minutes, the floating material suspended was collected and passed through a series of sieves (63 µm, 150 µm, 250 µm). This step was repeated until the water became clear. Then 100 ml CsCl (Fisher Scientific) solution with a specific gravity of 1.8 was added into the jar and mixed. After settling for three minutes, the floating material and the CsCl solution was collected and passed through the same series of sieves. At this point the sediment had been separated into five fractions including one residual heavy fraction mostly consisting of sand, three light fractions on sieves, and one light fine fraction (particle size < 63 µm). The first four fractions were rinsed with water to remove residual CsCl. The light fine fraction was centrifuged (2000 g for 20 minutes) and washed with water 3 times to remove CsCl. The heavy fraction was sieved using 63 µm sieve and split into two fractions.

Thus, the sediment was separated into six fractions, four light fractions which were <63 µm L, 63~150 µm L, 150~250 µm L, >250 µm L and two heavy fractions which were <63 µm H and >63 µm H. Fraction <63 µm L consisted of mostly clay, silt, and organic matter, fractions 63~150 µm L, 150~250 µm L, and >250 µm L consisted of mainly organic matter, and fractions <63 µm H and >63 µm H consisted mainly sand.

The mass and phenanthrene concentration in each fraction was measured after each fraction was air-dried at the completion of fractionation of the sediment. The apparent partition coefficients were measured in each of the size and density fractions using the methods described in chapter 2.
3.3 Results and Discussion

3.3.1 Contaminant Distribution in Different Fractions

Table 3.2 shows that the phenanthrene concentration in organic fractions (63~150 µm L, 150~250 µm L, and >250 µm L) were similar to each other and were significantly higher than in fractions rich in inorganic material. Phenanthrene concentrations in these three fractions were up to 18 times higher than the corresponding whole sediment loading. The phenanthrene concentration in fine light fraction (<63 µm L) was in the same order of magnitude as that in the corresponding whole sediment. Phenanthrene concentrations in heavy fractions were much less than in the corresponding whole sediment. Sediment mass and phenanthrene concentration in each fraction as well as the phenanthrene distribution in each fraction in sediments used are displayed in Figures 3.1 to 3.5.

Table 3.2 Phenanthrene concentration (mg/Kg) for fractionated Bayou Manchac sediment with different concentrations of desorption-resistant phenanthrene

<table>
<thead>
<tr>
<th>Sediment</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading</td>
<td>49.99±1.73</td>
<td>38.97±0.27</td>
<td>13.39±0.78</td>
<td>10.16±0.14</td>
<td>3.81±0.14</td>
</tr>
<tr>
<td>&lt;63 µm L</td>
<td>74.44±2.35</td>
<td>54.05±1.57</td>
<td>18.45±0.05</td>
<td>18.91±0.70</td>
<td>7.46±0.02</td>
</tr>
<tr>
<td>63-150 µm L</td>
<td>754.68±15.82</td>
<td>630.76±28.39</td>
<td>86.07±4.71</td>
<td>49.64±2.64</td>
<td>43.10±2.19</td>
</tr>
<tr>
<td>150-250 µm L</td>
<td>422.32±17.35</td>
<td>451.03±21.94</td>
<td>86.02±3.74</td>
<td>42.50±0.58</td>
<td>8.55±0.26</td>
</tr>
<tr>
<td>&gt;250 µm L</td>
<td>892.7±3.57</td>
<td>547.86±16.89</td>
<td>165.20±26.56</td>
<td>145.10±3.19</td>
<td>30.14±1.35</td>
</tr>
<tr>
<td>&lt;63 µm H</td>
<td>9.63±0.47</td>
<td>3.97±0.24</td>
<td>2.16±0.21</td>
<td>1.69±0.11</td>
<td>0.61±0.03</td>
</tr>
<tr>
<td>&gt;63 µm H</td>
<td>5.92±0.26</td>
<td>2.89±0.13</td>
<td>3.96±0.16</td>
<td>1.85±0.09</td>
<td>0.92±0.05</td>
</tr>
</tbody>
</table>
Figure 3.1 Phenanthrene distribution in fractionated Bayou Manchac sediment Level I

Note: Top figure shows the sediment mass distribution in each fraction, middle shows phenanthrene concentration in each fraction and bottom shows phenanthrene percentage in each fraction out of the total phenanthrene in the whole sediment for separation.
Figure 3.2 Phenanthrene distribution in fractionated Bayou Manchac sediment Level II

Note: Top figure shows the sediment mass distribution in each fraction, middle shows phenanthrene concentration in each fraction and bottom shows phenanthrene percentage in each fraction out of the total phenanthrene in the whole sediment for separation.
Figure 3.3 Phenanthrene distribution in fractionated Bayou Manchac sediment Level III

Note: Top figure shows the sediment mass distribution in each fraction, middle shows phenanthrene concentration in each fraction and bottom shows phenanthrene percentage in each fraction out of the total phenanthrene in the whole sediment for separation.
Figure 3.4 Phenanthrene distribution in fractionated Bayou Manchac sediment Level IV

Note: Top figure shows the sediment mass distribution in each fraction, middle shows phenanthrene concentration in each fraction and bottom shows phenanthrene percentage in each fraction out of the total phenanthrene in the whole sediment for separation.
Figure 3.5 Phenanthrene distribution in fractionated Bayou Manchac sediment Level V

Note: Top figure shows the sediment mass distribution in each fraction, middle shows phenanthrene concentration in each fraction and bottom shows phenanthrene percentage in each fraction out of the total phenanthrene in the whole sediment for separation.
About 55 to 73% of the phenanthrene in the corresponding whole sediment was associated with the fine light fraction (<63 µm L). Three light fractions rich in organic matter (63~150 µm L, 150~250 µm L, and >250 µm L) were almost three percent of the sediment mass, but 17 to 36 percent of the phenanthrene in the corresponding whole sediment. Taking light fraction <63 µm L into account, the phenanthrene in all these four fractions consists about 90 percent of the total phenanthrene in the corresponding whole sediment.

These findings were consistent with the observations reported in literature. Ghosh et al. (2000) found that coal/wood-derived particles in their sediments constitute only 5% of the sediment by weight but contain 62% of the total PAHs. Rockne et al. (2002) observed 50-80% of the PAHs in two sediments were associated with the low-density fractions which represents only 3-15% of total sediment.

**3.3.2 Apparent Partition Coefficients of Contaminants in Sediment Fractions**

The organic carbon contents and apparent partition coefficients of phenanthrene in whole sediments and sediment fractions were determined. Table 3.3 shows the apparent organic carbon normalized partition coefficients of phenanthrene in fractionated Bayou Manchac sediments with different concentrations of desorption-resistant phenanthrene.

The logarithm of the organic carbon normalized apparent partition coefficient of phenanthrene for whole sediment and fractions separated from the corresponding whole sediment increased as the phenanthrene concentration in whole sediment decreased. At lower concentration the desorption-resistant phenanthrene represented a larger fraction of the total phenanthrene in the sediment. However, no trend or significant difference was
observed between fractions separated from a single whole sediment. This suggested that the size and density separation of sediment does not provide a separation of the organic fractions responsible for desorption resistance.

Table 3.3 Apparent partition coefficients (LogK_{OC}) for fractionated Bayou Manchac sediment with different concentrations of desorption-resistant phenanthrene

<table>
<thead>
<tr>
<th>Sediment</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole sediment</td>
<td>4.51±0.01</td>
<td>4.59±0.01</td>
<td>4.72±0.01</td>
<td>4.79±0.01</td>
<td>4.92±0.02</td>
</tr>
<tr>
<td>&lt;63 µm L</td>
<td>4.60±0.02</td>
<td>4.64±0.01</td>
<td>4.88±0.03</td>
<td>5.05±0.02</td>
<td>5.02±0.02</td>
</tr>
<tr>
<td>63-150 µm L</td>
<td>4.60±0.02</td>
<td>4.74±0.03</td>
<td>4.51±0.02</td>
<td>4.47±0.02</td>
<td>4.95±0.03</td>
</tr>
<tr>
<td>150-250 µm L</td>
<td>4.47±0.03</td>
<td>4.60±0.03</td>
<td>4.52±0.02</td>
<td>4.48±0.01</td>
<td>4.57±0.03</td>
</tr>
<tr>
<td>&gt;250 µm L</td>
<td>4.67±0.01</td>
<td>4.64±0.02</td>
<td>4.84±0.02</td>
<td>4.99±0.03</td>
<td>4.90±0.02</td>
</tr>
<tr>
<td>&lt;63 µm H</td>
<td>4.60±0.02</td>
<td>4.40±0.02</td>
<td>4.90±0.02</td>
<td>4.89±0.03</td>
<td>4.83±0.03</td>
</tr>
<tr>
<td>&gt;63 µm H</td>
<td>4.25±0.02</td>
<td>4.28±0.02</td>
<td>4.82±0.01</td>
<td>4.85±0.02</td>
<td>4.86±0.01</td>
</tr>
</tbody>
</table>

\( f_{oc} \)'s were 1.95\% for fractions <63 µm L, with condensed phase carbon content/\( f_{oc} \) of 49\%;
\( f_{oc} \)'s were 18.81\% for fractions 63-150 µm L, 150-250 µm L and >250 µm L, with condensed phase carbon content/\( f_{oc} \) of 46\%;
\( f_{oc} \)'s were 0.40\% for Heavy fractions.

3.4Summary

Size and density separation were used to separate Bayou Manchac sediments into six fractions. Phenanthrene concentrations in light fractions rich in organic matter were significantly greater than in light fractions rich in clay and silt and than in heavy fractions rich in sand. The apparent partition coefficients, however, were not significantly different for different fractions. Thus, size and density separation does not help us to understand what types of organic matter are responsible for the phenomena of desorption resistance.
CHAPTER 4 COARSE PARTICLES IN FIELD-CONTAMINATED SEDIMENTS

4.1 Introduction

Coal/coal-derived particles, soot particles and other condensed phase organic matter particles have been considered to be responsible for the sequestration of HOCs in sediment (Ghosh et al., 2001; Huang and Weber, 1997a; Xing and Pignatello, 1997; Ghosh et al., 2003).

As described in Chapter 3, size and density fractionation did not allow separation of the organic fractions responsible for desorption resistance phenomena. Although the majority of the organic matter is found in fine fractions, significant organic matter is also found in coarse fractions. In the coarse fractions, it is relatively easy to separate different types of organic matter.

In this chapter, visually-based separation of the coarse particles is used in an attempt to differentiate organic matrices responsible for desorption resistance from those exhibit fast desorption characteristics. Although the focus of the characterization work in this chapter is on these coarse organic particles, it is assumed that coarse particles exhibit identical behavior to fine organic particles of similar character. The test of this assumption is whether the separated coarse organic particles exhibit the same fast and slow desorption phenomena observed in the bulk sediment.

4.2 Materials and Methods

4.2.1 Sediments

Two field-contaminated sediments, Utica Harbor sediment and Rouge River sediment, were also used in this research. Utica Harbor sediment was collected from Utica Harbor, Utica, NY and was not sieved when received. The sediment was
contaminated over many decades ago during the operation of a coal gasification plant. Rouge River sediment was collected from Rouge River, MI and had been sieved through 2 mm sieves when received. The sediment was contaminated in early 20th century by both sewer pipe and industrial waste discharges.

4.2.2 Obtaining Coarse Particles from Sediments

In order to obtain these particles, the Utica Harbor and Rouge River sediments were coarsely sieved. Coarse particles from Utica Harbor sediment were collected in a 2 mm sieve and coarse particles from Rouge River sediment were collected in a 400 µm sieve. The different sizes were necessary to collect a sufficient volume of coarse particles. Coarse particles were air-dried at room temperature.

Different categories of coarse particles were selected manually from those particles remaining on the sieve. Four main categories of particles rich in organic matter were collected and they were denoted as coal-like, coal-cinder, woody and charcoal. Black, shiny and nonporous particles were identified as coal-like particles. Grey-black porous particles were identified as coal-cinder particles due to their burned coal like appearance. Woody particles, charred wood, charcoal-like particles were readily identifiable. Inorganic silica, sandy particles were also readily identifiable and discarded as they represent a minimal sink for organic matter.

4.2.3 Particle Characterization

A variety of PAHs were identified in the coarse organic particles as listed in Table 2.5 with literature values of Kow and Koc which indicate the expected partition coefficient associated with that compound if sorption is fast and reversible. Contaminant concentrations were determined directly in the separated fractions of coarse particles
from Rouge River sediment following the procedures for solid samples stated in Chapter 2. The coarse particles from Utica Harbor sediment were ground and passed through 2 mm sieve to assure that they possessed similar particle size as the Rouge River sediment. Total organic carbon contents, amorphous and condensed phase organic carbon contents as indicated by the method of thermal oxidation at 375°C by Gustafsson et al. (1997) were measured for these particles. Apparent partition coefficients of contaminants were also measured in different categories of particles using methods described in Chapter 2.

4.2.4 Sorption of Phenanthrene to Different Particles

A single compound, phenanthrene, was employed to evaluate the short-term sorption characteristics on the various coarse fractions. Phenanthrene in an aqueous solution was added to glass jars containing pre-weighed coarse particles and the aqueous phenanthrene concentration was measured after 1 day and 2 days. The amount of phenanthrene sorbed was determined by mass balance. Aqueous phenanthrene solution (objective concentration of 750 µg/L) was prepared by diluting 100 mg/L phenanthrene stock solution in methanol into electrolyte solution (0.01M NaCl, 0.01M CaCl$_2$·2H$_2$O, and 0.01M NaN$_3$ in deionized water) in a volumetric flask. The aqueous phenanthrene solution was stirred using magnetic stirring bar for 24 hours and the exact phenanthrene concentration after aqueous solution preparation was measured before it was used for the experiment.

4.2.5 pH Effect on Availability of PAHs in Coarse Particles

An additional factor that might influence the sorption capacity and uptake rate for the coal-like particles is pH. Humic acid in sediment organic matter has been reported to be able to bind PAHs and other HOCs (Laor and Rebhun, 2002). Humic acid is able to be
dissolved under basic condition (Weber et al., 1992). Thus, the apparent partition coefficients for a variety of PAHs on those coarse particles were determined under neutral condition and basic condition (pH 7.5 and pH 10). The electrolyte solution used in the normal apparent partition coefficient measurement described in Chapter 2 exhibited a pH value of 7.5. Buffer solution with pH value of 10 replaced the electrolyte solution in the normal apparent partition coefficient methodology described in Chapter 2.

4.3 Results and Discussion

4.3.1 Characterization of Different Coarse Particles

Organic carbon contents of different particles with high organic carbon contents from Utica Harbor sediment were determined and are presented in Table 4.1. Organic carbon contents of these particles ranged from 28.82% to 83.13%. These observations were comparable to organic carbon contents reported in Jonker and Koelmans (2002) for coal-like particles of 90.8%, coal soot of 32.2% and charcoal of 82.2%.

Table 4.1 Organic carbon content of different particles from Utica Harbor sediment

<table>
<thead>
<tr>
<th>Particles</th>
<th>( f_{oc} )</th>
<th>( f_{oc}^A )</th>
<th>( f_{oc}^C )</th>
<th>( f_{oc}^A/f_{oc} )</th>
<th>( f_{oc}^C/f_{oc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-like</td>
<td>80.90±0.23%</td>
<td>39.37±0.67%</td>
<td>41.52±0.62%</td>
<td>48.67±0.83%</td>
<td>51.33±0.79%</td>
</tr>
<tr>
<td>Coal-cinder</td>
<td>28.82±0.12%</td>
<td>7.40±0.22%</td>
<td>21.42±0.19%</td>
<td>25.68±0.79%</td>
<td>74.31±0.73%</td>
</tr>
<tr>
<td>Wood</td>
<td>56.04±0.38%</td>
<td>56.04±0.38%</td>
<td>0.00%</td>
<td>100.00±0.96%</td>
<td>0.00%</td>
</tr>
<tr>
<td>Charcoal</td>
<td>83.13±0.33%</td>
<td>82.71±0.33%</td>
<td>0.41±0.01%</td>
<td>99.50±0.56%</td>
<td>0.50±0.01%</td>
</tr>
</tbody>
</table>

\( f_{oc} \): total organic carbon content of sediment; 
\( f_{oc}^A \): amorphous organic carbon content; 
\( f_{oc}^C \): condensed phase organic carbon content.
Concentrations of contaminants in coarse particles from Utica Harbor, Rouge River sediment and concentrations of contaminants in corresponding whole sediment are listed in Table 4.2 and 4.3 respectively. PAHs concentrations in the coal-like particles and coal-cinder particles were significantly higher than in the corresponding whole sediment. This is consistent with the observation of Ghosh et al. (2000) in which the coal/wood-derived particles constituted only 5% of the sediment by weight but contained 62% of the total PAHs. It is also in accord with results by Rockne et al. (2002) that 50-80% PAHs were associated with the low density fraction which represented only 3-15% of total sediment mass in the two sediments they studied.

Table 4.2 Concentrations of PAHs in coarse particles from Utica Harbor sediment

<table>
<thead>
<tr>
<th>Compound</th>
<th>Whole Sediment (mg/Kg)</th>
<th>Coal-like (mg/Kg)</th>
<th>Coal-cinder (mg/Kg)</th>
<th>Wood (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHE</td>
<td>6.53(±0.22)</td>
<td>177.45(±9.51)</td>
<td>287.33(±13.68)</td>
<td>49.13(±2.34)</td>
</tr>
<tr>
<td>ANT</td>
<td>5.80(±0.10)</td>
<td>74.37(±1.34)</td>
<td>333.97(±11.25)</td>
<td>25.39(±0.75)</td>
</tr>
<tr>
<td>PYR</td>
<td>23.75(±0.45)</td>
<td>227.68(±5.01)</td>
<td>289.86(±8.65)</td>
<td>78.12(±1.39)</td>
</tr>
<tr>
<td>CHR</td>
<td>24.25(±1.03)</td>
<td>550.13(±20.32)</td>
<td>347.38(±10.34)</td>
<td>5.90(±0.23)</td>
</tr>
<tr>
<td>BbF</td>
<td>8.91(±0.31)</td>
<td>347.28(±12.93)</td>
<td>348.45(±15.22)</td>
<td>8.63(±0.31)</td>
</tr>
<tr>
<td>BkF</td>
<td>4.15(±0.05)</td>
<td>148.81(±5.21)</td>
<td>147.82(±4.89)</td>
<td>0.64(±0.05)</td>
</tr>
<tr>
<td>BaP</td>
<td>12.67(±0.36)</td>
<td>334.19(±13.74)</td>
<td>358.21(±7.81)</td>
<td>10.28(±0.42)</td>
</tr>
<tr>
<td>DBahA</td>
<td>7.63(±0.08)</td>
<td>267.52(±7.58)</td>
<td>424.79(±13.66)</td>
<td>8.35(±0.33)</td>
</tr>
<tr>
<td>BghiPER</td>
<td>5.38(±0.21)</td>
<td>79.36(±3.62)</td>
<td>198.46(±6.35)</td>
<td>6.72(±0.21)</td>
</tr>
<tr>
<td>Total</td>
<td>99.07</td>
<td>2206.79</td>
<td>2736.27</td>
<td>193.16</td>
</tr>
</tbody>
</table>
Table 4.3 Concentrations of PAHs in coarse particles from Rouge River sediment

<table>
<thead>
<tr>
<th>Compound</th>
<th>Whole sediment (mg/Kg)</th>
<th>Coal-like (mg/Kg)</th>
<th>Coal-cinder (mg/Kg)</th>
<th>Wood (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHE</td>
<td>22.93(±0.48)</td>
<td>24.10(±0.50)</td>
<td>58.69(±1.06)</td>
<td>15.68(±0.35)</td>
</tr>
<tr>
<td>ANT</td>
<td>8.05(±0.23)</td>
<td>3.40(±0.05)</td>
<td>9.34(±0.31)</td>
<td>2.80(±0.11)</td>
</tr>
<tr>
<td>PYR</td>
<td>36.51(±1.25)</td>
<td>37.84(±1.19)</td>
<td>94.93(±2.24)</td>
<td>2.04(±0.07)</td>
</tr>
<tr>
<td>CHR</td>
<td>22.44(±1.01)</td>
<td>3.36(±0.16)</td>
<td>168.49(±4.39)</td>
<td>4.58(±0.16)</td>
</tr>
<tr>
<td>BbF</td>
<td>15.43(±0.54)</td>
<td>3.22(±0.13)</td>
<td>53.29(±1.97)</td>
<td>2.01(±0.06)</td>
</tr>
<tr>
<td>BkF</td>
<td>8.75(±0.37)</td>
<td>1.12(±0.04)</td>
<td>60.42(±1.68)</td>
<td>2.17(±0.04)</td>
</tr>
<tr>
<td>BaP</td>
<td>11.60(±0.28)</td>
<td>2.69(±0.10)</td>
<td>68.93(±1.72)</td>
<td>3.52(±0.08)</td>
</tr>
<tr>
<td>DBahA</td>
<td>21.18(±0.46)</td>
<td>-</td>
<td>63.49(±1.59)</td>
<td>-</td>
</tr>
<tr>
<td>BghiPER</td>
<td>14.50(±0.32)</td>
<td>-</td>
<td>11.44(±0.52)</td>
<td>1.57(±0.04)</td>
</tr>
<tr>
<td>Total</td>
<td>161.39</td>
<td>75.74</td>
<td>589.00</td>
<td>34.36</td>
</tr>
</tbody>
</table>

4.3.2 Sorption of Phenanthrene to Different Particles in Utica Harbor Sediment

The previous analyses indicated that the coal-cinder fraction displayed significant capacity (high apparent partition coefficient) for PAH contaminants. The coal-like particles also showed a significant capacity, at least for the Utica Harbor sediment. Woody particles showed no evidence of enhanced sorption capacity. Similarly, the coal-cinder and to a less extent, the coal-like particles showed a significant fraction of condensed phase as defined by the nonvolatile carbon which is retained after heating to 375°C for 24 hours. Sorption experiments were conducted to evaluate if fractions
exhibiting high capacity and high condensed phase fraction exhibit slow sorption kinetics.

