

**IMPACT OF SOIL ORGANIC MATTER HETEROGENEITY AND SOIL  
AGGREGATION ON THE SORPTION OF HERBICIDES BY SOILS**

By

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## **ABSTRACT OF THE DISSERTATION**

### **IMPACT OF SOIL ORGANIC MATTER HETEROGENEITY AND SOIL AGGREGATION ON THE SORPTION OF HERBICIDES BY SOILS**

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Experiments were performed in pursuit of understanding of interactions between herbicides and soils, focusing on the effects of heterogeneity within soil organic matter (SOM), and the aggregation of SOM with mineral matter in soils, on equilibrium sorption and sorption rates of herbicides. For this purpose, sorption of three herbicides – atrazine, metolachlor and napropamide – was studied on a bulk soil, a bulk peat and three fractions that were chemically isolated from it. Studies were also performed using the well studied polynuclear aromatic hydrocarbon (PAH) phenanthrene to provide a comparison for the herbicides. The sorbents extracted from the soil and peat – Base extracted fraction (BE), humic acids fraction (HA) and kerogen and black carbon fraction (KB) were characterized with elemental analysis, scanning electron microscopy and surface area measurements and subjected to sorption and desorption equilibrium studies and sorption rate investigations.

The herbicides were found to exhibit nonlinear sorption isotherms on all the sorbents; they exhibited least nonlinear isotherms and fastest sorption rates for HA

among all the sorbents. HA fraction also showed the least dependence of equilibrium or time dependent organic carbon normalized sorption capacity on initial aqueous solute concentration. This result was in accordance with the amorphous nature of the HA material and similar to that observed for PAHs. Herbicide atrazine was found to react with HA and was transformed to hydroxyatrazine in its presence. High sorption capacity of KB dominated the sorption for all the herbicides, with this capacity being diminished by the aggregation structure of the soil. Significant sorption hysteresis was not observed for the sorption of herbicides on the KB fraction, unlike that observed for phenanthrene, indicating large herbicide molecules do not penetrate nanopores of KB. Hysteresis observed for the bulk soil and BE for atrazine was attributed to chemical interactions between the sorbents and the herbicide. Overall this dissertation found that the herbicides exhibit hydrophobic interactions with soils, but owing to their large molecular sizes and polarities may exhibit site specific interactions and lack of hysteresis that call for changes in existing fate and transport models and further microscopic understanding.

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[All praise and thanks belongs to Allah, the Lord and Sustainer of all the worlds]

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## LIST OF SYMBOLS AND ABBREVIATIONS

$a, r$	Particle radius
ATZ	Atrazine
$b$	Langmuir surface affinity parameter
BC	Black carbon
BE	Base extracted
$C$	Aqueous phase concentration of the solute a radius $r$ inside a particle at time $t$
C	Carbon
$C_0$	Initial aqueous phase solute concentration ( $\mu\text{g/L}$ )
$C_{\text{aq}}$	Aqueous phase concentration at time $t$
$C_{\text{b}}$	Solute concentration in bulk water at time $t$
$C_{\text{be}}$	Solute concentration in bulk water at equilibrium
$C_{\text{bi}}$	Initial solute concentration in bulk water
$C_{\text{e}}$	Aqueous phase solute concentration at equilibrium ( $\mu\text{g/L}$ )
$C_{\text{T}}$	Initial total concentration of solute
$D_{\text{a}}$	Apparent diffusivity coefficient $D_{\text{a}}$
$D_{\text{b}}$	Bulk aqueous diffusivity
$D_{\text{p}}$	Effective pore diffusion coefficient
DRM	Distributed Reactivity Model
$D_{\text{s}}$	Effective surface diffusion coefficient
EDAX	Energy Dispersive X-Ray

$F$	Equilibrium fractional uptake of solute
$f$	Fraction of the sorbent in which equilibrium is instantaneously achieved
$f_d$	Sorption capacity that exhibits diffusively limited sorption
$f_{oc}$	fraction of total organic carbon in a sorbent
FA	Fulvic acid
FEMVTF	FIFRA Exposure Modeling Validation Task Force
FIFRA	Federal Insecticide Fungicide and Rodenticide Act
FOCUS	Forum for the Coordination of Pesticide Fate Models and their Use
FTIR	Fourier transform infrared (spectrometry)
H	Hydrogen
HA	Humic acid
HI	Hysteresis index
HOC	Hydrophobic organic chemical
KB	Kerogen and black carbon
$K_D$	Linear distribution coefficient of a solute between a solid and an aqueous phase
$K_d^{app}$	Apparent distribution coefficient at time $t$
$K_{di}$	Internal distribution coefficient for intra particle diffusion
$K_{Dr}$	Sum of linear distribution coefficients in DRM
$K_F$	Freundlich sorption capacity parameter ( $\mu\text{g}^{1-n}\text{kg}^{-1}\text{L}^{-n}$ )
$k_i$	First order mass transfer rate coefficient in compartment $i$ of the sorbent
$K_{OC}$	Organic carbon normalized distribution coefficient (L/kg-OC)
$K_{OW}$	Octanol-Water partitioning coefficient

$K_r$	Constrictivity factor
MET	Metolachlor
$m_s$	Mass of the sorbent
$n$	Freundlich isotherm linearity parameter (dimensionless)
NAP	Napropamide
O	Oxygen
$p(k_i)$	Probability density function of $k_i$
PAH	Poly chlorinated aromatic hydrocarbon
PBDE	Poly brominated diphenyl ether
PCB	Poly chlorinated biphenyl
PCDD	Poly chlorinated dibenzo dioxin
PCDF	Poly chlorinated dibenzo furan
PDR	Phase distribution relationship
PHEN	Phenanthrene
$Q$	Langmuir maximum sorption capacity parameter
$q$	Solid phase concentration of the solute a radius $r$ inside a particle at time $t$
$q_e$	Solid phase solute concentration at equilibrium ( $\mu\text{g}/\text{kg}$ )
$R_{\text{int}}$	Internal retardation factor for intra particle diffusion
$S$	Solid phase concentration at time $t$
$S_1$	Solid phase concentration in instantaneously sorbing fraction of the sorbent
$S_2$	Solid phase concentration at time $t$ in diffusively limited compartment of the sorbent

SEM	Scanning Electron Microscopy
SOM	Soil Organic Matter
$t$	time (min, hr, d)
$t_{0.95}$	Time to reach 95% equilibrium
$T_g$	Glass transition temperature ( $^{\circ}\text{C}$ )
$V_w$	Volume of the aqueous phase
$X_i$	Fraction of sorption capacity that equilibrates instantaneously
$x_l$	sum of domain fractions of exhibiting linear sorption isotherms in DRM
$x_{nl}$	any of the domain fractions exhibiting nonlinear sorption isotherms in DRM
$\alpha$	Shape factor defining the $\Gamma$ distribution (dimensionless)
$\beta$	Scale factor defining the $\Gamma$ distribution (hr)
$\chi$	Tortuosity factor
$\chi_e$	Effective tortuosity factor
$\varepsilon_i$	Internal porosity of sorbent particles
$\rho_a$	Apparent particle density in intra particle diffusion model
$\tau$	Dimensionless time in intra particle diffusion
$\nabla^2$	Second differential with respect to time $t$

## CHAPTER 1 – INTRODUCTION

### 1.1 Significance

Pesticides continue to be one of the major pollutants of surface and ground water systems in the US. The recent decadal national water-quality assessment (NAQWA) conducted by the USGS (1992-2001) has revealed the extent of pesticide contamination in US surface streams and shallow groundwater wells, with herbicides such as atrazine topping the list with most detections. Pesticides are a non-point source of pollution and as such off-site remediation methods such as “pump and treat” usually are not applicable to areas contaminated with pesticides and in situ mitigation methods need to be explored. Also, unlike most other pollutants, the term ‘pesticides’ represents an extremely diverse set of chemicals including fungicides, insecticides, herbicides and rodenticides. They range in chemical composition from metallic compounds to oils and various classes of organic compounds. Thus, the study of the interaction of pesticides with soils and sediments is as complex as it is vital.

Soil components have been shown to interact with pesticides in a manner that can retard or immobilize them and thus prevent groundwater pollution. An understanding of the mechanisms that govern such interactions could thus lead to development of more effective application strategies and more robust models for predicting their fate, transport and risks. Among these interactions, sorption of pesticides to soils and sediments is a major phenomenon that affects their mobility in the subsurface. Our understanding of the mechanisms underlying sorption of hydrophobic organic contaminants (HOCs) to soils and sediments has dramatically improved over the past 15 years. For example, the

previously expounded linear partition-like model for the sorption of hydrophobic organic contaminants (HOCs) has given way to more robust multi-domain, limited sorption-site and -energy models and the differential sorption properties of various soil components have been elucidated for HOCs.

This study attempts to extend the current state of understanding of sorption phenomena to mechanisms of pesticide sorption by soils, for which an unambiguous agreement seems to be lacking. The recently discovered behavior of soil components and newly expounded theories, if true for pesticides as they are for the non polar hydrophobic compounds originally investigated, could have wide ranging implications for predicting fate and transport of pesticides. This study was thus undertaken with the intent to provide the experimental evidence for facts overlooked by simplistic pesticide sorption models and to provide a framework under which behavior of HOCs and pesticides should be differentiated or treated similarly in terms of sorption studies.

## **1.2 Major Hypothesis and Objectives**

Broadly considered, soils are heterogeneous mixtures of inorganic and organic components. The inorganic components constitute a majority of the soil, but have been shown to play a minor role in the sorption of HOCs such as phenanthrene (PHEN). Given the more polar nature of pesticide molecules, it was hypothesized that the interactions of pesticides with inorganic soil components may be significant. The soil organic matter has been implicated for being responsible for most of the sorption of HOCs to soils, even when present in small quantities. We hypothesized that this could be true for organic pesticides too. The heterogeneity within SOM recently has been investigated. It has been

found that some of the SOM components are highly oxidized and provide liquid-like matrix for solutes to “dissolve” into, while others have reduced, aromatic structures and are characterized by strong binding capacities for HOCs. It was assumed that this behavior of SOM components would be evident for pesticides also, but possibly to a different extent than HOCs. It was further hypothesized that the functional groups of pesticides might exhibit specific interactions with the functionalities of oxidized, amorphous SOM components and that their rates of sorption on these components might be different from the reduced, condensed components. As shown for HOCs, the reduced SOM components were expected to dominate the sorption of pesticides.

The major objectives of this dissertation were to:

- Isolate and characterize amorphous and condensed SOM components from a soil
- Quantify the sorption equilibria between isolated SOM components and three pesticides – atrazine, metolachlor and napropamide
- Investigate the effects of SOM heterogeneity on sorption of pesticides
- Elucidate the contribution of SOM components towards sorption of pesticides into the bulk soil
- Elucidate the sorption and desorption mechanisms between SOM components and herbicides
- Measure the sorption rates of pesticides on SOM components and determine mass transfer rate coefficients
- Understand the effect of aggregation on sorption to soils

### **1.3 Overview**

This dissertation contains 8 chapters. Chapter 2 summarizes the current state of knowledge and research on sorption and desorption of pesticides to soils and sediments. It briefly describes the conceptual framework of sorption theories currently employed in understanding pesticide sorption phenomena. Chapter 3 describes the experimental methodologies and analytical techniques employed for obtaining the data that forms the basis of the Chapters 4, 5, 6 and 7. Chapter 4 characterizes the sorption behavior of three herbicides on a top soil and its SOM fractions and Chapter 5 discusses desorption of these herbicides from the same sorbents. Chapter 6 investigates the rates of sorption of an herbicide and a PAH on various SOM fractions of the same soil and Chapter 7 investigates the effect of inorganic coatings on high sorption capacity SOM fractions. Chapter 8 summarizes the major conclusions of this study and proposes future research to further our understating of herbicide sorption.

## CHAPTER 2 – LITERATURE REVIEW

### Overview

Sorption is a biphasic phenomenon of distribution of a compound, especially between a gas-solid or a liquid-solid phase. The term sorption includes the accumulation of a solute on the surface of a solid, known as *adsorption*, and the distribution of a solute into the entire matrix of the solid, known as *absorption* (Schwarzenbach et al., 2003). Sorption of contaminants (solutes) from pore water (liquid phase) onto soils and sediments (solid phase) is of particular environmental concern as it controls the concentration of these pollutants in ground and surface waters (Schwarzenbach et al., 2003). This chapter details the role of previous studies in identifying prevailing mechanisms during sorption of hydrophobic organic contaminants (HOCs) to soils and soil organic matter (SOM). Various sorption models developed for studying SOM sorption are discussed in brief along with their assumptions and limitations. It should be noted that the term “sorption” throughout this Chapter signifies both sorption equilibrium and sorption kinetics, as it is usually the norm to talk about “sorption parameters” (equilibrium sorption parameters) and “slow” vs. “fast” sorption (which refers to sorption rates). Thus unless specified the term sorption has both meanings. Since pesticides may or may not classify as HOCs, and since a comparison between HOCs such as polynuclear aromatic hydrocarbons (PAHs) and pesticides will be regularly made throughout this study, pesticides have been excluded from the term ‘HOCs’. This Chapter emphasizes the differences between sorption of nonpolar HOCs and pesticides – which are slightly polar

and moderately hydrophobic compounds. The questions that arise from previous studies and those that experiments in this study aim to answer have been highlighted.

## 2.1 Sorption Isotherm Models

Sorption phenomena are usually quantified on the basis of phase distribution relationships of the solute between the liquid and the solid phase. Such a relationship measured at constant temperature is termed as a sorption isotherm. Various types of sorption isotherms have been proposed and variously applied to the observed SOM sorption data. A brief description of the most commonly used models follows.

### 2.1.1 Linear Isotherm Model

The linear sorption model describes a linear relationship between a solute's aqueous and solid phase concentrations as:

$$q_e = K_D C_e \quad (2.1)$$

where  $q_e$  = equilibrium solid phase concentration ( $\mu\text{g}/\text{kg}$ ),  $C_e$  = equilibrium liquid phase concentration ( $\mu\text{g}/\text{L}$ ) and  $K_D$  = partitioning coefficient between the two phases ( $\text{L}/\text{kg}$ ). This model is analogous to partitioning of a solute between two liquid phases. This model assumes unlimited capacity of a sorbent to sorb a solute and that the distribution coefficient  $K_D$  is independent of initial solute concentration. It also inherently assumes a homogeneous solid phase in which sorption sites are not solute specific and into which the solute can partition instantaneously. The solute partitions into the whole body of the

solid phase, a phenomenon now distinguished as absorption. Until 1985, the linear model was extensively used to describe sorption to soil organic matter, which was thought to be a “gel” like matrix, analogous to partitioning into an organic solvent. The values of  $K_D$  measured using this model were often different for different soils and a parameter

$$K_{OC} = K_D/f_{OC} \quad (2.2)$$

where  $f_{OC}$  = fraction of organic carbon in the soil, was defined to normalize  $K_D$  to organic carbon content of soils in an attempt to obtain a universal partitioning coefficient between different soils (Chiou et al., 1979, 1981, 1983; Means et al., 1980, 1982; Karickhoff et al., 1979; Karickhoff, 1981, 1984; Schwarzenbach and Westall, 1981).

The extensive use and applicability of this model to describe sorption to SOM (Hance 1965, 1967; Lambert, 1967; Briggs, 1969; Chiou et al., 1979) is now thought to be because the tested solute concentrations were high enough to conform to the linear model and short solute-solid contact times were employed for sorption measurements (Cornelissen et al., 2005). In the late 1980’s, many researchers made observations challenging the assumptions of this model, including deviation of the isotherm data from the linear fits, i.e., isotherm non-linearity (Grathwohl, 1990; Huang et al., 1997; Huang et al., 1998; Chiou et al., 1998; Karapanagioti et al., 2000, 2001; Xia and Ball, 1999), competition between solutes (McGinley et al., 1993), sorption-desorption hysteresis (Huang and Weber, 1997), dependence of  $K_{OC}$  on initial aqueous solute concentration (Huang and Weber, 1998) and increased  $K_{OC}$  values in the field compared to predicted values (Bucheli and Gustafsson, 2001; Gustafsson et al., 1997). To describe such

phenomena, two nonlinear sorption models were borrowed from physical chemistry and were variously applied to sorption data. These were the Langmuir and Freundlich sorption models as described below.

### 2.1.2 Langmuir Isotherm Model

The theoretical Langmuir Model assumes single layer surface coverage of a solute onto the solid phase. It assumes a limited number of uniform, energetically similar sorption sites that become saturated with increasing aqueous phase concentration. It is mathematically represented as:

$$q_e = \frac{QbC_e}{1+bC_e} \quad (2.3)$$

where  $Q$  represents the maximum sorption capacity of the solid and  $b$  represents the affinity of the solid surface for the solute (Weber et al., 1992). At very high  $C_e$  ( $bC_e \gg 1$ ),  $q_e$  is equal to the maximum sorption capacity  $Q$ , indicating a saturation of the sorption sites and at very low  $C_e$  ( $bC_e \ll 1$ ), the equation transforms into equation (2.1), the linear sorption model.

### 2.1.3 Freundlich Isotherm Model

The Freundlich model is an empirical relationship between  $q_e$  and  $C_e$  described as

$$q_e = K_F C_e^n \quad (2.4)$$

The parameters  $K_F$  and  $n$  are fitted from experimental observations of  $q_e$  and  $C_e$  and termed as the sorption capacity and isotherm non-linearity factors, respectively. This model assumes multiple types of sorption sites, which exhibit different sorption free energies and act in parallel. The nonlinearity parameter  $n$  is an indicator of both the relative magnitude and diversity of sorption energies of a solid and depicts the sequence in which sorption sites are accessed by the solute (Weber et al., 1992; Weber and Huang 1996). This model, being empirical in nature, fits most of the observed sorption data very well. However, researchers have shown that a sum of multiple Langmuir terms (equation 2.3) results in an isotherm that is similar in shape to the Freundlich isotherm. The  $n$  value is observed to be  $< 1$  for sorption of organic chemicals for most soils. At  $n = 1$ , this model transforms into the linear model. At  $n < 1$ , the model predicts lesser and lesser sorption energies available for incoming solute with increasing  $C_e$ .

#### **2.1.4 Distributed Reactivity Model**

It was found that the above linear and nonlinear models could variously describe the sorption data observed and there was no consensus as to which model is representative of sorption behavior of SOM. In early 1990's, Weber et al. (1992) proposed a Distributed Reactivity Model (DRM) to reconcile these seemingly conflicting observations. This model recognizes that soils are heterogeneous mixtures of components and each of these components has its own sorption reactivity. Some of these components were hypothesized to exhibit linear sorption isotherms, while others would exhibit nonlinear isotherms. The total sorption to a soil would be a sum of individual reactivities of the sorption sites as:

$$q_e = x_l K_{D_r} C_e + \sum_{i=1}^m (x_{nl})_i K_{F_i} C_e^{n_i} \quad (2.5)$$

The first and subsequent papers based on this model (Weber et al., 1992; Weber and Huang, 1996) classified soils as consisting of three domains: the mineral domain, the amorphous organic matter or “soft” carbon domain, and the condensed organic matter or “hard” carbon domain, the latter two comprising the SOM in soils. The amorphous organic matter domain was hypothesized to exhibit fast and linear sorption and the condensed organic matter domain to exhibit slow, nonlinear and hysteretic sorption, so that the model describes sorption to soils as the sum of linear as well as nonlinear components. Thus the multi component DRM model reconciled conflicting observations regarding linear sorption to some SOM and non linear sorption to other types of SOM.

## 2.2 Sorption Rate Models

Sorption rate models are predicated on the assumption of a rate limiting step in the sorption process. Sorption rate models are valid only when the assumption of instantaneous equilibrium of the solute with the solid phase is not true, at least partially, and a slow approach to equilibrium is observed. The slow rate of sorption is thought to be result from diffusive resistances due to either i) intra-particle diffusion of solute through pre-existing mineral micro pores or ii) diffusion of a solute through intra organic matter matrices. Two types of rate models have generally been applied to observed soil sorption rate data: 1) the intra particle pore diffusion model and 2) the two site intra SOM mass transfer model. A “gamma” distribution model has been used in recent studies and is discussed in the following text.

### 2.2.1 Intra-Particle Pore Diffusion Model

Ball and Roberts (1991) developed the following intra particle diffusion model for transient conditions of uptake into a sorbent. Mass balance over a volume element of porous sorbent can be combined with Fick's first law of diffusion as:

$$\rho_a \left( \frac{\partial q}{\partial t} \right) + \varepsilon_i \left( \frac{\partial C}{\partial t} \right) = \varepsilon_i D_p \nabla^2 (C) + \rho_a D_s \nabla^2 (q) \quad (2.6)$$

where  $\rho_a$  = apparent particle density,  $\varepsilon_i$  = internal porosity of the sorbing particles,  $D_p$  = effective pore diffusion coefficient,  $D_s$  is the effective surface diffusion coefficient and  $q$  and  $C$  are the solid and aqueous phase concentration of the solute, respectively, a radius  $r$  inside the particle and time  $t$ .

For linear partitioning and reversible equilibrium within the pores this equation can be transformed to spherical coordinates as:

$$\frac{\partial C}{\partial t} = \left( \frac{D_a}{r^2} \right) \frac{\partial}{\partial r} \left[ r^2 \left( \frac{\partial C}{\partial r} \right) \right] \quad (2.7)$$

Where the apparent diffusivity coefficient  $D_a$  is defined as:

$$D_a = \frac{\varepsilon_i D_p}{(\varepsilon_i + \rho_a K_{di})} + \frac{\rho_a K_{di} D_s}{(\varepsilon_i + \rho_a K_{di})} \quad (2.8)$$

$K_{di}$  being the internal distribution coefficient, considering only the diffusion limited sorbed phase. In cases where diffusion of sorbed species is not believed to play an important role in the overall uptake rate, a pore diffusion interpretation is made. The diffusion is thus only in the aqueous phase and the equation can be simplified to:

$$D_a = \frac{D_p}{\left[ 1 + \left( \frac{\rho_a}{\epsilon_i} \right) K_{di} \right]} \quad (2.9)$$

The denominator in this equation can be equated to an internal retardation factor for intraparticle diffusion  $R_{int}$  and the equation can be further simplified as:

$$D_a = \frac{D_p}{R_{int}} \quad (2.10)$$

The effective pore diffusivity is thought to be less than the bulk aqueous diffusivity (diffusivity in bulk water) due to pore tortuosities and constrictivities.  $D_p$  can thus be expressed as:

$$D_p = \frac{D_b K_r}{\chi} \quad (2.11)$$

where  $K_r$  is the constrictivity factor ( $\leq 1$ ) and  $\chi$  is the tortuosity factor ( $\geq 1$ ). In practice it is almost impossible to separate the effects of  $K_r$  and  $\chi$  on  $D_p$  and an effective tortuosity

factor that also incorporates steric effects is used to replace the two terms as:

$$D_p = \frac{D_b}{\chi_e} \quad (2.12)$$

where,

$$\chi_e = \frac{\chi}{K_r} \quad (2.13)$$

With respect to approach to equilibrium, two types of fractions are defined for the sorbent. It is assumed that some substantial fraction of sorption capacity equilibrates sufficiently rapidly to be considered instantaneous uptake. The remaining sorption capacity exhibits diffusively limited sorption and the fraction of sorbent is represented by  $f_d$ , where

$$f_d = (C_{bi} - C_b) / (C_{bi} - C_{be}) \quad (2.14)$$

where  $C_{bi}$ ,  $C_b$ , and  $C_{be}$  are the solute concentrations in the bulk water initially, at time  $t$  and at equilibrium, respectively, and are expressed in terms of initial total concentration of the solute  $C_T$  as:

$$C_{bi} = C_T / (1 + X_i K_d m_s / V_w) \quad (2.15a)$$

$$C_b = C_T / (1 + K_d^{\text{app}} m_s / V_w) \quad (2.15b)$$

$$C_{be} = C_T / (1 + K_d m_s / V_w) \quad (2.15c)$$

where  $K_d^{\text{app}}$  is the apparent distribution coefficient (ratio of  $q/C$ ) measured prior to equilibrium),  $X_i$  is the fraction of sorption capacity that equilibrated instantaneously,  $m_s$  is the mass of the sorbent, and  $V_w$  is the volume of the aqueous phase.

Now, an equilibrium fractional uptake  $F$  is defined as:

$$F = (C_{bi} - C_{be}) / C_{bi} \quad (2.16)$$

And a dimensionless time parameter is defined as

$$\tau = D_a t / a^2 \quad (2.17)$$

where  $a$  is the particle radius.

A computer simulation is then used to find a diffusion rate constant ( $D_a/a^2$ ) that minimizes the weighted sum of square residuals of model estimated fractional uptake ( $f_d$ ) vs. those experimentally measured, for each sample, calculated by using samples  $F$  values and time of contact. The fraction of instantaneous sorption is thus a fitting parameter, the results obtained are  $X_i$ , diffusion rate constant  $D_a/a^2$  and time to reach 95% of equilibrium  $t_{0.95}$ .

### 2.2.2 The Two Site Model

The two site model, such as the intraparticle diffusion model, assumes two compartments, one where sorption is instantaneous and another where sorption rate is mass transfer limited, but the cause of this limitation is assumed to be slow solute accessibility of condensed SOM matrices. It is thus essentially an intra-SOM diffusion model. According to this model, equilibrium in fraction  $f$  of the sorbent is instantaneously achieved and is described by:

$$S_1 = fK_D C_{aq} \quad (2.18)$$

where  $S_1$  is the solid phase concentration in the instantaneous fraction of sorbent and

$$dS_2/dt = S_2 - (1-f)K_d C_{aq} \quad (2.19)$$

Total sorption in the sorbent is thus  $S = S_1 + S_2$

### 2.2.3 Gamma ( $\Gamma$ ) Distribution Model

The gamma distribution model assumes a gamma distribution of mass transfer rate coefficients in a continuum of physical compartments in a soil aggregate with each compartment characterized by its own sorption rate coefficient. The variation in solid phase concentration  $S$  is thus given by:

$$\frac{dS}{dt} = \sum_{i=1}^n p(k_i) * k_i * (S - K_{OC} C_{aq}) \quad (2.20)$$

and  $p(k_i)$ , the probability density function of  $k$  is defined as:

$$p(k) = \frac{\beta^\alpha k^{\alpha-1} \exp(-\beta k)}{\int_0^\infty x^{\alpha-1} \exp(-x) dx} \quad (2.21)$$

where  $\alpha$  and  $\beta$  are the fitting parameters that determine the shape and scale of the  $\Gamma$  distribution respectively and  $x$  is a dummy variable of integration. This model comes close to the DRM on a kinetic basis, as it assumes variable reactivities for various compartments of the sorbent.

### 2.3 Soil components and their sorption behavior for HOCs

After the proposal of DRM, many studies tried to investigate the individual sorption behavior of isolated soil components as well as of model compounds that are representative of those soil components. A typical soil consists of inorganic and organic components, with inorganic minerals constituting a majority of the soil. Other inorganic components may include small precipitates such as calcites and insoluble hydroxides. The organic components of the soil (i.e. SOM) further consists of several fractions, such as biopolymers, fulvic acids (FAs), humic acids (HAs), and kerogen and black carbon (KB). Biopolymers are derived from recently dead organic matter and are the precursors of humic acids (Weber et al., 2001). They include polysaccharides (cellulose, chitin, starch, glycogen), lignin, proteins and polynucleic acids. Fulvic acids, thought to be the first products of metamorphosis of biopolymers, are operationally defined as SOM components soluble in both acids and bases and have a significant number of functional

groups in their structure. SOM components soluble in bases but insoluble in acids are defined as HAs. These have lesser oxygen contents and functionalities, but are rich in carboxylic and phenolic groups. The SOM component that is acid and base resistant is defined as kerogen (Stevenson, 1994), which is a coal-like material originated from bacterial and algal remains, and exhibits coal-like properties such as high aromaticity and low functionality. Another component, black carbon, is the carbon that becomes associated with soil as residue of incomplete combustion processes, both industrial and natural. It is chemically very difficult to isolate kerogen from black carbon without substantially altering their structure as both are recalcitrant to acid and base treatment and solvent extraction. They have been thus collectively termed KB and have been examined as a whole in this study.

### **2.3.1 Sorption to Mineral Phase**

Sorption to the mineral phase has been shown to be fast and linear for HOCs such as PHEN, primarily because competition by polar water molecules prevents significant sorption of HOC to the mineral phase, a process that is energetically unfavorable in the first place. The surface coverage of HOCs on minerals is thus thought to be low and governed by the linear isotherm model. Huang et al. (1996) showed that for minerals such as silica gels of various particle sizes, alumina, quartz and kaolinite, sorption of PHEN was fast and linear. However, researchers have pointed out that sorption to the mineral phase may be important for soils with very low moisture contents, very low organic carbon content, or high clay content with hydrophobic surfaces (Pignatello et al., 2006).

### 2.3.2 Sorption to Amorphous Organic Carbon

Several trends regarding sorption properties of these substances have been observed. It has been shown that the greater the age of an SOM in the process of its diagenetic metamorphosis, the greater its sorption capacity and the more nonlinear its isotherm. It has been experimentally demonstrated that FA and HA typically have linear isotherms for PAHs, indicating that they may comprise the hypothesized soft or amorphous carbons in SOM, while kerogen and black carbon have nonlinear isotherms, indicating they are akin to the hard or condensed SOM. Like polymers, SOM has been shown to transform from a condensed state to an amorphous state above a characteristic temperature known as the glass transition temperature,  $T_g$ . A  $T_g$  value of  $-45^\circ\text{C}$  has been found for cellulose (Akim, 1978) and a value of  $43^\circ\text{C}$  has been shown for HA by LeBoeuf and Weber (1997), who also showed that at temperatures close to its  $T_g$ , the HA behaved as an amorphous sorbent, while at temperatures much below its  $T_g$ , it exhibited non-linear isotherms. Thus under environmental conditions, cellulose will always exhibit an amorphous character whereas HA could exhibit either of two characteristics, depending on the ambient temperature.