Coarse particles from Utica Harbor sediment were used to conduct the sorption experiment to investigate the rate and extent of sorption of HOCs into different particles. Particles from Utica Harbor sediment were selected due to the ease of obtaining sufficient quantity of coarse particles.

Table 4.4 Sorption of phenanthrene onto different coarse particles from Utica Harbor sediment

<table>
<thead>
<tr>
<th>Particles</th>
<th>Initial concentration on particle (mg/Kg)</th>
<th>Adsorbed after 1 day (mg/Kg)</th>
<th>Adsorbed after 2 days (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-like</td>
<td>177.45(±9.51)</td>
<td>24.66(±0.82)</td>
<td>27.31(±0.64)</td>
</tr>
<tr>
<td>Coal-like, Crushed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal-cinder</td>
<td>287.33(±13.68)</td>
<td>20.68(±0.77)</td>
<td>21.50(±0.81)</td>
</tr>
<tr>
<td>Coal-cinder, Crushed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>49.13(±2.34)</td>
<td>162.57(±5.39)</td>
<td>163.66(±6.91)</td>
</tr>
<tr>
<td>Charcoal</td>
<td>25.74(±0.94)</td>
<td>133.41(±5.08)</td>
<td>143.59(±4.38)</td>
</tr>
</tbody>
</table>

The amount sorbed after 1 and 2 days exposure to phenanthrene contaminated water was used to indicate sorption rate. The results are summarized in Table 4.4. The sorption of phenanthrene onto these particles showed different rate and extent for different fractions. Table 4.4 showed that the sorption of phenanthrene onto coal-like and coal-cinder particles were much slower than that onto woody and wood charcoal particles. Note that the total concentrations after two days sorption for each category of particles were still far less than the sorption capacities, thus the small sorption associated
with the coal-like and coal-cinder particles was associated with slow diffusion into these matrices. Note that crushed coal-like particles showed a significant increase in sorption over 1 and 2 days than the uncrushed particles. This suggests that the sorption of phenanthrene onto the coal-like particles is limited by available surface area. This may be the cause of the difference in capacity for this fraction between Rouge River and Utica Harbor sediments.

4.3.3 Apparent Partition Coefficients of Contaminants in Different Particles and pH Effect

In order to compare the apparent partition coefficients measured for the whole Utica Harbor sediment and that for the coal-like and coal-cinder particles, the coal-like and coal-cinder particles in this experiment were ground and passed through a 2 mm sieve.

The apparent partition coefficients of PAHs in coal-like particles and coal-cinder particles under pHs of 7.5 and 10 are presented in Table 4.5 and 4.6. The apparent partition coefficients of PAHs in both coal-like and coal-cinder particles under neutral condition (pH of 7.5) were significantly greater than predicted from Koc estimates (Equation 2.4). This confirms that the condensed phase carbon in these fractions exhibits high capacity as well as slow kinetics.

For the case of pH of 10, the apparent partition coefficients of PAHs in coal-like particles were, however, roughly equal to the predicted LogKOC values and significantly less than those measured under pH of 7.5. The basic condition under high pH may cause dissolution of bound humic acid (Weber et al., 1992), reducing the capacity of the solid phase. Thus the apparent partition coefficients of PAHs in coal-like particles under basic
condition were significantly less than those under neutral condition. No such effect was noted in coal-cinder particles.

Table 4.5 Apparent partition coefficients of PAHs in coal-like particles from Utica Harbor sediment and pH value effect

<table>
<thead>
<tr>
<th>Compound</th>
<th>Literature LogK&lt;sub&gt;OC&lt;/sub&gt;</th>
<th>Conc. (mg/Kg)</th>
<th>LogK&lt;sub&gt;OC&lt;/sub&gt; @ pH 7.5</th>
<th>LogK&lt;sub&gt;OC&lt;/sub&gt; @ pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHE</td>
<td>4.36</td>
<td>177.45</td>
<td>5.23±0.01</td>
<td>4.11±0.02</td>
</tr>
<tr>
<td>ANT</td>
<td>4.33</td>
<td>74.37</td>
<td>5.40±0.02</td>
<td>4.56±0.01</td>
</tr>
<tr>
<td>PYR</td>
<td>4.97</td>
<td>227.68</td>
<td>5.01±0.01</td>
<td>4.66±0.02</td>
</tr>
<tr>
<td>CHR</td>
<td>5.65</td>
<td>550.13</td>
<td>6.35±0.03</td>
<td>5.60±0.02</td>
</tr>
<tr>
<td>BbF</td>
<td>5.59</td>
<td>347.28</td>
<td>6.23±0.02</td>
<td>5.30±0.02</td>
</tr>
<tr>
<td>BkF</td>
<td>5.79</td>
<td>148.81</td>
<td>6.14±0.02</td>
<td>5.52±0.03</td>
</tr>
<tr>
<td>BaP</td>
<td>5.83</td>
<td>334.19</td>
<td>6.32±0.02</td>
<td>5.71±0.02</td>
</tr>
</tbody>
</table>

LogK<sub>OC</sub> was calculated from LogK<sub>OW</sub> compiled in Mackay et al. (1991) using correlation reported Karickhoff et al. (1979) (Equation 2.4: LogK<sub>OC</sub> = 1.0 × LogK<sub>OW</sub> – 0.21); f<sub>oc</sub> for coal-like particles from Utica Harbor sediment is 80.90%, f<sub>oc</sub><sup>A</sup> is 39.37% and f<sub>oc</sub><sup>C</sup> is 41.52%.

4.3.4 Apparent Partition Coefficients of Contaminants in Field-contaminated Sediments and in Condensed Phase Organic Carbon

The potential importance of coal-cinder particles on the desorption resistance can be illustrated by comparing the coal-cinder partition coefficients with the bulk sediment partition coefficients. As shown previously, the partitioning is largely governed by the fast desorbing fraction when one exists. Therefore, XAD-2 was used to remove effectively all of this fraction and create resistance dominated sediment before comparing partition coefficients. Figure 4.1 shows the resistance dominated sediment partition
coefficient versus the partition coefficient measured on coal-cinder particles. In these experiments the coal-cinder equilibrium coefficient reasonably approximated the observed resistant contaminant partition coefficient. There is some tendency to underpredict observed partition coefficients although this may simply represent mass transfer resistances in the relatively short desorption experiment.

Table 4.6 Apparent partition coefficients of PAHs in coal-cinder particles from Utica Harbor sediment and pH value effect

<table>
<thead>
<tr>
<th>Compound</th>
<th>LogK_{OC} literature</th>
<th>Conc. (mg/Kg)</th>
<th>LogK_{OC} @ pH 7.5</th>
<th>LogK_{OC} @ pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHE</td>
<td>4.36</td>
<td>287.33</td>
<td>5.10±0.01</td>
<td>5.01±0.02</td>
</tr>
<tr>
<td>ANT</td>
<td>4.33</td>
<td>333.97</td>
<td>5.07±0.02</td>
<td>5.22±0.02</td>
</tr>
<tr>
<td>PYR</td>
<td>4.97</td>
<td>289.86</td>
<td>5.25±0.02</td>
<td>5.28±0.01</td>
</tr>
<tr>
<td>CHR</td>
<td>5.65</td>
<td>347.38</td>
<td>6.62±0.01</td>
<td>6.72±0.02</td>
</tr>
<tr>
<td>BbF</td>
<td>5.59</td>
<td>348.45</td>
<td>6.79±0.02</td>
<td>6.74±0.03</td>
</tr>
<tr>
<td>BkF</td>
<td>5.79</td>
<td>147.82</td>
<td>6.56±0.03</td>
<td>6.58±0.02</td>
</tr>
<tr>
<td>BaP</td>
<td>5.83</td>
<td>358.21</td>
<td>6.86±0.02</td>
<td>6.58±0.02</td>
</tr>
</tbody>
</table>

Literature values of LogK_{OC} was calculated from LogK_{OW} compiled in Mackay et al. (1991) using correlation reported Karickhoff et al. (1979) (Equation 2.4: LogK_{OC} = 1.0 \times \text{LogK}_{OW} – 0.21);

\[ f_{oc} \text{ for coal-cinder particles from Utica Harbor sediment is 28.82%}, \ f_{oc}^A \text{ is 7.40%}, \ f_{oc}^C \text{ is 21.42%}. \]

4.4 Summary

Separation of coarse particles followed by chemical analysis showed that coal-like and coal-cinder particles exhibited very high PAH concentration. These particles also exhibited significantly higher condensed phase organic carbon contents. This is in
agreement with observations reported in Ghosh et al. (2000) and Jonker et al. (2002) that PAHs contamination in sediments was predominantly associated with “black” particles.

Figure 4.1 Comparison of apparent partition coefficients in desorption-resistant fraction and in coal-cinder particles in Utica Harbor sediment

Phenanthrene sorption experiments onto these separated fractions showed slow sorption onto coal-like and coal-cinder particles relative to woody particles. This was also consistent with the concept that condensed phase carbon exhibits higher capacity but slowed adsorption/desorption rates compared to amorphous carbon. The capacity of the coal-like particles was less than coal-cinder particles but crushing the coal-like particles improved uptake over 1 and 2 days of exposure, consistent with significant surface area limitation in the coal-like particles. Coal-like particles also showed a sensitivity to pH, presumably due to humic acid dissolution under basic condition.
The apparent partition coefficients of PAHs in the coal-cinder particles were a good indication of the apparent partition coefficients in the resistant fraction of the Utica Harbor sediment, further emphasizing that these particles or similar may largely describe the condensed phase carbon desorption resistance phenomena.
CHAPTER 5 MODELING SORPTION AND DESORPTION PHENOMENA

5.1 Introduction

The experimental work in the proceeding chapters suggests the following:

- Sorption and desorption in sediment can be described as a combination of fast and slow processes.
- Contaminants that sorb and desorb rapidly can be effectively removed by XAD-2 over 20 hours.
- The fast and slow processes are associated with organic carbon heterogeneity with an amorphous phase carbon (as defined by organic carbon lost upon 24 hours heating at 375°C) associated with fast sorption and desorption and reduced capacity relative to condensed phase carbon (carbon retained after heating at 375°C for 24 hours).
- Particles characterized as coal-cinder are consistent with this conceptional model exhibiting significant sorption capacity, slow sorption desorption kinetics as well as stability to heating at 375°C for 24 hours. Conversely, woody organic matter is lost under heating at 375°C for 24 hours and shows fast sorption and desorption rates and capacity consistent with literature predicted Koc values.

Some mechanistic models, e.g., Distributed Reactivity Model (Weber et al. 1992), Dual Mode Model (Xing, et al., 1996), and biphasic models (Kan et al., 1998; Gustafsson et al., 1997) have been proposed to address sorption and desorption behavior of HOCs in sediments. These models appear, however, to have limited prediction capability. A model that can predict physical partitioning of contaminants in sediment water systems would be useful. A two domain diffusion model was utilized by Rockne et al. (2002) to fit
desorption data. However, the assumption that PAHs were initially uniformly distributed throughout sediment aggregates undermined their efforts because microscopic observations show that PAHs may only reside in a very thin layer near external surface of the coal-derived particles in the sediment (Ghosh et al., 2001).

This chapter is focused on the development of a predictive model of sorption/desorption behavior of HOCs in natural sorbents in the environment. The model is designed to predict both kinetics and apparent equilibrium partitioning.

5.2 Development of the Model

5.2.1 Structure of the Model

The biphasic sorption behavior of organic contaminants in sediments has been attributed to the heterogeneity of soil/sediment organic matter. Amorphous organic carbon exhibits less sorption capacity and fast kinetics while condensed phase organic carbon exhibits greater sorption capacity and slow kinetics. The partitioning behavior of contaminants in sediment represents the balance between the kinetics and capacity of various organic carbon matrices in sediment. The slow kinetics is most likely attributed to the slow diffusion of contaminants in the condensed phase organic carbon and limited exposed surface area. Conversely, fast kinetics is most likely associated with porous structures where diffusion is not constrained by slow transport rates through a solid phase. Figure 5.1 characterizes schematically amorphous and condensed phase SOM in sediment.

The model is based on the following major assumptions:

1. Hydrophobic organic contaminants (HOCs) are mostly associated with sediment/soil organic matter.
2. Soil/sediment organic matter is classified as two broad categories—amorphous and condensed phase organic carbon. The amorphous organic carbon is porous having a lower sorption capacity and faster effective diffusivity for contaminant. The condensed carbon is physically compact having a greater sorption capacity and a slower effective diffusivity for contaminant;

3. Contaminant in intraparticle pore water is locally in equilibrium with contaminant sorbed in solid phase, with organic carbon normalized partition coefficient $K_{OC}$. 

Figure 5.1 Amorphous and condensed phase organic matter in sediment
4. Sorption capacity of organic matter for contaminant is characterized by the organic carbon normalized partition coefficient $K_{oc}$.

5. Contaminants migrate in amorphous organic matter by retarded diffusion in pore spaces and through condensed phase carbon by solid phase diffusion.

6. For simplicity, diffusion is assumed to be one-dimensional.

The governing equation for amorphous organic matter is

$$\frac{\partial C^{A}_{t}}{\partial t} = D^{A}_{eff} \frac{\partial^{2} C^{A}_{w}}{\partial x^{2}}$$

$$C^{A}_{t} = C^{A}_{w} (\varepsilon + \rho^{A} \cdot K^{A}_{OC} \cdot OC^{A})$$

$$\frac{\partial C^{A}_{w}}{\partial t} = \frac{D^{A}_{eff} \cdot \partial^{2} C^{A}_{w}}{R^{A}_{f} \cdot \partial x^{2}}$$

where

$$D^{A}_{eff} = D \cdot \varepsilon^{A/3}$$

$$R^{A}_{f} = \varepsilon + \rho^{A} \cdot K^{A}_{OC} \cdot OC^{A}$$

$C^{A}_{t}$ is the total contaminant concentration in amorphous organic matter including both contaminant in pore water and in solid phase (mg/L),

$C^{A}_{w}$ is contaminant concentration in amorphous organic matter pore water (mg/L),

$D$ is the diffusivity of contaminant in water (m$^2$/s),

$\varepsilon$ is the porosity of amorphous organic matter,

$\rho^{A}$ is the bulk density of amorphous organic matter (kg/L),

$OC^{A}$ is the organic carbon content of amorphous organic matter,
$K_{OC}^A$ is the organic carbon normalized partition coefficient of contaminant in amorphous organic matter,

$R_f^A$ is retardation factor for amorphous organic matter,

$D_{eff}^A$ is the effective diffusivity of contaminants in amorphous organic matter.

The governing equation for condensed phase organic matter is

$$\frac{\partial C_s^C}{\partial t} = D^C \frac{\partial^2 C_s^C}{\partial x^2}$$  \hspace{1cm} (5.4)

where $C_s^C$ is the contaminant concentration in condensed phase organic matter (mg/kg), $D^C$ is the diffusivity of the contaminant in condensed phase organic matter (m$^2$/s).

If we define a virtual contaminant concentration ($C_w^C$) in the condensed phase organic matter which is equivalent to the pore water concentration in amorphous organic matter,

$$C_w^C = C_s^C = \frac{C_s^C}{K_p^C} = \frac{C_s^C}{K_{OC}^C \cdot OC^C}$$  \hspace{1cm} (5.5)

Equation (5.4) can be rewritten as

$$\frac{\partial C_w^C}{\partial t} = D^C \frac{\partial^2 C_w^C}{\partial x^2}$$  \hspace{1cm} (5.6)

where

$OC^C$ is the organic carbon content of condensed phase organic matter,

$K_{OC}^C$ is the organic carbon normalized partition coefficient of contaminant to condensed phase organic matter.
Equations 5.1 and 5.6 were used to solve for \( C_w^A(x,t) \) and \( C_w^C(x,t) \) given different boundary conditions and initial conditions for sorption, desorption, portioning and aging processes. Contaminant concentration in sediment was quantified from \( C_w^A(x,t) \) and \( C_w^C(x,t) \).

### 5.2.2 Parameters for the Model

Parameters included in the model and their descriptions are listed in Table 5.1. Some of them are related to sediment or sediment organic matter properties and are not compound-specific.

\( \varepsilon \) is the porosity of the amorphous organic matter. Wu and Gschwend (1986) fitted their experimental data and reported the overall porosity for sediment to be in a range of 0.07-0.17. Arocha et al. (1996) reported simulation parameters for porosity of a loam and to be 0.48. Deane et al. (1999) used porosity of 0.5 for their sediments. The porosity was chosen to be 0.4.

The bulk density of the amorphous, \( \rho^A \), was chosen to be 1.5 g/cm\(^3\), and the bulk density of the condensed phase organic matter, \( \rho^C \), was chosen to be 1.8 g/cm\(^3\).

The organic carbon content for amorphous \( \text{OC}^A \) and condensed phase organic matter (\( \text{OC}^C \)) were 0.58 and 0.80 respectively. \( \text{OC}^A \) was chosen to be 0.58 based on that the organic matter can be converted to organic carbon content using the factor 1.72 (Allison, 1965; Waksman and Hutchings, 1953). The \( \text{OC}^C \) was chosen to be 0.80 based on the organic carbon content for coal-like particle in Utica Harbor sediment and literature values (Jonker and Koelmans, 2002).
The total organic carbon content in sediment, $f_{oc}$, the amorphous organic carbon content in sediment, $f_{oc}^A$, and the condensed phase organic carbon content, $f_{oc}^C$, were obtained by experimental measurements. The condensed phase organic carbon content was operationally defined by heating the sediment under 375°C for 24 hours (Gustafsson et al., 1997). The volume to surface area ratio, $(V/A)$, has a dimension of length. It represents a half of the characteristic length of the amorphous or condensed phase organic matter particle. The $(V/A)$ for the amorphous organic matter was assumed to be 20 µm and the model was not sensitive to it value. The $(V/A)$ for the condensed phase organic matter was obtained by fitting experimental data.

Other parameters are compound-specific. The diffusivity of contaminant in pure water, $D$, was obtained from USEPA (1996). The diffusivity of contaminant in condensed phase organic matter, $D^C$, was obtained by fitting experimental data. The organic carbon normalized partition coefficient of contaminant for the amorphous organic matter ($K_{OC}^A$) was obtained from literature (Mackay et al., 1991; Karickhoff et al., 1979). The organic carbon normalized partition coefficient of contaminant for the condensed phase organic matter ($K_{OC}^C$) was obtained from experimental measurement under neutral condition for coal-cinder particles in Chapter 4. The only exception was that the $K_{OC}^C$ for pyrene was modified from the measured value of 5.25 to be 5.60. $K_{OC}^C$ of 5.25 for pyrene was too low because the differences between measured $K_{OC}^C$ and literature $K_{OC}$ values for other compounds were 0.7 to 1.2 logarithmic units (Table 4.6). Thus the $K_{OC}^C$ for pyrene was adjusted to be 5.60 accordingly to be used for the model.

These partial differential equations with corresponding boundary conditions and initial conditions were solved simultaneously utilizing finite element method (Refer to
Appendix II for details) and Matlab program (Appendix III, Appendix IV) was written to implement the computation needed for the model.

### Table 5.1 Denotation of parameters used in the model

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varepsilon)</td>
<td>Porosity of the amorphous organic matter</td>
</tr>
<tr>
<td>D</td>
<td>Diffusivity of contaminant in pure water</td>
</tr>
<tr>
<td>(D_C)</td>
<td>Diffusivity of contaminant in condensed phase organic matter</td>
</tr>
<tr>
<td>(K_{OC})</td>
<td>Organic carbon normalized partition coefficient for amorphous and condensed phase organic matter</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Density of the amorphous and condensed phase organic matter</td>
</tr>
<tr>
<td>(OC)</td>
<td>Organic carbon content for amorphous and condensed phase organic matter</td>
</tr>
<tr>
<td>(f_{oc})</td>
<td>Total organic carbon content in sediment</td>
</tr>
<tr>
<td>(f_{oc}^C)</td>
<td>Condensed phase organic carbon content in sediment</td>
</tr>
<tr>
<td>(f_{oc}^A)</td>
<td>Amorphous organic carbon content in sediment</td>
</tr>
<tr>
<td>((V/A))</td>
<td>Volume to surface area ratio for the amorphous and condensed phase organic matter</td>
</tr>
</tbody>
</table>

The assumption of one-dimensional diffusion (in rectangular coordinates) is effectively assuming that organic matter is a slab with a length scale normal to the exposed surface defined by the volume to surface area ratio \((V/A)\). The sorption and desorption results are not sensitive to the assumption of geometry. This is illustrated in Figures 5.2 and 5.3 showing concentration predictions at 1 hour and 100 hours in both slab and spherical geometry.
Figure 5.2 Comparison of sorption progress of slab and spherical geometry at 1 hour

Note: Solid line denotes results for slab, and dashed line denotes results for spherical geometry.

Figure 5.3 Comparison of sorption progress of slab and spherical geometry at 100 hours

Note: Solid line denotes results for slab, and dashed line denotes results for spherical geometry.
5.2.3 Model Predicted Sorption and Desorption Behavior

5.2.3.1 Sorption Process

During sorption, the porewater concentration is maintained constant and the solid concentration was initially zero. Boundary conditions and initial condition for sorption are as follows.

Boundary conditions for amorphous organic matter,

\[
\begin{align*}
\frac{\partial C_w^A}{\partial x} &= 0 \quad \text{at} \quad x = 0 \\
C_w^A &= C_{w0} \quad \text{at} \quad x = \pm (V/A)
\end{align*}
\] (5.7)

and for condensed phase organic matter,

\[
\begin{align*}
\frac{\partial C_w^C}{\partial x} &= 0 \quad \text{at} \quad x = 0 \\
C_w^C &= C_{w0} \quad \text{at} \quad x = \pm (V/A)
\end{align*}
\] (5.8)

where \( C_{w0} \) is the concentration of contaminant in aqueous phase.

Initial conditions were \( C_w^A = 0 \) and \( C_w^C = 0 \).

The modeling of phenanthrene in a model sediment with organic carbon content of 2%, among which 1.8% is amorphous organic carbon and 0.2% is condensed phase organic carbon, was utilized to demonstrate the model. The modeling results for other processes in this section including desorption, aging and apparent partitioning and desorption isotherms were obtained based on this model sediment as well.