### 2.3.3 Sorption to KB

As said earlier, the KB fraction includes kerogen and black carbon; studies have reported extensive and non-linear sorption of HOCs on these inert, condensed and aromatic materials (Grathwohl, 1990; Huang et al., 1997; Huang et al., 1998; Young and Weber, 1995; Karapanagioti et al., 2000; Kleineidam et al., 1999, 2002; Huang et al., 2003; Jonker and Koelmans, 2002; Gustafsson et al., 1997; Hong et al., 2003). All these

forms of carbon are operationally recalcitrant to acid or base treatment and organic solvents. In their review on KB sorption studies in the past decade, Cornelissen et al. (2005) propose that all these forms of carbon exhibit properties characteristic of the hard or condensed carbon fraction hypothesized in the DRM by Weber's group (Weber et al., 1992; Young and Weber, 1995; Weber and Huang, 1996; Huang et al., 1997; Huang and Weber, 1998), and that they constituted the SOM fraction primarily responsible for the isotherm non-linearity and slow and hysteretic sorption behavior of HOCs. These observed sorption properties can have major consequences for the fate and transport of HOCs in the environment, for example, predicted protracted desorption rates, reduced bioavailability and limited biodegradation potential. Therefore, the characterization and investigation of sorption behavior of this SOM fraction is warranted (Cornelissen et al., 2005; Huang et al., 2003).

*Origin, Distribution and Composition of KB:* KB constituents are characterized by condensed, rigid and aromatic structures, high carbon contents and relatively little polar functionality (Huang et al., 2003; Cornelissen et al., 2004; Goldberg, 1985; Tissot, 1984). BC is ubiquitous in soils and sediments as a result of both natural and anthropogenic combustion activities and atmospheric transport (Bucheli et al., 2004; Middelburg et al., 1999; Gustafsson and Gschwend, 1998). On the other hand, coal is not frequently encountered in soils because most of it is buried deep in soil strata (Goldberg, 1985). However, coal is a significant constituent in SOM of soils near coal mining, transporting (major rivers and harbors), and burning facilities (Karapanagioti et al., 2000, 2004). Kerogen is thought to be more widely distributed in soils than coal (Goldberg, 1985). In

90 soils, Cornelissen et al. (2005) found BC at median levels of 4% of total organic carbon content of soils. Studies, however, show that for soils impacted by burning activities, charcoal BC may be present at levels of 30-45% of total organic carbon content of soils (Schmidt et al., 1999; Skjemstad et al., 1996). Song et al. (2002) found 24-48% of TOC was kerogen in one soil and three sediment samples. The sources and mechanisms of formation of these hard carbon fractions, along with their major structural distinctions, have been summarized in Table 2.1 (adapted from Cornelissen et al., 2005).

*Sorption Behavior of KB for HOCs:* The reported properties of KB that have generated much interest are its extensive sorption capacities, highly non-linear isotherms, and slow sorption rates that range from months to years. Due to these observed properties, this fraction is thought to determine the amount of contaminant that will ultimately sorb onto a soil and, be permanently bound or sequestered in the environment on practical time scales. Sorption behavior of KB has been mostly studied using PAHs, and more hydrophobic compounds such as PCBs and a few studies on PCDDs/Fs and PBDEs. Among these, the PAH PHEN has been used widely as a probe for investigating KB sorption properties.

*Mechanism of Sorption:* The structure of KB can be thought to be consisting of large aromatic sheets that are held together by side aliphatic side chains via covalent bonds. Only a few of these side chains may have polar functionalities with which to bind to mineral surfaces and more polar SOMs such as FA and HA. This tightly knit three

dimensional aromatic sheet structure provides large surface area as well as nano scale voids that are highly favorable energetically for sorption of HOCs.

Two types of sorption sites are thought to be acting in the sorption of HOCs, surface adsorption sites and nanoporous sites – which are not necessarily different from each other; the nanoporous sites provide further surface to adsorb into the pores (Cornelissen et al., 2005). Another, third type of site consists of inaccessible nanopores, called “occlusion site” that might be accessible to very small molecules only (McGroddy and Farrington, 1995; Jonker and Koelmans, 2002).

Two mechanisms of HOC sorption on KB have been proposed: adsorption on the surface of KB materials, and adsorption to and/or entrapment in their nanopores, comparable to dissolution of HOC into the matrix of amorphous organic matter. The actual sorption reaction may include partial phase transition (partial condensation) of the HOC molecule onto the KB surface (Gustafsson and Gschwend, 1997), which has been corroborated by the observation of decreased energies of rotation and translation of the sorbate (Gustafsson and Gschwend, 1997; Van Noort, 2003).

Both the size and the shape of HOC molecules have been found to be important in sorption to KB. Small planar molecules such as PHEN have been shown to bind more strongly (higher restriction of free energies, higher  $\log K_F$ ) and extensively (able to access the nanopores of KB) to KB. Thus although PHEN is only moderately hydrophobic, its relatively extensive sorption with KB (compared to amorphous organic matter) is comparable to more hydrophobic compounds (Van Noort, 2003). For example, on average the coefficient of sorption of PHEN to KB exceeds the amorphous carbon coefficients by a factor of 100-1000 (Cornelissen et al., 2005). Higher  $K_{OC}$  values have

been found in the field studies for sorption of PAHs than could be predicted by sorption to amorphous organic matter alone, indicating the presence of this high sorption capacity fraction (Accardi-Dey and Gschwend, 2002). Planarity effects on KB sorption have also been observed for PCBs; BC sorption coefficients of planar PCBs are up to an order of magnitude higher than those of nonplanar PCBs having similar log  $K_{OWs}$  (Bucheli and Gustafsson, 2003). These observations have been explained as the inaccessibility of nanoporous sorption sites to nonplanar molecules, compared to the planar molecules having similar molecular thickness to average nanopore widths in KB (Van Noort et al., 2003, 2004).

Sorption of HOCs to KB has also been shown to be slow, ranging from days to years to achieve equilibrium. This phenomenon also stems from the condensed, rigid nature of the KB matrix into which diffusion of HOCs is mass transfer limited (Pignatello and Xing, 1996). In some cases for very small molecules, this phenomenon has also been attributed to the physical entrapment and condensation of the molecules in the pores of the KB matrix. A similar phenomenon of slow desorption of HOCs from the KB matrix to the pore water, due to the energies required to overcome the strong hydrophobic bonding and phase transition, is expected. This observation is relevant dealing with achievement of remediation goals, where slow desorption and release could mean that a contaminant could present itself into the environment long after remediation is thought to be complete. A summary of sorption properties of various soil components for HOCs is presented in Table 2.2.

*Effect of KB on Sorption Capacities of Soil Aggregates:* Limited studies show that sorption of PHEN to black carbon is an order of magnitude lower when it is present along with amorphous organic matter and organic compounds native to soils are also present (Cornelissen and Gustafsson, 2004). This decrease in sorption capacity is thought to be caused by competition for BC sorption sites from small SOM molecules and native organic compounds. It has also been suggested that the amorphous organic matter particles can “block” BC sorption sites analogous to activated carbon fouling by humic substances (Cornelissen et al., 2005; Kilduff and Wigton, 1999; Carter and Weber, 1994). Studies suggest that such attenuation can also be expected for kerogen since it exhibits similar sorption properties to black carbon. However, the effects of presence of KB in soil aggregates – which are complex structures formed by inter-layering of mineral matter, small inorganic and organic molecules, amorphous organic matter and KB – have not been explored until now.

## **2.4 Pesticide Sorption, Desorption and Rates**

### **2.4.1 Nature of Pesticide Molecules**

Unlike most other classes of organic compounds, pesticides include diverse classes of chemicals such as organochlorines, triazines, carbamates, organophosphates and acetamides, which have diverse physicochemical properties. In contrast to compounds that have been traditionally used to study sorption to soils, pesticides are larger and non-planar molecules. They are also often more polar by design to increase

their aqueous solubility and facilitate plant uptake and hence efficacy; some may even exist in ionic form under prevailing soil pH ranges.

#### **2.4.2 Sorption to Soils**

A large but conceptually varied data set exists for the sorption of pesticides to soils. Recent reviews show that most of the studies treat soils as a single gel-like sorbent exhibiting linear sorption isotherms and constant partition coefficients,  $K_D$  (Wachoupe et al., 2002; Weber et al., 2000). Many studies have attempted to overcome observed variations in  $K_D$  by normalizing sorption data to organic carbon content of soils, using the parameter  $K_{OC}$ . Despite increasing evidence of isotherm non-linearity in pesticide sorption to soils, the linear  $K_{OC}$  coefficient is still widely applied to predict pesticide sorption to soils, including studies by the European FOCUS (Forum for the Coordination of Pesticide Fate Models and their Use) and the US FEMVTF (FIFRA Exposure Modeling Validation Task Force) work groups (Wachoupe et al., 2002). Sorption studies of pesticides to soils have in many cases focused on the agricultural aspects such as the effects of soil tillage systems or soil amendments on pesticide sorption. From an agricultural perspective, the major concern in the interaction of pesticides and soils is their efficacy, and sorption is generally regarded as a negative factor in this regard.

Many defining and widely quoted studies on sorption of pesticides for SOM consider SOM to be “humic material” and have linked the variations in sorption capacities of various soils to the degree of aromaticity of this SOM (Kulikova and Perminova, 2002). Others have hypothesized that SOM can be modeled by properties of biopolymers such as lignin, chitin and collagen (Torrents et al., 1997). Some studies also

exist on the role of minerals and clays in the sorption of pesticides, but the presence and role of KB in pesticide sorption has been generally overlooked (Cornelissen et al., 2005).

Sorption to SOM has been linked to retardation of herbicide movement in the subsurface (Schwarzenbach et al., 2003), thus controlling herbicide concentrations in runoff and leachate, and hence potentially controlling concentrations in surface and ground waters. Sorption behavior of ATZ and MET has been studied on various soils (Loiseau and Barriuso, 2002; Kulikova and Perminova, 2002; Laird et al., 1994; Wietresen et al., 1993; Seybold and Mersie, 1996; Yu et al., 2006; Lesan and Bhandari, 2003; Liu et al., 2000; Weber et al., 2003). These studies have observed the strong sorption of ATZ to the fine particle fraction ( $< 0.2$  mm) that contains most of the SOM, and increased ATZ sorption with increasing SOM aromaticity (Loiseau and Barriuso, 2002; Kulikova and Perminova, 2002). In a soil clay, 11% SOM has been shown to contribute 68% towards overall ATZ sorption (Laird et al., 1994), demonstrating the importance of SOM towards sorption of herbicides. The mobility of MET in soils has been shown to be inversely related to SOM and soil clay contents (Wietresen et al., 1993), and MET has been shown to be more mobile than ATZ in soil column studies (Seybold and Mersie, 1996). Many studies have found that ATZ and MET exhibit nonlinear sorption isotherms on a variety of soils (Yu et al., 2006; Lesan and Bhandari, 2003; Liu et al., 2000; Weber et al., 2003). Researchers have also shown that sorption capacity of soils for ATZ is a function of time (Yu et al., 2006; Lesan and Bhandari, 2003). Very few studies exist on the sorption behavior of NAP despite its wide application; it is not clear whether it exhibits linear or non linear isotherms for sorption to soils.

### 2.4.3 Sorption to Mineral Phase

Although strong positive correlations have been found between organic carbon contents of soils and soil  $K_{OC}$  for pesticides, a review by Wauchope et al. (2002) noted that SOM may not be the only sorbent important in sorption of pesticides. For soil with low organic matter content, and for more polar pesticides, mineral surfaces may become important sorbents (Koskinen and Harper, 1990; Means et al., 1982, Cox et al., 1998; Sukop and Cogger, 1992). Chen et al. (2000) have shown that particularly for soils that are very dry and where water molecules are not available for sorption to mineral sites, mineral and SOM domains may be equally important for sorption of pesticides (Chen et al., 2000; Unger et al., 1996), in contrast to the negligible contribution of the mineral phase in sorption of PHEN. Urea, triazine and chloroacetanilide herbicides have been shown to sorb on clays (Hance et al., 1969; Liu et al., 2000). Other specific interactions possible between inorganic sorption sites and pesticides include sorption to soil phosphorus sites for organophosphorus pesticides such as glyphosate (de Jong et al., 2001) and ligand exchange mechanisms for 2,4-D (Sannino et al., 1997).

Another way in which the mineral phase is thought to influence the sorption of pesticides is in the determination of the location of SOM, since SOM always exists intimately associated with mineral surfaces. Liu et al. (2002) found in FTIR analysis studies that sorption of three acetanilide herbicides increased with the increasing acidity of homoionic montmorillonite. A study on sorption of various pesticides on smectite clay by Sheng et al. (2001) showed that ATZ was sorbed to a similar extent by K- saturated smectite clay and SOM (Houghton muck soil), while for 4,6-dinitro-*o*-cresol, dichlobenil and carbaryl, the clay was a better sorbent than SOM and for parathion, diuron and

biphenyl, sorption to SOM exceeded the sorption to the clay. Their sorption equilibrium experiments were, however, carried out for 10 min to 3 d of equilibration time. In another study Laird et al. (1994) found that 11 % organic and 89% inorganic components of a clay contributed 68 % and 32 %, respectively, towards sorption of atrazine; their equilibration time was 24 hr. A study by Cruz-Guzman et al. (2004) showed that the addition of organic cations such as thiamine, cystine dimethyl ester and carnitine enhanced the sorption of simazine on a montmorillonite clay by factors ranging from 4-350.

#### **2.4.4 Sorption to Amorphous Organic Matter**

Amorphous organic matter, including biopolymers and FA and HA, have been thought to be the primary SOM component in the sorption of pesticides. In a study of 16 humic materials and peat soils, Kulikova and Perminova (2002) showed that the  $K_{OC}$  for atrazine sorption was positively correlated with the aromatic carbon content of the sorbents. Further, due to the complex functionalities in pesticide molecules, they specifically interact with SOM components having high numbers of polar functionalities, viz, the FA and HA. Studies have shown transformation of atrazine to hydroxyatrazine via a hydrogen bonding mechanism during its interactions with HA (Martin-Neto et al., 2001; Wang et al., 1992). This has led to speculation of the possibilities of permanent binding and assimilation of large molecules into the SOM structure itself (Loiseau et al., 2002). It is not clear whether this binding is due to chemical reactions or simply the above stated phenomena of slow sorption to KB and subsequent slow release.

#### **2.4.5 Sorption to KB**

Whether the SOM fraction exhibits similar characteristics for pesticides as for PAHs is not yet clear. For example, the high sorption capacity of the KB fraction has not been demonstrated for pesticides. However, this might be attributable to the fact that the strong sorption to KB has been studied mostly using PAHs, planar PCBs, chlorobenzenes, PCDDs/Fs and PBDEs. Very few studies exist regarding the sorption behavior of KB for pesticides. One study found that the magnitude of atrazine sorption was comparable to its sorption on the amorphous organic matter. The sorption of diuron was studied (Cornelissen et al., 2005) on a soil containing particulate matter from crop residue burns and it was found that the burned wheat and rice residues (ashes) were 400-2500 times more effective in sorbing diuron than the soil. Further studies are lacking in this area.

#### **2.5 Limitations of Existing Studies**

The following gaps in the current understanding of pesticide sorption were observed during the review of existing literature:

- 1) One major consequence of assuming linear partitioning in the case of pesticide sorption is that instantaneous equilibrium is often assumed. Many studies on pesticide sorption have used insufficient equilibration times, on the order of 1-2 days, thus introducing substantial errors in the estimation of the sorption properties of pesticides on SOM. Studies have shown that sorption isotherms become more nonlinear ( $n$  value decreases) and the sorption capacity ( $\log K_F$ ) increases with time both for PAHs (Huang et al., 1997) and pesticides such as

atrazine (Lesan and Bhandari, 2002). Nevertheless, linear isotherms and short equilibration times are repeatedly employed in studies. If the sorption of pesticides on soils is non-linear, however, consequences of this isotherm non-linearity on sorption such as desorption hysteresis and dependence of  $K_{OC}$  and sorption rates on aqueous phase concentration of incoming solute need to be examined for pesticides.

- 2) Most of these sorption models have been based on experiments with chemicals that are more nonpolar and hydrophobic than pesticides. It has been recognized that the varied functionalities, polar characteristics and higher aqueous solubilities of pesticides might elicit very different sorption behavior among soils and SOM components. These differences need to be explored before non-linear and multiple reactivity models are applied to pesticide sorption.
- 3) Whether large molecules such as organochlorines, triazines and carbamates are able to penetrate nanopores of the hard carbon domain KB as observed for PAHs is not clear. Such accessibility of pores has been cited as the cause of sorption desorption hysteresis and slow sorption rates for PHEN; these phenomena would have major consequences for the fate and transport of pesticides in the environment.
- 4) Most studies on these special interactions of herbicides with certain SOM components (e.g. HAs) have been conducted with isolated SOM domains, and no information exists on soil aggregates, which are a complex mix of minerals and SOM.

This dissertation aims to systematically quantify sorption of three herbicides on soil and SOM components, to obtain insights into the behavior of SOM components *vis a vis* bulk soil. In this work, a single soil is chemically isolated into individual SOM domains and subjected to sorption studies to analyze their contribution towards bulk soil sorption and to determine the extent to which the mechanisms observed in isolated domains exist in the bulk soil. A comparison of observed herbicide sorption parameters and isotherms with PAH sorption studies was also attempted.

The major questions that this study aims to answer are:

- Which sorption model best describes pesticide sorption?
- What are the roles of different SOM components in sorption to bulk soils?
- Does soil KB exhibit high sorption capacity for pesticides?
- Do SOM components show similar properties in bulk soil as in the isolated, purified form?
- What is the effect of soil aggregation on sorption properties of amorphous and condensed SOM components?
- How do observed herbicide sorption parameters and isotherms compare with PAH sorption studies?

Three herbicides (atrazine, metolachlor and napropamide) were selected for this purpose. Starting from the study of equilibrium sorption of herbicides as described in Chapter 4, each set of experiments paved the way for new hypotheses and further experiments, which will be described in the relevant chapters.

Table 2.1 Physicochemical properties of condensed organic matter (adapted from Cornelissen et al., 2005)

<b>SOM Component</b>	<b>Formation</b>	<b>Source</b>	<b>Structure</b>	<b>Distinct Features</b>	<b>Specific Surface Area<sup>a</sup></b>
BC					
Soot	Incomplete combustion	Fossil fuels, biomass	Sub mm conglomerates of aromatic layers	Onion-like structures, inter layer spacing of 4 – 20 Å; 20-90 % C	63 m <sup>2</sup> /g
Char and charcoal	Incomplete combustion		1-100 mm particles with identifiable features of the original fuel	Less structured material; 20-90% C	201 m <sup>2</sup> /g
Coke	Coal pyrolysis	Bituminous coal	Similar to char		
Lampblack	High temp decomposition of crude oil	Crude oil	Probably similar to char		
Atmospheric tar balls	Incomplete biomass combustion	Biomass	Lack of microscopic structure	~ 90% C	
Coal	Diagenesis and catagenesis of plants, maturation sequence: peat, brown coal, bituminous coal, anthracite	Terrestrial higher plants	Disordered macromolecules of variable condensation, aromaticity increases and functionality decrease as a function of coal maturation	50-90 % C	2.4 m <sup>2</sup> /g
Kerogen	Diagenesis and catagenesis of bacteria and algae, type –III kerogen structurally similar to coal	Bacteria and algae	Large disordered macromolecules of condensed cyclic nuclei linked by heteroatomic bonds or aliphatic chains	Interlayer distances 3.4-3.7 Å; 70-90% C	5.1 m <sup>2</sup> /g

<sup>a</sup> median values

Table 2.2 Summary of sorption behavior of soil components for HOCs

Sorption to Water-Wet Mineral Surfaces	
<b>Kinetics</b>	<b>Fast (&lt; minutes)</b>
<b>Isotherm</b>	<b>Linear, because of competition with water</b>
<b>Activation Energy</b>	<b>Low</b>
<b>Heat of Sorption</b>	<b>Low</b>
<b>Competitive</b>	<b>No, because surface coverage is small</b>
<b>Sorbate steric effects</b>	<b>Important</b>
<b>Solvent Extractability</b>	<b>High</b>
Sorption to Amorphous SOM	
<b>Kinetics</b>	<b>Fast (&lt; minutes)</b>
<b>Isotherm</b>	<b>Linear</b>
<b>Activation Energy</b>	<b>Low</b>
<b>Heat of Sorption</b>	<b>Low</b>
<b>Competitive</b>	<b>No</b>
<b>Sorbate steric effects</b>	<b>Not important</b>
<b>Solvent Extractability</b>	<b>High</b>
Sorption to Condensed SOM	
<b>Kinetics</b>	<b>Slow (&gt; days), Sorption-desorption hysteresis</b>
<b>Isotherm</b>	<b>Nonlinear, linear isotherm possible after very long equilibration</b>
<b>Activation Energy</b>	<b>High</b>
<b>Heat of Sorption</b>	<b>Moderate to high with increasing density of SOM</b>
<b>Competitive</b>	<b>Yes</b>
<b>Sorbate steric effects</b>	<b>Important for diffusion through matrix</b>
<b>Solvent Extractability</b>	<b>Low</b>

## CHAPTER 3 – METHODOLOGY

### Overview

This chapter details the materials and methods used for the experiments conducted in this study. Chemicals and their properties have been listed and the preparation and characterization – which included elemental analysis, scanning electron microscopy (SEM) imaging and energy dispersive X-ray (EDAX) imaging of the sorbents – have been presented. A detailed procedure for conducting sorption equilibrium experiments, used to obtain data for Chapters 4 and 7, is described. Also delineated are procedures for desorption experiments and rate experiments which form the basis for Chapter 5 and 6, respectively. Analytical procedures utilizing high performance liquid chromatography (HPLC) for determining chemical concentrations are presented next, followed by sorption isotherm models used to analyze the data obtained from sorption and desorption equilibrium experiments and a brief introduction to sorption rate data modeling, which will be described in greater detail in Chapter 6.

### 3.1 Chemicals and Solutions

The three herbicides used in this study were atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine] (ATZ), metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)-acetamide] (MET) and napropamide [N,N-diethyl-2-(1-naphthoxy)-propanamide] (NAP). ATZ (98% pure) was obtained from Chem Service Inc. (Chester, PA) and Pestanal<sup>®</sup> Analytical grade MET (98.4% pure) and NAP (97% pure) were purchased from Sigma-Aldrich Corp (St. Louis, MO). The three

ring PAH phenanthrene (PHEN) (98% purity, Aldrich Chemical Company, Milwaukee, WI) was also used for certain experiments. The molecular structures and relevant physicochemical properties of these compounds are listed in Table 3.1 (Schwarzenbach et al., 2003). These three herbicides were chosen because they represent completely different chemical classes and are among the most detected pesticides in US surface and groundwater (Barbash et al., 2001; Larson et al., 1999).

Primary stock solutions of each herbicide and PHEN were obtained by dissolving a desired amount in HPLC grade methanol. Working methanol stock solutions of each were then obtained by sequential dilutions of the primary solution. Methanol solutions of each herbicide at 10 concentration levels, ranging from 20 to 20,000  $\mu\text{g/L}$  for ATZ, 50 to 50,000  $\mu\text{g/L}$  for MET, 50 to 25,000  $\mu\text{g/L}$  for NAP and 11 concentration levels from 0.5 to 1000  $\mu\text{g/L}$  for PHEN to be used as calibration standards for HPLC analysis, were also obtained by the sequential dilution of the primary stock solution.

Four different types of aqueous solutions were prepared according to their requirement in the experiments. The first background solution contained 0.005 M  $\text{CaCl}_2$  as the main electrolyte to simulate electrolytes present in groundwater, 100 mg/L of  $\text{NaN}_3$  as a microbial inhibitor and 0.02 g/L of  $\text{NaHCO}_3$  as a pH buffer. The pH of this solution was  $7.0 \pm 0.2$ . The second type of background solution contained the same chemicals as the first but its pH was adjusted to  $2.0 \pm 0.2$  by dilute HCl. The third background solution had no buffer and its pH was  $6.8 \pm 0.2$ . The fourth type of background solution had similar composition to the first, except that 100 mg/L of  $\text{HgCl}_2$  was added as a microbial inhibitor instead of  $\text{NaN}_3$ , following a recent study (Chefetz et al., 2006) that indicated microbial degradation of ATZ at  $\text{NaN}_3$  concentrations of  $> 200$  mg/L, although no

microbial degradation was observed for any herbicide or PHEN in this study at the 100 mg/L  $\text{NaN}_3$  level used.

Aqueous background solutions were spiked with appropriate amounts of stock solutions to obtain initial aqueous solutions for sorption, desorption and rate experiments. The concentrations of initial aqueous solution ranged from 40 to 20,000  $\mu\text{g/L}$  for ATZ, 250 to 25,000  $\mu\text{g/L}$  for MET, and 100 to 25,000  $\mu\text{g/L}$  for NAP for sorption equilibrium experiments. Initial aqueous concentrations employed for MET sorption rate experiments were 500  $\mu\text{g/L}$  and 5,000  $\mu\text{g/L}$  and for PHEN sorption rate experiments were 80  $\mu\text{g/L}$  and 800 $\mu\text{g/L}$ . PHEN initial aqueous concentrations used for inorganic coatings experiments ranged from 25 to 750  $\mu\text{g/L}$ . All initial aqueous solutions contained < 0.5% of methanol to prevent any co-solute effects on sorption and desorption experiments.

### **3.2 Sorbents**

The primary sorbents used for the study were Chelsea Soil (a topsoil from Chelsea, MI) and three chemically distinct SOM fractions extracted from Chelsea Soil. A high organic matter peat Pahokee Peat (Pahokee, FL) and three isolated SOM fractions extracted from Pahokee Peat were also used for ATZ sorption and desorption experiments. Sorbents employed in inorganic coatings experiments included Illinois #6 Coal (Argonne National Laboratories, Argonne, IL), Chelsea Soil SOM, and their modified forms as described below.

### 3.2.1 Sorbent Preparation

To obtain the sorbents used in this study, Chelsea Soil was fractionated into three fractions by wet chemical procedures modified from an earlier work (Song et al., 2002). Figure 3.1 depicts a flow chart of the extraction process used.

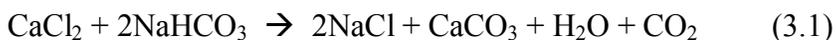
The bulk soil was first repetitively extracted with dilute alkali solution (0.1 M NaOH, 12 times) until the supernatant became colorless, following the standard procedure recommended by the International Humic Substances Society (IHSS) (available online at <http://ihss.gatech.edu>). The supernatant was separately collected and acidified with 6 M HCl to precipitate the humic acid fraction. This fraction was treated with 0.3 M HCl and 0.3 M HF mixture for 12 hrs in a water bath maintained at 60 °C to remove mineral impurities. The remaining solids were centrifuged and re-dissolved in 0.1 M NaOH and re-precipitated to obtain a more purified humic acid. This fraction was washed with Milli Q water and freeze dried to obtain the humic acid used in this study and termed as Soil HA.

A part of the alkali extracted soil residue was neutralized, centrifuged and freeze-dried to obtain the Base Extracted Soil (Soil BE). The remaining solid residue from the original repetitive extraction was subjected to a hot mineral acid treatment for 24 hr in a water bath maintained at 60°C. Initial treatment with 6 M HCl was followed by a 6 M HCl, 12 M HF mixture to dissolve silicates and metal oxides and hydroxides, yielding a solid residue enriched in kerogen and black carbon particles. After cleaning it sequentially with 6 M HCl, 1 M HCl, and MilliQ water, the solid residue was extracted with 0.1 M NaOH to dissolve bound humic acids. The humic acid fraction thus obtained was termed as HA-II and was not used in this study. This enriched solid material

obtained from the soil was freeze dried and defined as Soil Kerogen and Black Carbon (Soil KB). All SOM fractions were stored in glass bottles at controlled temperature and humidity until further use. The relative contents of the sorbents obtained from the bulk soil are presented in Table 3.3.

Three fractions similarly extracted from Pahokee Peat by Song et al. (2002) – Peat BE, Peat KB and Peat HA were also used in the study. A bituminous coal, Illinois # 6 from St. Louis, IL (Argonne National Laboratory, Argonne, IL) was used in inorganic coating studies for comparison with the Soil KB fraction.

To obtain the sorbents to be used in inorganic coating experiments, two hard carbon or particulate organic matter samples – Soil KB, obtained as described above and Illinois Coal #6 were loaded with  $\text{CaCO}_3$  and  $\text{Fe}(\text{OH})_3$  precipitated in situ. Three levels of  $\text{CaCO}_3$  loadings for each sorbent were obtained by preparing three different sets of  $\text{NaHCO}_3$  and  $\text{CaCl}_2$  aqueous solutions with concentrations of 0.005 M, 0.01 M and 0.02 M for  $\text{CaCl}_2$  and 0.01 M, 0.02 M and 0.04 M for  $\text{NaHCO}_3$ . In solution, the  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  reaction occurs as follows:



Thus the stoichiometric ratio of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  to form  $\text{CaCO}_3$  is 1:2. The  $\text{CaCO}_3 \rightleftharpoons \text{Ca}(\text{HCO}_3)_2$  chemistry dictates that  $\text{CaCO}_3$  is the dominant species in solution at  $\text{pH} > 8.3$ . Thus to form  $\text{CaCO}_3$  precipitates, the sorbent was placed in Pyrex glass centrifuge bottles and 15 mL each from a set of  $\text{NaHCO}_3$  and  $\text{CaCl}_2$  solutions were added. The pH was raised to above 8.3 with 0.1 M NaOH. Enough NaOH was added to

precipitate all  $\text{CaCO}_3$ . This process was repeated with other concentrations of the  $\text{NaHCO}_3$  and  $\text{CaCl}_2$  solutions and with the coal sample. Similarly, three concentration levels of  $\text{Fe(OH)}_3$  were coated on the KB and the coal sample by employing three different concentration of  $\text{FeCl}_3$  (0.01 M, 0.05 M and 0.1 M). A given concentration of  $\text{FeCl}_3$  was added to glass centrifuge bottles containing a pre-weighed amount of KB or coal. Brownish red  $\text{Fe(OH)}_3$  precipitates were formed by raising the pH of the solution to 8.0 by adding 0.1M NaOH.

The 12 centrifuge bottle systems obtained in this manner were capped immediately after  $\text{CaCO}_3$  or  $\text{Fe(OH)}_3$  precipitation and shaken first manually and later on a shaker at 125 rpm for 24 hrs to ensure equilibration of  $\text{CaCO}_3$  or  $\text{Fe(OH)}_3$  with the sorbents. After 24 hrs, the bottles were centrifuged and the samples were freeze dried and stored at room temperature until characterization and use. Samples were characterized with SEM equipped with EDAX as described below.

### **3.2.2 Sorbent Characterization**

*Surface Area Analysis:* Argon BET surface area of the sorbents was obtained. The results are presented in Table 3.2.

*Elemental Analysis:* The sorbents were characterized with an elemental analyzer to determine their C, H, N and O; the results are summarized in Table 3.3.

*Scanning Electron Microscopy (SEM) Imaging:* The SEM micrographs of Pahokee Peat and fractions were obtained by Song et al. (2002) and are presented in Figure 3.2. The

SEM micrographs of the samples extracted from Chelsea Soil were obtained using an Amray 1830I machine (Amray Inc., Bedford, MA). The pictures, presented in Figure 3.3, exhibit the differences in physical structure among the fractions. These are further discussed in Chapter 4.

*Energy Dispersive X-Ray (EDAX) Analysis:* This analysis was done for the inorganic coating samples to determine the differences in Ca and Fe composition of the samples of coated and uncoated samples. The results are presented in Figure 3.4.

### **3.3 Sorption and Desorption Experiments**

Sorption equilibria were measured with a constant dosage batch technique using flame-sealed glass ampules as the reactors. The constant soil to solution ratio used for each sorbent-sorbate system was determined from preliminary variable-dosage tests with an aim of achieving approximately 50% reduction in initial aqueous phase concentrations of the herbicides. The results of the preliminary rate tests showed that an equilibration time of 21 d was sufficient for attainment of equilibrium for all the sorbent-sorbate systems. This time period was employed for final sorption tests reported here for all systems except the ATZ-HA system. The ATZ-HA system showed ATZ degradation in about 4 d, therefore a reaction time of 2 days was chosen to obtain a phase distribution relationship between the solid phase and aqueous phase ATZ concentration.

In the final sorption experiments, 10 mL duplicate glass ampules (Wheaton) containing a pre-weighed amount of sorbent were filled with an appropriate volume of the initial solution of each concentration, leaving approximately 2.5 mL of headspace to

facilitate mixing and were flame sealed immediately. After checking for leakage, the sealed ampules were shaken end to end at  $22 \pm 1$  °C at 125 rpm to ensure complete mixing. After 21 d of equilibration time, the ampules were centrifuged at 2000 rpm and flame opened. An aliquot of ~ 3 mL of the supernatant was carefully withdrawn from each reactor, and mixed with ~ 2 mL of HPLC grade methanol in pre-prepared 5 mL glass vials for HPLC analysis.

For all sorbent-sorbate systems, control experiments were conducted using reactors prepared similarly but contained no sorbent for assessing loss of solutes to the reactor components during sorption tests. Results of triplicate reactors showed that the average solution phase concentrations of each solute were within 98–102% of the respective initial concentration of the aqueous solutions in the reactors. Hence, no correction was made during reduction of the sorption data.

### **3.4 Sorption Rate Experiments**

Rate experiments were conducted with MET and PHEN, with Chelsea Soil and its three extracted fractions (BE, KB and HA) as the sorbents. Glass vials (10 mL) with Teflon lined septa were used for the experiment. A preliminary run showed no loss of mass from the vials after shaking for > 30 days. Thus vials were preferred over centrifuge tubes, which showed losses with reaction time, and flame sealed ampules, which are time consuming to seal and open and thus not suitable for the time sensitive rate experiments.

To obtain the rate data, equal amounts of each sorbent were added into 10 vials along with aqueous solution having the same concentration of solute. These vials were shaken at 125 rpm on a constant temperature incubator-shaker maintained at  $22 \pm 1$ °C. At

designated times duplicate vials were centrifuged, opened and 2 mL of the supernatant carefully transferred into a vial containing approximately 3 mL of methanol. The vials were sacrificed at 20 min, 80 min, 6 hr, 1, 2, 4, 8, 14, 22 and 30 d from the start of the reaction (the first contact between solid and solute).

The same experiment was run in parallel for two concentration levels each of MET and PHEN. Duplicate controls, prepared in the same way as the reactors but containing no solids, were run for each time point. Change in the concentration of controls over the 30 d of reaction time was within 2% of the initial value, and thus losses due to degradation or sorption to reactor components were considered negligible.

### **3.5 Solute Analysis**

Aqueous phase herbicide concentrations were analyzed with a reverse phase HPLC (Agilent 1100 series) equipped with an ultraviolet diode array detector (UV-DAD) and a Fluorescence Detector (FLD). The UV-DAD at absorption wavelengths of 220, 197 and 213 nm was used to analyze ATZ, MET and NAP, respectively. FLD at 250 nm excitation and 364 nm emission was used to measure PHEN at low concentrations (0.5 to 30  $\mu\text{g/L}$ ) and UV-DAD at 250 nm absorption wavelength was used to measure higher concentrations (60 to 1000  $\mu\text{g/L}$ ). A Hypersil column (ODS, 5  $\mu\text{m}$ , 2.1  $\times$  250 mm, Phenomenex, Torrance, CA) was used for ATZ and PHEN analysis and a Luna column (ODS, 5  $\mu\text{m}$ , 4.0  $\times$  250 mm, Phenomenex, Torrance, CA) was used for MET and NAP analysis. The mobile phase was a mixture of acetonitrile and water at a 50:50 volumetric ratio and a flow rate of 0.3 mL/min for ATZ, at a 70:30 volumetric ratio and a flow rate of 1.2 mL/min for MET, at a 65:35 volumetric ratio and a flow rate of 1.2 mL/min for

NAP and 90:10 volumetric ratio and flow rate of 0.5 mL/min for PHEN. External standards in methanol were used to obtain linear calibration curves for the four chemicals.  $R^2$  of  $> 0.99$  were obtained for all standard curves. Aqueous phase herbicide concentrations were obtained by multiplying the concentrations measured by HPLC with the respective methanol dilution factors for the samples.

### 3.6 Data Analysis

#### 3.6.1 Sorption Equilibrium Data Reduction

The Freundlich sorption model discussed in Chapter 2 was used to fit the equilibrium sorption data obtained. A linearized logarithmic form of equation 2.4 was used for each sorbent-sorbate system as follows:

$$\log q_e^i = \log K_F^i + n^i \log C_e^i \quad (3.2)$$

where  $q_e^i$  and  $C_e^i$  are the equilibrium solid- and solution-phase concentrations in  $\mu\text{g}/\text{kg}$  and  $\mu\text{g}/\text{L}$ , respectively, for a sorbent 'i';  $K_F^i$  is the Freundlich isotherm coefficient with units  $\mu\text{g}^{1-n}\text{kg}^{-1}\text{L}^{-n}$ ; and  $n^i$  is the isotherm linearity index. The Freundlich model parameters were obtained by a linear regression on the data using a statistical software (SYSTAT, version 10.0, SYSTAT Inc.).

Single-point  $K_{OC}$  values ( $= K_F C_e^{n-1}/f_{OC}$ ) were obtained for all the sorbent-sorbate systems at constant  $C_e$  levels of the herbicides using  $K_F$  and  $n$  values presented in Chapter 4. The expected contributions of BE, HA and KB to the overall sorption capacity

exhibited by the bulk soil were calculated by multiplying the observed Freundlich parameters for these fractions with their relative contents in the bulk soil as:

$$q_e^i = f_M * K_F^i C_e^{n^i} \quad (3.3)$$

where  $q_e^i$  is the contribution of sorbent 'i';  $f_M$  is the mass fraction of sorbent 'i' isolated from the bulk soil;  $K_F^i$  and  $n^i$  are the Freundlich isotherm parameters for the sorbent 'i'.

### 3.6.2 Sorption Rate Data Modeling

The data obtained for sorption rate experiments included  $q(t)^i$  and  $C(t)^i$ , which are the solid and aqueous phase solute concentrations for sorbent 'i' in  $\mu\text{g}/\text{kg}$  and  $\mu\text{g}/\text{L}$ , respectively at a time ' $t$ '. To determine the mass transfer rate coefficients in the sorption process and to delineate the differences among different sorbents, a gamma probability function (developed by Ahn et al., 1999; Ju and Young, 2005) was used to describe the rate data. The model, which is discussed in detail in Chapter 6, assumes sorption into each fraction as consisting of a two step process: instantaneous equilibrium in fraction  $f$  of the sorbent having solid phase concentration =  $S_1$  and mass transfer limited sorption in fraction  $(1-f)$  of the sorbent, having solid phase concentration =  $S_2$  at time  $t$ . The sorption in  $S_1$  is described by the equation:

$$\frac{dS_1}{dt} = f * K_{oc} \frac{dC_{aq}}{dt} \quad (3.4)$$

where  $K_{OC} = \text{equilibrium } K_{OC} = q_{30d}/(C_{30d} * f_{OC})$ . The fraction  $S_2$  is hypothesized to consist of  $n$  number of compartments, each having a different mass transfer rate coefficient for the solute. The distribution of mass transfer rate coefficient  $k$  in each compartment is assumed to be defined by a continuous Gamma distribution as:

$$p(k) = \frac{\beta^\alpha k^{\alpha-1} \exp(-\beta k)}{\int_0^\infty x^{\alpha-1} \exp(-x) dx} \quad (3.5)$$

where  $\alpha$  and  $\beta$  are parameters that determine the shape and scale of the  $\Gamma$  distribution, respectively, and the denominator is the statistical  $\Gamma$  function of  $x$ . The total sorption in  $(1-f) = S_2$  is then represented as the sum of sorption in the  $n$  compartments as:

$$\frac{dS_2}{dt} = (1-f) * \sum_{i=1}^n p(k_i) * k_i * \left( S_{2i} - \frac{K_{OC} C_{aq}}{n} \right) \quad (3.6)$$

An  $n = 100$  was used. The modeled solid phase concentration at time  $t$  is thus obtained as:

$$q_m = S1 + S2 \quad (3.7)$$

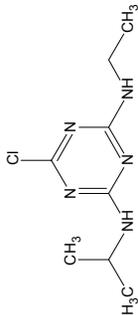
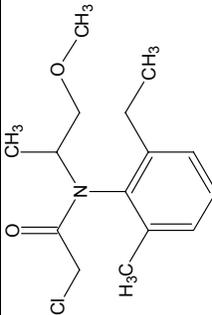
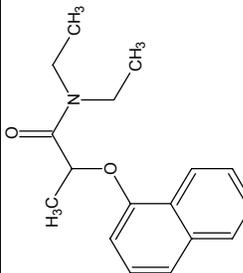
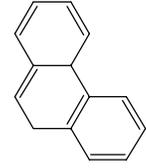
Equations 3.4 and 3.6 are numerically integrated for 1000 time steps of 1 min each initially, followed by 1 hr steps until the 30 d time period of the experiment. The

model parameters  $f$ ,  $\alpha$  and  $\beta$  are minimized simultaneously by minimizing the error between the modeled and the observed solid phase concentration  $q_o$ , defined as:

$$\text{error (\%)} = 100 \times \left[ \frac{\sum_{i=1}^N (q_o - q_m)^2 / q_o^2}{N} \right]^{0.5} \quad (3.8)$$

using the Solver function of MS Excel. (See Appendix A for a sample MS Excel sheet and Appendix B for details on model parameter behavior).

Table 3.1 Relevant physicochemical properties and toxicity of the atrazine, metolachlor, napropamide and phenanthrene

Compound	Structure	M.W. <sup>a</sup>	C <sub>s</sub> <sup>b</sup>	log K <sub>ow</sub> <sup>c</sup>	Source of contamination <sup>d</sup>	Half life <sup>e</sup>	Toxicity <sup>f</sup>	Use in this study
Atrazine		216	30	2.18	High mobility in soils, Storm water runoff for surface waters, soil leachates for ground water	90-120 d (lab) 13-261 d (field)	Endocrine disruptor, teratogen in frogs, LD <sub>50</sub> = 1750 mg/kg in mice LC <sub>50</sub> = 15 ppm for fish	Sorption - Desorption equilibria
Metolachlor		284	500	3.13	Moderate to high mobility in soils, Storm water runoff for surface waters, soil leachates for ground water	67-81 d	LD <sub>50</sub> = 2780 mg/kg in rats LC <sub>50</sub> = 8.2 ppm for fish	Sorption - Desorption equilibria, Sorption Rates
Napropamide		271	73	3.36	Low mobility in soils, Storm water runoff for surface waters, soil leachates for ground water	446 d (lab) 17-131 d (field)	LD <sub>50</sub> = 5000 mg/kg in rats LC <sub>50</sub> = 12.6 ppm for fish	Sorption - Desorption equilibria
Phenanthrene		178	1.29	4.57	Air deposition into surface waters, leaking underground fuel storage tanks, petroleum and coal processing	69-180 d (field)	Possible carcinogen LC <sub>50</sub> = 0.435 ppm for fish	Sorption Rates, Sorption equilibria of inorganic coated sorbents

<sup>a</sup> Molecular weight; <sup>b</sup> Aqueous solubility, mg/L; <sup>c</sup> Octanol-water partition coefficient (values from Schwarzenbach et al., 2003); <sup>d</sup> (EPA mobility classification); <sup>e</sup> (values from EPA contaminant fact sheets); <sup>f</sup> (values from EPA pesticide fact sheets and USGS Pesticide Toxicity Index for Fresh Water Aquatic Organisms, 2<sup>nd</sup> ed., 2006)

Table 3.2 BET surface area and total organic carbon (TOC) of the sorbents

Sorbent	Source	Ar – BET Surface	
		Area (m <sup>2</sup> /g)	TOC
Pahokee Peat	Pahokee, FL	NA	45.18 <sup>a</sup>
Peat BE	Extracted from Peat	NA	47.82 <sup>a</sup>
Peat KB	Extracted from Peat	NA	58.82 <sup>a</sup>
Peat HA	Extracted from Peat	NA	55.71 <sup>a</sup>
Chelsea Soil	Chelsea, MI	3.07 <sup>b</sup>	5.29 <sup>b</sup>
Soil BE	Extracted from Soil	3.90 <sup>b</sup>	3.33 <sup>b</sup>
Soil KB	Extracted from Soil	16.66 <sup>b</sup>	30.40 <sup>b</sup>
Soil HA	Extracted from Soil	0.15 <sup>b</sup>	51.48 <sup>b</sup>
Illinois #6 Coal	St. Louis, IL	14.1 <sup>c</sup>	77.7 <sup>d</sup>

<sup>a</sup> Song et al., unpublished data, <sup>b</sup> this study, <sup>c</sup> Larsen and Wernett (1987),  
<sup>d</sup> Argonne National Laboratory

Table 3.3 Elemental composition of the sorbents

Sorbent	C <sup>a</sup>	O <sup>a</sup>	H <sup>a</sup>	Ash (%)	O/C <sup>b</sup> Ratio	H/C <sup>b</sup> Ratio	Relative Contents <sup>a</sup> (%)
Pahokee Peat	45.18	32.22	3.81	14.8	0.53	1.01	-
Peat BE	47.82	28.45	4.98	15.3	0.45	1.26	ND
Peat KB	58.82	27.28	5.54	5.91	0.35	1.12	30.9
Peat HA	55.71	33.16	4.92	1.82	0.45	1.06	49.7
Chelsea Soil	5.29	6.76	0.90	ND	0.96	2.04	-
Soil BE	3.33	3.53	0.68	ND	0.79	2.44	89.9
Soil KB	30.4	14.02	2.91	48.2	0.35	1.15	3.6
Soil HA	51.5	30.62	5.04	5.21	0.45	1.17	3.9
Illinois # 6 Coal	77.7 <sup>c</sup>	13.5 <sup>c</sup>	5.00 <sup>c</sup>	14.25	0.77	0.13	-

<sup>a</sup> weight %; <sup>b</sup> weight ratio; <sup>c</sup> ash free basis

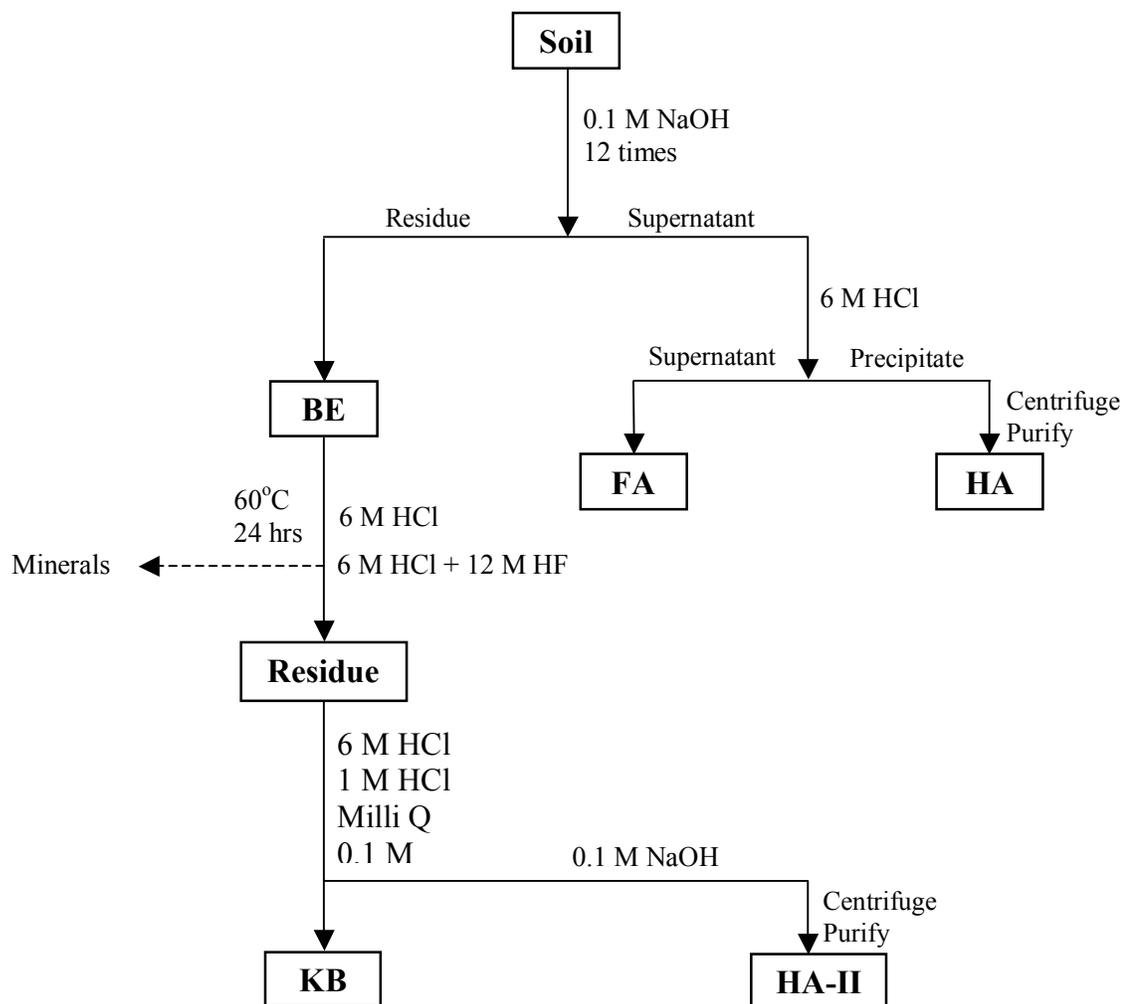


Figure 3.1 Schematic of chemical extraction procedure used to obtain soil organic matter fractions

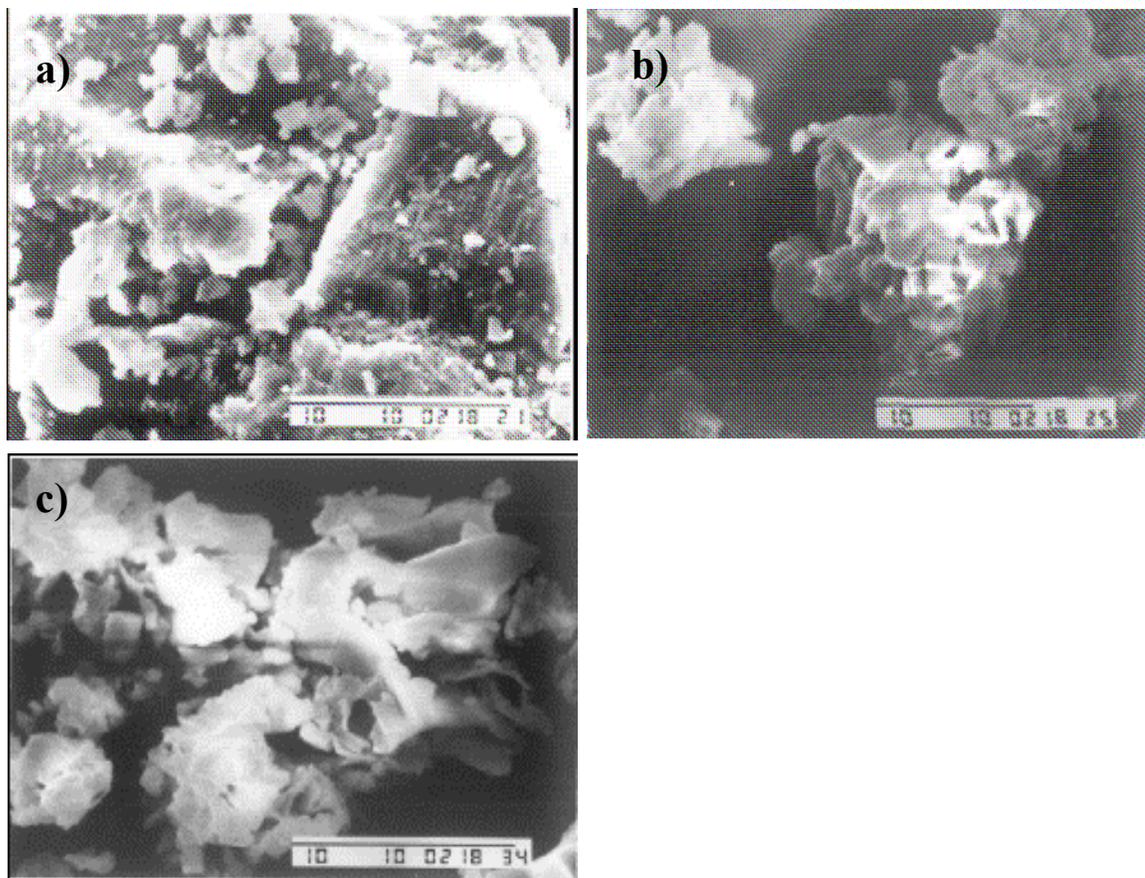


Figure 3.2 SEM micrographs of a) Pahokee Peat, b) Peat BE, and c) Peat KB.

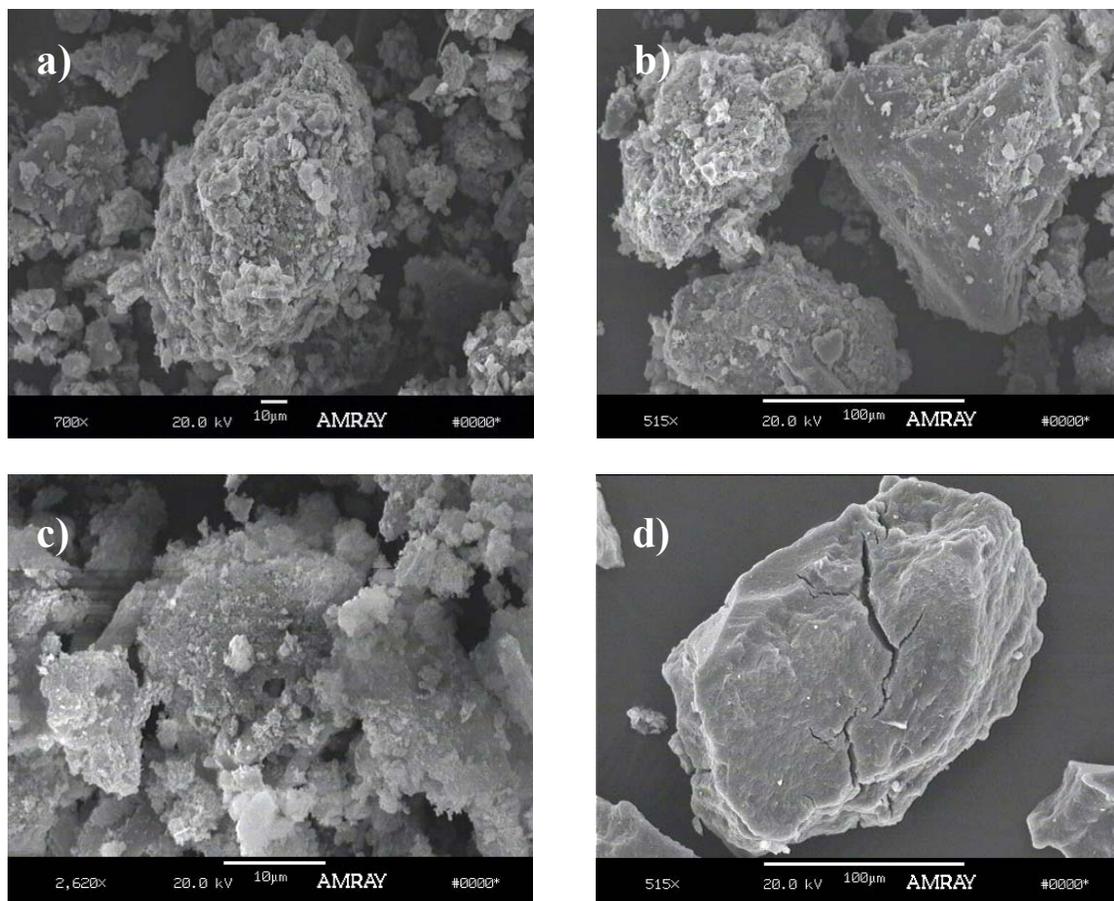


Figure 3.3. SEM micrographs of a) Chelsea Soil, b) Soil BE, c) Soil KB and d) Soil HA.

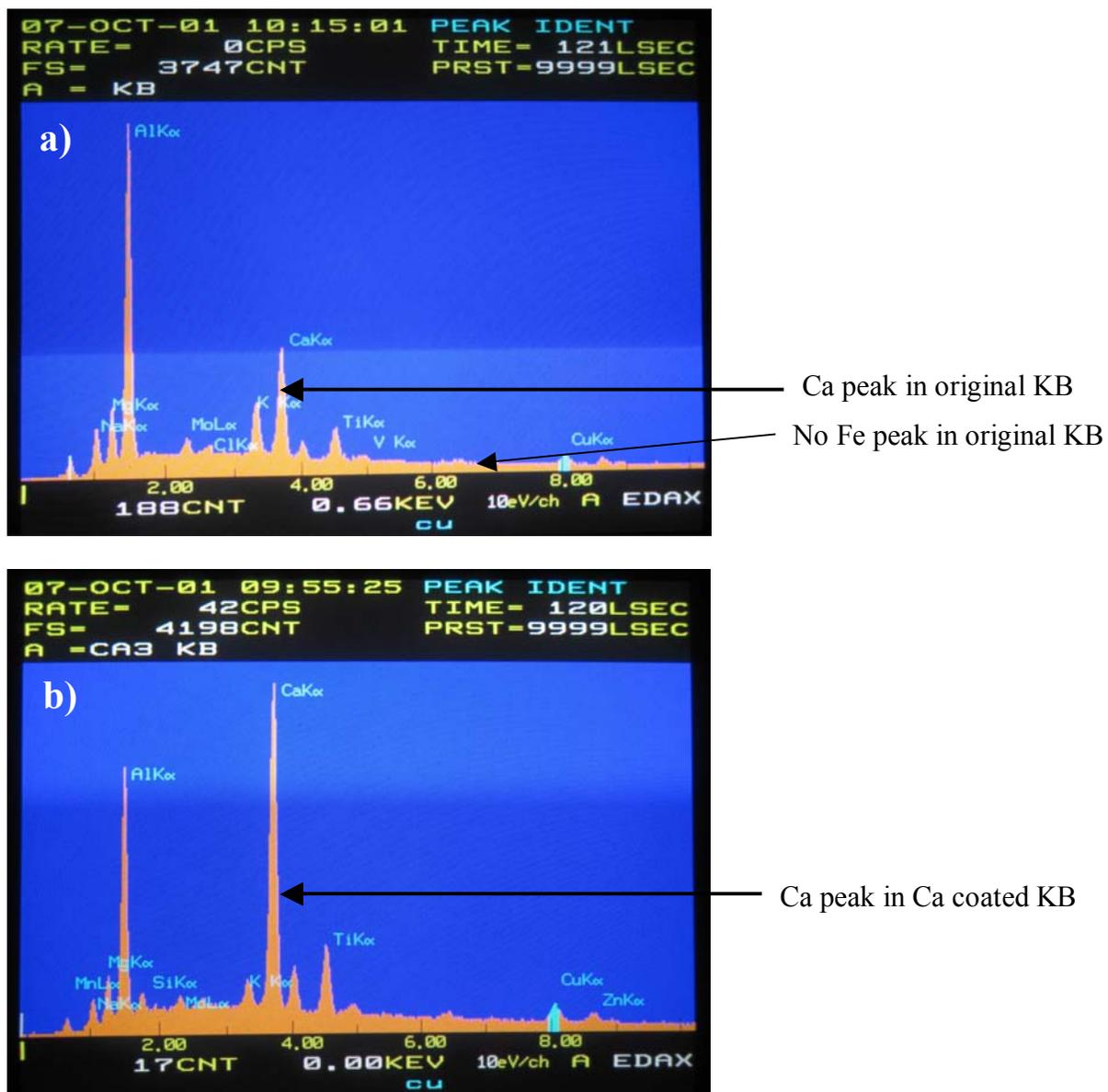


Figure 3.4. EDAX analysis of coated samples: a) untreated KB b) Ca coated KB  
 (continued on next page)

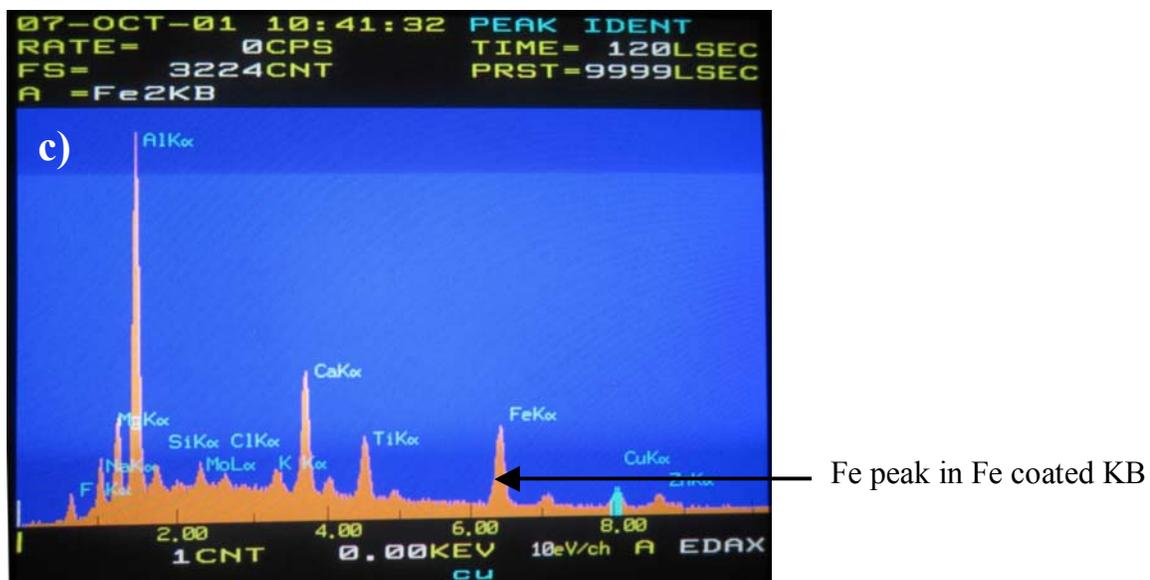


Figure 3.4 (contd.) c) Fe coated KB.