Considering sorption of phenanthrene from a porewater concentration maintained at 1 mg/kg, the intraparticle porewater concentration profile of phenanthrene in the amorphous organic matter and the virtual equivalent porewater concentration profile of
phenanthrene in the condensed phase organic matter at different times are shown in Figure 5.4.

Figure 5.4 Model predicted sorption of phenanthrene in model sediment

Note: Left half denotes the concentration profile in intraparticle porewater in the amorphous organic matter, right half denotes the virtual equivalent porewater concentration in the condensed phase organic matter.

The porewater concentration is maintained at 1 mg/L at position zero. Sorption into the amorphous phase is shown to the left while diffusion into the condensed phase is to the right. The phenanthrene saturated the amorphous organic matter after a short time of sorption while it is far from equilibrium for the condensed phase organic matter.

The phenanthrene concentration in sediment with respect to time during sorption process is presented in Figure 5.5. The phenanthrene concentration in sediment rises dramatically in the early stage of the sorption period because of movement into the
amorphous organic matter and then it increases very slowly while the condensed phase organic matter is continuing to adsorb phenanthrene.

![Figure 5.5 Model predicted phenanthrene concentration in sediment during sorption in model sediment](image)

**5.2.3.2 Desorption Process**

During desorption, the phenanthrene concentration in sediment porewater was assumed to be essentially zero. Boundary conditions for desorption process are stated below.

For the amorphous organic matter,

\[
\begin{align*}
\frac{\partial C_w^A}{\partial x} &= 0 & \text{at } x = 0 \\
C_w^A &= 0 & \text{at } x = \pm(V/A)
\end{align*}
\] (5.9)
Initial concentration profiles of intraparticle porewater concentration in the amorphous phase organic matter, \( C_w^A \), and the virtual equivalent porewater concentration in the condensed phase organic matter, \( C_w^C \), were defined by the concentration at the end of the sorption phase.

Model predicted intraparticle porewater concentration in the amorphous phase organic matter, \( C_w^A \), and the virtual equivalent porewater concentration in the condensed phase organic matter, \( C_w^C \), at different times during desorption are shown in Figure 5.6. On the \( x \) axis, the position at 0 \( \mu \text{m} \) represents the porewater interface while movement into the amorphous organic matter is to the left and movement into the condensed phase organic matter is to the right. The amorphous organic matter rapidly achieves equilibrium while the condensed phase remains well away from equilibrium even after long times. Note that desorption is occurring at the surface of the condensed phase organic matter even as slow diffusion further into the condensed phase organic matter is occurring.

Modeling result for the cumulative desorption of phenanthrene from the model sediment is shown in Figure 5.7. It is consistent with the biphasic desorption curve depicted by Hawthorne et al. (2001).

### 5.2.3.3 Apparent Partition Coefficient and Desorption Isotherms

The model was used to predict an apparent partition coefficient and desorption isotherms. The desorption isotherm was established in the following way: A series of
sediments with different initial contaminant concentrations were simulated. The apparent partition coefficient of contaminant in each sediment was estimated from predicted changes in porewater and solid concentrations. Different equilibration times, 10 days and 60 days, for apparent partition coefficient estimation were simulated to show the importance of equilibration time in determining the desorption isotherm.

Figure 5.6 Model predicted desorption of phenanthrene in model sediment

Note: Left half denotes the concentration profile in intraparticle porewater in the amorphous organic matter, right half denotes the virtual equivalent porewater concentration in the condensed phase organic matter.
Figure 5.7 Model predicted desorption kinetics of phenanthrene from model sediment

Boundary conditions for apparent partition coefficient estimation are

\[
\begin{align*}
\frac{\partial C_w^A}{\partial x} &= 0 \quad \text{at } x = 0 \text{ for the amorphous organic matter} \\
\frac{\partial C_w^C}{\partial x} &= 0 \quad \text{at } x = 0 \text{ for the condensed phase organic matter} \\
\left.\frac{\partial C_w}{\partial t}\right|_{x=(V/A)A} &= -\frac{D_{\text{eff}}}{v_1} \frac{\partial C_w^A}{\partial x} + \frac{D^C}{v_2} \frac{K_{OC}^C \rho^C}{\rho} \frac{\partial C_w^C}{\partial x} \quad \text{at the interface of organic matters and sediment porewater}
\end{align*}
\]

(5.11)
where $v_i$ (i=1,2) is the ratio of water to organic matter by volume for the amorphous and the condensed phase organic matter respectively, $C_w$ is the aqueous concentration of contaminant. And

$$v_1 = \left( \frac{W}{S} \right) \frac{\rho^A}{\rho_{\text{water}}} \frac{OC^A}{f_{oc}^A} \left( \frac{V}{A} \right)^A$$

$$v_2 = \left( \frac{W}{S} \right) \frac{\rho^C}{\rho_{\text{water}}} \frac{OC^C}{f_{oc}^C} \left( \frac{V}{A} \right)^C$$

where $\left( \frac{W}{S} \right)$ is the mass ratio of water to sediment for the apparent partition coefficient estimation.

Figure 5.8 Model predicted desorption isotherms of phenanthrene in freshly inoculated model sediment at equilibration time of 10 days and 60 days
The desorption isotherms determined at an equilibration time of 10 days and 60 days are shown in Figure 5.8. The results show that equilibration time plays an important role in determining the desorption isotherms. Desorption resistance may not be observed if the equilibration time is long enough for contaminants to achieve true equilibrium. These desorption isotherms were similar in shape to the biphasic desorption isotherms reported in Kan et al. (1998).

5.2.3.4 Modeling the Aging Effect

The effect of aging was modeled by simulating continued diffusion during storage (in this case for 1000 days) after sorption (inoculation). Boundary conditions are the same as those for the estimation of the apparent partition coefficient. During storage, however, a very small water to solid ratio was employed to simulate the wet sediment. The water to solid ratio for the wet sediment is 0.67 to 1 g/g. The initial condition for the aging process is the endpoint of the sorption process. Model demonstration of porewater concentration in amorphous organic matter and the virtual equivalent porewater concentration in condensed phase organic matter at different times during aging for the model sediment is shown in Figure 5.9. The contaminant migrated from the amorphous organic matter into the condensed phase organic matter at a very slow rate during the aging process.

Desorption kinetics were obtained after the aging process, assuming zero concentration in sediment porewater. Figure 5.10 shows modeling results for desorption kinetics after aging. A larger fraction of slowing desorbing contaminant is observed.

Figure 5.11 shows modeled desorption isotherms for freshly inoculated and aged model sediment. Aging increased the mass of phenanthrene resistant to desorption, $q_{res}$. 
Figure 5.9 Model predicted aging process in model sediment

Note: Left half denotes the concentration profile in intraparticle porewater in the amorphous organic matter, right half denotes the virtual equivalent porewater concentration in the condensed phase organic matter.
Figure 5.10 Model predicted desorption kinetics of phenanthrene from freshly inoculated and aged (for 1000 days) model sediment

Figure 5.11 Model predicted desorption isotherms of phenanthrene in freshly inoculated and aged (for 1000 days) model sediment
5.3 Modeling Results and Discussion

The model was then used to predict observations in both laboratory-inoculated and field-contaminated sediments.

5.3.1 Laboratory-inoculated Sediment

Modeling results for desorption kinetics of phenanthrene in freshly inoculated and aged Bayou Manchac sediment are shown in Figure 5.12. Also shown are the measured desorption rates as shown in Chapter 2.

![Figure 5.12 Comparison of model predicted and measured desorption kinetics of phenanthrene in freshly inoculated and aged Bayou Manchac sediment](image)

The model predicted desorption kinetics was obtained from the following parameters. The sorption time was 35 days which was the inoculation time for the experiment. Desorption time was selected to be 600 days to assure that the concentration remaining in sediment after desorption was low enough and it covered the scope of the
desorption experiment. The diffusivity of phenanthrene in water was $7.74 \times 10^{-10}$ m$^2$/s (Assumed same as anthracene because of identical molecular weight, diffusivity for anthracene from USEPA, 1996). The organic carbon normalized partition coefficient for phenanthrene in the amorphous organic carbon was estimated to be $\log K_{OC} = 4.36$ using Equation 2.6. The organic carbon normalized partition coefficient for phenanthrene in the condensed phase organic carbon was taken to be $\log K_{OC}=5.10$ (refer to measurements in Chapter 4 for coal-cinder particles). The total organic carbon content of Bayou Manchac sediment was 1.54%. Given the phenanthrene concentration in sediment porewater during the inoculation period to be the solubility of phenanthrene in water, which is 1.0 mg/L, the best fit for the diffusivity of phenanthrene in the condensed phase organic matter and the volume to surface area ratio of the condensed phase organic matter were $3.2 \times 10^{-17}$ m$^2$/s and $2.0 \times 10^{-5}$ m. The R-squared values for the model fitting of these desorption kinetics were both 0.998. The amorphous organic carbon ($f_{oc}^A/f_{oc}$) and the condensed phase organic carbon ($f_{oc}^C/f_{oc}$) percentages were 97% and 3% respectively. Note that the measured amorphous and condensed phase organic carbon percentages for Bayou Manchac sediment were 52% and 48%. It is unclear why the observed behavior was consistent with only a very small fraction of the condensed phase carbon.

Lick et al. (1997) reported a correlation to correlate the overall effective diffusion coefficient, $D'$, with the first order rate constant, $k$, for particles with diameter of $d$.

$$k = \frac{D'}{0.0165d^2}$$  \quad (5.14)
The overall effective diffusion coefficient, $D'$, in the above equation is corresponding to the $\frac{D_{\text{eff}}^A}{R_f^A}$ for the amorphous organic matter or the $D^C$ for the condensed phase organic matter. And note that the volume to surface area ratio $(V/A)$ for spherical particle is equal to $d/6$. Substituting the values of $\frac{D_{\text{eff}}^A}{R_f^A}$ and $(V/A)$ for the amorphous organic matter, $D^C$ and $(V/A)$ for the condensed phase organic matter in this study into Equation 5.14 gave the fast desorbing rate constant, $k_f$, of $0.163 \text{ h}^{-1}$, and the slow desorbing rate constant, $k_s$, of $4.85 \times 10^{-4} \text{ h}^{-1}$ for Bayou Manchac sediment. These estimations coincided with experimental measurements of $\sim 0.1 \text{ h}^{-1}$ for $k_f$ and $\sim 6 \times 10^{-4} \text{ h}^{-1}$ for $k_s$ in Chapter 2 of the study.

The model predicted and measured desorption isotherms for freshly inoculated Bayou Manchac sediment at equilibration time of 10 days and 60 days are shown in Figure 5.13. The comparison of model predicted and measured desorption isotherms for freshly inoculated and aged Bayou Manchac sediments at equilibration time of 10 days are shown in Figure 5.14. Good agreement was achieved between the experimental data and model prediction. The R squared values for the model fitting of these isotherms were 0.965 for the freshly inoculated Bayou Manchac sediment determined at equilibration time of 10 days, 0.999 the aged Bayou Manchac sediment determined at equilibration time of 10 day, and 0.943 for the freshly inoculated Bayou Manchac sediment determined at equilibration time of 60 days. The basic parameters were identical to those used for the desorption kinetics. The best fit results for the diffusivity of phenanthrene in the condensed phase organic matter was $3.2 \times 10^{-17} \text{ m}^2/\text{s}$ and the volume to surface area ratio
was $2.0 \times 10^{-5}$ m. The amorphous organic carbon ($f_{oc}^A/f_{oc}$) and the condensed phase organic carbon ($f_{oc}^C/f_{oc}$) percentages were 99.3% and 0.07% respectively. Again, the best fit was achieved assuming that only a small fraction of the condensed phase carbon was contributing to the sorption and desorption behavior.

Figure 5.13 Comparison of model predicted and measured desorption isotherms for freshly inoculated Bayou Manchac sediment at different equilibration times

Note: Circles are experimental data determined at equilibration time of 10 days; Dashed line is model prediction for isotherm at equilibration time of 10 days; Diamonds are experimental data determined at equilibration time of 60 days; Dash dotted line is model prediction for isotherm at equilibration time of 60 days.

5.3.2 Field-contaminated Sediments

The primary goal of the model, however, was prediction of sorption and desorption behavior in the field-contaminated sediment. The initial distribution of contaminants in the condensed phase fraction of the field-contaminated sediments was not known. To estimate this distribution, sorption over 50 years was modeled.
Figure 5.14 Comparison of model predicted and measured desorption isotherms for freshly inoculated and aged Bayou Manchac sediment

Note: Squares are experimental data for aged Bayou Manchac sediment; Solid line is model prediction for aged Bayou Manchac sediment; Circles are experimental data for freshly inoculated Bayou Manchac sediment; Solid line is model prediction for aged Bayou Manchac sediment. Both isotherms were determined at equilibration time of 10 days.

The fast desorbing fraction of the sediments was estimated by predicting the desorption by maintaining zero water concentration for 20 hours to simulate XAD-2 addition. The results for the Utica Harbor and Rouge River sediment are shown in Figure 5.15. The experimentally determined fast desorbing fractions for PAHs in both sediments were in good agreement with the model prediction. The model underpredicted the desorption of benzo(a)pyrene (BaP) perhaps due to the neglect of colloidaly associated BaP which would increase the effective desorption rate for that compound. Excluding BaP data (two outliers in Figure 5.15), the linear regression using the regression model of
Experimental fast desorbing fraction = Estimated fast desorbing fraction gave R squared value of 0.79.

![Desorption Estimation](image)

Figure 5.15 Experimental results and model prediction on the fast desorbing fraction for PAHs in Utica Harbor and Rouge River sediment

Note: Black points for Utica Harbor sediment, Red points for Rouge River sediment.

The measured and model predicted apparent partition coefficients for PAHs in Utica Harbor and Rouge River sediment before and after XAD-2 treatment are shown in Figure 5.16. In general, the model predicted values were consistent with the experimental data. The R squared value was 0.80 for the linear regression using a regression model of Experimental LogKOC = Estimated logKOC.

The parameters used for the modeling of Utica Harbor and Rouge River sediment are listed in Table 5.2. The estimated diffusivities of PAHs in condensed phase organic matter was 8.5×10^{-20} m^2/s for all compounds, the volume to surface area ratio were 20×10^{-5} m. Surprisingly, the same set of parameters worked very well for both Utica
Harbor and Rouge River sediment even though they differed from each other by their total organic carbon contents and the amorphous/condensed phase organic carbon contents.

Koc estimation

![Koc estimation graph](image)

Figure 5.16 Experimental results and model prediction on the apparent partition coefficients for PAHs in Utica Harbor and Rouge River sediment

Note: Black points for Utica Harbor sediment, Red points for Rouge River sediment. The apparent partition coefficients were determined at 10 days of equilibration time.

Table 5.2 Parameters used for Utica Harbor and Rouge River sediments

<table>
<thead>
<tr>
<th>Compound</th>
<th>D (m²/s)</th>
<th>Porosity</th>
<th>D^C (m²/s)</th>
<th>(V/A) (µm)</th>
<th>logKoc^A</th>
<th>logKoc^C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHE</td>
<td>7.74E-10</td>
<td>0.4</td>
<td>8.50E-20</td>
<td>20</td>
<td>4.36</td>
<td>5.10</td>
</tr>
<tr>
<td>ANT</td>
<td>7.74E-10</td>
<td>0.4</td>
<td>8.50E-20</td>
<td>20</td>
<td>4.33</td>
<td>5.07</td>
</tr>
<tr>
<td>PYR</td>
<td>7.24E-10</td>
<td>0.4</td>
<td>8.50E-20</td>
<td>20</td>
<td>4.97</td>
<td>5.60</td>
</tr>
<tr>
<td>BaP</td>
<td>5.80E-10</td>
<td>0.4</td>
<td>8.50E-20</td>
<td>20</td>
<td>5.83</td>
<td>6.86</td>
</tr>
</tbody>
</table>
The extremely small diffusivities of PAHs in the condensed phase organic matter estimated in this study were comparable to the reported diffusivities of HOCs. Ghosh et al. (2001) estimated PAHs diffusivities in coal-derived particles to be in the range from $10^{-21}$ to $10^{-23}$ m$^2$/s. Carroll et al. (1994) calculated effective diffusivity for PCBs in the range of $10^{-24}$ to $10^{-25}$ m$^2$/s in polymeric soil organic matter.

Sensitivity analysis was conducted by varying the diffusivity of contaminants ($D^C$) and the volume to surface area ratio (V/A) in the condensed phase organic matter. The relative error and correlation coefficient for the model estimated fast desorbing fractions in Utica Harbor and Rouge River sediment are shown in Table 5.3.

Table 5.3 The average relative error and correlation coefficient for model estimated fast desorbing fraction (F) in Utica Harbor and Rouge River sediments

<table>
<thead>
<tr>
<th>Scenario</th>
<th>$D^C$ (m$^2$/s)</th>
<th>(V/A) µm</th>
<th>Average Err% (with BaP)</th>
<th>R-squared (with BaP)</th>
<th>Average Err% (without BaP)</th>
<th>R-squared (without BaP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$8.5 \times 10^{-20}$</td>
<td>20</td>
<td>28.21</td>
<td>0.45</td>
<td>11.39</td>
<td>0.79</td>
</tr>
<tr>
<td>2</td>
<td>$8.5 \times 10^{-20}$</td>
<td>2</td>
<td>29.65</td>
<td>0.05</td>
<td>14.45</td>
<td>0.18</td>
</tr>
<tr>
<td>3</td>
<td>$8.5 \times 10^{-19}$</td>
<td>20</td>
<td>33.95</td>
<td>-0.19</td>
<td>17.61</td>
<td>-0.18</td>
</tr>
<tr>
<td>4</td>
<td>$8.5 \times 10^{-21}$</td>
<td>20</td>
<td>79.58</td>
<td>-0.16</td>
<td>87.4</td>
<td>-6.1</td>
</tr>
<tr>
<td>5</td>
<td>$8.5 \times 10^{-20}$</td>
<td>200</td>
<td>122.3</td>
<td>-1.1</td>
<td>152.2</td>
<td>-17.4</td>
</tr>
</tbody>
</table>

Note: R-squared values were obtained by fixing the regression model: Model estimated F = Experimental F; R-squared value could be negative because the regression model was fixed to be Model estimated F = Experimental F; Model estimated F is approaching experimental F when R-squared value approaches 1.

The relative error and correlation coefficient for the model estimated porewater concentration and apparent partition coefficient in Utica Harbor and Rouge River
sediment are shown in Table 5.4. Results were relatively insensitive to decreases in the volume to surface area ratio. The results were more sensitive to the diffusivity of the condensed phase organic carbon fraction, primarily seen by its effect on reducing the correlation of the model-estimated data with the experimental data. Changes in diffusivity of an order of magnitude or more were required to significantly impact the correlation between the model and observations.

Table 5.4 The average relative error and correlation coefficient for model-estimated porewater concentration and apparent partition coefficient in Utica Harbor and Rouge River sediments

<table>
<thead>
<tr>
<th>Scenario</th>
<th>$D^C$ (m$^2$/s)</th>
<th>(V/A) $\mu$m</th>
<th>Average Err% for $C_w$</th>
<th>R-squared for $C_w$</th>
<th>Average Err% for logK$_{OC}$</th>
<th>R-squared for logK$_{OC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$8.5 \times 10^{-20}$</td>
<td>20</td>
<td>84.98</td>
<td>0.60</td>
<td>6.27</td>
<td>0.80</td>
</tr>
<tr>
<td>2</td>
<td>$8.5 \times 10^{-20}$</td>
<td>2</td>
<td>46.55</td>
<td>0.80</td>
<td>3.49</td>
<td>0.90</td>
</tr>
<tr>
<td>3</td>
<td>$8.5 \times 10^{-19}$</td>
<td>20</td>
<td>50.39</td>
<td>0.75</td>
<td>7.30</td>
<td>0.57</td>
</tr>
<tr>
<td>4</td>
<td>$8.5 \times 10^{-21}$</td>
<td>20</td>
<td>346.2</td>
<td>-0.26</td>
<td>10.57</td>
<td>0.12</td>
</tr>
<tr>
<td>5</td>
<td>$8.5 \times 10^{-20}$</td>
<td>200</td>
<td>568.2</td>
<td>-0.58</td>
<td>13.77</td>
<td>-0.47</td>
</tr>
</tbody>
</table>

Note: R-squared values was obtained by fixing the regression model: $Y_{Estimated} = Y_{Experimental}$; R-squared value could be negative because the regression model was fixed to be $Y_{Estimated} = Y_{Experimental}$; $Y_{Estimated}$ is approaching $Y_{Experimental}$ when R-squared value approaches 1.

5.4 Summary

A model based on relative rapid porous diffusion in amorphous carbon and slow solid phase diffusion in condensed phase carbon was used to predict sorption and desorption phenomena. The basic character of the prediction was consistent with biphasic sorption desorption behavior. The model could not quantitatively describe observed
behavior in laboratory-inoculated sediments without modifying measured parameters. In particular, only a small fraction of the condensed phase carbon appeared to take part in sorption and desorption over the short time scale of the experiment.

Model simulations of sorption and desorption in field-contaminated sediments were more successful. Model parameters were estimated by separate measurements and from literature sources except for the diffusivity of contaminants in the condensed phase organic matter and the volume to surface area ratio of the condensed phase organic matter. Best fit for the diffusion coefficient in the condensed phase organic matter, $D^c$, was $8.5 \times 10^{-20}$ m$^2$/s and volume to surface area ratio ($V/A$) was 20 µm, which described desorption of PAHs in two sediments.

Modeling results were relatively insensitive to decreases in the volume to surface area ratio. The results were more sensitive to the diffusivity of the condensed phase organic carbon fraction, primarily seen by its effect on reducing the correlation of the model-estimated data with the experimental data. Changes in diffusivity of an order of magnitude or more were required to significantly impact the correlation between the model and observations.
CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

- The desorption resistance of laboratory-inoculated contaminants in Bayou Manchac and University Lake sediment was not observed to be significantly different, though the two sediments have different condensed phase carbon contents based upon the carbon remaining after combustion at 375°C. Only 3-4% of the original saturated phenanthrene in Bayou Manchac and University Lake sediment were considered to be slow desorbing fraction based on the desorption kinetics. Aged sediment exhibited slightly higher desorption resistance for both Bayou Manchac and University Lake sediment, but no differences between sediments were noted.