## CHAPTER 4: SORPTION EQUILIBRIA OF ATRAZINE, METOLACHLOR AND NAPROPAMIDE

### Overview

This Chapter examines the roles of different soil organic matter (SOM) fractions in the sorption of three chemically different herbicides – atrazine (ATZ), metolachlor (MET) and napropamide (NAP) – by soils. As described in Chapter 3, a base-extraction procedure was employed to obtain humic acids (HA) and base extracted (BE) fraction from a peat and a soil, and subsequent demineralization of BE yielded the kerogen and black carbon (KB) fractions. These fractions, along with the Bulk Peat and Soil, were used as the sorbents for sorption equilibrium experiments. The sorption equilibrium data indicated that all the herbicides exhibited nonlinear isotherms, with the nonlinearity index being close to unity for both Peat HA and Soil HA.

### 4.1 Rationale and Objectives

A majority of sorption equilibrium studies to date for pesticides have used either inadequate reaction times or have assumed linear sorption isotherms, or both (Chapter 2). Studies have also assumed SOM to be a homogenous sorbent into which the pesticide molecules partition. It was assumed that both the above scenarios might not hold true, however, because significant heterogeneity within SOM has been observed, with SOM components variously showing linear and nonlinear isotherms for PAHs; if the sorption isotherms for pesticides are nonlinear, it will have important consequences for determination of pesticide distribution coefficients which need to be examined. Given the

reported extensive sorption of other classes of organic compounds on KB (PAHs, PCBs), it was expected that the KB fraction will dominate the sorption of pesticides. The objectives of the experiments in this Chapter were specifically to: i) quantify sorption equilibria for ATZ, MET and NAP using two bulk soils and their extracted HA and KB as the sorbents; ii) to correlate the sorption behavior with properties of bulk soils and SOM; iii) quantify the contribution of the HA and KB fractions to the overall herbicide sorption by the bulk soil; and iv) to examine the effect of isotherm nonlinearity towards prediction of sorption capacity of soils.

#### 4.2 Experiments and Data Analysis

The materials and methods used for sorption equilibrium experiments have been detailed in Chapter 3. In brief sorption equilibrium experiments were conducted for ATZ on two bulk samples: Pahokee Peat and Chelsea Soil and three fractions isolated from each of them: BE, KB and HA. Experiments with MET and NAP were conducted on Chelsea Soil and its BE, KB and HA fractions only. Short term sorption experiments (with reaction times of 36 hr and 72 hr) for ATZ on the Bulk Peat and Bulk Soil were conducted to investigate the time dependence of sorption parameters. Sorption equilibrium data was collected after 21 d of equilibration, the data obtained by HPLC analysis and mass balance were the solid and aqueous phase concentrations of the herbicides  $q_e$  and  $C_e$  respectively.

Equation 3.1 [ $\log q_e^i = \log K_F^i + n^i \log C_e^i$ ] was used to fit both the short term and the equilibrium sorption data obtained for a given sorbent-sorbate system. The results are presented in Tables 4.1 and 4.2 respectively. Also shown in Table 4.2 are the single point

KOC values obtained using equation 3.2 [ $K_{OC} = K_F C_e^{n-1}/f_{OC}$ ] for all the sorbent-sorbate systems at three  $C_e$  levels of the herbicides ( $C_e/C_S = 0.5, 0.05, 0.005$ ; where  $C_S$  = aqueous solubility of the herbicide) using the observed  $\log K_F$  and  $n$  values listed in Table 4.2. The obtained sorption equilibrium isotherms are presented in Figure 1. The expected contributions of BE, HA and KB to the overall sorption capacity exhibited by the bulk soil were calculated by equation 3.3 [ $q_e^i = f_M^i * K_F^i C_e^{ni}$ ] and the results are presented in Table 4.3.

### 4.3 Results and Discussion

The elemental composition and relative contents of the distinct SOM domains extracted from the Bulk Peat and Soil were presented in Table 3.3. The results indicated that the HA and KB fractions extracted from the Bulk Soil have much higher  $f_{OC}$  content than the Bulk Soil and Soil BE. The  $f_{OC}$  of the Soil BE is even lower than that of the bulk soil due to the removal of high  $f_{OC}$  HA fraction. The Peat KB and Peat HA sample do not exhibit a similarly large difference from  $f_{OC}$  contents of the Bulk Peat, which is expected as Peat is an exceptionally high  $f_{OC}$  SOM end member and coal precursor. The higher oxygen content of both the HA fractions relative to other fractions indicates the abundance of oxygen containing functional groups in agreement with the established literature on structure of HAs (Stevenson, 1994). The higher hydrogen content of both the KB fractions suggests the presence of a relatively more reduced aromatic structure. This fraction is primarily thought to consist of kerogen and black carbon (Luthy et al., 1997, Feng et al., 2006) – it is thus located closer to graphite, compared to other domains,

in the chronology of metamorphosis of dead organic matter to graphite (Feng et al., 2006).

These distinct properties of SOM domains as well as the physicochemical properties of ATZ, MET and NAP (Table 3.1) determine the sorption mechanisms exhibited by these sorbents in the equilibrium sorption of the herbicides.

#### 4.3.1 Time Dependence of ATZ Sorptive Phase Distribution Relationships (PDRs)

A comparison of sorption parameters in Tables 4.1 and 4.2 indicates that the PDRs measured for the original peat or the soil at non equilibrium conditions (36 and 72 hr) (Table 4.1) are more linear than the isotherm at the equilibrium condition (21 d) (Table 4.2). The  $n(t)$  values of PDRs obtained for the Bulk Peat are 0.933 and 0.920, respectively, at 36 and 72 hr, and for the Bulk Soil are 0.934 and 0.939, respectively. These  $n(t)$  values are greater than the isotherm  $n$  values of 0.722 and 0.773 measured for the Bulk Peat and Bulk Soil, respectively. Similarly, the  $\log K_F(t)$  values of the PDRs measured for the Bulk Peat are 2.039 and 2.168, respectively, at 36 and 72 hr, and for the Bulk Soil are 1.014 and 1.012, respectively. These non equilibrium values are lower than the isotherm  $\log K_F$  parameters of 3.021 and 1.694 measured for the Bulk Peat and Soil, respectively. A similar increase was observed between the calculated  $\log K_{OC}$  values for 36 and 72 hr and the 21 d equilibrium period. For example at  $C_s/C_s = 0.05$ , the  $\log K_{OC}(t)$  values for the original peat are 148.3 and 181.5, for 36 and 72 hr, respectively, while the equilibrium  $\log K_{OC}$  value is 304.7; the  $\log K_{OC}(t)$  for the original soil at  $C_s/C_s = 0.05$  are 120.5 and 124.4, for 36 and 72 hr, respectively, while the equilibrium  $\log K_{OC}$  value is 177.7. This data clearly indicates that sorption has not attained apparent equilibrium

within 72 hr. This is consistent with several prior studies. Weber and Huang (1996) found that the PDRs measured for phenanthrene, a less polar sorbate, and four soil/sediment samples become increasingly nonlinear and the PDR capacities increase rapidly as the solid-solution contact time increases from 5 min to 1 d. The decrease of the  $n(t)$  parameter and the increase of  $K_F(t)$  parameter become gradual to approach the equilibrium values as the contact time increases from 1 d to 14 d. Huang and Weber (1998) observed similar trends for sorption of phenanthrene on shale and kerogen materials, but the time required for attainment of apparent sorption equilibrium was much longer due to the very slow rates of sorption into the tightly knit kerogen matrix. They explained that the changes of time dependent PDR parameters reflect the sequence in which sorbing molecules access the relatively labile sites (rapid sorption) versus the more resistant sites (slow sorption) within heterogeneous SOM matrices. The SOM fractions exhibiting more linear and fast sorption rates are accessed first by the sorbing molecule, and the SOM fractions exhibiting more nonlinear isotherms and slow rates likely dominate the sorption phenomena in later stages after saturation of the fast sorbing SOM fraction sites. This is consistent with slow rates of intra-particle and matrix diffusion of the sorbates within rigid and condensed SOM fractions. Xing and Pignatello (1997) found time-dependent isotherm shapes and sorption parameters for the sorption of 1,3-dichlorobenzene, 2,4-dichlorophenol and metolachlor by SOM. Their data for 1,3-dichlorophenol, for instance, revealed that as the solid-solution contact time increased from 1 to 30 to 180 d, the  $n$  parameter for a soil SOM gradually decreased from 0.806 to 0.720 to 0.715, and  $\log K_F$  increased from 1.478 to 2.164 and to 2.190. Lesan and Bhandari (2003) investigated the changes of PDR parameters for ATZ on two soils as a

function of contact times ranging from 0.01 to 84 d and found a corresponding decrease in the  $n$  value from 0.931 to 0.904 and increase in the  $\log K_F$  value from 0.595 to 0.931.

It is apparent that the sorption data collected with a contact time of 1 to 2 d may underestimate the equilibrium sorption capacity. Compared to several literature studies that used 1 to 2 d as the solid-solution contact times, ATZ sorption isotherms obtained here are more nonlinear with relatively greater  $K_{OC}$  values at comparable  $C_e$  levels. For example, Xing et al. (1996) measured the ATZ sorption on the same Pahokee peat sample used in this study, using 2 d as the contact time. Their reported  $n$  and  $\log K_F$  values were 0.916 and 2.122, respectively, which were quite close to our data collected at 36 and 72 hr, but their  $n$  value is a factor of 1.3 greater and  $K_F$  value is a factor of 8 lower than our 21 day isotherm parameters presented in Table 4.2.

The 4 sorbents and the 3 herbicides represent 12 sorbent-sorbate systems that exhibit 12 different sorption isotherms shown in Figure 4.1 a)-d). The logarithmic Freundlich model equation 3.1 fitted the data excellently, with the  $R^2$  values of the obtained isotherms ranging from 0.997 to 1.000.

#### **4.3.2 Sorption of Herbicides to Bulk Soil**

A  $\log K_F$  value of 1.694 and  $n$  value of 0.773 was observed for sorption of ATZ on the bulk soil. These values are fairly close to the  $\log K_F$  values observed by previous studies for sorption of ATZ on various soils, which range from 0.063 to 1.65 and the  $n$  values which range from 0.49 to 0.98 (Xing et al., 1996; Lesan and Bhandari, 2003; Nemeth-Konda et al., 2002; Daniel et al., 2002; Lu et al., 2002; Socias-Viciana et al., 1999). For MET a  $\log K_F$  value of 1.352 and  $n$  value of 0.903 was observed. The

reported  $\log K_F$  values for MET for a variety of soils are in the range of 0.650 – 1.635 and  $n$  values are in range of 0.75 to 0.94 for a variety of soils (Weber et al., 2003; Lu et al., 2002; Liu et al., 2000; Xing et al., 1996). Our values fall between these observed values. The  $\log K_F$  and  $n$  values observed for sorption of NAP on bulk soil were 2.182 and 0.795. A  $\log K_F$  value of 0.023 and an  $n$  value of 0.993 have been reported for the sorption of NAP on a soil for a sorption period of 24 hours (Turin and Bowman, 1997). However, the  $\log K_F$  value is expected to increase and the  $n$  value is expected to decrease with increased equilibration time and the system mentioned in the study might not have attained equilibrium within 24 hours. Thus we observed that the Bulk Chelsea Soil has the greatest sorption capacity for NAP and the lowest sorption capacity for MET, with the sorption capacity for ATZ lying in between (Figure 4.1a). This observation is according to the expected trend because NAP is the most hydrophobic of the three herbicides, having the greatest  $\log K_{OW}$  (Table 3.1). On the other hand, while MET does not have the lowest  $\log K_{OW}$  value among the three, it possibly has the lowest affinity for bulk soil due to the presence of polar oxygen containing groups in its molecular structure that increase its affinity for the aqueous phase, as indicated by its highest aqueous solubility limit among the three herbicides (Table 3.1). The lower sorption capacity of the bulk soil for MET than ATZ is also supported by previous studies that show that MET is more mobile than ATZ in soil columns (Seybold et al., 1996).

#### **4.3.3 Sorption of Herbicides to HA and BE**

As indicated in Table 4.2 and Figure 4.1 d), the  $\log K_F$  and  $n$  values for sorption of MET on the Soil HA fraction are 2.140 and 0.985 and for the sorption of NAP are

2.844 and 0.952, respectively. Thus the same trend in sorption capacity as seen for the Bulk Soil is also observed for HA, with HA having the greatest sorption capacity for NAP and the lowest for MET. It is notable, however, that  $n$  values for the HA fraction differ substantially from the bulk soil values, being closer to unity, implying both that the HA fraction is more homogenous than the bulk soil and also indicating the fact that HA fraction mostly consists of soft carbon that exhibits partitioning-like sorption phenomena and linear sorption isotherms.

The ATZ-HA systems showed degradation of ATZ at a reaction time greater than 4 days, thus sorption experiments of ATZ on the HA fraction were run for only 2 days and the resulting phase distribution parameters  $\log K_F(t)$  and  $n(t)$  are 2.646 and 0.950. A previous study reported  $\log K_F$  and  $n$  values of 2.612 and 0.886 for 2 day sorption of ATZ on a soil HA (Xing et al., 1996). A number of studies have reported that HA facilitated degradation of ATZ with a reaction time of 4 days or more. In our study, this was evidenced by the appearance of a hydroxyatrazine peak in the chromatogram for ATZ at 238 nm. A detailed discussion of this observation can be found elsewhere (Yu et al., 2006). This special role of HA in degradation of ATZ has been attributed to the presence of acidic groups such as carboxylic acids in the HA structure and basic amide groups in herbicides such as ATZ (Molecular Structure, Table 3.1) that result in hydrogen bonding or proton transfer between the two, resulting in the replacement of the chlorine atom by a hydroxyl group (Sposito et al., 1996, Martin-Neto et al., 2001). Thus the amount of HA present in a particular soil may be important in determining both the efficacy and final concentration of an applied herbicide. No such transformation was observed for the MET-HA and NAP-HA systems or for other sorbents, indicating the specific nature of

the interactions involved in the ATZ-HA system. Also, no transformation of ATZ was observed for the Bulk Soil-ATZ system, indicating that the HA functional groups needed for such transformations are modified or less accessible to ATZ in the bulk soil. This observation might also arise from the fact that HA-ATZ interactions are predominant at low pH conditions, such as those maintained for the HA experiments to prevent dissolution of HA in the background solution. Marti-Neto et al. (2001) have shown negligible ATZ degradation above pH 6.

The  $\log K_F$  and  $n$  values for ATZ sorption on BE are 1.791 and 0.760, for sorption of MET on BE are 1.603 and 0.779, and for the sorption of NAP are 2.374 and 0.708, respectively, thus again exhibiting the same trend in sorption capacities for the three herbicides. The  $n$  values for the BE fraction are the lowest among the SOM fractions, indicating the heterogeneous nature of this fraction.

#### **4.3.4 Sorption of Herbicides to KB**

Figure 4.1 c) presents the sorption isotherms of the three herbicides on the KB fraction. The  $\log K_F$  and  $n$  values for sorption of ATZ on the KB fraction are 3.239 and 0.849, respectively. A  $\log K_F$  of 3.1 and an  $n$  value of 0.97 were observed for sorption of ATZ on black carbon derived from lake sediment (Cornelissen and Gustafson ES&T, 2005). The  $\log K_F$  and  $n$  values for sorption of MET on KB are 2.831 and 0.839 and for the sorption of NAP are 3.469 and 0.832, respectively. The few studies that have been conducted on the sorption of MET and NAP on KB, including black carbon and activated carbon, do not provide explicit  $\log K_F$  and  $n$  values.

Thus the KB fraction exhibits the same trend in sorption capacities, having the highest sorption capacity for NAP and the lowest for MET. The  $n$  values for the three herbicides for the KB fraction are higher than the base extracted and bulk soil values (apart from MET bulk soil  $n$  value), indicating the less heterogeneous nature of the KB fraction compared to both the bulk soil and BE fraction.

The values of  $\log K_F$  for KB are much greater than those of other sorbents, but direct comparison of the sorption capacities (e.g.,  $\log K_F$ ) among the sorbents for the same herbicide is misleading due to the differences in the  $f_{OC}$  of the four sorbents, necessitating the normalization of the solid phase equilibrium sorption data to the  $f_{OC}$  of the sorbents. Thus the solid phase equilibrium concentration was normalized to organic carbon by using the relation  $q_{eOC} = q_e/f_{OC}$  (and  $K_{F-OC} = K_F/f_{OC}$ ) to obtain the organic carbon normalized isotherms for the herbicides for each sorbent, as presented in Figure 4.2 a) and b) for ATZ on Bulk Peat and fractions and Bulk Soil and fractions and in Figure 4.3 a) to c) representing isotherms for ATZ, MET and NAP on Chelsea Soil and fractions.

Figures 4.2 and 4.3 reveal that even after normalization to organic carbon contents both the Peat and the Soil KB fractions show greater sorption capacities than all other fractions. The calculated  $K_{F-OC}$  values range from 386 to 5710 for ATZ, 273 to 2260 for MET and 1357 to 9683  $\mu\text{g}^{1-n} \text{kg}_{OC}^{-1} \text{L}^{-n}$  for NAP for the Bulk Soil and its fractions; the lowest  $\log K_{F-OC}$  in all cases exhibited by HA and the highest by KB. The  $K_{F-OC}$  values for the HA fraction are 0.4 to 0.6 times that of the original soil for all the herbicides. The  $K_{F-OC}$  values for the BE fraction are 2-2.5 times that of the original soil for all the herbicides. In contrast the  $K_{F-OC}$  values exhibited by the isolated KB fraction are 3-6

times higher than the bulk soil values. For example, the log  $K_{F-OC}$  of Bulk soil for MET sorption is 474 and for the HA fraction is 273 while the values for the BE and KB fractions are 1126 and 2260  $\mu\text{g}^{1-n} \text{kg}_{OC}^{-1} \text{L}^n$ , respectively. These observations reveal two important facts described below.

Firstly, they elucidate the variability exhibited by these organic carbon normalized isotherms indicating the differences in intrinsic sorption properties of organic matter with different structural composition and degree of diagenetic alteration. Thus the sorption capacity of a soil is not a linear function of its SOM content; sorption capacity is further dependent on the “quality” and fractional composition of the SOM it contains. This suggests that normalization to organic carbon alone may not be an adequate method to predict sorption of a particular organic compound to soil.

Secondly, the isolated HA fraction has similar sorption capacity for the three herbicides to those of the Bulk Soil, the BE and the KB fraction. The KB fraction in particular has a greater affinity for the three herbicides than any other fraction. This is consistent with previously reported properties of KB as an extremely good sorbent for organic chemicals (Xiao et al., 2004; Cornelissen et al. 2005). On the other hand, the organic carbon normalized sorption capacity of the HA fraction is even lower than the bulk soil and the BE fraction. This observation together with the fact that the HA fraction has the highest organic carbon content ( $f_{OC}$ ) among all fractions, implies that organic matter in HA is a comparatively weaker sorbent than KB or the mineral phase in BE. Earlier studies have pointed out the possibility of such differences in sorption properties among organic matter that is derived from diverse sources and that has undergone varying degrees of diagenesis (Luthy et al., 1997, Weber et al., 2001). Thus in

regard to sorption capacity of HA, which is a less reduced and diagenetically altered SOM component than KB, the observation of higher sorption capacity of highly altered SOM seems to hold true. The greater organic carbon normalized sorption capacity of the left over BE fraction than the bulk soil, after the removal of HA, from the bulk soil also alludes to the low sorption capacity of the HA fraction. The lower sorption capacity of the HA fraction was also observed in a previous study by our group (Xiao et al., 2004) and was attributed to low content of HA in the sorbent soil and sediment samples. Therefore the HA fraction will play a significant role in sorption only when it is the main component of SOM, such as in pristine forest soils. In industrially weathered soils, where KB is abundant due to fossil fuel and crop residue combustion, KB could dominate the sorption of organic compounds.

#### **4.3.5 Contribution of SOM Fractions to Bulk Soil Sorption.**

Theoretical contribution of each SOM domain towards bulk soil sorption was calculated based on their relative contents in the bulk soil by employing equation 2. This equation essentially conveys how much the contribution of an SOM fraction toward bulk soil sorption would be, provided if it exhibited the same sorption capacity in the bulk soil as observed in the isolate form. The expected solid phase concentrations in each fraction were calculated for the same aqueous phase concentrations. The results are presented in Table 4.3 and indicate that for all three herbicides, the calculated sum of solid phase concentrations of the fractions exceeds the observed solid phase concentration of the bulk soil. The sum of BE and HA are expected to essentially represent the bulk soil isotherm if the two fractions were contributing their full potential towards sorption in the bulk soil.

Similarly, the sum of KB and HA represents the expected sorption capacity of the organic matter in soil. But as is apparent from the bulk soil isotherm and the expected contribution of the isolated fractions, the calculated (expected) solid phase concentration of BE + HA and KB + HA are both greater than that of bulk soil for all the herbicides. For example, at a 100  $\mu\text{g/L}$  equilibrium aqueous phase concentration of MET, the solid phase concentration for the bulk soil is 1439  $\mu\text{g/kg}$ , while the calculated sums of BE + HA fractions is 1806 and KB + HA is 1665  $\mu\text{g/kg}$ , respectively. The difference of BE and KB values would essentially reflect the expected sorption to the mineral phase. It was expected that the sorption capacity of the bulk soil would be equal to the sum of its individual components or higher due to loss of some organic matter during the process of isolation of fractions. On the contrary, the sum of solid phase sorbed concentrations of the herbicides on individual components is greater than the bulk soil concentrations, in some 300 – 400 % greater. This is true for all the herbicides examined. This illustrates an important point – that the observed sorption capacity of the bulk soil is lower than the weighted sum of its constituents, indicating that the SOM fractions are unable to fully contribute towards sorption of the herbicides in the bulk soil.

Thus, while the isolated fractions have higher sorption capacities, their presence in the bulk soil somehow renders them less accessible for the sorbing molecules. This is likely due to the aggregation structure of the bulk soil in which SOM domains are tightly bound to the mineral matrix, which causes the sorption sites of the SOM fractions to be only partially available to solute molecules. Researchers in both geochemistry and environmental science have proposed the structure of soil aggregates as consisting of coexisting KB and HA bound to soil minerals (Weber and Huang, 1996). Some studies

have proposed that such a structure essentially protects the SOM within the mineral matrix from further decomposition.

It is proposed that this type of configuration within the soil aggregates renders at least some of the external and internal SOM sorption sites inaccessible due to the blocking of its pores by small organic and inorganic molecules present in the soil. This type of aggregation structure is further supported by our observation that another fraction of HA (named HA-II and not used in this study) was obtained when the HM fraction was treated with hot acids to release the minerals. When the SOM fractions are isolated and purified, more of their sorption sites are accessible for sorbing molecules and thus they exhibit greater sorption capacity in the isolated form.

Earlier, our group has studied the sorption of PAHs on sandy soils and fresh water and marine sediments and found a similar reduced role of “soil/sediment matrix-bound” KB compared to the isolated KB fraction (Xiao et al., 2004). In that study, however the reduction in sorption capacity of the KB fraction was much more pronounced, possibly due to the differences in the hydrophobicity of PAHs as compared to the herbicides used in this study. The bulk soil and the BE fraction in our case are expected to have a relatively higher sorption capacity for the slightly polar herbicides than PAHs due to the affinity of the herbicides for the mineral phase in bulk soil and BE.

Another study from our group (Kim et al., 2007) focusing on the sorption of male and female hormones on Chelsea soil and its isolated SOM fractions also found the sum of BE and KB sorption contributions to be greater than the bulk soil. Other researchers have similarly suggested the inaccessibility of benzene to the internal sorption sites of char due to coating by model lipid compounds (Kwon and Pignatello, 2005), and the

reduction of the ATZ diffusion coefficient for granular activated carbon loaded with model dissolved organic matter by around three orders of magnitude (Li et al., 2003). Less than expected sorption on a clay and HA mixture than the sum of individual components has also been observed for MET (Liu et al., 2000). We believe that this observation should have an impact on the protocols of soil remediation using natural or synthetic KB because the KB incorporated in or amended to soils is expected to show reduced sorption capacities compared to their intrinsic values. We therefore suggest that the sorption behavior of such sorbents should be tested with the mixtures of soils to which they are to be applied. Also, since the soil system is always dynamic with organic and inorganic coatings always being added and removed from a particular soil aggregate, the SOM may never exhibit its ultimate sorption capacity in the environment. Thus any equilibrium attained in such soil-solute systems in laboratory experiments should be considered “apparent”.

#### **4.3.6 Effect of Isotherm Non-linearity**

The  $n$  value, or the isotherm linearity index, reflects the diversity of free energies of sorption and thus the diversity of sorption sites within a sorbent and is a measure of its physicochemical heterogeneity. It has been elucidated that sorption of a solute onto a sorbent begins with the occupation of lowest sorption energy sites and continues to higher sorption energy sites until the sorption capacity of the sorbent is reached (Weber and Huang, 1996); this point the  $n$  value essentially becomes constant. The numeric value of  $n$  elucidates the mechanism involved in the sorption process. Hence an  $n$  value = 1 represents uniform sorption energies for all sorption sites and is indicative of partitioning-

like distribution of the solute between the solid and aqueous phases. As stated earlier, near linear isotherms ( $n$  values ranging from 0.950 to 0.985) were observed for sorption of all herbicides on the HA fraction, while all the other fractions exhibited non-linear isotherms. Previous researchers have described that certain HAs (those having their glass transition temperature below room temperature) have flexible or “rubbery” matrices that accommodate solute molecules analogous to a liquid-liquid partitioning phenomena and thus exhibit near linear isotherms. Our observations indicate that Chelsea soil HA fraction may predominately have such type of constituents. On the other hand the KB fraction is comprised of tightly knit hard carbon matrices and exhibits a diversity of sorption site energies, and thus has nonlinear isotherms ( $n$  values ranging from 0.832 to 0.849). The KB fraction is less heterogeneous than the BE fraction which exhibits the lowest  $n$  values (from 0.708 to 0.779) and the bulk soil ( $n$  values range from 0.773 to 0.903).

Non-linearity of isotherms causes the sorption capacity of organic compounds to be dependent on the initial aqueous phase concentration of sorbing compound. This greatly impacts the accuracy of assessment of sorption properties of soils for applied herbicides. To illustrate this point, single point  $K_{OC}$  values were calculated based on the sorption isotherm parameters obtained for each compound at  $C_e/C_S = 0.005, 0.05$  and  $0.5$  (where  $C_S$  is the aqueous solubility limit of the herbicide), and are presented in Table 4.2. Thus, for example, the organic carbon normalized sorption capacity  $K_{OC}$  for bulk soil for ATZ at  $C_e/C_S = 0.5$  or  $C_e = 15$  mg/L is 105 L/kg, while at a  $C_e/C_S = 0.005$  or  $C_e = 150$   $\mu$ g/L, the  $K_{OC}$  value is 300 L/kg. Extrapolating this calculation further to  $C_e = 1.5$   $\mu$ g/L,

the  $K_{OC}$  value at this aqueous phase concentration is 853 L/kg. A similar trend is seen for all the three herbicides.

The reported average  $K_{OC}$  value in the literature for ATZ is 160 L/kg (Schwarzenbach et al., 2003) for a range of soils. Based on measurements of ATZ  $K_{OC}$  on several soils, it has been suggested that this average value may vary by a factor of 2 (Schwarzenbach et al., 2003). Clearly, the values observed by us for a single soil at different aqueous phase concentrations are more than a factor of 2 different, showing the inherent change in  $K_{OC}$  values due to its dependence on the  $n$  value of the sorption isotherm. Thus the percent uptake of an herbicide from an aqueous solution will be greater at lower concentrations than at higher concentrations. Although  $K_{OC}$  was originally employed in sorption literature as a correcting mechanism for the variability of the linear partitioning coefficient  $K_D$ , the variability in  $K_{OC}$  itself signifies that it cannot be used as the defining parameter for sorption of an herbicide onto a soil. The error lies in the fact that the concept of  $K_{OC}$  employs the same assumption that the normalization to organic carbon or organic matter content will yield a linear relationship between equilibrium solid and aqueous phase concentration, while the isotherm itself is non-linear. Thus even the single point  $K_{OC}$  values calculated from the Freundlich model parameters will not be similar at all aqueous phase concentrations.

Recently, there have been attempts to standardize the soil-solution herbicide distribution coefficients reported in literature by applying certain mathematical normalizations within the data set, for example, normalization of soil properties (Weber et al., 2000). However, as noted above, the values of parameters reported in the literature depend on the herbicide concentrations employed during the study. Researchers have

cautioned against the use of  $K_{OC}$  estimated from  $K_{OC} - K_{OW}$  correlations known as single parameter linear free energy relationships (LFERs) for assessment of sorption properties. Such relationships have been suggested to be useful for narrow compound classes and  $K_{OC}$  values estimated for higher solute concentrations may underestimate sorption at lower concentrations by a factor of 2 or greater (Schwarzenbach et al., 2003). As demonstrated by our study, this error may be as large as an order of magnitude.

To conclude, the amount of organic carbon alone does not control the sorption capacity of soils. Relative abundance of different types of SOM also plays a role in determining a soil's sorption behavior. Further, not only the quality of SOM present but the amount of accessible SOM in the aggregated soil structure (as determined by the bulk soil sorption capacity and  $n$  value) is the key factor in determining the sorption capacity of a soil for a particular herbicide. Thus it is inaccurate to apply the  $K_{OC}$  values calculated from one soil or one particular concentration to another soil or another concentration. For the study of a small set of compounds, we suggest that performing sorption experiments with the environmentally expected concentrations of herbicides and with representative samples of the soils in question can be expected to yield the most accurate results in evaluating the fate and transport of herbicides in those soils. This study shows that caution should be exercised while using intrinsic KB sorption capacities for fate and transport studies, as well as for evaluating synthetic based remediation strategies; capacities of these sorbents need to be measured in their aggregated form.

#### 4.4 Summary and Implications

The sorption equilibrium data indicated that all the herbicides exhibited nonlinear isotherms, with the nonlinearity index being close to unity for both Peat HA ( $n = 0.983$  for ATZ) and Soil HA ( $n = 0.950$  for ATZ,  $0.985$  for MET and  $0.952$  for NAP) indicating their amorphous nature. All sorbents exhibited highest sorption capacity for NAP ( $\log K_F = 2.182 - 3.469$ ) among the three herbicides and the lowest for MET ( $\log K_F = 1.352 - 2.831$ ), consistent with their degree of hydrophobicity. It was observed that the isolated Peat and Soil KB fractions, were exceptionally good sorbents for the herbicides, and played a more important role than Peat or Soil HA in the sorption of herbicides, with  $\log K_{F-OC}$  values ranging from  $2.138 - 2.844$  for HA and  $3.348 - 4.416$  for KB. The super-sorbent property of Soil KB was, however, observed to be diminished in the Bulk Soil, with the Bulk Soil exhibiting 30% less (on average) sorption capacity than the sum of its components, suggesting reduced access of solute molecules to KB aggregated within soil matrices. Organic carbon normalized uptake ratios ( $K_{OC}$ ) for the herbicides were found to be dependent on the initial aqueous concentration of the herbicides, varying factor of 2 on an average for 2 orders of magnitude change in equilibrium aqueous phase concentration.

The sorption equilibrium experiments thus show that isotherms for herbicide sorption to soil are decidedly non linear, unless the soil is entirely made up of humic acids, which is rare considering mineral matter is the major soil constituent and kerogen and black carbon are ubiquitous in soils. The use of short reaction times and linear sorption isotherms should thus be replaced by experiments that attempt to obtain sorption data under equilibrium (at least three weeks of reaction time) and Freundlich type models for obtaining more realistic sorption isotherm parameters. Whereas the presence of KB

greatly enhances sorption capacities of soils compared to what would be otherwise predicted from treating SOM as amorphous organic matter, the determination of HA and KB content of a soil cannot be solely utilized to predict soil sorption capacities. The complex aggregation structure of soils and the attenuation of KB sorption capacity in soils need to be considered as well. The sorption desorption phenomena and mass transfer limited sorption rates said to be associated with KB have been further explored in the next chapters.

Table 4.1 Phase distribution relationship (PDR) parameters for Bulk Peat and Soil

Sorbent	$n(t)$	$\log K_F(t)$ ( $\mu\text{g}/\text{kg}$ )/( $\mu\text{g}/\text{L}$ ) <sup><math>n(t)</math></sup>	N	R <sup>2</sup>	$K_{OC}(t)$ (L/kg)	$C(t)/C_S$	$C(t)/C_S$	$C(t)/C_S$
Bulk Peat					$C(t)/C_S$ = 0.005	$C(t)/C_S$ = 0.05	$C(t)/C_S$ = 0.5	
36 h	0.933 (0.035) <sup>a</sup>	2.039 (0.103) <sup>a</sup>	10	0.987	173.1	148.3	127.1	
72 h	0.920 (0.031)	2.168 (0.092)	10	0.990	218.2	181.5	151.0	
21 d	0.722 (0.015)	3.021 (0.039)	10	0.996	577.5	304.7	160.7	
Bulk Soil								
36 h	0.934 (0.024)	1.014 (0.066)	9	0.995	140.3	120.5	103.5	
72 h	0.939 (0.083)	1.012 (0.083)	9	0.992	143.1	124.4	108.1	
21 d	0.773 (0.014)	1.694 (0.037)	10	0.997	300.0	177.7	105.4	

<sup>a</sup> standard error of estimate

Table 4.2 Freundlich sorption isotherm parameters and single point  $K_{oc}$  values for atrazine, metolachlor and napropamide

Herbicide	Sorbent	$n$	$\log K_f$ ( $\mu\text{g}/\text{kg}/(\mu\text{g}/\text{L})^n$ )	N	$R^2$	$C_d/C_s = 0.005$	$C_d/C_s = 0.05$	$C_d/C_s = 0.5$
Atrazine	Bulk Peat	0.722 (0.015) <sup>a</sup>	3.021 (0.039) <sup>a</sup>	10	0.996	577	304	160
	Peat BE	0.781 (0.011)	3.388 (0.029)	10	0.998	1704	1029	621
	Peat KB	0.821 (0.017)	3.899 (0.044)	10	0.996	5490	3635	2407
	Peat HA <sup>b</sup>	0.983 (0.013)	2.712 (0.030)	5	0.999	849	817	785
Metolachlor	Bulk Soil	0.773 (0.014) <sup>a</sup>	1.694 (0.037) <sup>a</sup>	10	0.997	300	178	105
	Soil BE	0.760 (0.013)	1.791 (0.034)	10	0.997	558	321	185
	Soil KB	0.849 (0.014)	3.239 (0.037)	10	0.997	2679	1892	1337
	Soil HA <sup>b</sup>	0.950 (0.009)	2.646 (0.023)	5	1.000	669	596	532
Napropamide	Bulk Soil	0.903 (0.020)	1.352 (0.063)	19	1.000	199	159	127
	Soil BE	0.779 (0.012)	1.603 (0.039)	20	1.000	263	158	95
	Soil KB	0.839 (0.015)	2.831 (0.049)	20	1.000	632	437	301
	Soil HA	0.985 (0.014)	2.140 (0.047)	20	1.000	238	230	222
Napropamide	Bulk Soil	0.795 (0.005)	2.182 (0.015)	20	1.000	858	535	334
	Soil BE	0.708 (0.008)	2.374 (0.023)	20	1.000	1269	648	331
	Soil KB	0.832 (0.013)	3.469 (0.034)	20	1.000	3595	2442	1658
	Soil HA	0.952 (0.011)	2.844 (0.031)	20	1.000	1021	914	819

<sup>a</sup> standard error of estimate, <sup>b</sup> 2 day phase distribution relationships (PDRs)

Table 4.3 Contribution of SOM fractions towards sorption in Bulk Soil

Herbicide	$C_e$ ( $\mu\text{g/L}$ )	$q_e$ ( $\mu\text{g/kg}$ )		
		Bulk Soil	BE + HA	HA + KB
Atrazine	1	49	73	80
	10	293	474	595
	100	1,738	3,213	4,485
	1000	10,304	22,818	34,214
	10000	61,094	169,897	264,256
Metolachlor	1	22	41	30
	10	180	269	220
	100	1,439	1,806	1,665
	1000	11,508	12,692	12,876
	10000	92,045	94,012	102,262
Napropamide	1	152	240	133
	10	948	1,331	975
	100	5,916	7,732	7,233
	1000	36,898	47,876	54,404
	10000	230,144	319,635	415,615

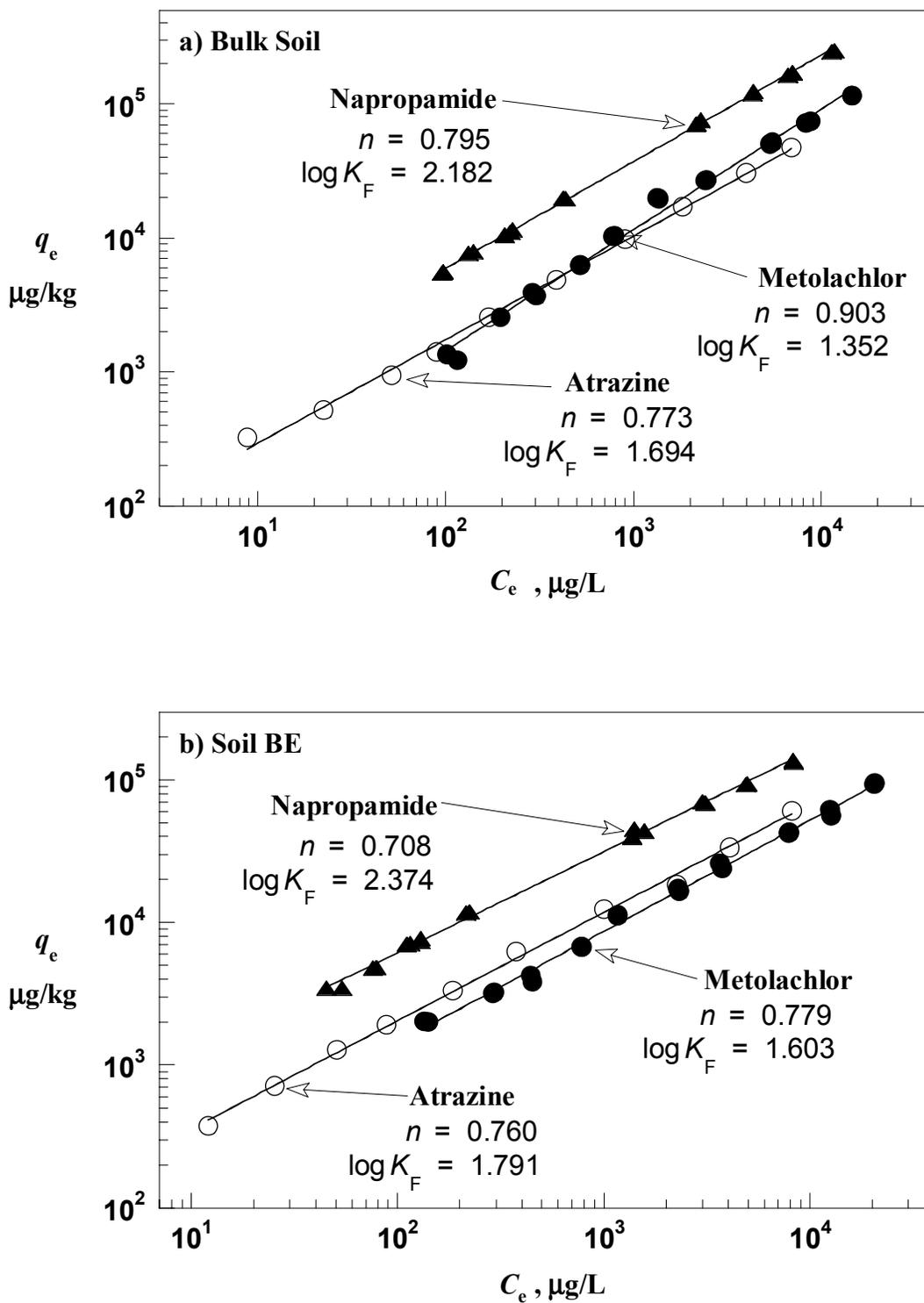


Figure 4.1 Sorption Isotherms for ATZ, MET and NAP on a) Bulk Soil, b) Soil BE (continued on next page).

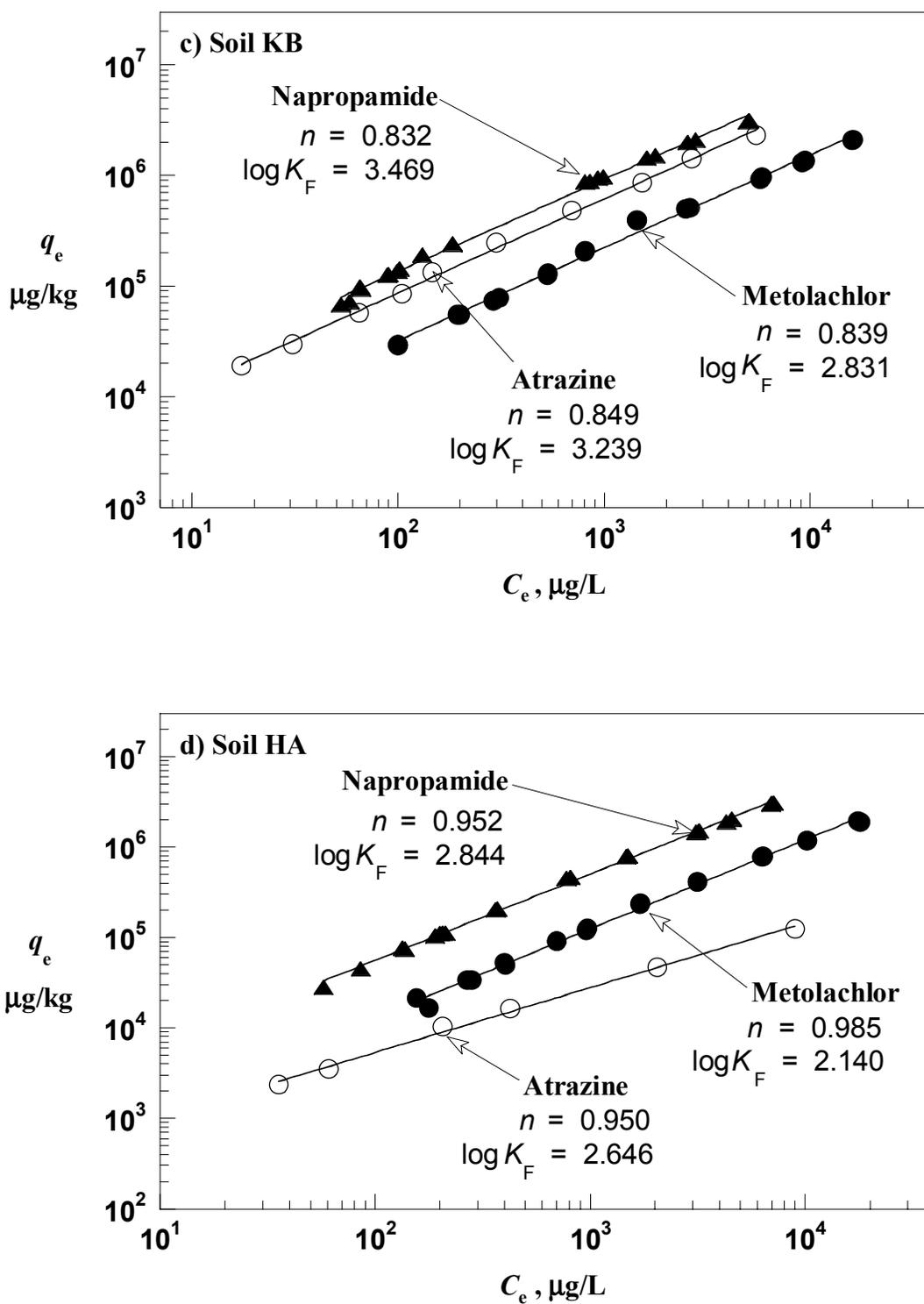


Figure 4.1 (contd.) c) Soil KB and d) Soil HA.

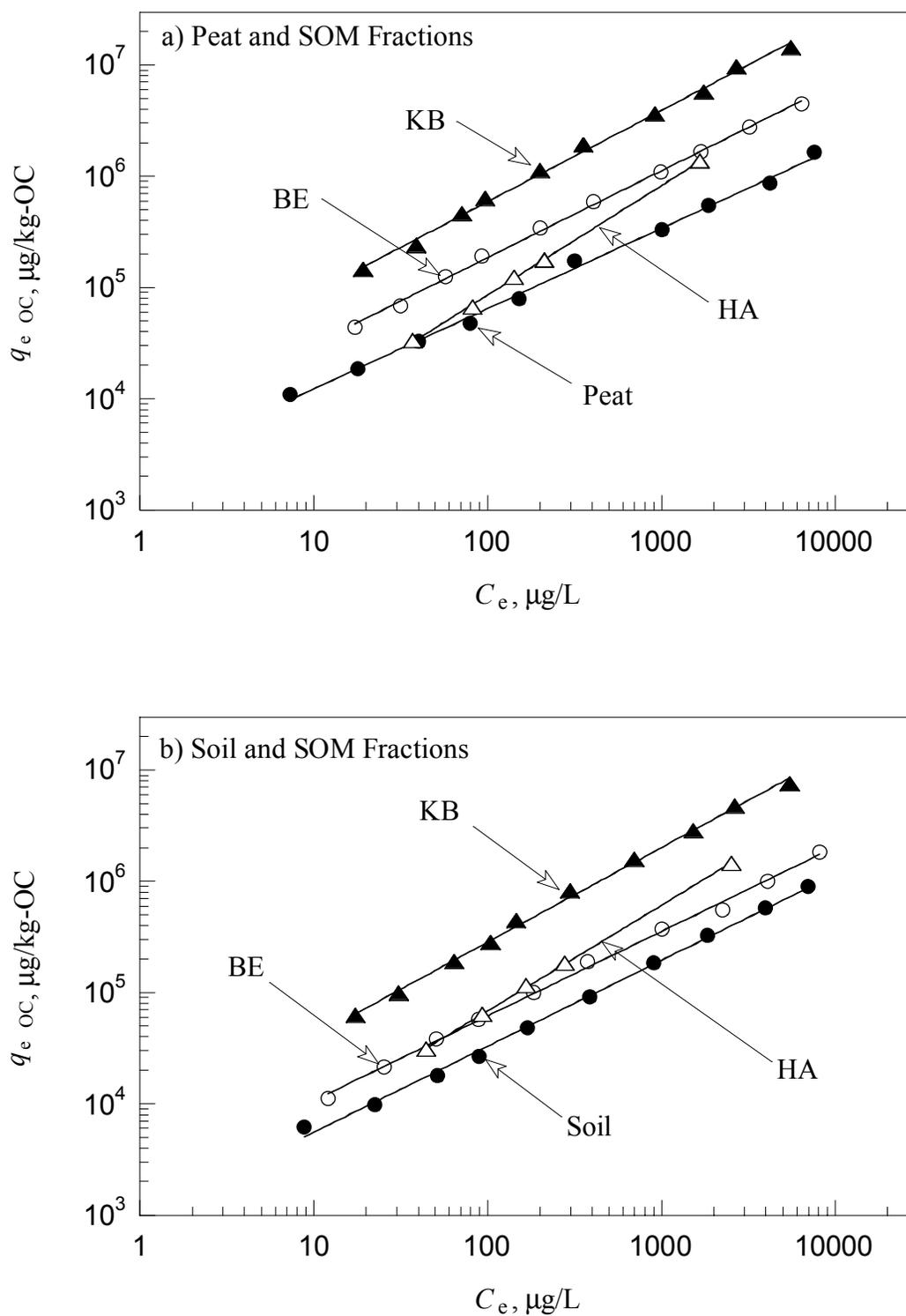


Figure 4.2 Organic carbon normalized sorption isotherms for ATZ on a) Bulk Peat and its isolated fractions and b) Bulk Soil and its isolated fractions

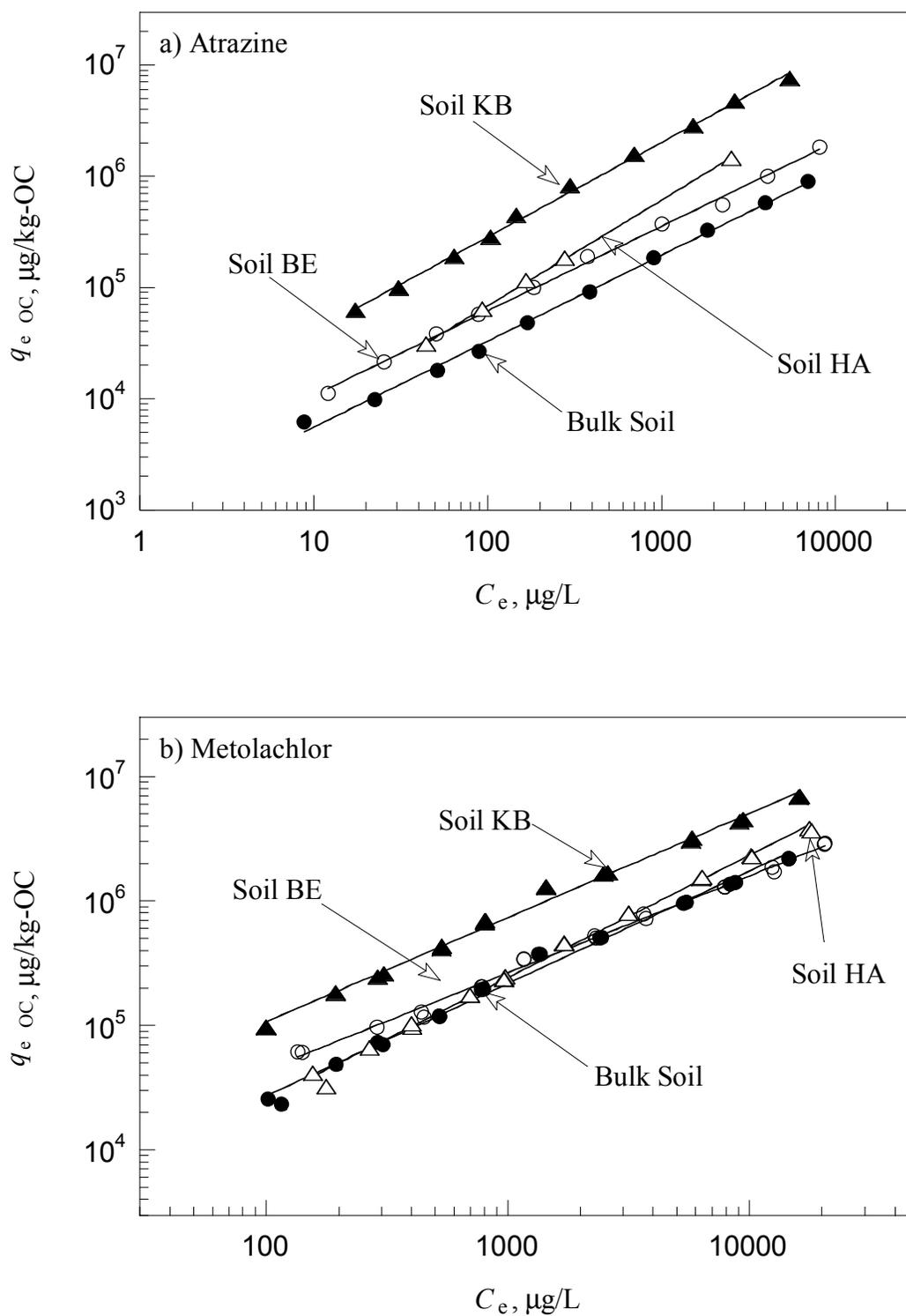


Figure 4.3 Organic carbon normalized sorption isotherms on Bulk Soil and its isolated fractions for a) ATZ, b) MET (continued on next page).

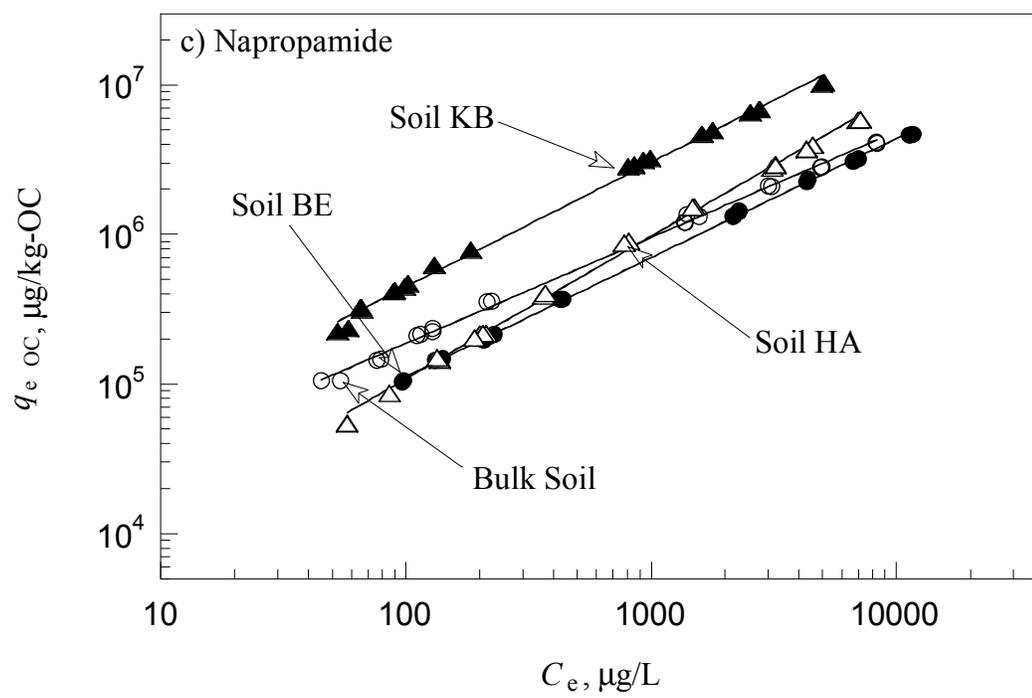


Figure 4.3 (contd.) c) NAP.

## **CHAPTER 5 – DESORPTION EQUILIBRIA OF ATRAZINE, METOLACHLOR AND NAPROPAMIDE**

### **Overview**

This Chapter describes the desorption experiments performed with the three herbicides atrazine (ATZ), metolachlor (MET) and napropamide (NAP) that were performed in conjunction with and immediately after the sorption equilibrium experiments, using the same reactors. Sorption-desorption graphs and Freundlich model parameters obtained are discussed. A hysteresis index was developed and used to mathematically interpret the differences observed in sorption and desorption isotherms. The overall objective of this chapter was to extend the understanding of sorption-desorption hysteresis to pesticide compounds, for which only a few studies exist.

### **5.1 Rationale and Objectives**

Sorption – desorption hysteresis has been observed for the sorption of the PAH PHEN to soils. When experimental artifacts are not present, desorption hysteresis has been attributed to the physical entrapment and condensation of HOC molecules into condensed SOM matrices. The phenomenon has been shown to occur to a greater extent in soils that have greater condensed organic matter content. We hypothesized that the existence or absence of sorption and desorption hysteresis could lead to a better understanding of herbicide sorption mechanisms. The objectives of this Chapter were to:

- i) examine and quantify the desorption behavior of ATZ, MET and NAP on Bulk Chelsea Soil and its isolated BE, KB and HA fractions employing a technique that minimizes

experimental artifacts; ii) to use the concept of hysteresis index to statistically investigate the existence of hysteresis among the herbicides; iii) to elucidate desorption mechanisms by comparing the desorption behavior of the herbicides to PHEN desorption.

## 5.2 Experiments and Data Analysis

The methodology followed for the desorption experiments has been detailed in Chapter 3. In brief a batch ampule system was used to evaluate desorption of the solutes from the solid phase into a solute free background solution after 21 days of sorption. Desorption experiments were also run for 21 days. The linearized Freundlich isotherm model was used to calculate  $\log K_F$  and  $n$  values.

## 5.3 Results and Discussion

Figures 5.1 and 5.2 present the sorption and desorption isotherms for ATZ on the Bulk Peat and its fractions and the Bulk Soil and its fractions, respectively. The data in Figures 5.1 (d) and 5.2 (d) for HA are the 2d phase distribution relationships; the sorption and desorption experiments in these cases were run only for 2 d following the observation of ATZ degradation by HA. The data have only been presented for comparison. The sorption and desorption isotherms measured for MET and NAP on the Bulk Soil and its fractions are presented in Figures 5.3 and 5.4, respectively. The Freundlich desorption parameters obtained are listed in Table 5.1; the equilibrium sorption parameters from Table 4.2 have been listed again for ease of comparison between the sorption and desorption values.

Sorption-desorption hysteresis is evidenced by the non singularity of sorption and desorption isotherms. A close comparison of the isotherms in Figures 5.1 to 5.4 indicates that sorption and desorption isotherms may be substantially different from each other only in a few cases. Specifically, the ATZ isotherms on Bulk Peat and Peat BE (Fig. 5.1 (a), (b)), ATZ isotherms on Bulk Soil and Soil BE (Fig. 5.2 (a), (b)) and MET isotherms on Bulk Soil and Soil BE (Fig. 5.3 (a), (b)) could imply sorption desorption hysteresis. It is interesting to note that the condensed carbon rich KB fraction does not show visible hysteresis for the three herbicides.