- The absence of a correlation between desorption resistance and condensed phase organic carbon content in laboratory-inoculated Bayou Manchac and University Lake sediment was most likely due to the extremely slow diffusion rate of contaminant in the condensed phase organic carbon. Prolonged equilibration time for Bayou Manchac sediment exhibited lower apparent partition coefficient. Different apparent partition coefficients with different equilibration times suggested deviations from equilibration were significant. The time scale of 5 weeks for inoculation and 0-2 or 3 years for aging was apparently not long enough for a considerable amount of contaminant to migrate into the condensed phase
organic carbon. Thus any differences in condensed phase capacity for contaminants between the two sediments were not detectable.

- This hypothesis was tested with field-contaminated sediments from Utica Harbor and Rouge River that had a lengthy (decades) period of exposure. The field-contaminated sediments showed significantly different desorption resistant behavior. The Utica Harbor sediment exhibited a more pronounced desorption resistant behavior (i.e., greater fractions of contaminants desorbed slowly or not at all over the course of the experiments) consistent with its greater fraction of condensed phase carbon.

- Size and density separation were used to separate Bayou Manchac sediments into six fractions. Phenanthrene concentrations in light fractions rich in organic matter were significantly greater than in light fractions rich in clay and silt and than in heavy fractions rich in sand. The apparent partition coefficients, however, were not significantly different for different fractions. Thus, size and density separation does not help us to understand what types of organic matter are responsible for the phenomena of desorption resistance.

- Separation of coarse particles followed by chemical analysis showed that coal-like and coal-cinder particles exhibited very high PAH concentration. These particles also exhibited significantly higher condensed phase organic carbon contents. This is in agreement with observations reported
in Ghosh et al. (2000) and Jonker et al. (2002) that PAHs contamination in sediments was predominantly associated with “black” particles.

- Phenanthrene sorption experiments onto these separated fractions showed slow sorption onto coal-like and coal-cinder particles relative to woody particles. This was also consistent with the concept that higher capacity but slowed adsorption/desorption rates compared to amorphous carbon. The capacity of the coal-like particles was less than coal-cinder particles but crushing the coal-like particles improved uptake over 1 and 2 days of exposure, consistent with significant surface area limitation in the coal-like particles. Coal-like particles also showed a sensitivity to pH, presumably due to humic acid dissolution under basic condition.

- The apparent partition coefficients of PAHs in the coal-cinder particles were a good indication of the apparent partition coefficients in the resistant fraction of the Utica Harbor sediment, further emphasizing that these particles or similar may largely describe the condensed phase carbon desorption resistance phenomena.

- A model based on relative rapid porous diffusion in amorphous carbon and slow solid phase diffusion in condensed phase carbon was used to predict sorption and desorption phenomena. The basic character of the prediction was consistent with biphasic sorption desorption behavior. The model could not quantitatively describe observed behavior in laboratory-inoculated sediments without modifying measured parameters. In particular, only a small fraction of the condensed phase carbon appeared to
take part in sorption and desorption over the short time scale of the experiment.

- Model simulations of sorption and desorption in field-contaminated sediments were more successful. Model parameters were estimated by separate measurements and from literature sources except for the diffusivity of contaminants in the condensed phase organic matter and the volume to surface area ratio of the condensed phase organic matter. Best fit for the diffusion coefficient in the condensed phase organic matter, \( D^C \), was \( 8.5 \times 10^{-20} \, \text{m}^2/\text{s} \) and volume to surface area ratio \( (V/A) \) was 20 µm, which described desorption of PAHs in two sediments.

- Modeling results were relatively insensitive to decreases in the volume to surface area ratio. The results were more sensitive to the diffusivity of the condensed phase organic carbon fraction, primarily seen by its effect on reducing the correlation of the model-estimated data with the experimental data. Changes in diffusivity of an order of magnitude or more were required to significantly impact the correlation between the model and observations.

**6.2 Recommendations**

The current work established the model to successfully address physical availability of PAHs as representative hydrophobic organic contaminants in sediments. Several future areas suggested by our results are summarized below.

- Explore other HOCs such as PCBs, chlorinated pesticides, dioxins etc. other than PAHs. PCBs, chlorinated pesticides and dioxins are also major
hydrophobic organic contaminants found in sediments and soils. It would be useful if the application of the model in this study could be extended to address the sorption and desorption behaviors for these contaminants in sediments and soils.

- Couple the current model with the conceptual model proposed by Lu (2003) to estimate bioavailability of HOCs. The ultimate goal of this study was not only the physical availability, i.e., sorption and desorption and effective partitioning behavior, of contaminants in sediments. Lu (2003) has developed a conceptual model regarding the bioaccumulation of contaminants in benthic organisms. It is intriguing, therefore, to explore the feasibility of the model in this study to estimate the bioaccumulation of contaminants associated with sediments.

- Characterize the amorphous and condensed phase organic matter using NMR or other approach. The chemical structure of the amorphous and condensed phase organic matter would be interesting. The microscopic association and migration of contaminants with/in different organic matter would be insightful as well to understand the desorption-resistant behavior.
REFERENCES


Allison, L. E., in Methods of Soil Analysis, Edited by A. Black, No. 9 in the Series of Agronomy, Part 2 (ASA, Madison, WI, 1965), 1367-1378.


APPENDIX A NOMENCLATURE

Symbols

$C_0$ Initial concentration of contaminant in sediment, mg/kg dry sediment

$C_{Des20hr}$ Concentration of contaminant in sediment after treatment with XAD2 for 20 hours, mg/kg dry sediment

$C_s$ Contaminant concentration in sediment, mg/kg dry sediment

$C_s^A$ Contaminant concentration in amorphous organic matter, mg/kg

$C_s^C$ Contaminant concentration in condensed phase organic matter, mg/kg

$C_{s,labile}$ The fast desorbing contaminant concentration in sediment, mg/kg

$C_w$ Contaminant concentration in aqueous phase, mg/L

$C_w^A$ Contaminant concentration in amorphous organic matter pore water, mg/L

$C_w^C$ Virtual contaminant concentration in condensed phase organic matter which is equivalent to the pore water concentration, $= C_s^C/K_w^C$

$D$ Diffusivity of contaminant in water, m$^2$/s

$D^C$ Diffusivity of contaminant in condensed phase organic matter, m$^2$/s

$D_{eff}^A$ Effective diffusivity of contaminants in amorphous organic matter

$F$ Fast desorbing fraction of contaminant

$f_{oc}$ Fraction of organic carbon content in sediment, g OC/g dry sediment

$f_{oc}^{375}$ Fraction of organic carbon content in sediment after combustion at 375°C

$f_{oc}^A$ Fraction of amorphous organic carbon content in sediment, g OC/g dry sediment

$f_{oc}^C$ Fraction of condensed phase organic carbon content in sediment, g OC/g dry sediment

$k_f$ Desorption rate constant for fast desoring fraction, h$^{-1}$
\( K_{OC} \) Organic carbon normalized sediment-water partition coefficient, L/kg

\( K_{OC}^A \) Organic carbon normalized partition coefficient of contaminant in amorphous organic matter, L/Kg

\( K_{OC, bulk} \) Organic carbon normalized apparent partition coefficient of contaminant in bulk sediment, L/Kg

\( K_{OC}^C \) Organic carbon normalized partition coefficient of contaminant to condensed phase organic matter, L/Kg

\( K_{OC}^{res} \) Organic carbon normalized sediment-water partition coefficient of desorption-resistant contaminants, L/Kg

\( K_{OW} \) Partition coefficient between octanol and water, L/Kg

\( K_P \) Partition coefficient between sediment and water at equilibrium, L/Kg

\( K_P^{res} \) Equilibrium partition coefficient of desorption-resistant contaminant, L/Kg

\( k_s \) Desorption rate constant for slow desorbing fraction, h\(^{-1}\)

\( OC^d \) Organic carbon content of amorphous organic matter

\( OC^C \) Organic carbon content of condensed phase organic matter

\( q_{max}^{irr} \) The maximum desorption-resistant capacity, mg/kg dry sediment

\( Rf^A \) Retardation factor for amorphous organic matter

\( S_0 \) The total initial mass of contaminant in sediment

\( Sol \) Solubility of contaminant in water, mg/L

\( S_t \) Mass of contaminant removed by sorbent at time \( t \)

\( t \) Time, hour or day

\( V/A \) Volume to surface area ratio

\( \varepsilon \) Porosity of amorphous organic matter
\( \rho^A \) Bulk density of amorphous organic matter, kg/L

\( \rho^C \) Bulk density of condensed phase organic matter, kg/L

*Abbreviations*

**ANT** Anthracene

**ASTM** American Society for Testing and Materials

**BaP** Benzo[a]pyrene

**BbF** Benzo[b]Fluoranthene

**BghiPER** Benzo[g,h,i]Perylene

**BkF** Benzo[k]Fluoranthene

**CHR** Chrysene

**DBahA** Dibenzo[a,h]Anthracene

**DOC** Dissolved organic carbon

**HOC** Hydrophobic organic contaminant

**HPLC** High performance liquid chromatography

**PAH** Polycyclic Aromatic Hydrocarbon

**PHE** Phenanthrene

**PYR** Pyrene

**SOM** Soil/sediment organic matter

**TOC** Total organic carbon

**USEPA** United States Environmental Protection Agency
APPENDIX B FINITE ELEMENT METHOD

Considering a one dimensional partial differential equation with the form of

\[ \alpha \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} \]

A fully implicit finite element method solution was obtained as follows, choosing linear shape function.

For the case of one element only,

Let

\[ \tilde{u}(x, t; a) = \sum_{i=1}^{2} a_i(t) \varphi_i(x) \]

where \( \varphi_i(x) \) are linear shape functions and

\[ \varphi_1(x) = \frac{x_b - x}{x_b - x_a} \quad \varphi_2(x) = \frac{x - x_a}{x_b - x_a} \]

\( x_a \) and \( x_b \) are values of \( x \) at the boundary.

For

\[ \alpha \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} \]

residual

\[ R(x, t; a) = \alpha \frac{\partial \tilde{u}}{\partial t} - \frac{\partial^2 \tilde{u}}{\partial x^2} \]
\[ \int_{s_a}^{s_b} R(x,t;a) \varphi_i(x) \, dx = \int_{s_a}^{s_b} \left( \alpha \frac{\partial \tilde{u}}{\partial t} - \frac{\partial^2 \tilde{u}}{\partial x^2} \right) \varphi_i(x) \, dx = 0 \quad i = 1, 2 \]

\[ \int_{s_a}^{s_b} \alpha \frac{\partial \tilde{u}}{\partial t} \varphi_i(x) \, dx = \frac{\partial \tilde{u}}{\partial x} \varphi_i(x) \bigg|_{s_a}^{s_b} + \int_{s_a}^{s_b} \frac{\partial \tilde{u}}{\partial x} \frac{d \varphi_i(x)}{dx} \, dx = 0 \quad i = 1, 2 \]

\[ \int \alpha \frac{\partial \tilde{u}}{\partial t} \varphi_i(x) \, dx + \int \frac{\partial \tilde{u}}{\partial x} \frac{d \varphi_i(x)}{dx} \, dx = \left[ - \frac{\partial \tilde{u}}{\partial x} \right] \varphi_i(x) \bigg|_{s_a}^{s_b} \quad \text{Equation 1} \]

Recall

\[ \tilde{u}(x,t;a) = a_1(t) \varphi_1(x) + a_2(t) \varphi_2(x) \]

\[ \frac{\partial \tilde{u}}{\partial t} = \frac{d a_1(t)}{dt} \varphi_1(x) + \frac{d a_2(t)}{dt} \varphi_2(x) \]

\[ \frac{\partial \tilde{u}}{\partial t} = a_1(t) \frac{d \varphi_1(x)}{dx} + a_2(t) \frac{d \varphi_2(x)}{dx} \]

Substitute into Equation 1:

\[ \int \alpha \left( \frac{d a_1(t)}{dt} \varphi_1(x) + \frac{d a_2(t)}{dt} \varphi_2(x) \right) \varphi_i(x) \, dx + \int \left( a_1(t) \frac{d \varphi_1(x)}{dx} + a_2(t) \frac{d \varphi_2(x)}{dx} \right) \frac{d \varphi_i(x)}{dx} \, dx \]

\[ = \left[ - \frac{\partial \tilde{u}}{\partial x} \right] \varphi_i(x) \bigg|_{s_a}^{s_b} \]

in matrix form,

\[ \begin{bmatrix} c \end{bmatrix} \frac{da(t)}{dt} + \begin{bmatrix} k \end{bmatrix} a(t) = F(t) \quad \text{Equation 2} \]

where

\[ a(t) = \begin{bmatrix} a_1(t) \\ a_2(t) \end{bmatrix} \quad F(t) = \begin{bmatrix} F_1(t) \\ F_2(t) \end{bmatrix} \]
\[ c_{ij} = \alpha \int_{x_a}^{x_b} \varphi_i(x) \varphi_j(x) \, dx \quad i = 1, 2 \quad j = 1, 2 \]

\[ k_{ij} = \int_{x_a}^{x_b} \frac{d\varphi_i(x)}{dx} \frac{d\varphi_j(x)}{dx} \, dx \quad i = 1, 2 \quad j = 1, 2 \]

\[ F_i(t) = -\left[ \tau(x, t; a) \varphi_i(x) \right]_{x_a}^{x_b} = \left[ -\frac{\partial \tilde{u}(x, t; a)}{\partial x} \varphi_i(x) \right]_{x_a}^{x_b} \quad i = 1, 2 \]

For the case of multi-elements,

\[
\begin{array}{cccc}
  & x_a & & \\
  x_1 & x_2 & x_3 & \\
  & x_n & x_{n+1} & \\
  x_{n-1} & x_n & x_{n+1} & x_b
\end{array}
\]

for the \( n \)th element, we have:

\[
[C]^{(e)} \frac{da_n(t)^{(e)}}{dt} + [k]^{(e)} a_n(t)^{(e)} = F_n(t)^{(e)}
\]

where

\[ c_{aij}^{(e)} = \alpha \int_{x_a}^{x_{ai+1}} \varphi_m(x)^{(e)} \varphi_n(x)^{(e)} \, dx \quad i = 1, 2 \quad j = 1, 2 \]

\[ k_{aij}^{(e)} = \int_{x_a}^{x_{ai+1}} \frac{d\varphi_m(x)^{(e)}}{dx} \frac{d\varphi_n(x)^{(e)}}{dx} \, dx \quad i = 1, 2 \quad j = 1, 2 \]

\[ F_i(t) = \left[ -\frac{\partial \tilde{u}(x, t; a)}{\partial x} \varphi_m(x)^{(e)} \right]_{x_a}^{x_{ai+1}} \quad i = 1, 2 \]

Recalling for the case of one element,

\[ \varphi_1(x) = \frac{x_b - x}{x_b - x_a} \quad \varphi_2(x) = \frac{x - x_a}{x_b - x_a} \]

then, for the \( n \)th element:
\[ \varphi_{n1}(x) = \frac{x_{n+1} - x}{\Delta x} \quad \varphi_{n2}(x) = \frac{x - x_n}{\Delta x} \]

\[ \frac{d\varphi_{n1}(x)}{dx} = -\frac{1}{\Delta x} \quad \frac{d\varphi_{n2}(x)}{dx} = \frac{1}{\Delta x} \]

\[ c_{n11} = \int_{x_n}^{x_{n+1}} \alpha \left( \frac{x_{n+1} - x}{\Delta x} \right)^2 dx = \frac{\alpha}{(\Delta x)^2} \left[ \frac{x_{n+1}^2}{x_{n+1}^2} \Delta x - x_{n+1} \left( x_{n+1}^2 - x_n^2 \right) + \frac{1}{3} \left( x_{n+1}^3 - x_n^3 \right) \right] \]

\[ c_{n22} = \int_{x_n}^{x_{n+1}} \alpha \left( \frac{x - x_n}{\Delta x} \right)^2 dx = -\frac{\alpha}{(\Delta x)^2} \left[ \frac{1}{3} \left( x_{n+1}^3 - x_n^3 \right) - \left( x_{n+1}^2 - x_n^2 \right) x_n + x_n^2 \Delta x \right] \]

\[ c_{n12} = c_{n21} = \int_{x_n}^{x_{n+1}} \alpha \frac{x_{n+1} - x}{\Delta x} \frac{x - x_n}{\Delta x} dx = \frac{\alpha}{(\Delta x)^2} \left[ -x_n x_{n+1} \Delta x + \frac{1}{2} (x_n + x_{n+1})^2 \Delta x - \frac{1}{3} \left( x_{n+1}^3 - x_n^3 \right) \right] \]

\[ k_{n11} = k_{n22} = \int_{x_n}^{x_{n+1}} \frac{1}{(\Delta x)^2} dx = \frac{1}{\Delta x} \]

\[ k_{n12} = k_{n21} = \int_{x_n}^{x_{n+1}} -\frac{1}{(\Delta x)^2} dx = -\frac{1}{\Delta x} \]

\[ F_{n1}(t) = \left[ -\frac{\partial u}{\partial x} \frac{x_{n+1} - x}{x_{n+1} - x_n} \right]_x^{x_{n+1}} = \left[ -\frac{\partial u}{\partial x} \right]^{(e)}_x \]

\[ F_{n2}(t) = \left[ -\frac{\partial u}{\partial x} \frac{x - x_n}{x_{n+1} - x_n} \right]_x^{x_{n+1}} = \left[ -\frac{\partial u}{\partial x} \right]^{(e)}_x \]

Sketch on a numbered line:

\[ x_a \quad x_1 \quad x_2 \quad x_3 \quad x_n \quad x_{n+1} \quad x_b \]

\[ \frac{x_b - x_a}{nx} \]

where \( nx \) is the total number of elements for \( x \) and \( \Delta x = \frac{x_b - x_a}{nx} \)
From Equation 3:

\[
[c]^{(e)} \frac{da_n(t)}{dt} + [k]^{(e)} a_n(t)^{(e)} = F_n(t)^{(e)}
\]

For the 1st element:

\[
\begin{bmatrix}
c_{111} & c_{112} \\
c_{121} & c_{122}
\end{bmatrix}
\begin{bmatrix}
\frac{da_{11}(t)}{dt} \\
\frac{da_{12}(t)}{dt}
\end{bmatrix} +
\begin{bmatrix}
k_{111} & k_{112} \\
k_{121} & k_{122}
\end{bmatrix}
\begin{bmatrix}
a_{11}(t) \\
a_{12}(t)
\end{bmatrix} =
\begin{bmatrix}
- \left( \frac{\partial u}{\partial x} \right)^{(e)} \\
- \left( \frac{\partial u}{\partial x} \right)^{(e)}
\end{bmatrix}
\]

For the 2nd element:

\[
\begin{bmatrix}
c_{211} & c_{212} \\
c_{221} & c_{222}
\end{bmatrix}
\begin{bmatrix}
\frac{da_{21}(t)}{dt} \\
\frac{da_{22}(t)}{dt}
\end{bmatrix} +
\begin{bmatrix}
k_{211} & k_{212} \\
k_{221} & k_{222}
\end{bmatrix}
\begin{bmatrix}
a_{21}(t) \\
a_{22}(t)
\end{bmatrix} =
\begin{bmatrix}
- \left( \frac{\partial u}{\partial x} \right)^{(e)} \\
- \left( \frac{\partial u}{\partial x} \right)^{(e)}
\end{bmatrix}
\]

\[
\vdots
\]

For the nxth element:

\[
\begin{bmatrix}
c_{nx1} & c_{nx2} \\
c_{nx1} & c_{nx2}
\end{bmatrix}
\begin{bmatrix}
\frac{da_{nx1}(t)}{dt} \\
\frac{da_{nx2}(t)}{dt}
\end{bmatrix} +
\begin{bmatrix}
k_{nx11} & k_{nx12} \\
k_{nx21} & k_{nx22}
\end{bmatrix}
\begin{bmatrix}
a_{nx1}(t) \\
a_{nx2}(t)
\end{bmatrix} =
\begin{bmatrix}
- \left( \frac{\partial u}{\partial x} \right)^{(e)} \\
- \left( \frac{\partial u}{\partial x} \right)^{(e)}
\end{bmatrix}
\]
Note that \( a_{n2}(t) = a_{(n+1)1}(t) \), put above equations together and rename \( a_{n1}(t) \) as \( a_n(t) \)

\[
\begin{bmatrix}
    c_{111} & c_{112} & 0 & 0 & 0 & 0 \\
    c_{121} & c_{122} + c_{211} & c_{212} & 0 & 0 & 0 \\
    0 & c_{221} & c_{222} + c_{311} & . & 0 & 0 \\
    0 & 0 & . & . & c_{(n-1)2} & 0 \\
    0 & 0 & 0 & c_{(n-1)21} & c_{(n-1)22} + c_{m11} & c_{m12} \\
    0 & 0 & 0 & 0 & c_{m21} & c_{m22}
\end{bmatrix}
\begin{bmatrix}
da_1(t) \\
da_2(t) \\
da_3(t) \\
d_a(t) \\
da_{m1}(t) \\
da_{m2}(t)
\end{bmatrix} +
\begin{bmatrix}
\frac{\partial u}{\partial x}^{(e)} \\
\frac{\partial u}{\partial x}^{(e)}
\end{bmatrix}
\]

That is,

\[
\begin{bmatrix}
c & c \\
k & k
\end{bmatrix}
a'(t) +
\begin{bmatrix}
k \\
k
\end{bmatrix}a(t) = F(t)
\]