To mathematically evaluate the existence of hysteresis, a hysteresis index (HI) was used (from Huang and Weber, 1997), which is described as:

$$HI = \frac{q_e^d - q_e^s}{q_e^s} \Big|_{T, C_e} \quad (5.1)$$

Where  $q_e^d$  and  $q_e^s$  are the equilibrium solid phase concentrations in the desorption and sorption steps, respectively, at the same temperature and  $C_e$ . This parameter thus essentially measures the “vertical” difference between a sorption and desorption isotherm on the graph at various  $C_e$  values. A zero or negative value thus implies no hysteresis among the sorption and desorption steps, while a positive value highlights hysteresis. The values of  $q_e^d$  and  $q_e^s$  were calculated for four arbitrary levels of 10, 100, 1,000 and 10,000  $\mu\text{g/L}$  (that are a subset of the concentration ranges used for the sorption experiments) using the  $\log K_F$  and  $n$  values for sorption and desorption from Table 5.1. To incorporate the statistical error in the estimation of  $\log K_F$  and  $n$ , lower and upper limits of HI were calculated using the following expressions:

$$HI_{\min} = \frac{q_e^d \min - q_e^s \max}{q_e^s \max} \Big|_{T, C_e} \quad (5.2)$$

where

$$q_e^d \min = 10^{\log K_F^d - e} * C_e^{n^d - e} \quad (5.3)$$

$$q_e^s \max = 10^{\log K_F^s + e} * C_e^{n^s + e} \quad (5.4)$$

$$HI_{\max} = \frac{q_e^d \max - q_e^s \min}{q_e^s \min} \Big|_{T, C_e} \quad (5.5)$$

$$q_e^d \max = 10^{\log K_F^d + e} * C_e^{n^d + e} \quad (5.6)$$

$$q_e^s \min = 10^{\log K_F^s - e} * C_e^{n^s - e} \quad (5.7)$$

where superscript ‘d’ and ‘s’ denote desorption and sorption respectively and ‘e’ represents the standard error of estimation of the parameters as reported in Table 5.1. The calculated values of HI along with the statistical upper and lower limits are presented in Table 5.2. Examination of the HI values in this table indicates that for NAP, the range of values includes the zero value. Hence, there was little or no hysteresis in the sorption and desorption isotherms for NAP for any of the sorbents. The same observation is also made for MET. For ATZ, however, hysteresis might be important for the Bulk Peat and Bulk

Soil and Peat BE and Soil BE fractions, especially at lower concentrations. Logarithmic plots of sorption and desorption isotherms for ATZ on these sorbents have been presented in Figure 5.5 to elucidate this observation. As the equilibrium aqueous phase concentration increases to 10,000  $\mu\text{g/L}$ , the hysteresis becomes less evident. Examination of HI values in Table 5.2 and their ranges also reveals that little hysteresis is evident for either the Peat or Soil HA or the Peat or Soil KB for any of the herbicides. Thus the observations made from the visual analysis of Figures 5.1 to 5.4 are corroborated by employing the more quantitative concept of HI.

The observed sorption-desorption phenomena for the herbicides is different from those observed for PHEN. Huang and Weber (1997) and Weber et al. (1998) evaluated sorption-desorption behavior of PHEN on 10 peat, HA and shale samples and 12 soil and sediment samples, respectively, that included Chelsea Soil (the Bulk Soil sample used in this chapter) and Chelsea Soil HA (the Soil HA used in this study). They observed that PHEN exhibited greater hysteresis for samples such as shale and shale kerogen that are comprised of more mature carbons compared to samples consisting mainly of less mature amorphous carbon. They attributed their observations to the slow desorption and entrapment of sorbing molecules within the condensed carbon matrices. They also observed that the mechanisms behind this slow desorption could be related to the heterogeneity of the condensed SOM micro pores that result in different energies of interaction between the sorbent and the solute in the sorption and desorption steps. Thus, sorption into hydrophobic micro pores might be more energetically favorable for hydrophobic solutes such as PHEN than desorption into the bulk aqueous phase, which

causes sorption and desorption rates to be non identical. In the case of amorphous SOMs such as HA, although they have large micro porosities, their matrices are not rigid and can swell in the presence of water to present a gel-like phase for sorbing solutes and hence no sorption desorption hysteresis is observed in their case. Weber et al. (1998) classified Chelsea Soil as mostly consisting of amorphous carbon matter and did not observe any hysteresis for this sample and its base extracted fraction (a sample processed similarly to the Soil BE used in this study) for PHEN. As noted above, our results show the opposite trend where hysteresis is observed for the Bulk Soil and Soil BE (and Bulk Peat and Peat BE) for ATZ, and no hysteresis is seen among the sorption and desorption steps of any of the herbicides on the condensed organic matter rich KB fraction. These differences between the herbicides and a typical PAH need to be examined in the context of physicochemical properties of these molecules as follows.

### **5.3.1 Molecular Size and Shape**

The size of a PHEN molecule is comparable to the size reported for nanopores of condensed matrices (Table 2.1) (Cornelissen et al., 2005). On the other hand, the herbicide molecules might be larger compared to the interlayer thicknesses of condensed KB matrices. The presence of Cl, amide, methyl and ethyl groups in ATZ; Cl, O, N and methyl groups in MET; and O, N and methyl groups in NAP contribute to their large molecular sizes. While the heteroatomic side chain of the “naphthalene” type nucleus of NAP might cause steric hindrance of this molecule for sorption into small pores, the MET and ATZ molecules have overall big “rounded” shapes that can prove to be too large to penetrate small pores.

### 5.3.2 Aqueous Solubility and Polarity

The aqueous solubility of PHEN is 1.29 mg/L whereas that of ATZ is 30 mg/L, of MET is 500 mg/L and of NAP is 73 mg/L (Table 3.1), which might be further attributed to their different functionalities. As evident from the molecular structures of these compounds listed in Table 3.1, PHEN is a polynuclear aromatic molecule with no functional groups. Its only interactions with SOM are thought to be van der Waal-type hydrophobic interactions. Although van der Waal interactions are weaker than any polar interactions that may be observed for the herbicides, the collective magnitude of hydrophobic interactions can be large for the planar PHEN molecule, considering that the SOM itself is made up of similar planar aromatic nuclei.

For the herbicide molecules, various other types of interactions may be expected based on their individual structures. ATZ has a heteroatomic N-containing ring at its nucleus. The N atom has a lone pair of electrons and thus acts as a strong electron donor. This ring further has two amide group side chains linked to the two carbons in the heterocyclic ring that can also act as potential electron donors. On the other end the third carbon has an electron withdrawing Cl atom attached to it. Thus the molecule is slightly polar and can effectively form hydrogen bonds with organic matter functionalities. The MET molecule can form localized dipoles around its N-C=O, CH<sub>3</sub>-Cl and CH<sub>3</sub>-O- bonds. Its polar nature is evident from the fact that it has the highest aqueous solubility among all the four chemicals, despite having the largest molecular weight. NAP exhibits one nitrogen and two oxygen atoms in its molecules, both of which can cause polar interactions, and the O atoms can potentially exhibit H bonding.

Considering the above mentioned possible interactions, it is likely that the sorption and desorption energies for each of the three herbicides are not that different from each other and hence they do not exhibit hysteresis when interacting with isolated SOMs such as HA and KB. On the other hand hysteresis observed for desorption of ATZ from Bulk Peat, Peat BE, Bulk Soil and Soil BE might be caused by polar interactions or chemisorption between ATZ and the sorbents.

### 5.3.3 Hydrophobicity

Hydrophobicity of compounds is generally measured by their octanol-water partitioning coefficient  $K_{OW}$ . The  $\log K_{OW}$  of PHEN is 4.57 whereas that of ATZ is 2.18, of MET is 3.13 and of NAP is 3.36 (Table 3.1). The  $\log K_{OW}$  value of a compound is an indicator of its hydrophobicity and also the strength of hydrophobic interactions it will exhibit in a hydrophobic environment. Thus PHEN has the greatest value, even though it is the smallest of all the four compounds. NAP is next with its naphthalene-like nucleus, and ATZ and MET have lower values due to their size and polar functional groups respectively.

It is reasonable to conclude that the interactions of a compound with the condensed organic matter will be dependent on its physicochemical properties. Thus, the PHEN molecule might be able to penetrate the condensed OM pores and might be entrapped in constricted pores that provide a much more energetically favorable environment for the molecules than the outside aqueous environment. On the other hand, the large herbicide molecules may not be able to access such small pores and their sorption to condensed organic matter may be limited to adsorption on the surface and

micropores. Their sorption to the condensed organic matter may be enhanced by the extent to which they can relax the matrix of the condensed organic matter, a phenomenon that is expected to be more visible for higher solute concentrations. Thus no sorption-desorption hysteresis is observed for these big molecules on the KB fraction in contrast with PHEN.

No substantial hysteresis is observed for the herbicides (except ATZ) for all the other fractions, which suggests interactions, such as entrapment and sequestration do not occur for these molecules. The hysteresis for ATZ observed for Bulk Peat and Soil samples and their BE fractions could indicate either electrostatic interactions of ATZ with the mineral phase of these sorbents, or interactions with the HA material contained in these two fractions. It would be valuable to compare the hysteresis in these fractions with the hysteresis on HA, but unfortunately the data for HA are not for equilibrium conditions, since ATZ was found to degrade in the presence of HA at times longer than 4 d; thus equilibrium isotherms could not be measured.

#### **5.4 Summary and Implications**

No substantial hysteresis was observed with any of the sorbents for MET and NAP. For ATZ, hysteresis was substantial only for the Bulk Peat, Bulk Soil and their BE fractions. Desorption hysteresis is an indicator of retardation and sequestration of contaminants in soils. Low or no hysteresis means that more solute is available for biodegradation on one hand and for leaching and run off on the other hand. This study indicates that in general, large polar molecules do not show sorption desorption hysteresis for sorption to the KB fraction, as observed for more hydrophobic molecules. Herbicides

may, however, show specific binding such as chemisorption that could cause the desorption step to appear hysteretic. It is reasonable to assume that a larger fraction of herbicide would be present in the aqueous phase rather than bound to soils in comparison to PAHs, as evidenced by the herbicides' detection frequency in ground and surface waters (Barbash et al., 2001; Larson et al., 1999).

Table 5.1. Freundlich sorption-desorption parameters

Herbicide	Sorbent	$n$	Sorption			Desorption			
			$\log K_F$ ( $\mu\text{g}/\text{kg}/(\mu\text{g}/\text{L})^n$ )	$N$	$R^2$	$n$	$\log K_F$ ( $\mu\text{g}/\text{kg}/(\mu\text{g}/\text{L})^n$ )	$N$	$R^2$
Atrazine	Bulk Peat	0.722 (0.015 <sup>a</sup> )	3.021 (0.039 <sup>a</sup> )	10	0.996	0.731 (0.019 <sup>a</sup> )	3.245 (0.042 <sup>a</sup> )	10	0.994
	Peat BE	0.781 (0.011)	3.388 (0.029)	10	0.998	0.659 (0.017)	3.918 (0.037)	10	0.994
	Peat KB	0.821 (0.017)	3.899 (0.044)	10	0.996	0.646 (0.009)	4.492 (0.021)	10	0.998
	Peat HA <sup>b</sup>	0.983 (0.013)	2.712 (0.030)	5	0.999	1.042 (0.076)	3.054 (0.138)	5	0.979
Metolachlor	Bulk Soil	0.773 (0.014)	1.694 (0.037)	10	0.997	0.709 (0.011)	2.083 (0.026)	10	0.998
	Soil BE	0.760 (0.013)	1.791 (0.034)	10	0.997	0.681 (0.011)	2.215 (0.025)	10	0.998
	Soil KB	0.849 (0.014)	3.239 (0.037)	10	0.997	0.720 (0.018)	3.648 (0.041)	10	0.995
	Soil HA <sup>b</sup>	0.950 (0.009)	2.646 (0.023)	5	1.000	0.986 (0.048)	2.948 (0.096)	5	0.990
Napropamide	Bulk Soil	0.903 (0.020)	1.352 (0.063)	19	1.000	0.998 (0.021)	1.159 (0.064)	18	0.992
	Soil BE	0.779 (0.012)	1.603 (0.039)	20	1.000	1.045 (0.036)	1.061 (0.093)	18	0.981
	Soil KB	0.839 (0.015)	2.831 (0.049)	20	1.000	0.978 (0.025)	2.484 (0.069)	20	0.988
	Soil HA	0.985 (0.014)	2.140 (0.047)	20	1.000	1.164 (0.038)	1.696 (0.107)	18	0.982
Napropamide	Bulk Soil	0.795 (0.005)	2.182 (0.015)	20	1.000	0.815 (0.014)	2.219 (0.039)	20	0.994
	Soil BE	0.708 (0.008)	2.374 (0.023)	20	1.000	0.730 (0.021)	2.383 (0.057)	10	0.992
	Soil KB	0.832 (0.013)	3.469 (0.034)	20	1.000	0.842 (0.013)	3.421 (0.036)	18	0.996
	Soil HA	0.952 (0.011)	2.844 (0.031)	20	1.000	0.937 (0.021)	2.984 (0.059)	8	0.996

<sup>a</sup> standard error of estimate, <sup>b</sup> 2 day phase distribution relationships (PDRs)

Table 5.2 Calculated hysteresis indices (HI) for atrazine, metolachlor and napropamide

Herbicide	Sorbent	HI		
		$C_e = 10 \mu\text{g/L}$	$C_e = 100 \mu\text{g/L}$	$C_e = 1000 \mu\text{g/L}$
Atrazine	Bulk Peat	0.710 (0.312 ~ 1.228)	0.746 (0.239 ~ 1.460)	0.782 (0.169 ~ 1.716)
	Peat BE	1.559 (1.061 ~ 2.177)	0.932 (0.459 ~ 1.559)	0.459 (0.033 ~ 1.061)
	Peat KB	1.618 (1.123 ~ 2.228)	0.750 (0.337 ~ 1.291)	0.169 (-0.159 ~ 0.626)
	Peat HA <sup>b</sup>	1.518 (0.393 ~ 3.550)	1.884 (0.300 ~ 5.379)	2.304 (0.213 ~ 7.995)
	Bulk Soil	1.113 (0.726 ~ 1.588)	0.824 (0.406 ~ 1.366)	0.574 (0.146 ~ 1.163)
	Soil BE	1.213 (0.828 ~ 1.679)	0.845 (0.442 ~ 1.360)	0.538 (0.138 ~ 1.080)
	Soil KB	0.905 (0.479 ~ 1.455)	0.416 (0.021 ~ 0.963)	0.052 (-0.295 ~ 0.570)
	Soil HA <sup>b</sup>	1.178 (0.452 ~ 2.266)	1.366 (0.384 ~ 3.046)	1.570 (0.318 ~ 4.012)
Metolachlor	Bulk Soil	-0.202 (-0.458 ~ 0.175)	-0.007 (-0.386 ~ 0.607)	0.236 (-0.305 ~ 1.198)
	Soil BE	-0.470 (-0.650 ~ -0.198)	-0.023 (-0.422 ~ 0.652)	0.803 (-0.045 ~ 2.404)
	Soil KB	-0.381 (-0.569 ~ -0.109)	-0.147 (-0.459 ~ 0.346)	0.175 (-0.321 ~ 1.032)
	Soil HA	-0.457 (-0.662 ~ -0.127)	-0.180 (-0.547 ~ 0.486)	0.239 (-0.393 ~ 1.529)
Napropamide	Bulk Soil	0.140 (-0.036 ~ 0.349)	0.194 (-0.034 ~ 0.476)	0.250 (-0.032 ~ 0.614)
	Soil BE	0.074 (-0.164 ~ 0.380)	0.130 (-0.178 ~ 0.552)	0.189 (-0.191 ~ 0.746)
	Soil KB	-0.084 (-0.245 ~ 0.112)	-0.062 (-0.253 ~ 0.177)	-0.041 (-0.260 ~ 0.244)
	Soil HA	0.334 (0.007 ~ 0.288)	0.288 (-0.096 ~ 0.837)	0.245 (-0.189 ~ 0.910)
				$C_e = 10000 \mu\text{g/L}$
				0.820 (0.104 ~ 1.999)
				0.102 (-0.269 ~ 0.660)
				-0.218 (-0.470 ~ 0.153)
				2.784 (0.132 ~ 11.647)
				0.358 (-0.067 ~ 0.977)
				0.282 (-0.103 ~ 0.832)
				-0.218 (-0.514 ~ 0.256)
				1.793 (0.256 ~ 5.209)
				0.538 (-0.213 ~ 2.006)
				2.327 (0.578 ~ 6.015)
				0.618 (-0.147 ~ 2.069)
				0.871 (-0.187 ~ 3.305)
				0.309 (-0.029 ~ 0.766)
				0.250 (-0.204 ~ 0.963)
				-0.018 (-0.268 ~ 0.316)
				0.202 (-0.272 ~ 0.986)

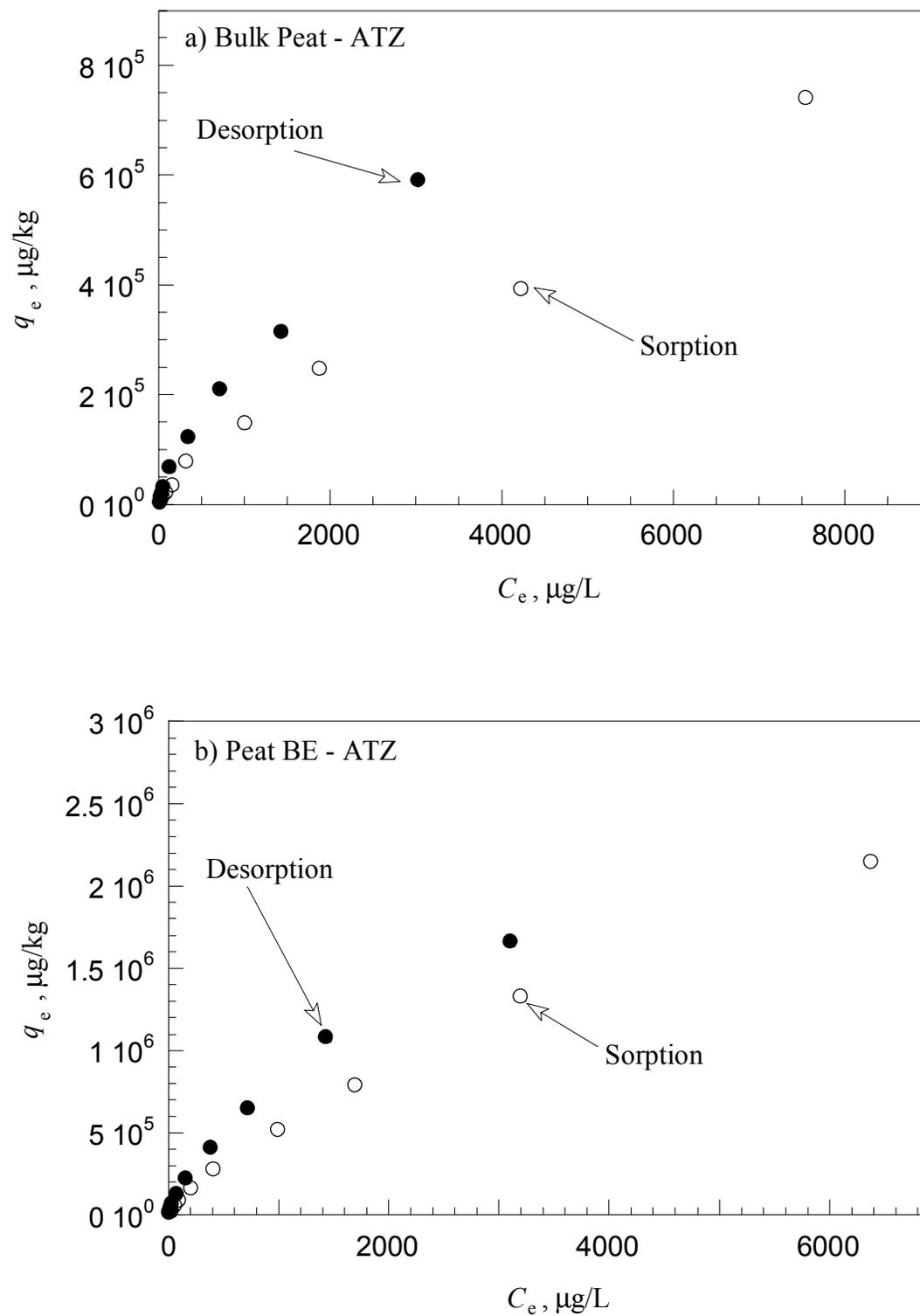


Figure 5.1 Sorption and Desorption Isotherms for Atrazine on (a) Bulk Peat, (b) Peat BE (continued on next page)

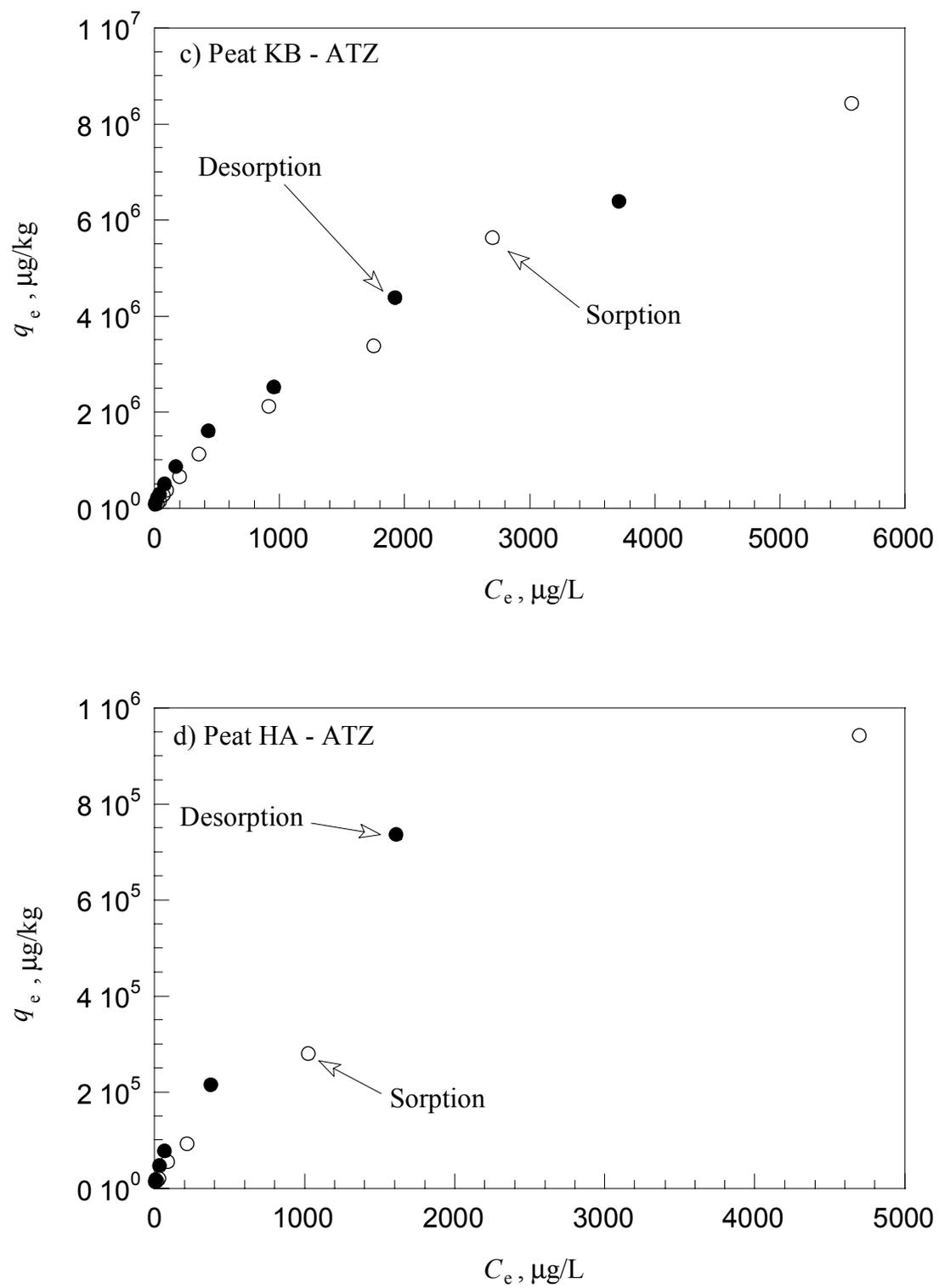


Figure 5.1 contd. (c) Peat KB and (d) Peat HA.

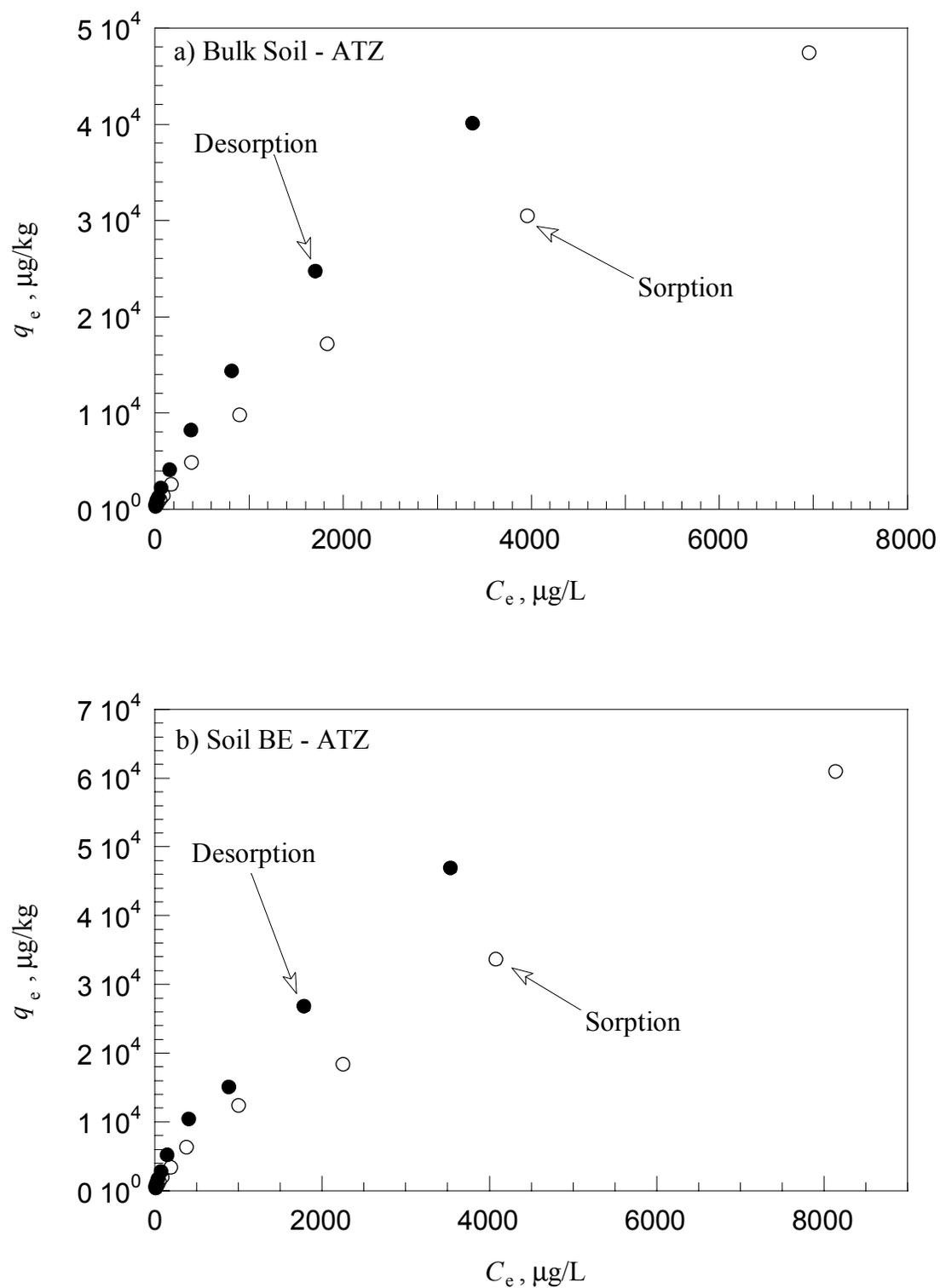


Figure 5.2 Sorption and Desorption Isotherms for Atrazine on (a) Bulk Soil, (b) Soil BE (continued on next page)

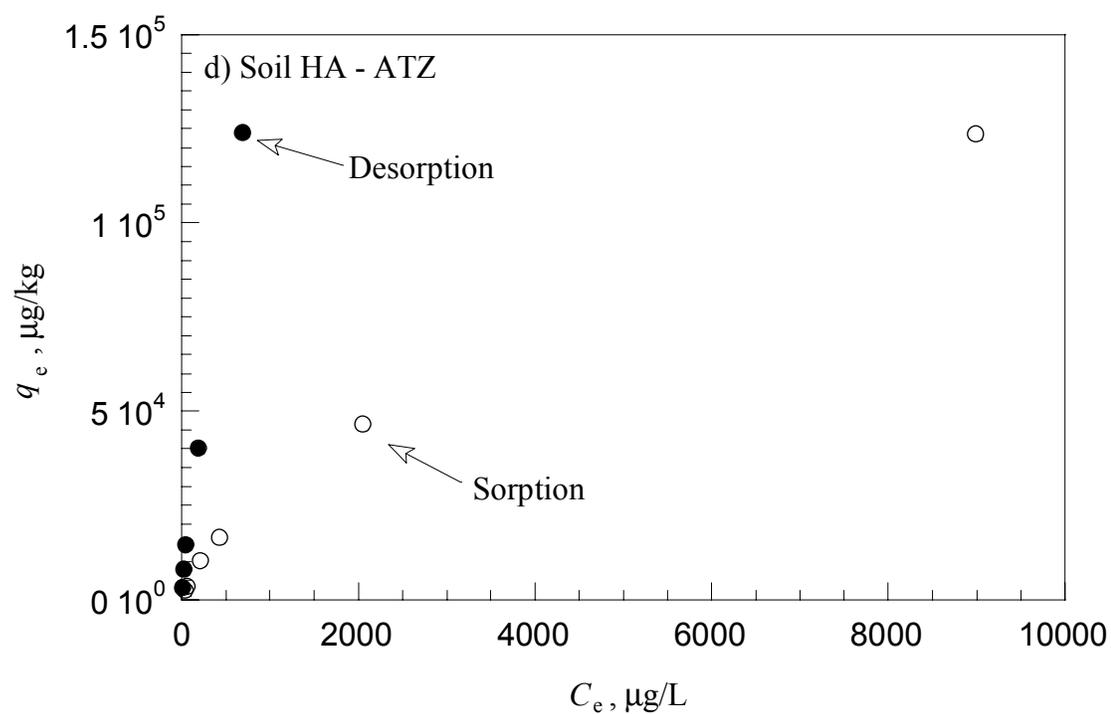
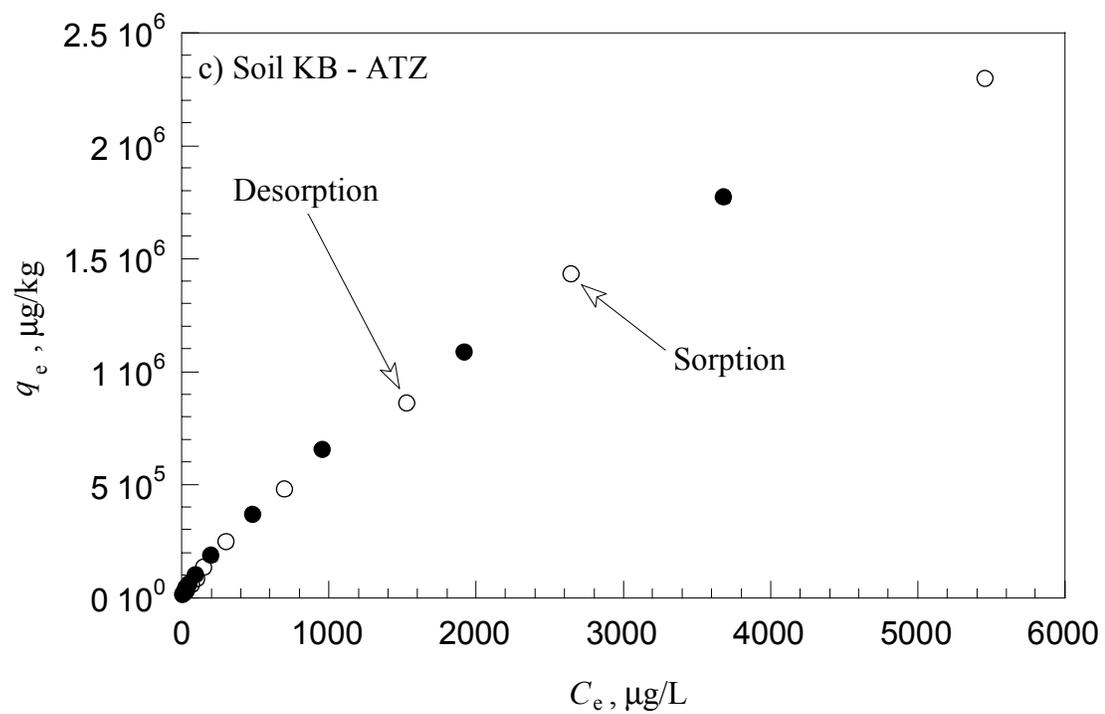


Figure 5.2 contd. (c) Soil KB and (d) Soil HA.