Equation 3

where

\[
c =
\begin{bmatrix}
c_{111} & c_{112} & 0 & 0 & 0 & 0 \\
    c_{121} & c_{122} + c_{211} & c_{212} & 0 & 0 & 0 \\
    0 & c_{221} & c_{222} + c_{311} & . & 0 & 0 \\
    0 & 0 & . & . & c_{(n-1)2} & 0 \\
    0 & 0 & 0 & c_{(n-1)21} & c_{(n-1)22} + c_{m11} & c_{m12} \\
    0 & 0 & 0 & 0 & c_{m21} & c_{m22}
\end{bmatrix}
\]
\[
\begin{bmatrix}
k_{111} & k_{112} & 0 & 0 & 0 & 0 \\
k_{121} & k_{122} + k_{211} & k_{212} & 0 & 0 & 0 \\
0 & k_{221} & k_{222} + k_{311} & 0 & 0 & 0 \\
0 & 0 & . & \cdot & k_{(n_x-1)21} & 0 \\
0 & 0 & 0 & k_{(n_x-1)22} & k_{nx11} & k_{nx12} \\
0 & 0 & 0 & 0 & k_{nx21} & k_{nx22}
\end{bmatrix}
\]

\[
a(t) = \begin{bmatrix}
a_1(t) \\
a_2(t) \\
. \\
. \\
a_{n_x+1}(t)
\end{bmatrix}
\]

\[
a'(t) = \begin{bmatrix}
a'_1(t) \\
a'_2(t) \\
. \\
. \\
a'_{n_x+1}(t)
\end{bmatrix}
\]

\[
F(t) = \begin{bmatrix}
F_1(t) \\
F_2(t) \\
. \\
. \\
F_{n_x+1}(t)
\end{bmatrix}
\]

At this point, boundary conditions are needed to determine, 
\[
a_i(t), \ a_{n_x+1}(t), \ \frac{da_1(t)}{dt}, \ \text{and} \ \frac{da_{n_x+1}(t)}{dt},
\]
or
\[
- \left( \frac{\partial u}{\partial x} \right)^{(e)} \right)_{x_e}, \text{ and } - \left( \frac{\partial u}{\partial x} \right)^{(e)} \right)_{x_u}
\]

Then Equation 3
\[
[c]a'(t) + [k]a(t) = F(t)
\]
could be solved using fully implicit method,
\[
[c]a(t_{m+1} - a(t_m) + [k]a(t_{m+1}) = F(t)
\]
\[
a(t_{m+1}) = \text{(Inverse of } (c[c] + \Delta t[k][a(t_{m+1})]) (F(t) + [c]a(t_m)))
\]
for \(t_0 = 0\), \(a(0)\) is determined by the initial condition. Once \(a(t_m)\) were obtained, the \(u(x,t)\)
was given by the following equation,
\[
u_n(x,t_m; a) = a_n(t_m)\phi_{n1}(x) + a_{n+1}(t_m)\phi_{n2}(x)
\]

The comparisons between numerical solutions and analytical solutions for simplified cases are shown in the following section. For the sorption process of phenanthrene in the amorphous organic matter, the governing equation and boundary conditions and initial condition are
\[
\begin{align*}
\frac{\partial C^A_{w}}{\partial t} &= \frac{D^A_{eff}}{R_f} \frac{\partial^2 C^A_{w}}{\partial x^2} \\
C^A_{w} &= 1 \text{ at } x = (V / A) \\
\frac{\partial C^A_{w}}{\partial x} &= 0 \text{ at } x = 0 \\
C^A_{w} &= 0 \text{ at } t = 0
\end{align*}
\]
where
\[ D_{\text{eff}}^A = D \cdot \varepsilon^{4/3} \]

\[ R_f^A = \varepsilon + \rho^A \cdot K_{OC}^A \cdot OC^A \]

\[ D = 7.74 \times 10^{-10} \text{ m}^2/\text{s}; \quad \varepsilon = 0.4; \quad \rho^A = 1.5 \text{ g/ml}; \quad K_{OC}^A = 10^{4.36} \text{ L/KG}; \quad OC^A = 0.58 \text{ and } V/A = 20 \mu\text{m}. \]

The analytical solution to this problem gives the following porewater concentration profile in the amorphous organic matter,

\[ C_w^A = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left\{ -\frac{\left(D_{\text{eff}}^A / R_f^A\right)(2n+1)^2 \pi^2 t}{4(V/A)^2} \right\} \cos\left(\frac{(2n+1)\pi x}{2(V/A)}\right) \]

and the overall phenanthrene concentration in solid phase amorphous organic matter \( C_{s,t}^A \) at time \( t \),

\[ \frac{C_{s,t}^A}{C_{s,\infty}^A} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left\{ -\frac{\left(D_{\text{eff}}^A / R_f^A\right)(2n+1)^2 \pi^2 t}{4(V/A)^2} \right\} \]

where \( C_{s,\infty}^A \) is the overall phenanthrene concentration in the solid phase organic matter after infinite time and

\[ C_{s,\infty}^A = K_{OC}^A \cdot OC^A \]

The comparison between analytical and numerical solution to phenanthrene porewater concentration profile in the amorphous organic matter is shown in Figure A-B.1. The comparison between analytical and numerical solution to phenanthrene sorption kinetics in the amorphous organic matter is shown in Figure A-B.2. The numerical solution was obtained with \( \Delta t = 0.5 \text{ hr} \) and \( \Delta x = 0.5 \mu\text{m} \) (the step size used in the modeling in the study was \( \Delta t = 1 \text{ hr} \), and this step size did not affect the accuracy of our
modeling results; $\Delta x = 0.5 \, \mu m$). These results showed that the numerical solution is a reasonable approximation.

Figure A-B.1 The comparison between analytical and numerical solution to phenanthrene porewater concentration profile in the amorphous SOM

Note: $\Delta t = 0.5 \, \text{hr}$, $\Delta x = 0.5 \, \mu m$

Figure A-B.2 The comparison between analytical and numerical solution to phenanthrene sorption kinetics in the amorphous SOM

Note: $\Delta t = 0.5 \, \text{hr}$, $\Delta x = 0.5 \, \mu m$
For condensed phase organic matter, the governing equation and boundary conditions and initial condition are

\[
\begin{aligned}
\frac{\partial C_w^C}{\partial t} &= D^C \frac{\partial^2 C_w^C}{\partial x^2} \\
C_w^C &= 1 \text{ at } x = (V / A) \\
\frac{\partial C_w^C}{\partial x} &= 0 \text{ at } x = 0 \\
C_w^C &= 0 \text{ at } t = 0
\end{aligned}
\]

\[D^C = 8.5 \times 10^{-20} \text{ m}^2/\text{s}; \quad \rho^C = 1.8 \text{ g/ml}; \quad K_{OC}^C = 10^{5.1} \text{ L/KG}; \quad OC^C = 0.8 \text{ and } V/A = 20 \mu m.\] The analytical solution to this problem gives the following porewater concentration profile in the amorphous organic matter,

\[
C_w^C = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left\{ - \frac{D^C (2n+1)^2 \pi^2 t}{4(V / A)^2} \right\} \cos \left( \frac{(2n+1)\pi x}{2(V / A)} \right)
\]

and the overall phenanthrene concentration in solid phase amorphous organic matter \(C_{s,t}^C\) at time \(t\),

\[
\frac{C_{s,t}^C}{C_{s,\infty}^C} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left\{ - \frac{D^C (2n+1)^2 \pi^2 t}{4(V / A)^2} \right\}
\]

where \(C_{s,\infty}^C\) is the overall phenanthrene concentration in the solid phase organic matter after infinite time and

\[C_{s,\infty}^C = K_{OC}^C OC^C\]

Results for condensed phase organic matter are shown in Figure A-B.3 and Figure A-B.4, which were obtained with \(\Delta t = 1 \text{ yr}\) and \(\Delta x = 0.5 \mu m\) (the step size used in the modeling in the study was \(\Delta t = 0.5 \text{ year or less; } \Delta x = 0.5 \mu m\)).
Figure A-B.3 The comparison between analytical and numerical solution to phenanthrene porewater concentration profile in the condensed phase SOM

Note: Δt = 1 yr, Δx = 0.5 μm

Figure A-B.4 The comparison between analytical and numerical solution to phenanthrene sorption kinetics in the condensed phase SOM

Note: Δt = 1 yr, Δx = 0.5 μm
APPENDIX C SAMPLE MATLAB PROGRAM FOR LABORATORY-INOCULATED SEDIMENTS

This section includes sample MatLab program used for modeling laboratory-inoculated sediments. The following MatLab files are required to be placed in the same subdirectory on computer in order to run the program.

1. File name: phe.m

% main program
%Bayou Manchac sediment
echo off; clc; % clear the command window before run this program
close('all'); % close all windows before running

sedimentName = 'Bayou Manchac Sediment';
tAds = 35; % sorption time, day
tDes = 600; % desorption time, day
tKoc = 10; % equilibration time for Koc estimation, day
tKoc60 = 60;
tAge = 1000; % days
ntAds = 60; % number of steps for sorption time
ntDes = 100; % number of steps for desorption time
ntKoc = 60; % number of time steps for Koc estimation
ntAge = 50; % number of time steps for aging

foc = 0.0154;
D = 7.7*10^-10;
Dhd = 2.2*10^-17;
VSAratio = 20*10^-6; % m
CwInit = 1;
wsRatio = 70; %

% all these parameters below denote--1st: amorphous carbon, 2nd: condensed phase carbon
shocM pct = [0.99 0.01];
oc = [0.58 0.8];
density = [1.5 1.8]; % kg/L
lgKoc = [4.4 5.10];
porosity = 0.4;
Lsft = 2.0*10^-5; % V/A for amorphous
nxSft = 40; % number of elements on x for amorphous carbon particles
nxHd = 40; % number of elements on x for condensed phase carbon particles

%write all basic parameters.
fid = fopen('run\paramOut.txt','w');
fprintf(fid,'Basic Parameters for %s:

', sedimentName);
fprintf(fid,'Lsft = %.4e; nxSft = %d; nxHd = %d; Lsft, nxSft, nxHd);
fprintf(fid,tAds = %d; ntAds = %d; tAds, ntAds);
fprintf(fid,tDes = %d; tDes, ntDes);
fprintf(fid,tKoc = %d; tKoc, ntKoc);
fprintf(fid,tAge = %d; tAge, ntAge);
fprintf(fid,'D = %.4e; Dhd = %.4e; D, Dhd);
fprintf(fid,'VSAratio = %.4e, VSAratio);
fprintf(fid,'logKoc = [%.4f %.4f], lgKoc);
fprintf(fid,'OC = [%.4f %.4f], oc);
fprintf(fid,'Density = [%.4f %.4f], density);
fprintf(fid,'shMPcnt = [%.4f %.4f], shocMpcnt);
fprintf(fid,'porosity = %.4f, porosity);
fprintf(fid,'CwInit = %.4f, CwInit);
fprintf(fid,'wsRatio = %.4f, wsRatio);
fprintf(fid,'foc = %.4f, foc);
fclose(fid);

DeffSft = D * porosity^(4/3);
om = (foc .* shocMpcnt) ./ oc;
SOM = sum(om);
shomMpct = om ./SOM;
wSOMmr = wsRatio/SOM; % overall mass ratio of water to total organic matter
wSftOMmr = wsRatio/om(1);
wHdOMmr = wsRatio/om(2);
wSftVolR = wSftOMmr * density(1);
wHdVolR = wHdOMmr * density(2);
Lhd = VSAratio;
Koc = 10.^lgKoc;
Kd = Koc .* oc;
Rfsft = porosity + density(1) * Kd(1);
DRf(1) = DeffSft / Rfsft;
Rfhd = density(2)* Kd(2);
DRf(2) = Dhd;
Rf = [Rfsft, Rfhd];
Deff = [DeffSft, Dhd];
a(1) = Lsft * wsftVolR;
a(2) = Lhd * whdVolR;
f = 1 / DRF;

n = nxSft +nxHd +1;
delXsft = Lsft/nxSft;
delXhd = Lhd /nxHd;
x = zeros(n,1);
for i=1:nxSft+1
    x(i,1)=0.0 + delXsft * (i-1);
end
for i=nxSft+2:n
    x(i,1)=x(nxSft+1,1) + delXhd * (i-nxSft-1);
end

%*******************************************************************
% stiﬀness matrix for each element
%*******************************************************************
[c, k] = ckElem(n, nxSft, nxHd, x, delXsft, delXhd, f);

%*******************************************************************
% sorption process below
%*******************************************************************
delTAds = tAds*24*3600.0/ntAds;

% cc overall stiffness matrix for sorption
[cc, kk] = cckkAds(n, nxSft, c, k);
ccAds=cc;
kkAds=kk;
ccDes=cc;
kkDes=kk;

FAds=zeros(n-1, 1);
FAds(nxSft,1) = - CwInit * k(nxSft,1,2);
FAds(nxSft+1,1) = - CwInit * k(nxSft+1,2,1);

% a (i, 1) from a(2) to a(nx) at time t0
a2 = zeros(n-1,ntAds+1);
% solve for a(i, tn) at time tn
aaAds = ccAds + delTAds* kkAds;
for j=2:ntAds+1
    a2(:, j) = inv(aaAds) * (delTAds*FAds + ccAds *a2(:, j-1));
end

a1= zeros(ntAds+1,n);
a1(:, 1:nxSft) = a2(1:nxSft, :)';
a1(:, nxSft+1) = CwInit;
a1(:, nxSft+2:n) = a2(nxSft+1:n-1, :); a1Ads = a1;
% display the results for adsorption process
plotAdsResult(a1,n,nxSft, x, delXsft, delXhd, Lsft, Lhd, ntAds, delTAds, Kd, om, foc);

%********************************************************************%
% desorption process below                                       %
%********************************************************************%

% cc and kk are the same as the adsorption process
[tDesArray, delTDesArray]= timeDes(tDes, ntDes);

Fdes=zeros(n-1, 1);
a2des = zeros(n-1, ntDes+1);
a2des(:, 1) = a2(:, ntAds+1);

% solve for a(i, tn) at time tn
for j=2:ntDes+1
    a2des(:, j) = inv(cc + delTDesArray(j-1,1)* kk) * (delTDesArray(j-1, 1)*Fdes + cc *a2des(:, j-1));
end
a1des= zeros(ntDes+1,n);
a1des(:, 1:nxSft) = a2des(1:nxSft, :)';
a1des(:, nxSft+1) = 0;
a1des(:, nxSft+2:n) = a2des(nxSft+1:n-1, :)';

% display desorption results
% plotDesResult(a1des, n,nxSft, x, delXsft, delXhd, Lsft,Lhd, ntDes, tDesArray, Kd, om, foc);

%********************************************************************%
% Koc estimation process                                         %
%********************************************************************%

delTKoc = tKoc*24*3600 / ntKoc;
[cc, kk] = cckkKoc(n, nxSft, Deff, a, c, k, Kd, Rf);
[ccKoc, kkKoc] = cckkKoc(n, nxSft, Deff, a, c, k, Kd, density);
% a (i,1) from a(2) to a(nx) at time t0
a2Koc = zeros(ntDes+1, n, ntKoc+1);
% solve for a(i, tn) at time tn
a2Koc(i, 1) = a1des(i, 1);
for i=2:ntDes+1
    temp2= zeros(n, ntKoc+1);
    for cnt=1:n
        a2Koc(i, cnt, 1) = a1des(i, cnt);
        temp2(cnt, 1) = a2Koc(i, cnt, 1);
    end
    a2Koc(i, ntKoc+1, :) = temp2;
end
for j=2:ntKoc+1
temp2(:, j) = inv(aaKoc10) * ccKoc *temp2(:, j-1);
end
a2Koc(i, :, :) = temp2(:, :);
end

a1Koc = zeros(ntDes+1, ntKoc+1, n);
for i=1:ntDes+1
    for j=1:ntKoc +1
        for cnt=1:n
            a1Koc(i, j, cnt) = a2Koc(i, cnt, j);
        end
    end
end
delTKoc60 = tKoc60*24*3600 / ntKoc;
% a (i,1) from a(2) to a(nx) at time t0
a2Koc60 = zeros(ntDes+1, n, ntKoc+1);
% solve for a(i, tn) at time tn
aaKoc60 = ccKoc + delTKoc60* kkKoc;
for i=1:ntDes+1
    temp2= zeros(n, ntKoc+1);
    for cnt=1:n
        a2Koc60(i, cnt, 1) = a1des(i, cnt);
        temp2(cnt, 1) = a2Koc60(i, cnt, 1);
    end
    for j=2:ntKoc+1
        temp2(:, j) = inv(aaKoc60) * ccKoc *temp2(:, j-1);
    end
    a2Koc60(i, :, :) = temp2(:, :);
end
a1Koc60 = zeros(ntDes+1, ntKoc+1, n);
for i=1:ntDes+1
    for j=1:ntKoc +1
        for cnt=1:n
            a1Koc60(i, j, cnt) = a2Koc60(i, cnt, j);
        end
    end
end

%*******************************************************************%
%            Aging process                                                  
%*******************************************************************%
delTAge = tAge*24*3600 / ntAge;
wsmRaging         = 0.67;
% overall mass ratio of water to total organic matter
wSOMmrAging = wsmRaging/SOM;

% water to SOM ratio
wSftOMmrAging = wsmRaging/om(1);

% water to HDOM ratio
wHdOMmrAging = wsmRaging/om(2);

% water to SOM mass ratio
wsftVolRaging = wSftOMmrAging * density(1);

% water to HDOM mass ratio
whdVolRaging = wHdOMmrAging * density(2);

% initial aging
aAging(1) = Lsft * wsftVolRaging;

% final aging
aAging(2) = Lhd * whdVolRaging;

% cc and kk are the same as the adsorption process
[ccAge, kkAge] = cckkAging(n, nxSft, Deff, aAging, c, k, Kd, density);

% solve for a(i, tn) at time tn
fAge = zeros(n, 1);
a2Age = zeros(n, ntAge+1);
a2Age(:, 1) = a1Ads(ntAds+1, :);%

% solve for a(i, tn) at time tn
aaAge = ccAge + delTAge* kkAge;
for j=2:ntAge+1
    a2Age(:, j) = inv(aaAge) * (delTAge*fAge + ccAge *a2Age(:, j-1));
end

% display Age results
plotAgeResult(a1Age, n, nxSft, x, delXsft, delXhd, Lsft, Lhd, ntAge, delTAge, Kd, om, foc)

% desorption process after aging below
[tDesArray, delTDesArray] = timeDes(tDes, ntDes);

% solve for a(i, tn) at time tn
fDes = zeros(n-1, 1);
a2AgeDes = zeros(n-1, ntDes+1);
a2AgeDes(1:nxSft, 1) = a2Age(1:nxSft, ntAge+1);
a2AgeDes(nxSft+1: n-1, 1) = a2Age(nxSft+2:n, ntAge+1);

% solve for a(i, tn) at time tn
for j=2:ntDes+1
a2AgeDes(:, j) = inv(ccAgeDes + delTDesArray(j-1, 1)* kkAgeDes) * 
(delTDesArray(j-1, 1)*fDes + ccAgeDes *a2AgeDes(:, j-1));
end

a1AgeDes= zeros(ntDes+1,n);
a1AgeDes(:, 1:nxSft) = a2AgeDes(1:nxSft, :)';
a1AgeDes(:, nxSft+1) = 0;
a1AgeDes(:, nxSft+2:n) = a2AgeDes(nxSft+1:n-1, :');

% display desorption results after aging
plotAgeDesResult(a1des, a1AgeDes, n, nxSft, x, delXsft, delXhd, Lsft, Lhd, ntDes, 
tDesArray, Kd, om, foc);

% Koc estimation process after aging
% delTKoc = tKoc*24*3600 / ntKoc;
% overall cc and kk stiffness matrice are the same as Koc estimation
ccAgeKoc = ccKoc;
kKocKoc = kkKoc;

aaAgeKoc = ccAgeKoc + delTKoc* kkAgeKoc;

% a (i,1) from a(2) to a(nx) at time t0
a2AgeKoc = zeros(ntDes+1, n, ntKoc+1);

% solve for a(i, tn) at time tn
for i=1:ntDes+1
    temp2= zeros(n, ntKoc+1);
    for cnt=1:n
        a2AgeKoc(i, cnt, 1) = a1AgeDes(i, cnt);
        temp2(cnt, 1) = a2AgeKoc(i, cnt, 1);
    end
    for j=2:ntKoc+1
        temp2(:, j) = inv(aaAgeKoc) * ccAgeKoc *temp2(:, j-1);
    end
    a2AgeKoc(i, :, :) =  temp2(:, :);
end

a1AgeKoc= zeros(ntDes+1,ntKoc+1, n);
for i=1:ntDes+1
    for j=1:ntKoc +1
        for cnt=1:n
            a1AgeKoc(i, j, cnt) = a2AgeKoc(i, cnt, j);
        end
    end
end
plotKoc(a1Koc, a1Koc60, a1AgeKoc, n, nxSft, x, delXsft, delXhd, Lsft, Lhd, ntKoc, delTKoc, delTKoc60, Kd, om, foc, ntDes, tDesArray);
open('run\paramOut.txt');

2. File name: ckElem.m

function [c, k] = ckElem (np, nxSftp, nxHdp, xp, delXsftp, delXhdp, fp)

% C stiffness matrix for each element
c = zeros(np, 2, 2);
for i=1:nxSftp
    c(i,1,1) = (fp(1)/delXsftp^2)*...
               [(xp(i+1,1)^2*delXsftp - xp(i+1,1)*(xp(i+1,1)^2-xp(i,1)^2) +(1/3)*(xp(i+1,1)^3-xp(i,1)^3));
    c(i,2,2) = (fp(1)/delXsftp^2)*...
               ((1/3)*(xp(i+1,1)^3-xp(i,1)^3)-xp(i,1)*(xp(i+1,1)^2-xp(i,1)^2)+xp(i,1)^2*delXsftp);
    c(i,1,2) = (fp(1)/delXsftp^2)*...
               (-xp(i+1,1)*xp(i,1)*delXsftp + (1/2)*(xp(i+1,1)+xp(i,1))^2*delXsftp -
                 (1/3)*(xp(i+1,1)^3-xp(i,1)^3));
    c(i,2,1) = c(i,1,2);
end
for i=nxSftp+1:np-1
    c(i,1,1) = (fp(2)/delXhdp^2)*...
               [(xp(i+1,1)^2*delXhdp - xp(i+1,1)*(xp(i+1,1)^2-xp(i,1)^2) +(1/3)*(xp(i+1,1)^3-xp(i,1)^3));
    c(i,2,2) = (fp(2)/delXhdp^2)*...
               ((1/3)*(xp(i+1,1)^3-xp(i,1)^3)-xp(i,1)*(xp(i+1,1)^2-xp(i,1)^2)+xp(i,1)^2*delXhdp);
    c(i,1,2) = (fp(2)/delXhdp^2)*...
               (-xp(i+1,1)*xp(i,1)*delXhdp + (1/2)*(xp(i+1,1)+xp(i,1))^2*delXhdp -
                 (1/3)*(xp(i+1,1)^3-xp(i,1)^3));
    c(i,2,1) = c(i,1,2);
end

% k stiffness matrix for each element
k = zeros(np, 2, 2);
for i=1:nxSftp
    k(i,1,1) = 1/delXsftp;
    k(i,2,2) = 1/delXsftp;
    k(i,1,2) = -1/delXsftp;
end
\[
k(i,2,1) = -1/delXsftp;
\]
end
for \(i=nxSftp+1:np-1\)
\[
k(i,1,1) = 1/delXhdp;
k(i,2,2) = 1/delXhdp;
k(i,1,2) = -1/delXhdp;
k(i,2,1) = -1/delXhdp;
\]
end

3. File name: cckAds.m

% cc overall stiffness matrix for sorption
function \([cc, kk] = cckAds(n, nxSftp, c, k)\)

% cc overall stiffness matrix
cc = zeros(n-1);
cc(1,1) = c(1, 1, 1);
c(1,2) = c(1, 1, 2);
for \(i=2:nxSftp-1\)
\[
cc(i, i-1) = c(i-1,2,1);
cc(i,i) = c(i-1,2,2) + c(i,1,1);
c(i, i+1) = c(i,1,2);
\]
end
cc(nxSftp, nxSftp-1) = c(nxSftp-1,2,1);
cc(nxSftp,nxSftp) = c(nxSftp-1,2,2) + c(nxSftp,1,1);

% (nxSftp+1)th row of stiffness matrix
cc(nxSftp+1,nxSftp+1) = c(nxSftp+1, 2, 2)+ c(nxSftp+2, 1, 1);
cc(nxSftp+1,nxSftp+2) = c(nxSftp+2, 1, 2);
for \(i=nxSftp+2:n-2\)
\[
cc(i, i-1) = c(i,2,1);
cc(i,i) = c(i,2,2) + c(i+1,1,1);
c(i, i+1) = c(i+1,1,2);
\]
end
%last row of stiffness matrix
cc(n-1,n-2) = c(n-1,2,1);
cc(n-1,n-1) = c(n-1,2,2);

% kk overall stiffness matrix
kk = zeros(n-1);
k(1,1) = k(1, 1, 1);
k(1,2) = k(1, 1, 2);
for \(i=2:nxSftp-1\)
\[
kk(i, i-1) = k(i-1,2,1);
\]
\[
\begin{align*}
\text{kk}(i,i) &= \text{k}(i-1,2,2) + \text{k}(i,1,1); \\
\text{kk}(i, i+1) &= \text{k}(i,1,2); \\
\end{align*}
\]
end
\[
\text{kk}(\text{nxsft}, \text{nxsft}-1) = \text{k}(\text{nxsft}-1,2,1); \\
\text{kk}(\text{nxsft},\text{nxsft}) = \text{k}(\text{nxsft}-1,2,2) + \text{k}(\text{nxsft},1,1);
\]

\% (\text{nxsft}+1)th row of stiffness matrix
\[
\begin{align*}
\text{kk}(\text{nxsft}+1,\text{nxsft}+1) &= \text{k}(\text{nxsft}+1,2,2)+\text{k}(\text{nxsft}+2,1,1); \\
\text{kk}(\text{nxsft}+1,\text{nxsft}+2) &= \text{k}(\text{nxsft}+2,1,2); \\
\end{align*}
\]
for \(i=\text{nxsft}+2:\text{n}-2\)
\[
\begin{align*}
\text{kk}(i, i-1) &= \text{k}(i,2,1); \\
\text{kk}(i,i) &= \text{k}(i,2,2) + \text{k}(i+1,1,1); \\
\text{kk}(i, i+1) &= \text{k}(i+1,1,2); \\
\end{align*}
\]
end
\% last row of stiffness matrix
\[
\begin{align*}
\text{kk}(\text{n-1},\text{n-2}) &= \text{k}(\text{n-1},2,1); \\
\text{kk}(\text{n-1},\text{n-1}) &= \text{k}(\text{n-1},2,2); \\
\end{align*}
\]

4. File name: cckkKoc.m

\% stiffness matrix for Koc estimation
function \([\text{cc}, \text{kk}] = \text{cckkKoc}(n, \text{nxsftp}, \text{Deff}, \text{a, c, k, kd, densityp})\)
\[
\begin{align*}
\text{cc} &= \text{zeros}(n); \\
\text{cc}(1,1) &= \text{c}(1, 1, 1); \\
\text{cc}(1,2) &= \text{c}(1, 1, 2); \\
\% \text{cc}(2,1) &= \text{c}(1, 2, 1); \\
\end{align*}
\]
for \(i=2:n-1\)
\[
\begin{align*}
\text{cc}(i, i-1) &= \text{c}(i-1,2,1); \\
\text{cc}(i,i) &= \text{c}(i-1,2,2) + \text{c}(i,1,1); \\
\text{cc}(i, i+1) &= \text{c}(i,1,2); \\
\end{align*}
\]
end
\% (\text{nxsftp}+1)th row of stiffness matrix
\[
\begin{align*}
\text{cc}(\text{nxsftp}+1, \text{nxsftp}) &= (\text{Deff}(1)/\text{a}(1))*\text{c}(\text{nxsftp},2,1); \\
\text{cc}(\text{nxsftp}+1, \text{nxsftp}+1) &= (\text{Deff}(1)/\text{a}(1))*\text{c}(\text{nxsftp},2,2)+ \\
& (\text{Deff}(2)*\text{kd}(2)*\text{densityp}(2)/\text{a}(2))*\text{c}(\text{nxsftp}+1,1,1)+1; \\
\text{cc}(\text{nxsftp}+1, \text{nxsftp}+2) &= (\text{Deff}(2)*\text{kd}(2)*\text{densityp}(2)/\text{a}(2))*\text{c}(\text{nxsftp}+1,1,2); \\
\end{align*}
\]
\% last row of stiffness matrix
\[
\begin{align*}
\text{cc}(\text{n},\text{n}-1) &= \text{c}(\text{n}-1, 2, 1); \\
\text{cc}(\text{n},\text{n}) &= \text{c}(\text{n}-1, 2, 2); \\
\end{align*}
\]
\% kk overall stiffness matrix
\[
\begin{align*}
\text{kk} &= \text{zeros}(n); \\
\text{kk}(1,1) &= \text{k}(1, 1, 1); \\
\end{align*}
\]
\( \text{kk}(1,2) = k(1, 1, 2); \)
for \( i=2:n-1 \)
  \( \text{kk}(i, i-1) = k(i-1,2,1); \)
  \( \text{kk}(i,i) = k(i-1,2,2) + k(i,1,1); \)
  \( \text{kk}(i, i+1) = k(i,1,2); \)
end
\( \text{kk}(nxsftp+1, nxsftp) = \left( \frac{\text{Deff}(1)}{a(1)} \right) k(nxsftp,2,1); \)
\( \text{kk}(nxsftp+1, nxsftp+1) = \left( \frac{\text{Deff}(1)}{a(1)} \right) k(nxsftp,2,2) + \)
\( \left( \frac{\text{Deff}(2) \cdot \text{kd}(2) \cdot \text{densityp}(2)}{a(2)} \right) k(nxsftp+1,1,1); \)
\( \text{kk}(nxsftp+1, nxsftp+2) = \left( \frac{\text{Deff}(2) \cdot \text{kd}(2) \cdot \text{densityp}(2)}{a(2)} \right) k(nxsftp+1,1,2); \)
\( \text{kk}(n,n-1) = k(n-1, 2, 1); \)
\( \text{kk}(n,n) = k(n-1, 2, 2); \)

5. File name: cckkAging.m

function \([\text{cc}, \text{kk}] = \text{cckkAging}(n, nxsftp, \text{Deff}, \text{ap}, c, k, \text{kd}, \text{densityp})\)

\( \text{cc} = \text{zeros}(n); \)
\( \text{cc}(1,1) = c(1, 1, 1); \)
\( \text{cc}(1,2) = c(1, 1, 2); \)
for \( i=2:n-1 \)
  \( \text{cc}(i, i-1) = c(i-1,2,1); \)
  \( \text{cc}(i,i) = c(i-1,2,2) + c(i,1,1); \)
  \( \text{cc}(i, i+1) = c(i,1,2); \)
end
% (nxsftp+1)th row of stiffness matrix
\( \text{cc}(nxsftp+1, nxsftp) = \left( \frac{\text{Deff}(1)}{\text{ap}(1)} \right) c(nxsftp,2,1); \)
\( \text{cc}(nxsftp+1, nxsftp+1) = \left( \frac{\text{Deff}(1)}{\text{ap}(1)} \right) c(nxsftp,2,2) + \)
\( \left( \frac{\text{Deff}(2) \cdot \text{kd}(2) \cdot \text{densityp}(2)}{\text{ap}(2)} \right) c(nxsftp+1,1,1) + 1; \)
\( \text{cc}(nxsftp+1, nxsftp+2) = \left( \frac{\text{Deff}(2) \cdot \text{kd}(2) \cdot \text{densityp}(2)}{\text{ap}(2)} \right) c(nxsftp+1,1,2); \%
% last row of stiffness matrix
\( \text{cc}(n,n-1) = c(n-1, 2, 1); \)
\( \text{cc}(n,n) = c(n-1, 2, 2); \)

% kk overall stiffness matrix
\( \text{kk} = \text{zeros}(n); \)
\( \text{kk}(1,1) = k(1, 1, 1); \)
\( \text{kk}(1,2) = k(1, 1, 2); \)
for \( i=2:n-1 \)
  \( \text{kk}(i, i-1) = k(i-1,2,1); \)
  \( \text{kk}(i,i) = k(i-1,2,2) + k(i,1,1); \)
  \( \text{kk}(i, i+1) = k(i,1,2); \)
end
\[
\begin{align*}
kk(nxsftp+1, nxsftp) &= \left( \frac{Deff(1)}{ap(1)} \right) k(nxsftp, 2, 1); \\
kk(nxsftp+1, nxsftp+1) &= \left( \frac{Deff(1)}{ap(1)} \right) k(nxsftp, 2, 2) + \\
&\quad \left( \frac{Deff(2)}{ap(2)} \right) \left( \frac{kd(2) \cdot \text{densityp}(2)}{ap(2)} \right) k(nxsftp+1, 1, 1); \\
kk(nxsftp+1, nxsftp+2) &= \left( \frac{Deff(2)}{ap(2)} \right) \left( \frac{kd(2) \cdot \text{densityp}(2)}{ap(2)} \right) k(nxsftp+1, 1, 2); \\
kk(n, n-1) &= k(n-1, 2, 1); \\
kk(n, n) &= k(n-1, 2, 2);
\end{align*}
\]

6. File name: plotAdsResult.m

function []=plotAdsResult(aa,np,nxSftp, x, delXsftp,delXhdp, Lsftp, Lhdp, ntp,delT, Kd, omp, Toc)

%plot results at the end of sorption process

nxsft2= 300;
nxhd2= 300;
dXsft2=Lsftp/nxsft2;
dXhd2 = Lhdp/nxhd2;

n2 = nxsft2+nxhd2 +2;
Cnum = zeros(ntp+2, n2);  % c
Fnum = zeros(ntp+2, n2);  % flux

for k=2:n2
    % the first row of each array is x value
    if (k<nxsft2+3)
        Cnum(1, k)= dXsft2*(k-2);
        Fnum(1, k)= Cnum(1, k);
        i= floor(dXsft2*(k-2)/delXsftp) +1;
    elseif (k<n2)
        Cnum(1, k)= Cnum(1, nxsft2+2)+ dXhd2*(k-2-nxsft2);
        Fnum(1, k)= Cnum(1, k);
        i= nxSftp + floor(dXhd2*(k-2-nxsft2)/delXhdp) +1;
    else
        Cnum(1, k)= Cnum(1, nxsft2+2)+ dXhd2*(k-2-nxsft2);
        Fnum(1, k)= Cnum(1, k);
        i= np-1;
    end

for m=2:ntp+2
    % the first column of each array is time value
    Cnum(m,1)= delT*(m-2);
    Fnum(m,1)= delT*(m-2);
end

if (i<nxSftp+1)
Cnum(m,k) = aa(m-1,i)* (x(i+1, 1) - Cnum(1,k))/delXsftp + aa(m-1,i+1)*
(Cnum(1,k) - x(i, 1))/delXsftp;
Fnum(m,k) = (aa(m-1,i) - aa(m-1,i+1))/delXsftp;
else
Cnum(m,k) = aa(m-1,i)* (x(i+1, 1) - Cnum(1,k))/delXhdp + aa(m-1,i+1)*
(Cnum(1,k) - x(i, 1))/delXhdp;
Fnum(m,k) = (aa(m-1,i) - aa(m-1,i+1))/delXhdp;
end
end
end

tPlot = Cnum(:,1)/(24*3600); % in days

mark = zeros(2, 2);
mark(1, 1) = Lsftp;
mark(1, 2) = Lsftp;
mark(2,1)  = 0;
mark(2,2)  = 1.2;

% plot results for C
figure(10); clf;
plot(Cnum(1, 2:n2)*10^6, Cnum(2:ntp+2, 2:n2),'-', mark(1, :)*10^6, mark(2, :), '--r');
xlabel('x, um (left part for amorphous, right part for condensed phase)');
ylabel('Porewater conc., Cw^A or Cw^C, mg/L');
YLim([0 1.2]);
title('Sorption: porewater conc. profile');
saveas(gcf, 'run\runFig\AdsCpwX', 'fig');
saveas(gcf, 'run\runBmp\AdsCpwX', 'bmp');

Ldg= zeros(ntp+2, 1);
for i=2:ntp+2
    Ldg(i,1) = Kd(1)*(0.5*(Cnum(i, 2)+Cnum(i, nxsft2+2)) + sum(Cnum(i, nxsft2+3:n2+1)))*(dxsft/Lsftp)*omp(1)+...
             Kd(2)*(0.5*(Cnum(i, nxslt2+2)+Cnum(i, n2))+sum(Cnum(i, nxslt2+4:n2-1)))*(dxhdp/Lhdp)*omp(2);
end
figure(11); clf;
plot(tPlot(2:ntp+2), Ldg(2:ntp+2, 1)/Toc,'-');
xlabel('Sorption time, day');  ylabel('Sediment loading, mg/(Kg OC)');
title('Sorption: loading vs time');
saveas(gcf, 'run\runFig\AdsCsT', 'fig');
saveas(gcf, 'run\runBmp\AdsCsT', 'bmp');
7. File name: plotDesResult.m

%plot desorption results
function []=plotDesResult(aa, np, nxSftp, x, delXsftp, delXhdp, Lsftp, Lhdp, nt, tArray, Kd, omp, Toc)

nxsft2= 300;
nxhd2= 300;
dXsft2=Lsftp/nxsft2;
dXhd2 = Lhdp/nxhd2;

n2 = nxsft2+nxhd2 +2;
Cnum = zeros(nt+2, n2); % c
Fnum = zeros(nt+2, n2); % flux

for k=2:n2
    % the first row of each array is x value
    if (k<nxsft2+3)
        Cnum(1, k)= dXsft2*(k-2);
        Fnum(1, k)= Cnum(1, k);
        i= floor(dXsft2*(k-2)/delXsftp) +1;
    else if (k<n2)
        Cnum(1, k)= Cnum(1, nxsft2+2)+ dXhd2*(k-2-nxsft2);
        Fnum(1, k)= Cnum(1, k);
        i= nxSftp + floor(dXhd2*(k-2-nxsft2)/delXhdp) +1;
    else
        Cnum(1, k)= Cnum(1, nxsft2+2)+ dXhd2*(k-2-nxsft2);
        Fnum(1, k)= Cnum(1, k);
        i= np-1;
    end

    for m=2:nt+2
        % the first column of each array is time value
        Cnum(m,1)= tArray(m-1, 1);
        Fnum(m,1)= tArray(m-1, 1);
        % numerical solution for U and flux
        if (i<nxSftp+1)
            Cnum(m,k)= aa(m-1,i)* (x(i+1, 1)- Cnum(1,k))/delXsftp + aa(m-1,i+1)*
                        (Cnum(1,k)- x(i, 1))/delXsftp;
            Fnum(m,k) = (aa(m-1,i)-aa(m-1,i+1))/delXsftp;
        else
            Cnum(m,k)= aa(m-1,i)* (x(i+1, 1)- Cnum(1,k))/delXhdp + aa(m-1,i+1)*
                        (Cnum(1,k)- x(i, 1))/delXhdp;
            Fnum(m,k) = (aa(m-1,i)-aa(m-1,i+1))/delXhdp;
        end
    end

end
end
end
end
tPlot = Cnum(:,1)/(24*3600);  % in days

% plot results for C
figure(20); clf;
plot(Cnum(1, 2:n2), Cnum(2:nt+2, 2:n2),'-');
xlabel('x');  ylabel('pw conc. ');
grid on;
title('Desorption: solid porewater conc. profile');
saveas(gcf, 'run\runJpg\DesCpwX', 'fig');
saveas(gcf, 'run\runFig\DesCpwX', 'bmp');

Ldg= zeros(nt+2, 1);
for i=2:nt+2
    Ldg(i,1) = Kd(1)*(0.5*(Cnum(i, 2)+Cnum(i, nxsft2+2)) + sum(Cnum(i, 3:nxsft2+1)))*(dXsft2/Lsftp)*omp(1)+...
        Kd(2)*(0.5*(Cnum(i, nxsft2+3)+Cnum(i, n2))+sum(Cnum(i, nxsft2+4:n2-1)))*(dXhd2/Lhdp)*omp(2);
end

figure(21); clf;
plot(tPlot(2:nt+2,1), Ldg(2:nt+2, 1),'-');
XLim([0 50]);
xlabel('t, day');  ylabel('loading, mg/kg');
grid on;
title('Desorption: loading vs time');
saveas(gcf, 'run\runJpg\DesCsT', 'bmp');
saveas(gcf, 'run\runFig\DesCsT', 'fig');

8. File name: plotAgeResult.m

%plot results at the end of aging process
function []=plotAgeResult(aa, np, nxSftp, x, delXsftp, delXhdp, Lsftp, Lhdp, nt, delT, Kd, omp, Toc)

nxsft2= 300;
nxhd2= 300;
dXsft2=Lsftp/nxsft2;
dXhd2 = Lhdp/nxhd2;
\( n2 = nxslt2 + nxhd2 + 2; \)
\( Cnum = zeros(nt+2, n2); \quad \% c \)
for \( k = 2:n2 \)
    \% the first row of each array is \( x \) value
    if \((k < nxslt2 + 3)\)
        \( Cnum(1, k) = dXslt2 \times (k-2); \)
        \( i =.floor(dXslt2 \times (k-2)/delXslt) + 1; \)
    elseif \((k < n2)\)
        \( Cnum(1, k) = Cnum(1, nxslt2 + 2) + dXhd2 \times (k-2-nxslt2); \)
        \( i = nxSftp + floor(dXhd2 \times (k-2-nxslt2)/delXhdp) + 1; \)
    else
        \( Cnum(1, k) = Cnum(1, nxslt2 + 2) + dXhd2 \times (k-2-nxslt2); \)
        \( i = np-1; \)
    end
for \( m = 2:nt+2 \)
    \% the first column of each array is time value
    \( Cnum(m,1) = delT \times (m-2); \)
\% numerical solution for \( c \)
    if \((i < nxSftp + 1)\)
        \( Cnum(m,k) = aa(m-1,i) \times (x(i+1, 1) - Cnum(1,k))/\text{delXslt} + aa(m-1,i+1)\times(Cnum(1,k) - x(i, 1))/\text{delXslt}; \)
    else
        \( Cnum(m,k) = aa(m-1,i) \times (x(i+1, 1) - Cnum(1,k))/\text{delXhdp} + aa(m-1,i+1)\times(Cnum(1,k) - x(i, 1))/\text{delXhdp}; \)
    end
end
tPlot = Cnum(:,1) / (24*3600); \quad \% in days
Ldg = zeros(nt+2, 1);
for \( i = 2:nt+2 \)
    \( Ldg(i,1) = Kd(1) \times (0.5 \times (Cnum(i, 2) + Cnum(i, nxslt2+2)) + \text{sum(Cnum(i, 3:nxslt2+1)))} \times (dXslt2/\text{Lsftp}) \times \text{omp(1)} + \ldots \)
    \( Kd(2) \times (0.5 \times (Cnum(i, nxslt2+3) + Cnum(i, n2)) + \text{sum(Cnum(i, nxslt2+4:n2-1)))} \times (dXhd2/\text{Lhdp}) \times \text{omp(2)}; \)
end
mark = zeros(2, 2);
mark(1, 1) = Lsftp;
mark(1, 2) = Lsftp;
mark(2, 1) = 0;
mark(2, 2) = 1.2;
% plot results for C
figure(22); clf;
plot(Cnum(1, 2:n2)*10^6, Cnum(2:nt+2, 2:n2),'-', mark(1, :)*10^6, mark(2, :), '--r');
xlabel('x, mum (left part for amorphous, right part for condensed phase)');
ylabel('Porewater conc. Cw^A or Cw^C, mg/L');
YLim([0 1.2]);
title('Aging: porewater conc. profile');
saveas(gcf, 'run\runFig\AgeCpwX', 'fig');
saveas(gcf, 'run\runBmp\AgeCpwX', 'bmp');

figure(23); clf;
plot(tPlot(2:nt+2,1), Ldg(2:nt+2, 1)/Toc,'-');
YLim([Ldg(2,1)*0.9/Toc Ldg(2,1)*1.1/Toc]);
xlabel('Aging time, day');  ylabel('loading, mg/(kg OC)');
title('Aging: loading vs time');
saveas(gcf, 'run\runFig\AgeCsT', 'fig');
saveas(gcf, 'run\runBmp\AgeCsT', 'bmp');