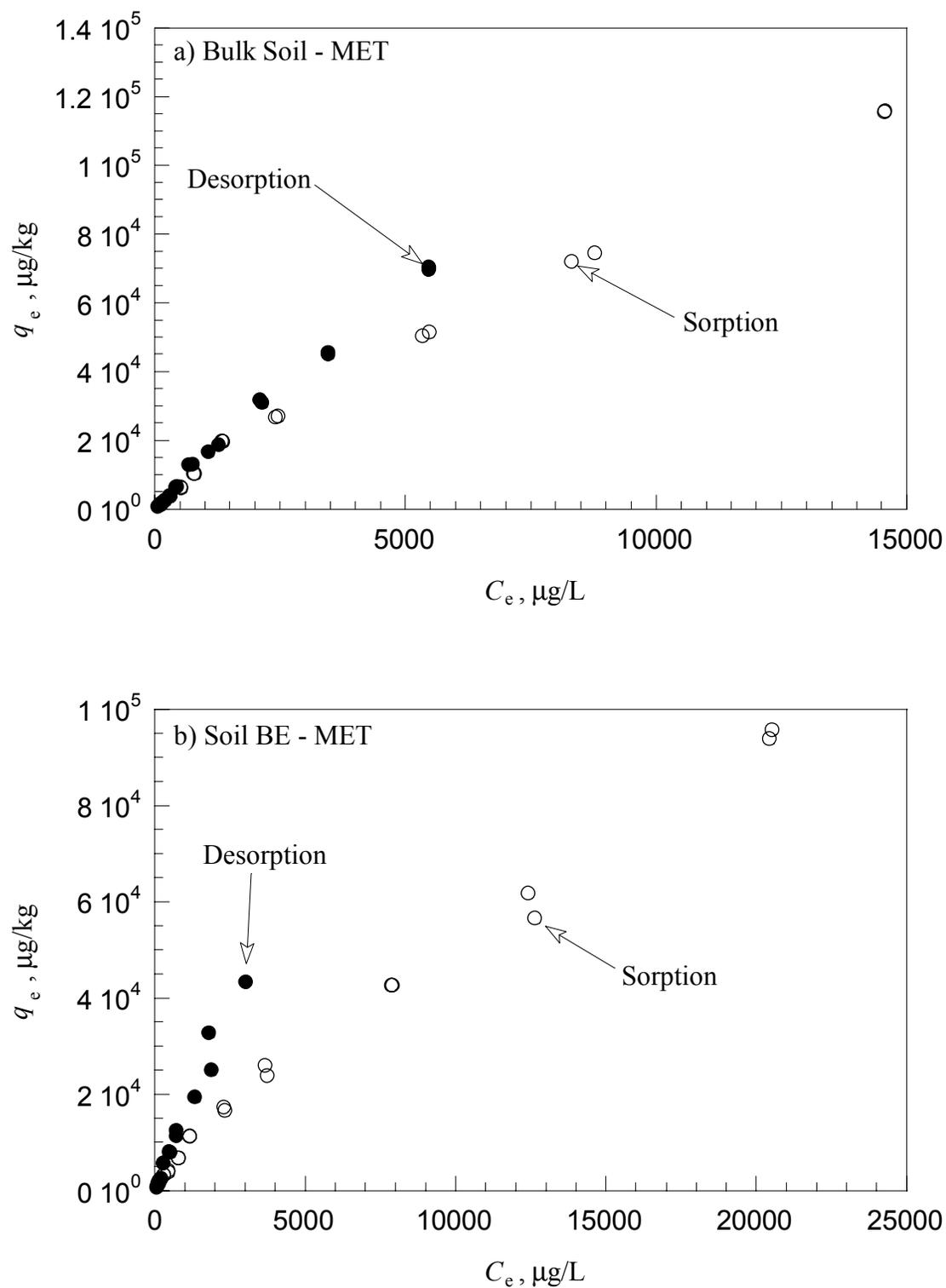


Figure 5.3 Sorption and Desorption Isotherms for Metolachlor (a) Bulk Soil, (b) Soil BE (continued on next page)

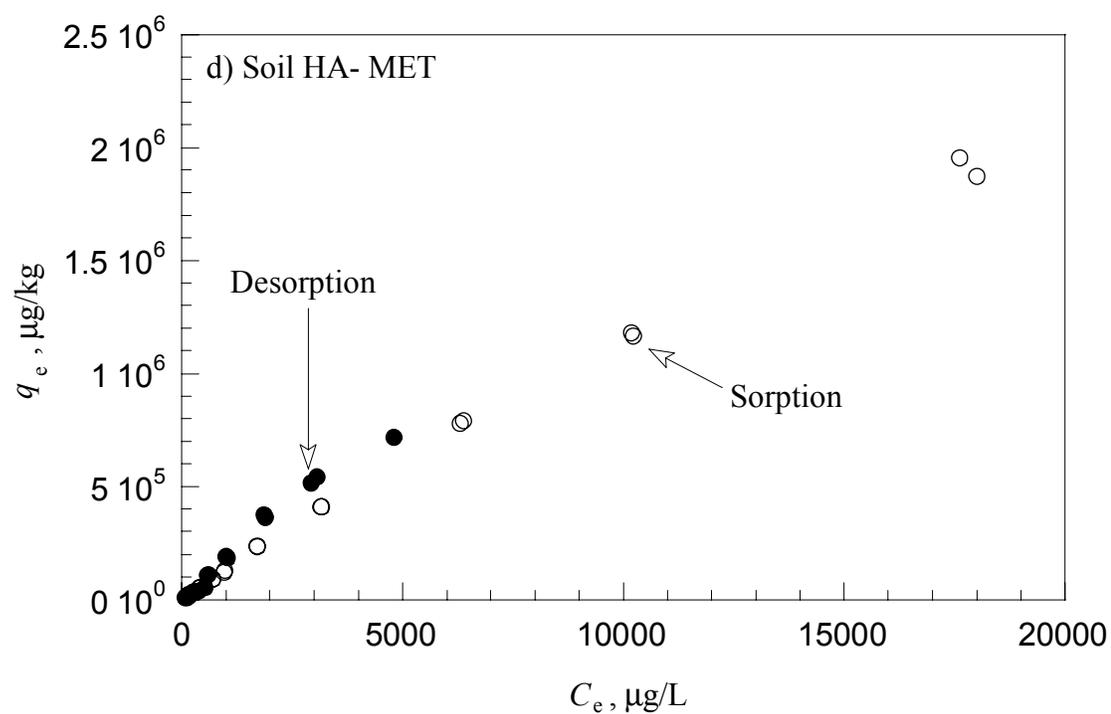
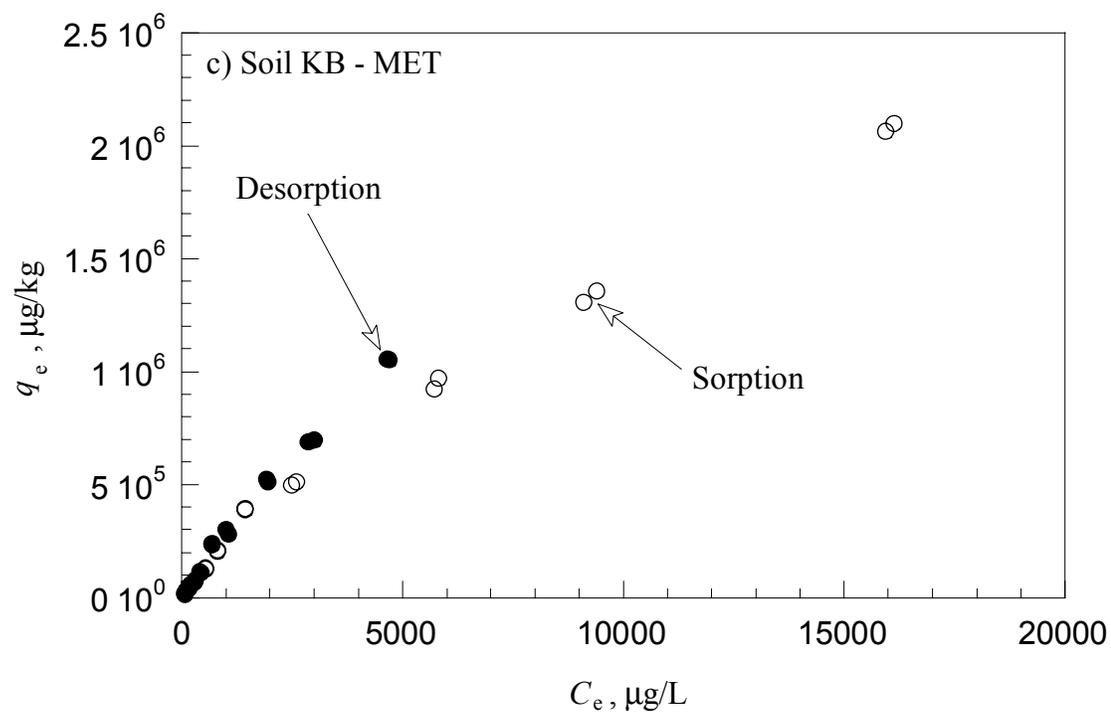


Figure 5.3 contd. (c) Soil KB and (d) Soil HA.

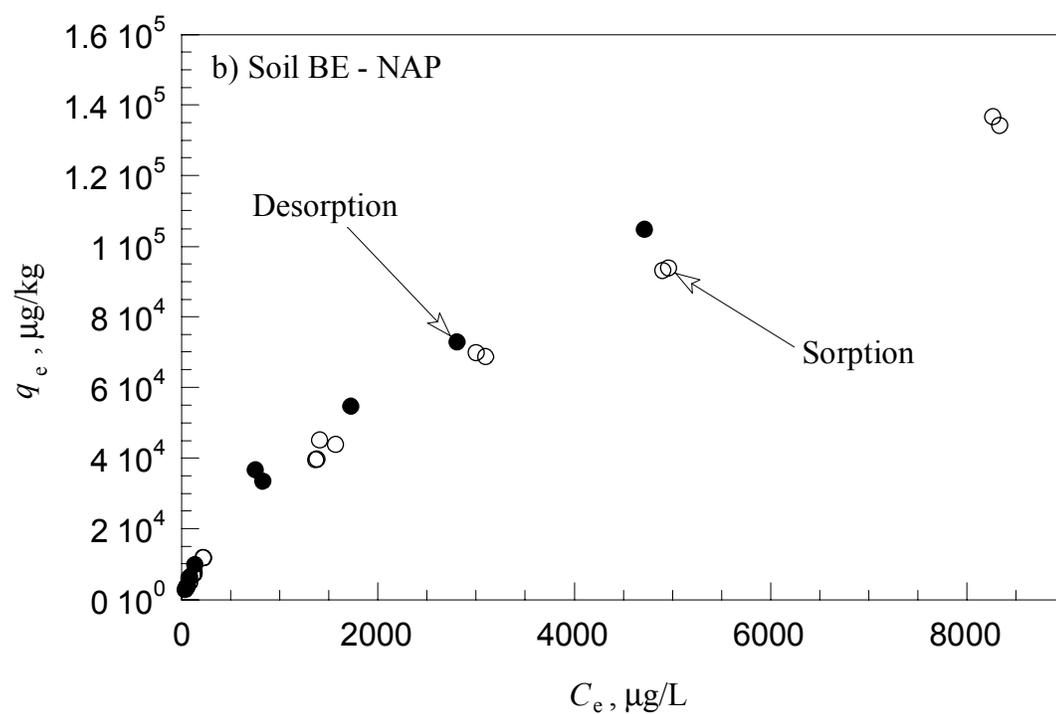
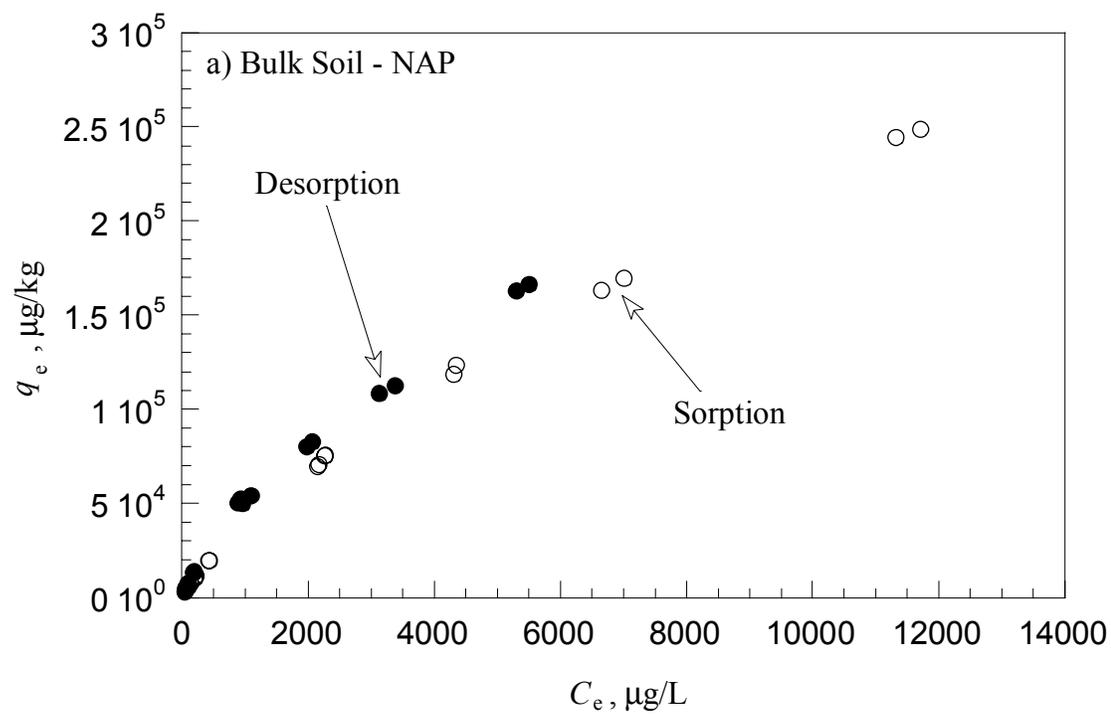


Figure 5.4 Sorption and Desorption Isotherms for Napropamide on (a) Bulk Soil, (b) Soil BE (continued on next page)

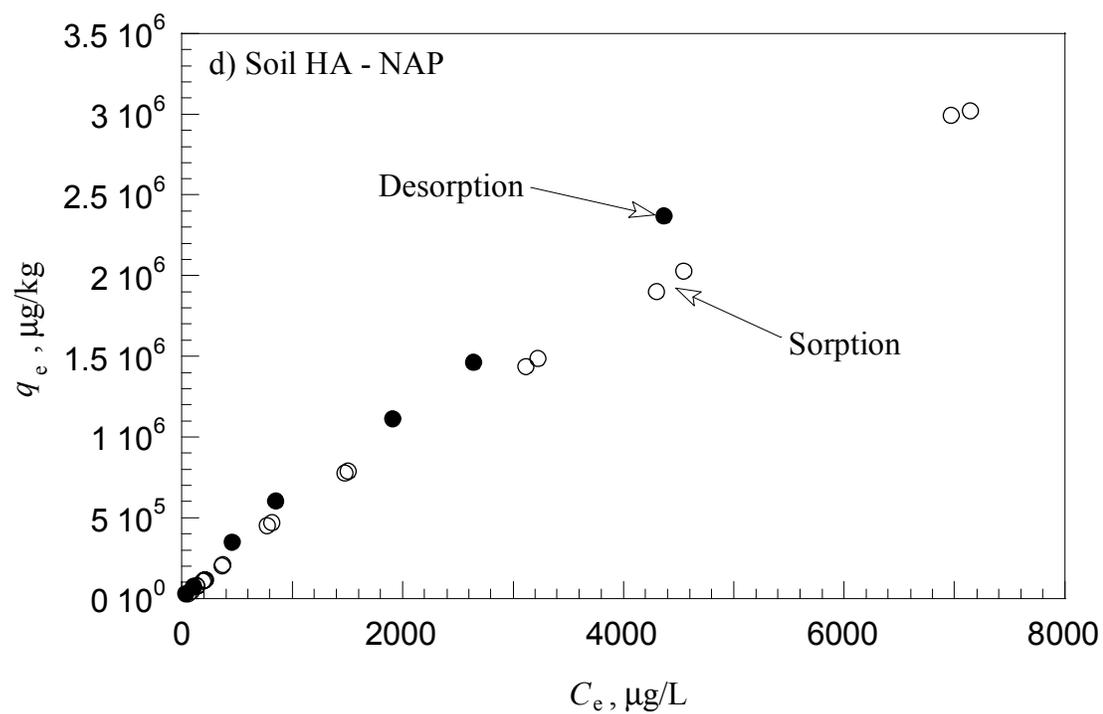
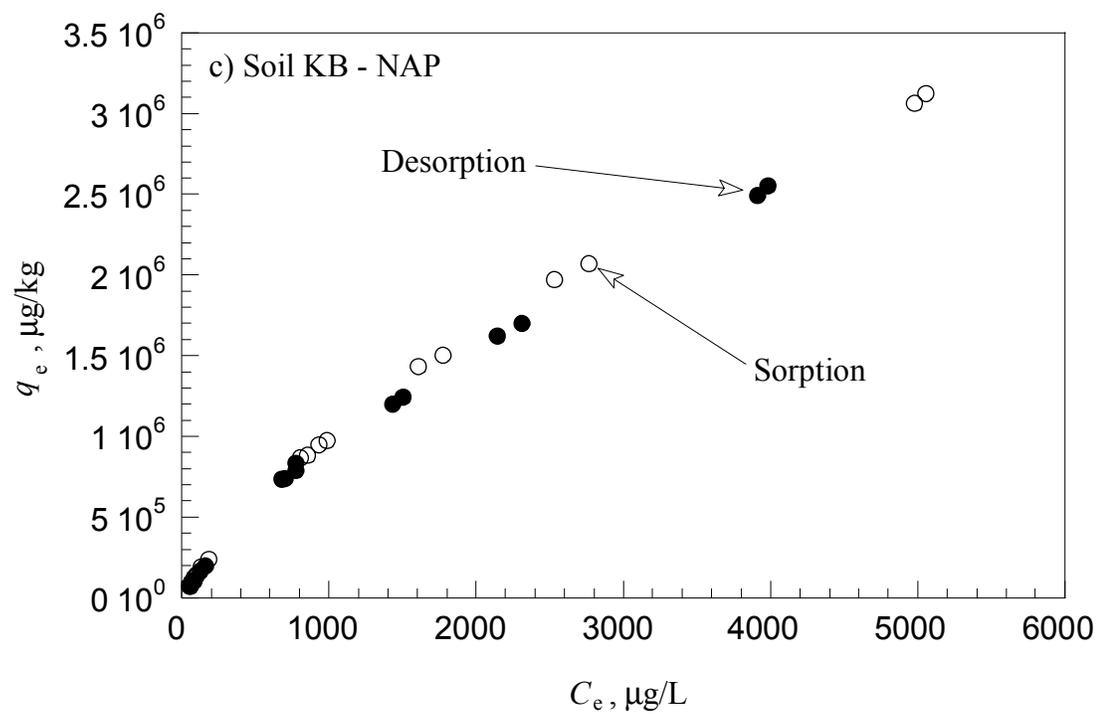


Figure 5.4 contd. (c) Soil KB and (d) Soil HA.

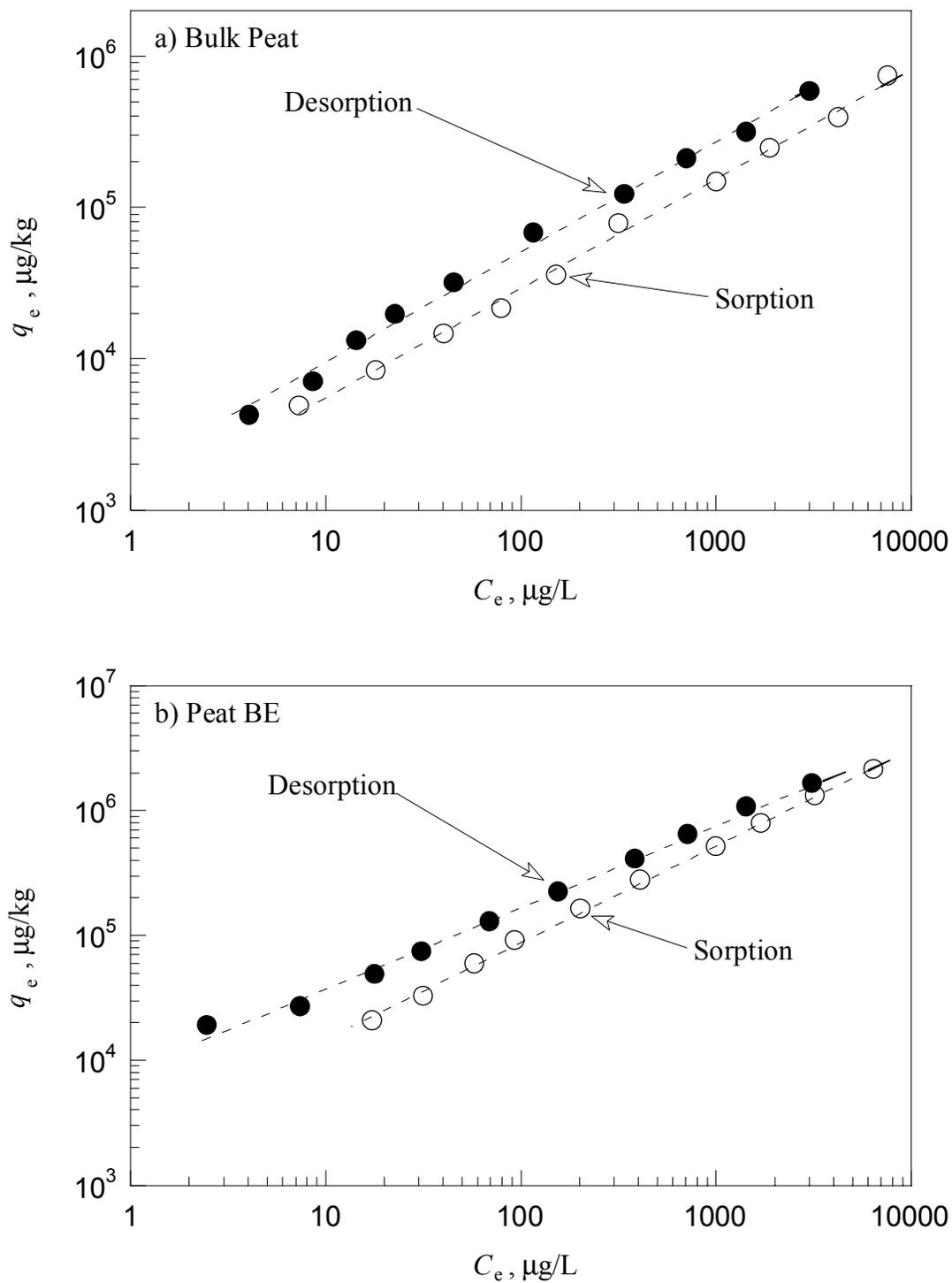


Figure 5.5 Logarithmic Sorption and Desorption Isotherms for Atrazine on (a) Bulk Peat, (b) Peat BE (continued on next page)

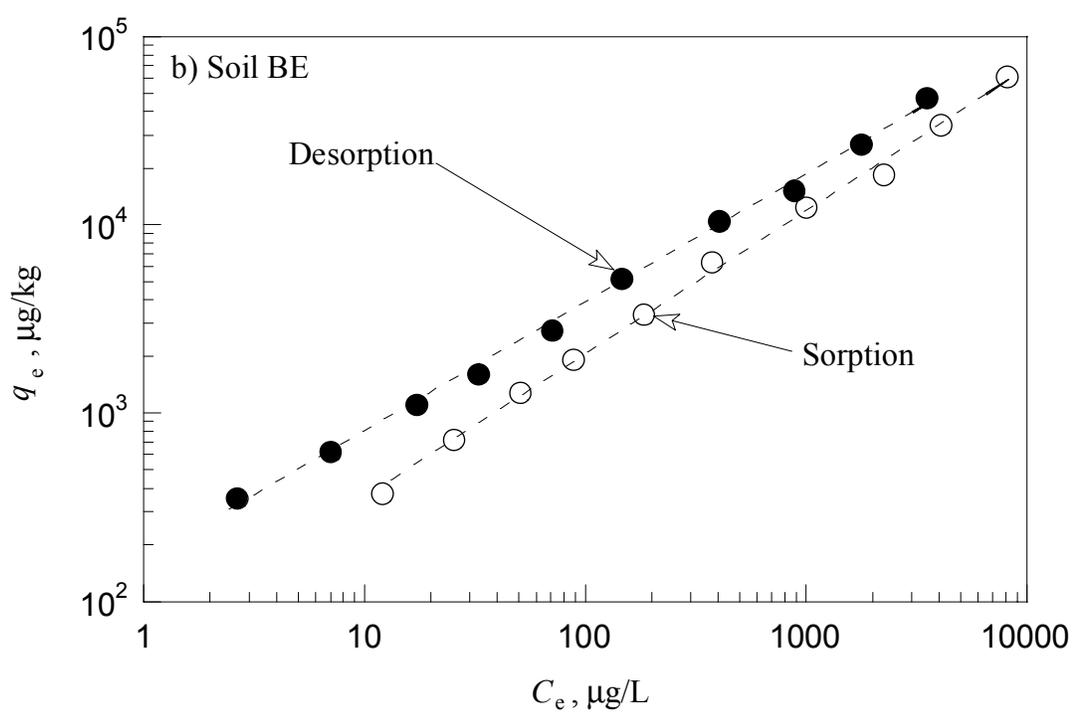
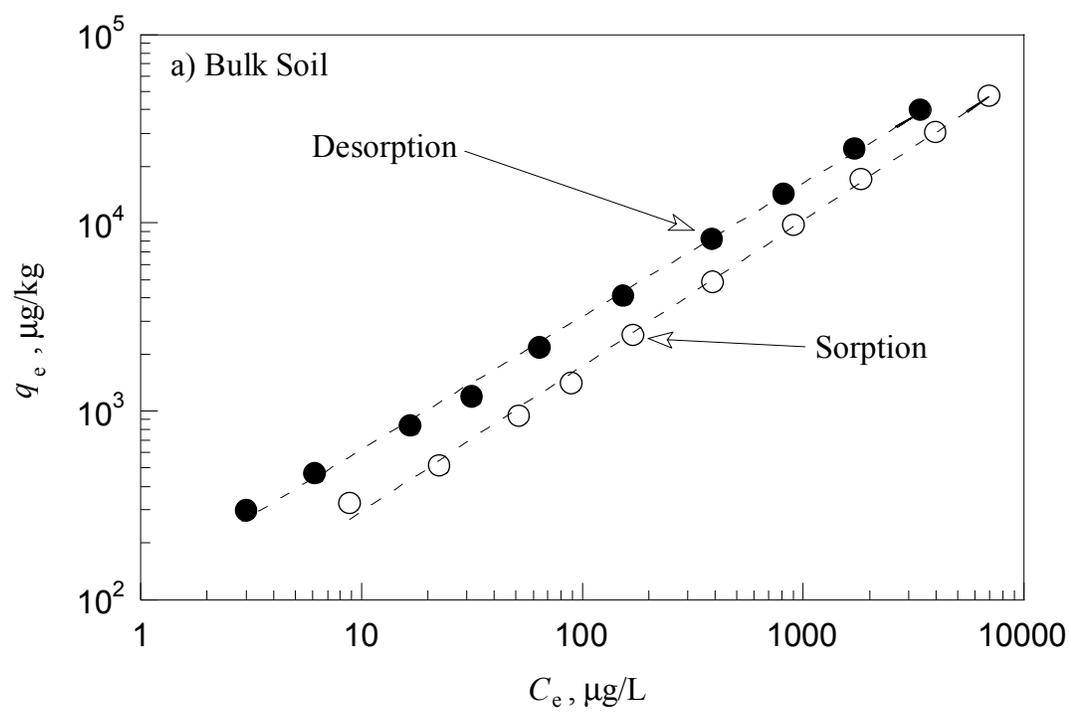


Figure 5.5 contd. c) Bulk Soil and d) Soil BE.