9. File name: plotAgeDesResult.m

%plot results for desorption process before and after aging
function []=plotAgeDesResult(aa, aa2, np, nxSftp, x, delXsftp, delXhdp, Lsftp, Lhdp, nt, tArray, Kd, omp, Toc)

nxsft2= 300;
nxhd2= 300;
dXsft2=Lsftp/nxsft2;
dXhd2 = Lhdp/nxhd2;

n2 = nxsft2+nxhd2 +2;
Cnum = zeros(nt+2, n2);  % c before aging
C2 = zeros(nt+2, n2);  % C after aging

for k=2:n2
    % the first row of each array is x value
    if (k<nxsft2+3)
        Cnum(1, k)= dXsft2*(k-2);
        C2(1, k)= Cnum(1, k);
        i= floor(dXsft2*(k-2)/delXsftp) +1;
    elseif (k<n2)
        Cnum(1, k)= Cnum(1, nxsft2+2)+ dXhd2*(k-2-nxsft2);
        C2(1, k)= Cnum(1, k);
    end

end
\[ i = \text{nxsftp} + \text{floor}(dXhd2*(k-2-nxsft2)/delXhdp) + 1; \]

\text{else}  
\[ \text{Cnum}(1,k) = \text{Cnum}(1,\text{nxsft2+2}) + dXhd2*(k-2-nxsft2); \]
\[ \text{C2}(1,k) = \text{Cnum}(1,k); \]
\[ i = \text{np-1}; \]
\text{end} 

\text{for } m=2:nt+2  
\text{% the first column of each array is time value}  
\[ \text{Cnum}(m,1) = tArray(m-1,1); \]
\[ \text{C2}(m,1) = tArray(m-1,1); \]
\text{% numerical solution for } c  
\text{if (i<nxsftp+1)}  
\[ \text{Cnum}(m,k) = \text{aa}(m-1,i) \times (x(i+1,1) - \text{Cnum}(1,k))/\text{delXsftp} + \text{aa}(m-1,i+1) \times (\text{Cnum}(1,k) - x(i,1))/\text{delXsftp}; \]
\[ \text{C2}(m,k) = \text{aa2}(m-1,i) \times (x(i+1,1) - \text{C2}(1,k))/\text{delXsftp} + \text{aa2}(m-1,i+1) \times (\text{C2}(1,k) - x(i,1))/\text{delXsftp}; \]
\text{else}  
\[ \text{Cnum}(m,k) = \text{aa}(m-1,i) \times (x(i+1,1) - \text{Cnum}(1,k))/\text{delXhdp} + \text{aa}(m-1,i+1) \times (\text{Cnum}(1,k) - x(i,1))/\text{delXhdp}; \]
\[ \text{C2}(m,k) = \text{aa2}(m-1,i) \times (x(i+1,1) - \text{C2}(1,k))/\text{delXhdp} + \text{aa2}(m-1,i+1) \times (\text{C2}(1,k) - x(i,1))/\text{delXhdp}; \]
\text{end}  
\text{end}  
\text{end}  
\text{tPlot} = \text{Cnum}(:,1)/(24*3600); \text{ % in days} 

\text{mark} = \text{zeros}(2,2); 
\text{mark}(1,1) = \text{Lsftp}; 
\text{mark}(1,2) = \text{Lsftp}; 
\text{mark}(2,1) = 0; 
\text{mark}(2,2) = 1.2; 
\text{Ldg} = \text{zeros}(nt+2,1); 
\text{for i=2:nt+2}  
\text{Ldg}(i,1) = \text{Kd}(1) \times (0.5 \times (\text{Cnum}(i,2)+\text{Cnum}(i,\text{nxsft2+2})) + \text{sum}(\text{Cnum}(i,3:\text{nxsft2+1}))) \times (dXsft2/\text{Lsftp}) \times \text{omp}(1)+... 
\text{Kd}(2) \times (0.5 \times (\text{Cnum}(i,\text{nxsft2+3})+\text{Cnum}(i,\text{n2})) + \text{sum}(\text{Cnum}(i,\text{nxsft2+4:n2-1}))) \times (dXhd2/\text{Lhdp}) \times \text{omp}(2); 
\text{Ldg2}(i,1) = \text{Kd}(1) \times (0.5 \times (\text{C2}(i,2)+\text{C2}(i,\text{nxsft2+2})) + \text{sum}(\text{C2}(i,3:\text{nxsft2+1}))) \times (dXsft2/\text{Lsftp}) \times \text{omp}(1)+...
Kd(2)*(0.5*(C2(i, nxsft2+3)+C2(i, n2))+sum(C2(i, nxsft2+4:n2-1)))*(dXhd2/Lhdp)*omp(2);
end

desFr = [0 100; 0.875 14.52; 7 3.45; 14 2.67; 30 2.45];
desAg = [0 100; 0.875 13.0; 7 6.76; 18 6.15];

figure(29); clf;
plot( desFr(:, 1), desFr(:, 2), 'd', desAg(:, 1), desAg(:, 2), 'o', ...
    tPlot(2:nt+2,1), 100*Ldg(2:nt+2, 1)/Ldg(2,1),'--', ...
    tPlot(2:nt+2,1), 100*Ldg2(2:nt+2, 1)/Ldg2(2,1),'-');
XLim([0 50]);
YLim([0 100]);
xlabel('Desorption time, day'); ylabel('Percentage remaining in sediment');
legend('Fresh, Exp', 'Aged, Exp','Fresh, model', 'Aged, model', 1);
title('Desorption kinetics before and after aging');
saveas(gcf, 'run\runFig\ageDesKinet2', 'fig');
saveas(gcf, 'run\runBmp\ageDesKinet2', 'bmp');

10. File name: plotKoc.m

%plot Koc estimation
function []=plotKoc(aa, aa60, aaAge, np,nxSftp, x, delXsftp, delXhdp, Lsftp,Lhdp, nt,
delT, delT60, Kd, omp, Toc, ntDes, tArray)
nxsft2= 300;
nxhd2= 300;
dXsft2=Lsftp/nxsft2;
dXhd2 = Lhdp/nxhd2;
n2 = nxsft2+nxhd2 +2;

Cnum = zeros(nt+2, n2);  % C
Loading= zeros(ntDes+1,nt+2);
Cwe = zeros(ntDes+1, 1);
Cnum60 = zeros(nt+2, n2);  % C
Loading60= zeros(ntDes+1,nt+2);
Cwe60 = zeros(ntDes+1, 1);

CnumAge = zeros(nt+2, n2);  % C
LoadingAge= zeros(ntDes+1,nt+2);
CweAge = zeros(ntDes+1, 1);

adsCal = [0.00001 0.00001*Toc*10^4.4; 1 1*Toc*10^4.4];
% experimental data
KocExp10 = [0.0021203.37 4.99; ... 0.0031257.14 4.92; ... 0.0109673.78 4.79; ... 0.0169875.60 4.72; ... 0.01911155.16 4.78; ... 0.02581370.24 4.73; ... 0.04461895.00 4.63; ... 0.06432478.16 4.59; ... 0.09603107.99 4.51; ... 0.726921597.87 4.47];

KocExp60 = [0.0032200.9 4.79; ... 0.00459 252.0 4.74; ... 0.01584659.4 4.62; ... 0.02617 1146.9 4.64; ... 0.05842 1865.5 4.50; ... 0.11883 3050.6 4.41; ... 0.84100 21359.5 4.40];

KocExp10Age = [0.00162289.2 5.25; ... 0.00279555.9 5.30; ... 0.070632451.2 4.54; ... 0.8194425514.1 4.49];

flag = 0;
for it= 1:ntDes+1
for k=2:n2
  % the first row of each array is x value
  if (k<nxsft2+3)
    Cnum(1, k)= dXsft2*(k-2);
    Cnum60(1,k) = Cnum(1, k);
    CnumAge(1,k) = Cnum(1, k);
    i= floor(dXsft2*(k-2)/delXsftp) +1;
  elseif (k<n2)
    Cnum(1, k)= Cnum(1, nxsft2+2)+ dXhd2*(k-2-nxsft2);
    Cnum60(1,k) = Cnum(1, k);
    CnumAge(1,k) = Cnum(1, k);
    i= nXsftp + floor(dXhd2*(k-2-nxsft2)/delXhdp) +1;
  else
    Cnum(1, k)= Cnum(1, nxsft2+2)+ dXhd2*(k-2-nxsft2);
    Cnum60(1,k) = Cnum(1, k);
  end
end

CnumAge(1,k) = Cnum(1, k);
i = np-1;
end

for m=2:nt+2
  % the first column of each array is time value
  Cnum(m,1) = delT*(m-2);
  Cnum60(m,1) = delT60*(m-2);
  CnumAge(m,1) = delT*(m-2);
  % numerical solution for Concentration
  if (i<nxSftp+1)
    Cnum(m,k) = aa(it,m-1,i)*(x(i+1, 1)- Cnum(1,k))/delXsftp + aa(it, m-1,i+1)*( Cnum(1,k)-x(i, 1))/delXsftp;
    Cnum60(m,k) = aa60(it,m-1,i)*(x(i+1, 1)- Cnum60(1,k))/delXsftp + aa60(it,m-1,i+1)*( Cnum60(1,k)-x(i, 1))/delXsftp;
    CnumAge(m,k) = aaAge(it,m-1,i)*(x(i+1, 1)- CnumAge(1,k))/delXsftp + aaAge(it,m-1,i+1)*( CnumAge(1,k)-x(i, 1))/delXsftp;
  else
    Cnum(m,k) = aa(it,m-1,i)*(x(i+1, 1)- Cnum(1,k))/delXhdp + aa(it,m-1,i+1)*( Cnum(1,k)-x(i, 1))/delXhdp;
    Cnum60(m,k) = aa60(it,m-1,i)*(x(i+1, 1)- Cnum60(1,k))/delXsftp + aa60(it,m-1,i+1)*( Cnum60(1,k)-x(i, 1))/delXhdp;
    CnumAge(m,k) = aaAge(it,m-1,i)*(x(i+1, 1)- CnumAge(1,k))/delXsftp + aaAge(it,m-1,i+1)*( CnumAge(1,k)-x(i, 1))/delXhdp;
  end
end

end

tPlot = Cnum(:,1)/ (24*3600);  % in days
for i=2:nt+2
  Loading(it,i) = Kd(1)*(0.5*( Cnum(i, 2)+Cnum(i, nxSftp2+2)) + sum(Cnum(i, 3:nxSftp2+1)))*(dXsftp/Lsftp)*omp(1)+...    Kd(2)*(0.5*(Cnum(i, nxSftp2+3)+Cnum(i, n2))+sum(Cnum(i, nxSftp2+4:n2-1)))*(dXhd2/Lhdp)*omp(2);
  Loading60(it,i) = Kd(1)*(0.5*( Cnum60(i, 2)+Cnum60(i, nxSftp2+2)) + sum(Cnum60(i, 3:nxSftp2+1)))*(dXsftp/Lsftp)*omp(1)+...    Kd(2)*(0.5*(Cnum60(i, nxSftp2+3)+Cnum60(i, n2))+sum(Cnum60(i, nxSftp2+4:n2-1)))*(dXhd2/Lhdp)*omp(2);
  LoadingAge(it,i) = Kd(1)*(0.5*( CnumAge(i, 2)+CnumAge(i, nxSftp2+2)) + sum(CnumAge(i, 3:nxSftp2+1)))*(dXsftp/Lsftp)*omp(1)+...    Kd(2)*(0.5*(CnumAge(i, nxSftp2+3)+CnumAge(i, n2))+sum(CnumAge(i, nxSftp2+4:n2-1)))*(dXhd2/Lhdp)*omp(2);
end
Cwe(it, 1) = Cnum(nt+2, nxSftp2+2);
Cwe60(it, 1) = Cnum60(nt+2, nxsf2+2);  
CweAge(it, 1) = CnumAge(nt+2, nxsf2+2);
end
KocApp    = zeros(it, 1);
KocApp60  = zeros(it, 1);
KocAppAge = zeros(it, 1);

logKocApp    = zeros(it, 1);
logKocApp60  = zeros(it, 1);
logKocAppAge = zeros(it, 1);

for cnt = 1:ntDes+1
    KocApp(cnt, 1)    =    Loading(cnt, nt+2)/(Toc*   Cwe(cnt,1));
    KocApp60(cnt, 1)  =  Loading60(cnt, nt+2)/(Toc* Cwe60(cnt,1));
    KocAppAge(cnt, 1) = LoadingAge(cnt, nt+2)/(Toc*CweAge(cnt,1));
    logKocApp(cnt, 1)    = log10(   KocApp(cnt, 1));
    logKocApp60(cnt, 1)  = log10( KocApp60(cnt, 1));
    logKocAppAge(cnt, 1) = log10(KocAppAge(cnt, 1));
end

figure(51); clf;
loglog(  adsCal(:, 1),      adsCal(:, 2)/Toc, '--', ...
    KocExp10Age(:, 1), KocExp10Age(:, 2), 's', ...
    KocExp10(:, 1),    KocExp10(:, 2), 'o', ...
    KocExp60(:, 1),    KocExp60(:, 2), 'd', ...
    CweAge(:, 1), LoadingAge(:, nt+2)/Toc, 's', ...
    Cwe(:, 1), Loading(:, nt+2)/Toc, 'o', ...
    Cwe60(:, 1), Loading60(:, nt+2)/Toc, 'd');
XLim([10^-4 1]);
YLim([10 10^5]);
xlabel('Cw, mg/L');  ylabel('Loading, mg/(Kg OC)');
legend('adsorption', 'Exp, Aged, 10d', 'Exp, Fresh, 10d','Exp, Fresh, 60d','Model, Aged, 10d','Model, Fresh, 10d','Model, Fresh, 60d', 2);
title('Desorption isotherms');
saveas(gcf, 'run\runFig\KocCsCw3', 'fig');
saveas(gcf, 'run\runBmp\KocCsCw3', 'bmp');

figure(52); clf;
semilogx(KocExp10Age(:, 2), KocExp10Age(:, 3), 's', ...
    KocExp10(:, 2),    KocExp10(:, 3), 'o', ...
    KocExp60(:, 2),    KocExp60(:, 3), 'd', ...
    (LoadingAge(:,nt+2))/Toc, logKocAppAge(:,1), 's', ...
    (Loading(:,nt+2))/Toc,    logKocApp(:,1), 'o', ...
    (Loading60(:,nt+2))/Toc,  logKocApp60(:,1), 'd');
function [tDesArray, delTDesArray] = timeDes(tDes, ntDes)

% adaptive time steps for desorption

tDesArray = zeros(ntDes +1, 1);
delTDesArray = zeros(ntDes, 1);
t1=1;
t2=15;
if (tDes <= t1)
    delTDes = tDes*24*3600/ntDes;
    for i=2:ntDes+1
        tDesArray(i,1) = (i-1)*delTDes;
        delTDesArray(i-1, 1)= delTDes;
    end
elseif (tDes<=t2)
    delt1 = t1*24*3600/(ntDes/2);
    delt2 = (tDes-t1)*24*3600/(ntDes/2);
    for i=2:(ntDes/2)+1
        tDesArray(i,1) = (i-1)*delt1;
        delTDesArray(i-1, 1)= delt1;
    end
    for i= (ntDes/2)+2:ntDes+1
        tDesArray(i,1) = tDesArray((ntDes/2)+1, 1) + (i- ntDes/2-1)*delt2;
        delTDesArray(i-1, 1)= delt2;
    end
else
    delt1 = t1*24*3600/floor(ntDes/3);
end

11. File name: timeDes.m
delt2 = (t2-t1)*24*3600/floor(ntDes/3);
delt3 = (tDes-t2)*24*3600/ (ntDes - 2*floor(ntDes/3));
for i=2:(floor(ntDes/3)+1)
    tDesArray(i,1) = (i-1)*delt1;
    delTDesArray(i-1, 1)= delt1;
end
for i= (floor(ntDes/3)+2): (2*floor(ntDes/3)+1)
    tDesArray(i,1) = tDesArray(floor(ntDes/3)+1, 1) + (i- floor(ntDes/3)-1)*delt2;
    delTDesArray(i-1, 1)= delt2;
end
for i= (2*floor(ntDes/3)+2):ntDes+1
    tDesArray(i,1) = tDesArray(2*floor(ntDes/3)+1, 1) + (i- 2*floor(ntDes/3)-1)*delt3;
    delTDesArray(i-1, 1)= delt3;
end
end
APPENDIX D SAMPLE MATLAB PROGRAM FOR FIELD-CONTAMINATED SEDIMENTS

This section includes sample MatLab program used for modeling field-contaminated sediments. The following MatLab files are required to be placed in the same subdirectory on computer in order to run the program.

1. File name: phe.m

% main program
% Utica sediment
% Sorption for 50 years
% Aging for 1 year

echo off; clc; % clear the command window before run this program
close('all');

sedimentName = 'Utica Harbor Sediment';

tAds = 18250; % adsorption time, day, 50 years = 18250 days
tDes = 3000; % desorption time, day
tKoc = 10; % equilibration time for Koc estimation, day
tKoc60 = 60;
tAge = 365; % days, 50 years = 18250 days
ntAds = 100; % number of steps for adsorption time
ntDes = 70; % number of steps for desorption time
ntKoc = 30; % number of time steps for Koc estimation
ntAge = 10;

foc = 0.021;
D = 7.74*10^-10;
Dhd = 8.5*10^-20;
VSAratio = 20*10^-6; % m
CwInit = 0.007;
wsRatio = 70; %

% all these parameters below denote--1st: soft carbon, 2nd: hard carbon
%shMPcnt = [1-var(1) var(1)];
shocMpcnt = [0.61 0.39];
oc = [0.58 0.8];
density = [1.5 1.8]; % kg/L
lgKoc = [4.36 5.1];
porosity = 0.4;
Lsft = 2.0*10^-5; % half thickness of slab for soft carbon particles
nxSft = 40; % number of elements on x for soft carbon particles
nxHd = 40;

%write all basic parameters.
fid = fopen('run\paramOut.txt','w');
fprintf(fid,'Basic Parameters for %s:

', sedimentName);
fprintf(fid,'Lsft = %.4e;	 nxSft = %d;	 nxHd = %d
', Lsft, nxSft, nxHd);
fprintf(fid,'tAds = %d;	 ntAds = %d
', tAds, ntAds);
fprintf(fid,'tDes = %d;	 ntDes = %d
', tDes, ntDes);
fprintf(fid,'tKoc = %d;	 ntKoc = %d
', tKoc, ntKoc);
fprintf(fid,'tAge = %d;	 ntAge = %d
', tAge, ntAge);
fprintf(fid,'D = %.4e;	 Dhd = %.4e
', D, Dhd);
fprintf(fid, 'VSAratio = %.4e
', VSAratio);
fprintf(fid,'logKoc =	 [%.4f	 %.4f]
', lgKoc);
fprintf(fid,'OC =		 [%.4f	 %.4f]
', oc);
fprintf(fid,'Density =	 [%.4f	 %.4f]
', density);
fprintf(fid,'shMPcnt =	 [%.4f	 %.4f]
', shocMpct);
fprintf(fid,'porosity = %.4f

', porosity);
fprintf(fid,'CwInit = %.4f
', CwInit);
fprintf(fid,'wsRatio= %.4f
', wsRatio);
fprintf(fid,'foc =		 %.4f
', foc);
fclose(fid);

DeffSft = D * porosity^(4/3);

om = (foc .* shocMpct) ./ oc;
SOM = sum(om);
shomMpct = om ./ SOM;
wSOMmr = wsRatio/SOM; % overall mass ratio of water to total organic matter
wSftOMmr = wsRatio/om(1);
wHdOMmr = wsRatio/om(2);
wSftVolR = wSftOMmr * density(1);
wHdVolR = wHdOMmr * density(2);
Lhd = VSAratio;
Koc = 10.^lgKoc;
Kd = Koc .* oc;
Rfsft = porosity + density(1) * Kd(1);
DRf(1) = DeffSft / Rfsft;
Rfhd = density(2) * Kd(2);
DRf(2) = Dhd;
Rf = [Rfsft, Rfhd];
Deff = [DeffSft, Dhd];
a(1) = Lsft * wSftVolR;
\[ a(2) = L_{hd} \cdot w_{hdVolR}; \]
\[ f = 1 / DRf; \]
\[ n = nxSft + nxHd + 1; \]
\[ delXsft = L_{sft} / nxSft; \]
\[ delXhd = L_{hd} / nxHd; \]
\[ x = zeros(n, 1); \]
\[ \text{for } i=1:nxSft+1 \]
\[ x(i,1) = 0.0 + delXsft \cdot (i-1); \]
\[ \text{end} \]
\[ \text{for } i=nxSft+2:n \]
\[ x(i,1) = x(nxSft+1,1) + delXhd \cdot (i-nxSft-1); \]
\[ \text{end} \]

%***************************************************************%
%                          stiffness matrix for each element                %
%***************************************************************%
% C stiffness matrix for each element
\[ [c, k] = ckElem(n, nxSft, nxHd, x, delXsft, delXhd, f); \]
%***************************************************************%
%                          adsorption process below                          %
%***************************************************************%
\[ \text{delTAds} = t_{Ads} \cdot 24 \cdot 3600.0 / nt_{Ads}; \]
\[ \text{cc overall stiffness matrix} \]
\[ [cc, kk] = cckkAds(n, nxSft, c, k); \]
\[ ccAds = cc; \]
\[ kkAds = kk; \]
\[ ccDes = cc; \]
\[ kkDes = kk; \]
\[ \text{FF} = zeros(n-1, 1); \]
\[ \text{FF(nxSft,1)} = - C_{wInit} \cdot k(nxSft,1,2); \]
\[ \text{FF(nxSft+1,1)} = - C_{wInit} \cdot k(nxSft+1,2,1); \]
\[ \text{a (i,1) from a(2) to a(nx) at time t0} \]
\[ a2 = zeros(n-1, nt_{Ads}+1); \]
% solve for a(i, tn) at time tn
AA = cc + delTAds* kk;
for j=2:ntAds+1
    a2(:, j) = inv(AA) * (delTAds*FF + cc *a2(:, j-1));
end

a1= zeros(ntAds+1,n);
a1(:, 1:nxSft) = a2(1:nxSft, :)';
a1(:, nxSft+1) = CwInit;
a1(:, nxSft+2:n) = a2(nxSft+1:n-1, :)';
a1Ads = a1;

% display the results for adsorption process
plotAdsResult(a1,n,nxSft, x, delXsft, delXhd, Lsft, Lhd, ntAds,delTAds, Kd, om, foc);

%****************************************************************************%
% desorption process below %
%****************************************************************************%

%cc and kk are the same as the adsorption process
[tDesArray, delTDesArray]= timeDes(tDes, ntDes);

Fdes=zeros(n-1, 1);
a2des = zeros(n-1, ntDes+1);
a2des(:, 1) = a2(:, ntAds+1);

% solve for a(i, tn) at time tn
for j=2:ntDes+1
    a2des(:, j) = inv(cc + delTDesArray(j-1,1)* kk) * (delTDesArray(j-1, 1)*Fdes + cc *a2des(:, j-1));
end

a1des= zeros(ntDes+1,n);
a1des(:, 1:nxSft) = a2des(1:nxSft, :)';
a1des(:, nxSft+1) = 0;
a1des(:, nxSft+2:n) = a2des(nxSft+1:n-1, :)';

% display desorption results
plotDesResult(a1des, n,nxSft, x, delXsft, delXhd, Lsft, Lhd, ntDes, tDesArray, Kd, om, foc);

% delTKoc = tKoc*24*3600 / ntKoc;
[ccKoc, kkKoc] = cckkKoc(n, nxSft, Deff, a, c, k, Kd, density);
delTAge = tAge*24*3600 / ntAge;

wsmRaging = 0.67; 

wsOMmrAging = wsmRaging/SOM; % overall mass ratio of water to total organic matter 

wSftOMmrAging = wsmRaging/om(1); 

wHdOMmrAging = wsmRaging/om(2); 

wsftVolRaging = wSftOMmrAging * density(1); 

whdVolRaging = wHdOMmrAging * density(2); 

aAging(1) = Lsft * wsftVolRaging; 

aAging(2) = Lhd * whdVolRaging; 

[ccAge, kkAge] = cckkAging(n, nxSft, Deff, aAging, c, k, Kd, density); 

fAge= zeros(n, 1); 

a2Age = zeros(n, ntAge+1); 

a2Age(:, 1) = a1Ads(ntAds+1, :)'; 

% solve for a(i, tn) at time tn 

aaAge = ccAge + delTAge* kkAge; 

for j=2:ntAge+1 
    a2Age(:, j) = inv(aaAge) * (delTAge*fAge + ccAge*a2Age(:, j-1)); 
end 

a1Age= zeros(ntAge+1,n); 

a1Age = a2Age'; 

% display Age results 

plotAgeResult(a1Age, n, nxSft, x, delXsft, delXhd, Lsft, Lhd, ntAge, delTAge, Kd, om, foc) 

[tDesArray, delTDesArray] = timeDes(tDes, ntDes);
%cc and kk are the same as the adsorption process
ccAgeDes = ccDes;
kkAgeDes = kkDes;

fDes=zeros(n-1, 1);
a2AgeDes = zeros(n-1, ntDes+1);
a2AgeDes(1:nxSft, 1) = a2Age(1:nxSft, ntAge+1);
a2AgeDes(nxSft+1: n-1, 1) = a2Age(nxSft+2:n, ntAge+1);

% solve for a(i, tn) at time tn
for j=2:ntDes+1
    a2AgeDes(:, j) = inv(ccAgeDes + delTDesArray(j-1, 1)* kkAgeDes) * (delTDesArray(j-1, 1)*fDes + ccAgeDes *a2AgeDes(:, j-1));
end

a1AgeDes= zeros(ntDes+1,n);
a1AgeDes(:, 1:nxSft) = a2AgeDes(1:nxSft, :)';
a1AgeDes(:, nxSft+1) = 0;
a1AgeDes(:, nxSft+2:n) = a2AgeDes(nxSft+1:n-1, :)';

% display desorption results
j20hr = plotAgeDesResult(a1des, a1AgeDes, n, nxSft, x, delXsft, delXhd, Lsft, Lhd, ntDes, tDesArray, Kd, om, foc);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%                                                                           
%            Koc estimation process after aging                             
%                                                                           
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

delTKoc = tKoc*24*3600 / ntKoc;
% overall cc and kk stiffness matrice are the same as Koc estimation
ccAgeKoc = ccKoc;
kkAgeKoc = kkKoc;

aaAgeKoc = ccAgeKoc + delTKoc* kkAgeKoc;
% a (i,1) from a(2) to a(nx) at time t0
a2AgeKoc = zeros(ntDes+1, n, ntKoc+1);
% solve for a(i, tn) at time tn
for i=1:ntDes+1
    temp2= zeros(n, ntKoc+1);
    for cnt=1:n
        a2AgeKoc(i, cnt, 1) = a1AgeDes(i, cnt);
        temp2(cnt, 1) = a2AgeKoc(i, cnt, 1);
    end
end
for j=2:ntKoc+1
    temp2(:, j) = inv(aaAgeKoc) * ccAgeKoc * temp2(:, j-1);
end
a2AgeKoc(i, :, :) = temp2(:, :);
end

a1AgeKoc = zeros(ntDes+1,ntKoc+1, n);
for i=1:ntDes+1
    for j=1:ntKoc+1
        for cnt=1:n
            a1AgeKoc(i, j, cnt) = a2AgeKoc(i, cnt, j);
        end
    end
end

plotKoc(a1AgeKoc, n, nxSft, x, delXsft, delXhd, Lsft, Lhd, ntKoc, delTKoc, Kd, om, foc, ntDes, j20hr, tDesArray);
open('run\paramOut.txt');

2. File name: timeDes.m

% time array for desorption process
function [tDesArray, delTDesArray] = timeDes(tDes, ntDes)

% adaptive time steps for desorption
tDesArray = zeros(ntDes+1, 1);
delTDesArray = zeros(ntDes, 1);
t1=1; t2=50;

if (tDes <= t1)
    delTDes = tDes*24*3600/ntDes;
    for i=2:ntDes+1
        tDesArray(i,1) = (i-1)*delTDes;
        delTDesArray(i-1, 1)= delTDes;
    end
elseif (tDes<=t2)
    delt1 = t1*24*3600/(ntDes/2);
    delt2 = (tDes-t1)*24*3600/(ntDes/2);
    for i=2:(ntDes/2)+1
        tDesArray(i,1) = (i-1)*delt1;
        delTDesArray(i-1, 1)= delt1;
    end
    for i= (ntDes/2)+2:ntDes+1

tDesArray(i,1) = tDesArray((ntDes/2)+1, 1) + (i- ntDes/2-1)*delt2;
  delTDesArray(i-1, 1)= delt2;
end
else
  delt1 = t1*24*3600/\text{floor}(ntDes/3);
  delt2 = (t2-t1)*24*3600/\text{floor}(ntDes/3);
  delt3 = (tDes-t2)*24*3600/ (ntDes - 2*\text{floor}(ntDes/3));
  for i=2:(\text{floor}(ntDes/3)+1)
    tDesArray(i,1) = (i-1)*delt1;
    delTDesArray(i-1, 1)= delt1;
  end
  for i= (\text{floor}(ntDes/3)+2):(2*\text{floor}(ntDes/3)+1)
    tDesArray(i,1) = tDesArray(floor(ntDes/3)+1, 1) + (i- \text{floor}(ntDes/3)-1)*delt2;
    delTDesArray(i-1, 1)= delt2;
  end
  for i= (2*\text{floor}(ntDes/3)+2):ntDes+1
    tDesArray(i,1) = tDesArray(2*\text{floor}(ntDes/3)+1, 1) + (i- 2*\text{floor}(ntDes/3)-1)*delt3;
    delTDesArray(i-1, 1)= delt3;
  end
end

3. \textbf{File name: plotKoc.m}

function [ ]=plotKoc(aaAge, np,nxSftp, x, delXsftp, delXhdp, Lsftp,Lhdp, nt, delT, Kd, omp, Toc, ntDes, cnt20hr, tArray)

nxsft2= 55;
 nxhd2= 55;
 dXsft2=Lsftp/nxsft2;
 dXhd2 = Lhdp/nxhd2;
 n2 = nxsft2+nxhd2 +2;

Cnum = zeros(nt+2, n2);  \% C
CnumAge = zeros(nt+2, n2);  \% C
LoadingAge= zeros(ntDes+1,nt+2);
CweAge = zeros(ntDes+1, 1);

adsCal = [0.00019 0.1; 0.019 10];

KocExp10Age = [0.002485 5.1 4.99; 0.005137 6.5 4.78];

flag = 0;
for it= 1:ntDes+1

164
for k=2:n2
    % the first row of each array is x value
    if (k<nxsft2+3)
        Cnum(1,k) = dXsft2*(k-2);
        CnumAge(1,k) = Cnum(1,k);
        i = floor(dXsft2*(k-2)/delXsftp) + 1;
    elseif (k<n2)
        Cnum(1,k) = Cnum(1,nxsft2+2)+ dXhd2*(k-2-nxsft2);
        CnumAge(1,k) = Cnum(1,k);
        i = nxSftp + floor(dXhd2*(k-2-nxsft2)/delXhdp) + 1;
    else
        Cnum(1,k) = Cnum(1,nxsft2+2)+ dXhd2*(k-2-nxsft2);
        CnumAge(1,k) = Cnum(1,k);
        i = np-1;
    end

for m=2:nt+2
    % the first column of each array is time value
    CnumAge(m,1) = delT*(m-2);
    % numerical solution for c
    if (i<nxSftp+1)
        CnumAge(m,k) = aaAge(it,m-1,i) * (x(i+1,1) - CnumAge(1,k))/delXsftp +
                      aaAge(it,m-1,i+1) * (CnumAge(1,k) - x(i,1))/delXsftp;
    else
        CnumAge(m,k) = aaAge(it,m-1,i) * (x(i+1,1) - CnumAge(1,k))/delXhdp +
                      aaAge(it,m-1,i+1) * (CnumAge(1,k) - x(i,1))/delXhdp;
    end
end

end

tPlot = Cnum(:,1)/(24*3600);    % in days

for i=2:nt+2
    LoadingAge(it,i) = Kd(1)*(0.5*(CnumAge(i,2)+CnumAge(i,nxsft2+2)) +
                              sum(CnumAge(i,3:nxsft2+1)))*(dXsft2/Lsftp)*omp(1)+...
                              Kd(2)*(0.5*(CnumAge(i,nxsft2+3)+CnumAge(i,n2))+sum(CnumAge(i,
                              nxsft2+4:n2-1)))*(dXhd2/Lhdp)*omp(2);
end

CweAge(it,1) = CnumAge(nt+2,nxsft2+2);

end
KocAppAge = zeros(it, 1);
logKocAppAge = zeros(it, 1);

for cnt = 1:ntDes+1
    KocAppAge(cnt, 1) = LoadingAge(cnt, nt+2)/(Toc*CweAge(cnt,1));
    logKocAppAge(cnt, 1) = log10(KocAppAge(cnt, 1));
end

%pass the time counter to compute the equilibrium

Cs20hrEquilCalc1 = LoadingAge(cnt20hr, nt+2)+ (LoadingAge(cnt20hr+1, nt+2)-LoadingAge(cnt20hr, nt+2))*...
(t20hr-tArray(cnt20hr,1))/(tArray(cnt20hr+1,1)-tArray(cnt20hr,1));
Cw20hrEquilCalc1 = CweAge(cnt20hr,1)+ (CweAge(cnt20hr+1,1)-CweAge(cnt20hr,1))*...
(t20hr-tArray(cnt20hr,1))/(tArray(cnt20hr+1,1)-tArray(cnt20hr,1));
logKocApp20hrCalc1 = log10(Cs20hrEquilCalc1/Cw20hrEquilCalc1/Toc);

%compute the equilibrium accroding the real concentration

jj=1;
while (LoadingAge(jj,nt+2)>= KocExp10Age(2,2) & LoadingAge(jj+1,nt+2)>=KocExp10Age(2,2) & jj < ntDes)
    jj=jj+1;
end
CwEqCalc2 = CweAge(jj,1)+ (CweAge(jj+1,1)-CweAge(jj,1))*...
((KocExp10Age(2,2)-LoadingAge(jj,nt+2))/(LoadingAge(jj+1,nt+2)-LoadingAge(jj,nt+2)));

while (LoadingAge(jj,nt+2)>= KocExp10Age(1,2) & LoadingAge(jj+1,nt+2)>=KocExp10Age(1,2) & jj < ntDes)
    jj=jj+1;
end
Cw20hrEqCalc2 = CweAge(jj,1)+ (CweAge(jj+1,1)-CweAge(jj,1))*...
((KocExp10Age(1,2)-LoadingAge(jj,nt+2))/(LoadingAge(jj+1,nt+2)-LoadingAge(jj,nt+2)));

logKocAppCalc2 = log10(KocExp10Age(2,2)/CwEqCalc2/Toc);
logKocApp20hrCalc2 = log10(KocExp10Age(1,2)/Cw20hrEqCalc2/Toc);

%writing results.
fid = fopen('run\paramOut.txt','a');
fprintf(fid,'Equilibrium results:
');
fprintf(fid,'Cs = %d, Cw = %d
', KocExp10Age(2,2), CwEqCalc2);
fprintf(fid,'Cs20hr = %d, Cw20hr = %d
', KocExp10Age(1,2), Cw20hrEqCalc2);
fprintf(fid,'logKocAppCalc2 = %.3f, logKocApp20hrCalc2= %.3f\n',logKocAppCalc2, logKocApp20hrCalc2);
fprintf(fid,'From time counter, for 20 hrs:\n');
fprintf(fid,'Cs20hr = %d, Cw20hr = %d, Cs20hrEquilCalc1, Cw20hrEquilCalc1);
fprintf(fid,'logKocApp20hrCalc1= %.3f\n', logKocApp20hrCalc1);
close(fid);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
figure(51); clf;
loglog(adsCal(:, 1), adsCal(:, 2), '--',  ...  
    KocExp10Age(:,1), KocExp10Age(:, 2), 's',...
    CweAge(:, 1), LoadingAge(:, nt+2),'-');
XLim([10^-6 1]);
YLim([0.1 100]);
xlabel('Cw, ppm'); ylabel('Loading, ppm');
legend('adsorption', 'Koc 10d, Aged','calc, 10, Aged', 2);
%grid on;
title('Koc estimation: Loading vs Cw, after different desorption time');
saveas(gcf, 'run\runJpg\KocCsCw', 'bmp');
saveas(gcf, 'run\runFig\KocCsCw', 'fig');

figure(52); clf;
plot(KocExp10Age(:, 2), KocExp10Age(:, 3), 's', ...  
    LoadingAge(:,nt+2), logKocAppAge(:,1), '-');
xlabel('loading, ppm'); ylabel('logKocApp');
YLim([4 7]);
legend('Koc 10d, aged', 'calc, 10d aged', 1);
%grid on;
title('Koc estimation: LogKocApp vs Loading, after different desorption time');
saveas(gcf, 'run\runJpg\KocLogKocCs', 'bmp');
saveas(gcf, 'run\runFig\KocLogKocCs', 'fig');

4. File name: plotAgeDesResult.m

% fast desorbing fraction
function [cnt20hr]=plotAgeDesResult(aa, aa2, np, nxSftp, x, delXsftp, delXhdp, Lsftp, 
Lhdp, nt, tArray, Kd, omp, Toc)

nxSftp2= 300;
nxhd2= 300;
dXsftp2=Lsftp/nxSftp2;
dXhd2 = Lhdp/nxhd2;
n2 = nxsft2+nxhd2 +2;
Cnum = zeros(nt+2, n2); % c
C2 = zeros(nt+2, n2); % flux

for k=2:n2
% the first row of each array is x value
if (k<nxsft2+3)
Cnum(1, k)= dXsft2*(k-2);
C2(1, k)= Cnum(1, k);
i= floor(dXsft2*(k-2)/delXsftp) +1;
elseif (k<n2)
Cnum(1, k)= Cnum(1, nxsft2+2)+ dXhd2*(k-2-nxsft2);
C2(1, k)= Cnum(1, k);
i= nxSftp + floor(dXhd2*(k-2-nxsft2)/delXhdp) +1;
else
Cnum(1, k)= Cnum(1, nxsft2+2)+ dXhd2*(k-2-nxsft2);
C2(1, k)= Cnum(1, k);
i= np-1;
end

for m=2:nt+2
% the first column of each array is time value
Cnum(m,1)= tArray(m-1, 1);
C2(m,1)= tArray(m-1, 1);
% numerical solution for c
if (i<nxSftp+1)
Cnum(m,k)= aa(m-1,i)* (x(i+1, 1)- Cnum(1,k))/delXsftp + aa(m-1,i+1)*
(Cnum(1,k)- x(i, 1))/delXsftp;
C2(m,k)= aa2(m-1,i)* (x(i+1, 1)- C2(1,k))/delXsftp + aa2(m-1,i+1)* (C2(1,k)-
x(i, 1))/delXsftp;
else
Cnum(m,k)= aa(m-1,i)* (x(i+1, 1)- Cnum(1,k))/delXhdp + aa(m-1,i+1)*
(Cnum(1,k)- x(i, 1))/delXhdp;
C2(m,k)= aa2(m-1,i)* (x(i+1, 1)- C2(1,k))/delXhdp + aa2(m-1,i+1)* (C2(1,k)-
x(i, 1))/delXhdp;
end
end

tPlot = Cnum(:,1)/(24*3600); % in days

% plot results for C
figure(25); clf;
plot(Cnum(1, 2:n2), Cnum(2:nt+2, 2:n2),'-');
xlabel('x'); ylabel('pw conc.');
grid on;
title('Desorption: solid porewater conc.');
saveas(gcf, 'run\runJpg\DesCpwX', 'jpg');
saveas(gcf, 'run\runFig\DesCpwX', 'fig');

figure(26); clf;
plot(C2(1, 2:n2), C2(2:nt+2, 2:n2), '-');
xlabel('x'); ylabel('pw conc.);
grid on;
title('Desorption after aging: solid porewater conc.');
saveas(gcf, 'run\runJpg\ageDesCpwX', 'jpg');
saveas(gcf, 'run\runFig\ageDesCpwX', 'fig');

Ldg = zeros(nt+2, 1);
for i=2:nt+2
    Ldg(i, 1) = Kd(1)*(0.5*(Cnum(i, 2)+Cnum(i, nxsft2+2)) + sum(Cnum(i, 3:nxsft2+1)))*(dXsft2/Lsftp)*omp(1)+...
                 Kd(2)*(0.5*(Cnum(i, nxsft2+3)+Cnum(i, n2))+sum(Cnum(i, nxsft2+4:n2-1)))* (dXhd2/Lhdp)*omp(2);
    Ldg2(i, 1) = Kd(1)*(0.5*(C2(i, 2)+C2(i, nxsft2+2)) + sum(C2(i, 3:nxsft2+1)))*(dXsft2/Lsftp)*omp(1)+...
                 Kd(2)*(0.5*(C2(i, nxsft2+3)+C2(i, n2))+sum(C2(i, nxsft2+4:n2-1)))* (dXhd2/Lhdp)*omp(2);
end

figure(27); clf;
plot(tPlot(2:nt+2,1), Ldg(2:nt+2, 1), '-');
XLim([0 50]);
xlabel('t, day'); ylabel('loading, mg/kg');
grid on;
title('Desorption: loading vs time');
saveas(gcf, 'run\runJpg\DesCsT', 'bmp');
saveas(gcf, 'run\runFig\DesCsT', 'fig');

figure(28); clf;
plot(tPlot(2:nt+2,1), Ldg2(2:nt+2, 1), '-');
XLim([0 50]);
xlabel('t, day'); ylabel('loading, mg/kg');
grid on;
title('Desorption after aging: loading vs time');
saveas(gcf, 'run\runJpg\ageDesCsT', 'bmp');
saveas(gcf, 'run\runFig\ageDesCsT', 'fig');

t20hr = 3600*20;
j=1;
while (tArray(j,1)<= t20hr & tArray(j+1,1)<=t20hr & j < nt+1)
   j=j+1;
end
C20hrCalc = Ldg2(j+1,1)+ (Ldg2(j+2,1)-Ldg2(j+1,1))*(t20hr-
   tArray(j,1))/(tArray(j+1,1)-tArray(j,1));
fract = 100-100*C20hrCalc/Ldg2(2,1);
cnt20hr=j;

%writing results.
fid = fopen('run\paramOut.txt','a');
fprintf(fid,'Desorption results:
');
fprintf(fid,'fraction = %.3f
', fract);
fclose(fid);

The other Matlab files needed for field-contaminated sediments are the same as
those in the Appendix III:

5. ckElem.m
6. cckkAds.m
7. cckkKoc.m
8. cckkAging.m
9. plotAdsReult.m
10. plotAgeResult.m
VITA

Mr. Yunzhou Chai was born in the winter of 1975 in a tiny village of Cili, Hunan, P. R. China, a mountainous village in the vicinity of the fantastic Wulinyuan scenic region in Zhangjiajie, Hunan, which is one of the world heritages located in central southern China. He lived in the village until he finished middle school. He went to the Cili No. 1 High School which was located in the county of Cili, Hunan and spent three years there.

In the fall of 1993, he traveled to Xiamen, Fujian, for his higher education, which had been in his dream for many years. He graduated from Xiamen University in July 1997, with a bachelor’s degree in chemical engineering. He spent almost two years toward his master’s degree in Xiamen University before he actually got the degree.

In August 1999, he flew over the Pacific Ocean to attend the graduate program in chemical engineering at Louisiana State University, working toward a doctoral degree, which will be conferred in May 2005.