## CHAPTER 6: SORPTION RATES OF METOLACHLOR AND PHENANTHRENE

### Overview

This Chapter describes the sorption rate studies conducted for metolachlor (MET) and phenanthrene (PHEN) using the Chelsea soil and its extracted fractions. The obtained batch experimental results are discussed with respect to the effect of initial aqueous phase concentration on observed sorption rates and the comparisons between MET and PHEN. The hybrid gamma distribution model used to fit the data is described next and the model fits to the data are presented. The obtained mass transfer rate coefficients and their probability distributions are presented. The obtained mean values of mass transfer rate coefficients are compared with respect to sorbent and sorbate properties as well as published studies. The scope of the model for evaluating sorption rates of pesticides are discussed along with the trends revealed in the obtained model parameters.

### 6.1 Rationale and Objectives

Given the differential equilibrium sorption behavior of the sorbents for MET, we hypothesized that SOM fractions would exhibit different sorption rates than the Bulk Soil and further elucidate herbicide sorption mechanisms observed during the sorption and desorption equilibrium studies. Kerogen and black carbon components of SOM have been shown to exhibit slow sorption rates for PHEN and this has been attributed to the slow diffusion of the solute into the KB matrix. Since the KB fraction showed nonlinear isotherms for MET, it was expected that it might exhibit slow sorption rates for MET.

The HA fraction, which showed an almost linear isotherm for MET, was expected to show relatively faster sorption, in accordance with its amorphous nature. The objectives of this Chapter were to: i) evaluate the sorption rates of MET and PHEN on Bulk Chelsea Soil and its components, ii) investigate the effect of initial aqueous phase concentration on sorption rates of MET and PHEN; iii) use a stochastic model to obtain mass transfer rate coefficients for sorption of MET and PHEN to mathematically compare the sorption rates.

## 6.2 Experiments and Data Analysis

The chemicals used and the methodology followed for rate experiments have been detailed in Chapter 3. In brief, the rates of sorption at two different concentration levels of MET (500  $\mu\text{g/L}$  and 5000  $\mu\text{g/L}$ ) and PHEN (80  $\mu\text{g/L}$  and 800  $\mu\text{g/L}$ ) were studied on Bulk Chelsea soil and its BE, KB and HA fractions. Sampling times of 20 min, 80 min, 6 hr, 1 d, 2 d, 4 d, 8 d, 14 d, 22 d and 30 d were used to assess the change in aqueous phase concentrations over time, and solid phase concentrations were calculated from mass balance.

## 6.3 Results and Discussion

Figures 6.1 (a)-(d) and 6.2 (a)-(d) present the  $K_{OC}(t)$  values vs. logarithmic time for metolachlor and phenanthrene, respectively. Here the  $K_{OC}(t)$  data were calculated using the following equation:

$$K_{OC}(t) = \frac{q(t)}{C(t)f_{OC}} \quad (6.1)$$

where  $C(t)$  and  $q(t)$  are the aqueous and solid phase solute concentrations at any observation time  $t$ , respectively, and  $f_{OC}$  is the fraction of total organic carbon of the sorbent.

A comparison among the  $K_{OC}(t)$  values obtained for MET in Figure 6.1 indicates the effect of initial aqueous phase concentration ( $C_0$ ) on the  $K_{OC}(t)$  values. It is observed that the  $K_{OC}(t)$  values approach apparent equilibrium faster when the rate experiment was initiated with a higher  $C_0$  than with a lower  $C_0$  for the Bulk Soil, Soil BE and Soil KB. There seemed to be no effect of two different starting concentration levels on the rate of approach to equilibrium of  $K_{OC}(t)$  values for the Soil HA for MET. Although equilibrium is not achieved under the 30 d experimental time for the Bulk Soil, Soil BE and Soil KB, the faster approach of  $K_{OC}(t)$  values at higher  $C_0$  is evident from the smaller % differences in consecutive  $K_{OC}(t)$  values compared to the lower  $C_0$ . The Soil HA however, shows apparent equilibrium within 2 d reaction time.

Figure 6.2 indicates that in the case of PHEN also, the  $K_{OC}(t)$  values approach equilibrium faster for higher  $C_0$  compared to the lower  $C_0$  for the Bulk Soil, Soil BE and Soil KB. The effect of  $C_0$  on  $K_{OC}(t)$  values for the Soil HA fraction for PHEN does not seem to be substantial. In the case of PHEN, the  $K_{OC}(t)$  values for Bulk Soil and Soil KB at higher  $C_0$  seem to achieve equilibrium at about 8 d of reaction time, while equilibrium is not achieved for the lower  $C_0$  values for these sorbents. For the Soil BE, equilibrium is not reached for either  $C_0$  level. On the other hand, for the Soil HA-PHEN systems, equilibrium is achieved at around 8 d of experimental time for both the  $C_0$  levels. These observations reveal underlying aspects of the system, that can help elucidate the

similarities and differences in controlling sorption mechanisms for the sorption of the herbicide MET and the PAH PHEN, as described below.

### **6.3.1 Rate of Sorption to KB**

*K<sub>OC</sub>(t)* values are greater for the KB fraction compared to other sorbents. As observed for the equilibrium *K<sub>OC</sub>* values in Chapter 4, the *K<sub>OC</sub>(t)* values under non equilibrium conditions are also larger for the KB fraction for both MET and PHEN. These values are a factor of 2-3 different than the Bulk Soil, Soil BE and Soil HA values. Thus the rate experiments confirm the higher sorption capacity of the isolated KB fraction compared to other sorbents and again points out to its diminished role in the Bulk Soil.

### **6.3.2 Rate of Sorption to HA**

*HA exhibits the fastest sorption rates among all the sorbents.* Clear approach to equilibrium is seen for MET (in 2 d) and PHEN (in 4 d) for the HA fraction. As noted in Chapter 4, the MET isotherm for HA were the least non-linear, while MET exhibited nonlinear isotherms on all other sorbents; this indicated that the Chelsea Soil HA is primarily comprised of amorphous carbon. The fast approach to equilibrium of MET and PHEN on HA compared to other sorbents is a typical property of amorphous organic matter (Table 2.2) and further confirms that Chelsea Soil HA is primarily amorphous in nature. Although the glass transition temperature (*T<sub>g</sub>*) of Chelsea Soil HA in the “dry” state has been found to be between 63-67 °C (Pignatello et al., 2006), it is possible that the incoming solutes can lower its *T<sub>g</sub>* to around room temperature and hence it exhibits

sorption properties characteristic of amorphous organic matter. The mechanism of sorption of MET or PHEN to HA thus involves the dissolution into the “gel-like” matrix of HA and therefore experiments initiated at both  $C_0$  levels achieve equilibrium at about the same time, and no difference in the  $K_{OC}(t)$  values for the two  $C_0$  levels is observed. Soil HA is probably the fraction soil that is assumed to exhibit “almost instantaneous” sorption in rate models.

### 6.3.3 Rate of Sorption to Bulk Soil

*Bulk Soil Exhibits Slower Sorption Rates than Isolated HA:* For both MET and PHEN, the Bulk Chelsea Soil approaches equilibrium slower than the Soil HA fraction extracted from it. The Bulk Soil appears to reach equilibrium only for the higher concentration of PHEN at around 8 d whereas for the lower  $C_0$ , equilibrium is not reached within the 30 d experiment. Equilibrium is also not achieved for the sorption of the two concentrations of MET on the Bulk Soil. This observation points out that the KB and possibly the mineral phase play an important role in determining the sorption rates of organic solutes on the Bulk Soil. Both the slow diffusion through the mineral matrix and the slow penetration of the condensed KB matrix can result in slower rates of sorption to the Bulk Soil. The role of Soil BE in this regard is elucidated from the fact that neither of the solutes reaches apparent equilibrium with the BE fraction, which contains less of the fast sorbing HA fraction. It is possible that the sorbates experience greater diffusive retardation in sorbing to the BE fraction than to the isolated KB fraction, which is largely free of mineral matter, due to the encapsulation of KB in the mineral phase that can cause slower rates of sorption.

#### 6.3.4 Effect of $C_0$ on Sorption Rates

*Sorption Approaches Apparent Equilibrium Faster at Higher Initial Aqueous Concentrations.* It appears that the higher the initial aqueous phase concentration, the faster a system approaches apparent equilibrium. This seems to hold true for both MET and PHEN and all the sorbents (Bulk Soil, Soil BE, Soil KB), except for Soil HA as discussed above. This reflects a different physicochemical nature of these sorbents compared to HA. As was suggested from the observations of high sorption capacity and isotherm nonlinearity in Chapter 4, the KB fraction is a condensed form of carbon. Penetration of high concentrations of a solute into it causes its condensed matrix to swell and expand, thus allowing for more sorbent to be sorbed on to it and thus exhibiting faster sorption rate.

Huang and Weber (1998) observed similar differences in  $K_{OC}(t)$  values at different  $C_0$  for shale and kerogen samples in sorption rate studies of PHEN. They concluded that the dependence of sorption rate on aqueous phase solute concentration was more important for kerogen containing samples compared to humus containing samples. This is in accordance with the observation made here for the HA and KB fractions. Since the Bulk Soil and the BE both contain KB, they exhibit a similar trend, showing differences in their  $K_{OC}(t)$  values, although not to the same extent. The mechanism of a high solute concentration expanding or relaxing the condensed carbon matrix has been termed as the “aging” of the sorbent due to continued exposure to high concentration of solute. When such a solute desorbs, the process is hysteretic, i.e. the sorbent may not be able to fully recover its original condensed form and is thus said to be permanently relaxed or aged. The solute thus permanently changed the sorbent’s

character from “condensed” to “amorphous” (Huang and Weber, 1998; Ju and Young, 2005). Also, the higher  $C_0$  causes the sorbent’s sorption sites to be saturated faster than at the lower  $C_0$ , as observed in the decreasing uptake of the solute (% differences in consecutive  $K_{OC}(t)$  values) for the higher  $C_0$ . Such phenomenon is not observed when the  $C_0$  is low since the sorption sites are not saturated and uptake of the solute into the sorbent continues to increase throughout the experimental time of 30 d.

### 6.3.5 Sorption Mechanisms

*Sorption sites appear to be accessed in a particular sequence during sorption.*

While the HA and KB fractions are comprised primarily of amorphous and condensed organic matter, respectively as noted above, Bulk Soil and Soil BE are mixtures of both of these fractions and mineral matter. An examination of the  $K_{OC}(t)$  values of these sorbents in Figure 6.1 and 6.2 indicates that at the beginning of the rate experiments, the  $K_{OC}(t)$  values are identical for both  $C_0$  levels for Bulk Soil and Soil BE for both MET and PHEN. It is possible that this reflects the solutes accessing the amorphous organic matter matrix of HA contained in these two sorbents, which does not exhibit dependence of  $K_{OC}(t)$  values on  $C_0$ . Later during the process of sorption, when these sites have been fully accessed, sorption continues into the condensed KB fraction and this is where differences in the  $K_{OC}(t)$  values for these sorbents become apparent. The higher  $C_0$  level of solute is able to relax and penetrate the sorbent matrix more than the lower  $C_0$ , and thus the  $K_{OC}(t)$  values for higher  $C_0$  reach equilibrium faster than the lower  $C_0$ , indicating faster approach to equilibrium. This sequence of sorption events was also proposed by Weber and Huang (1996), who observed increasing  $\log K_F$  values and decreasing  $n$

values as a function of time for sorption of PHEN on soils. They observed an “initiation” in which the solute accesses the energetically more favorable sorption sites and then a “logarithmic” stage where the solute gains access to the remote condensed organic matter sites (possibly due to relaxation of the condensed matrix due to solute sorption) and finally an apparent equilibrium stage where no further sorption takes place. As seen in Figures 6.1 and 6.2, the final equilibrium stage in most cases is not reached in the 30 d reaction time.

To interpret the rate data mathematically and to enable the prediction of sorption rate of other compounds on the sorbents used in this study required the data to be fit to a conceptual sorption rate model. Among the various models described in Chapter 2, it has been reported that the intra particle diffusion model, which assumed slow desorption to be explicitly a consequence of slow diffusion through tortuous path and small pores inside a soil aggregate (Ball and Roberts, 1991; Farrell and Reinhard, 1994), is unable to completely describe certain phenomena related to slow sorption, such as the tailing of sorption rate curves and the differences in rate of sorption and desorption steps (Ahn et al., 1999; Deitsch et al., 1998, 2000). Others have reported that the intraparticle diffusion models that employ diffusion lengths as model parameters have expounded diffusion lengths that are several hundred times the particle size of the sorbents, which is a highly impractical result. On the other hand, stochastic models that assume slow sorption to be a result of intra organic matter diffusion and assume a distribution of mass transfer rate coefficients acting in parallel, have been found to satisfactorily describe observed sorption rate phenomena. A hybrid gamma model is one such model that was chosen to fit the rate data presented in Figures 6.1 and 6.2.

## 6.4 Rate Data Modeling

The hybrid Gamma distribution model is a “hybrid” of the traditional two site model and the gamma model described in Chapter 2 (Section 2.2). It assumes a soil to consist of two compartments, the ‘ $f$ ’ fraction equilibrating instantaneously with the incoming solute and the  $(1-f)$  fraction exhibiting mass transfer limited sorption, which is described by a  $\Gamma$  distribution of mass transfer rate coefficients in sub-compartments of  $(1-f)$ . The equations governing this model were presented in the data reduction section in Chapter 3 (Section 3.6.2), but are shown here again for convenience and ease of discussion.

$$\frac{dS_1}{dt} = f * K_{OC} \frac{dC_{aq}}{dt} \quad (3.4)$$

where  $K_{OC}$  = equilibrium  $K_{OC} = q_{30d}/(C_{30d}*f_{OC})$ . The fraction  $S_2$  is hypothesized to consist of  $n$  number of compartments, each having a different mass transfer rate coefficient for the solute. The distribution of mass transfer rate coefficients  $k$  in each compartment is assumed to be defined by a continuous Gamma distribution as:

$$p(k) = \frac{\beta^\alpha k^{\alpha-1} \exp(-\beta k)}{\int_0^\infty x^{\alpha-1} \exp(-x) dx} \quad (3.5)$$

where  $\alpha$  and  $\beta$  are parameters that determine the shape and scale of the  $\Gamma$  distribution respectively and the denominator is the statistical  $\Gamma$  function of  $x$ . The total sorption in

$(1-f) = S_2$  is then represented as the sum of sorption in the  $n$  compartments as:

$$\frac{dS_2}{dt} = (1-f) * \sum_{i=1}^n p(k_i) * k_i * \left( S_{2i} - \frac{K_{oc} C_{aq}}{n} \right) \quad (3.6)$$

An  $n = 100$  was used. The modeled solid phase concentration at time  $t$  is thus obtained as:

$$q_m = S_1 + S_2 \quad (3.7)$$

Equation 3.4 and 3.6 are numerically integrated for 1000 time steps of 1 min each initially and 1 hr each later till the end of the 30 d time period of the experiment. The model parameters  $f$ ,  $\alpha$  and  $\beta$  are minimized simultaneously by minimizing the error between the modeled and the observed solid phase concentration  $q_o$ , defined as:

$$\text{error (\%)} = 100 \times \left[ \frac{\sum_{i=1}^N (q_o - q_m)^2 / q_o^2}{N} \right]^{0.5} \quad (3.8)$$

using the Solver function of MS Excel. A sample spreadsheet for the modeling exercise can be found in Appendix A.

The hybrid model used here has been shown to give better results than either the two site model or the gamma model alone (Ahn et al., 1999). This should be expected as the model incorporates an instantaneously sorbed fraction that accounts for fast sorption

exhibited by certain fractions in the Bulk Soil, while the gamma model accounts for the distributed reactivities that may be encountered by the solute among other more condensed soil components. The  $f$ ,  $\alpha$  and  $\beta$  values that were obtained using the Solver function in MS Excel have been presented in Table 6.1. The obtained distributions of mass transfer rate coefficients are presented in Figure 6.3 and 6.4 for MET and PHEN, respectively. The modeled fits to the experimental rate data are presented in Figures 6.5 (a)-(d) and 6.6 (a)-(d).

It should be noted that our data set presented here for one herbicide and one PAH is relatively small to make adequate quantitative comparison of the rate parameters among different sorbents. Our quantitative assessment is also limited due to the fact that no prior data existed in the literature for comparison. However, some general trends can be observed, which are summarized and discussed here.

Firstly, it can be seen from the Table 6.1 that, for both MET and PHEN, a greater value  $f$  – the fraction of sorbent that equilibrates instantaneously with the incoming solute was observed for the same sorbent for the higher  $C_0$ . This observation essentially extends our earlier suggestion in this Chapter that the higher incoming solute concentration exhibits faster approach to equilibrium at higher  $C_0$ , which in turn points to the ability of the solute at  $C_0$  to penetrate or transform the condensed nature of the sorbent to an amorphous character, as indicated by higher  $f$  values for higher  $C_0$ .

Only a few other researchers have used this model for sorption and desorption rate studies and have made similar observations. Ju and Young (2005) used this model to investigate the sorption and desorption behavior of 1,2-dichlorobenzene (1,2-DCB) and 1,2,4-trichlorobenzene (1,2,4-TCB) on two surface soils and a shale. They observed that

the magnitude of the instantaneously sorbing and desorbing fraction was inversely related to the hard (condensed) carbon content of the soils and invoked the sorbent transformation from condensed to amorphous form to explain their findings. They hypothesized that the sorbent with the highest condensed carbon content was also the one most resistant to this conformational change by incoming solutes. For three soils having  $f_{OC}$  values between 1.08 – 5.52, they observed  $f$  values between 0.09 – 0.59, with the  $f$  values increasing for sorbents with higher condensed organic matter contents

Secondly, although there are large standard deviations on the estimated mean mass transfer rate coefficients ( $k$ ), the mean  $k$  values appear to be larger for the higher  $C_0$  in comparison to the smaller  $C_0$  for the Bulk Soil and the Soil KB. This is in agreement with the  $K_{OC}(t)$  vs. time plots, which suggested faster rates of sorption were observed for the higher  $C_0$ . Among the different sorbents for PHEN, the mean  $k$  values are the lowest for the KB fraction and the largest for the HA fraction. Also, no major difference is observed between the mean  $k$  values (Table 6.1) or the distribution of mass transfer rate coefficients for HA (Figure 6.4), similar to the  $K_{OC}(t)$  values for HA, confirming its mainly amorphous nature. Similarly, the mean  $k$  values and the distribution of mass transfer rate coefficients for BE are identical at both  $C_0$ . Observed mean  $k$  values and distribution of mass transfer rate coefficients follow a similar pattern for MET, except that the largest  $f$  and mean  $k$  value among the sorbents were obtained for the KB fraction which was unexpected. Ahn et al. (1999) reported mean  $k$  values of  $6.08 - 6.13 \times 10^{-3} \text{ hr}^{-1}$  for 1,2 DCB and between  $6.08 - 7.36 \times 10^{-3} \text{ hr}^{-1}$  for 1,2,4-TCB, values that are close to the values obtained for the current experiments.

Thirdly, the parameters  $\alpha$  and  $\beta$  determine the size and shape of the  $\Gamma$  probability distribution respectively, but a trend in their values among the sorbent or among the two  $C_0$  was lacking and hence no physical meaning could be assigned to these parameters. Ahn et al. (1999) validated this model for describing desorption of the two-ring PAH naphthalene in a batch and column study; their modeled  $\alpha$  and  $\beta$  values ranged from 0.33 – 0.51 and 47.06 – 83.3 hr respectively. Deitsch et al. (2000) used the simple  $\Gamma$  distribution model (detailed in Chapter 2) to investigate sorption and desorption mass transfer rate coefficients for 1,2-DCB and found significant difference between the sorption and desorption rate steps indicative of desorption hysteresis. For their 7 d sorption experiments on various sands, clays and peat, they obtained  $\alpha$  values ranging from 0.147 – 0.678 and  $\beta$  values ranging from 0.023 – 0.44.

In general it can be said that since good model fits are obtained from this modeling exercise, inorganic matter diffusion appears to be the cause of slow sorption of MET and PHEN observed among the sorbents. This statement is supported by the observations of faster attainment of equilibrium by the HA fraction (within 2 – 4 d) and nonattainment of equilibrium for other sorbents in this 30 d study. However, this model has previously been used only for low  $f_{OC}$  soils samples and  $f$  and mean  $k$  values for the KB and HA fractions obtained with this model are not as expected from the  $K_{OC}(t)$  vs. time graphs and the model fits to the HA sorption rate data (Figures 6.5 (d) and 6.6 (d)). This indicate that the model might not be able to “catch up” with these higher  $f_{OC}$  fractions, in these case it over-predicts the initial low uptake in the favor of high values at longer times. The model was also found to give non-singular optimum values, where two values of  $\alpha$  and  $\beta$  varied across orders of magnitude gave similar minimum error values.

Effect of change in  $\alpha$  and  $\beta$  on distribution of mass transfer rate coefficients is presented in Appendix B.

The model used here is essentially similar in concept to the distributed reactivity model (DRM) model explained in Chapter 2, in that it assumes soil to be consisting of a “linear” or “instantaneously sorbing” component and a distribution of “non-linear” or “mass transfer limited” components, each having individual reactivities that act in parallel. However, as pointed out by Johnson et al. (2001) in desorption rate studies, single or two parameter models such as the pore-diffusion model, the two parameter  $\Gamma$  model and other more complex models involving 3-5 fitting parameters failed to fit their observed desorption data. They suggested the use of a biphasic (slow and rapid desorption) first order models to model desorption rate data. We suggest that given the slow sorption rates exhibited the mineral rich BE fraction for both MET and PHEN, it might be reasonable to assume that intra aggregate pore diffusion also influences the rate of sorption to some extent and a model that accounts for both the diffusion limitations of solutes on the intra particle scale and the mass transfer limitation in the intra organic matter domain might be needed to describe sorption rates of pesticides. The development of mathematical correlations between sorbents characteristics and model parameters would be possible only if the model studies are expanded to other solutes.

## **6.5 Summary and Implications**

Based on the time to attain equilibrium for the herbicide MET with the Bulk Soil, our study indicates that sorption rate phenomena could be more important than evaluation of sorption equilibrium data for soils. Given that apparent sorption equilibrium is not

reached within the 30 d time period of this experiment, concentrations of pesticides in runoff and leachate could be several times higher than equilibrium predicted values in case of flash storm events that happen right after pesticide application. This Chapter also emphasizes further the importance of inclusion of KB fraction in sorption studies of herbicides. Our data suggest that the KB fraction and its aggregated conformation in soils contributes to slower rates of sorption than those suggested by assuming soils as consisting of amorphous “humus” matter as is usually the case for pesticide sorption studies (Wauchope et al., 2002) Since the KB fraction is ubiquitous in the environment (Cornelissen et al., 2005), any study that assumes soils can be represented by humic acids or lignin is unrealistic. According to Cornelissen et al. (2005) our paradigm for sorption to soils needs to be changed to incorporate the presence of KB in the SOM. The effect of aggregation behavior of this KB fraction is further investigated in the next chapter.

Table 6.1 Model parameters for MET and PHEN

Sorbent	Conc. Level	$f$	$\alpha$	$\beta$	mean $k$	Std. Dev.	Error (%)
Metolachlor							
Bulk Soil	Low	0.281	0.736	86	8.56E-03	9.98E-03	2.93
	High	0.357	0.559	40	1.40E-02	1.87E-02	3.59
Soil BE	Low	0.163	0.519	86	6.03E-03	8.38E-03	5.51
	High	0.352	0.517	86	6.01E-03	8.36E-02	3.24
Soil KB	Low	0.492	0.177	3.3	5.36E-02	1.27E-01	4.79
	High	0.599	0.300	4.9	6.12E-02	1.12E-01	2.75
Soil HA	Low	0.396	0.127	400	3.18E-04	8.91E-04	9.21
	High	0.528	0.157	447.4	3.51E-04	8.86E-04	4.95
Phenanthrene							
Bulk Soil	Low	0.151	0.428	86	4.98E-03	7.61E-03	2.51
	High	0.289	0.263	43.4	6.06E-03	1.18E-02	3.95
Soil BE	Low	0.127	0.355	86	4.13E-03	6.93E-03	2.04
	High	0.384	0.352	81.9	4.30E-03	7.24E-03	6.54
Soil KB	Low	0.052	4.87	8620.7	5.65E-04	2.56E-04	8.94
	High	0.163	0.665	480	1.39E-03	1.70E-03	3.70
Soil HA	Low	0.058	0.906	73.6	1.23E-02	1.30E-02	3.53
	High	0.080	0.778	86	9.05E-02	1.03E-02	6.49

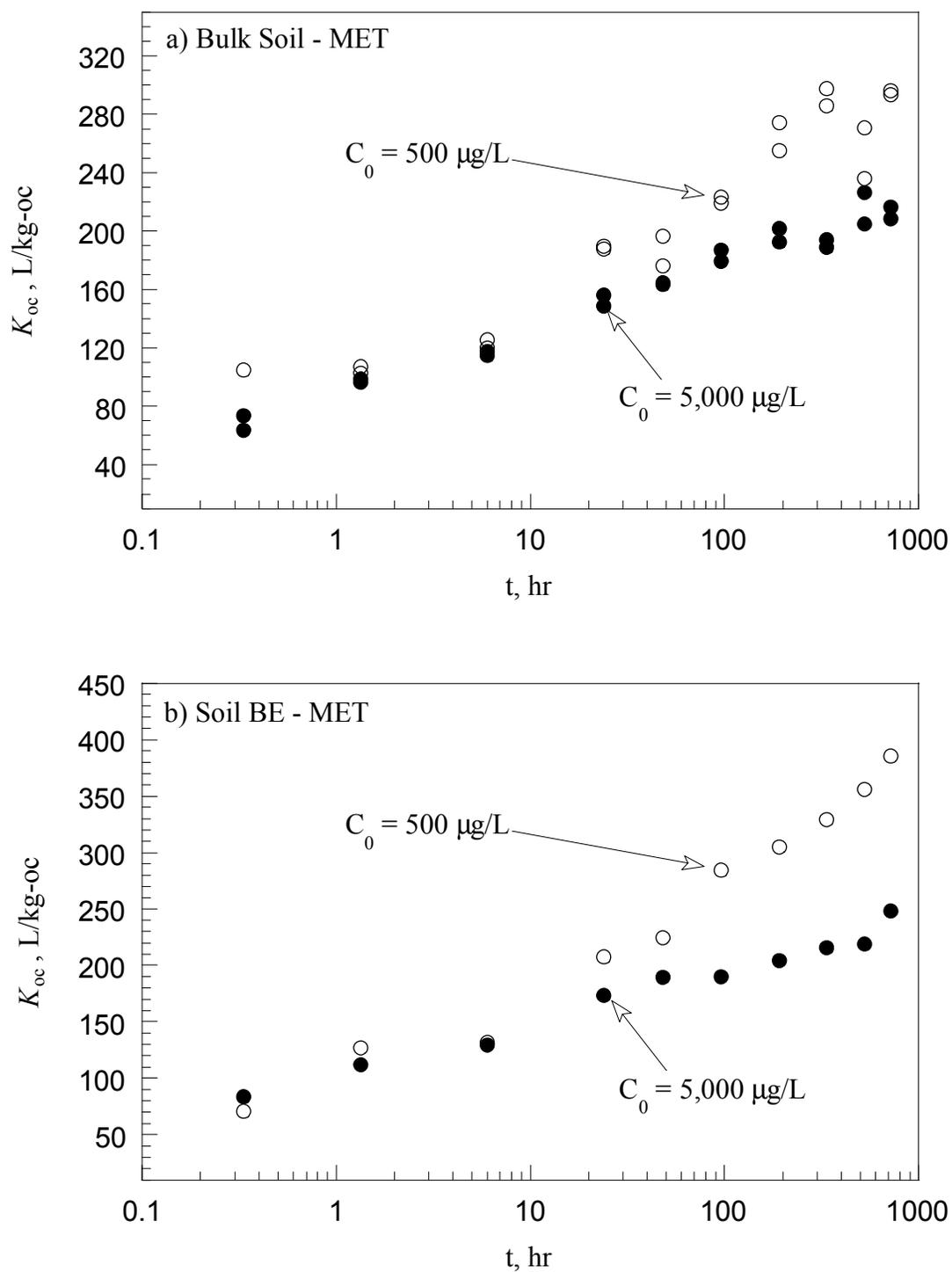


Figure 6.1.  $K_{OC}$  vs.  $t$  graphs for metolachlor sorption on a) Bulk Soil, b) Soil BE

(continued on next page)

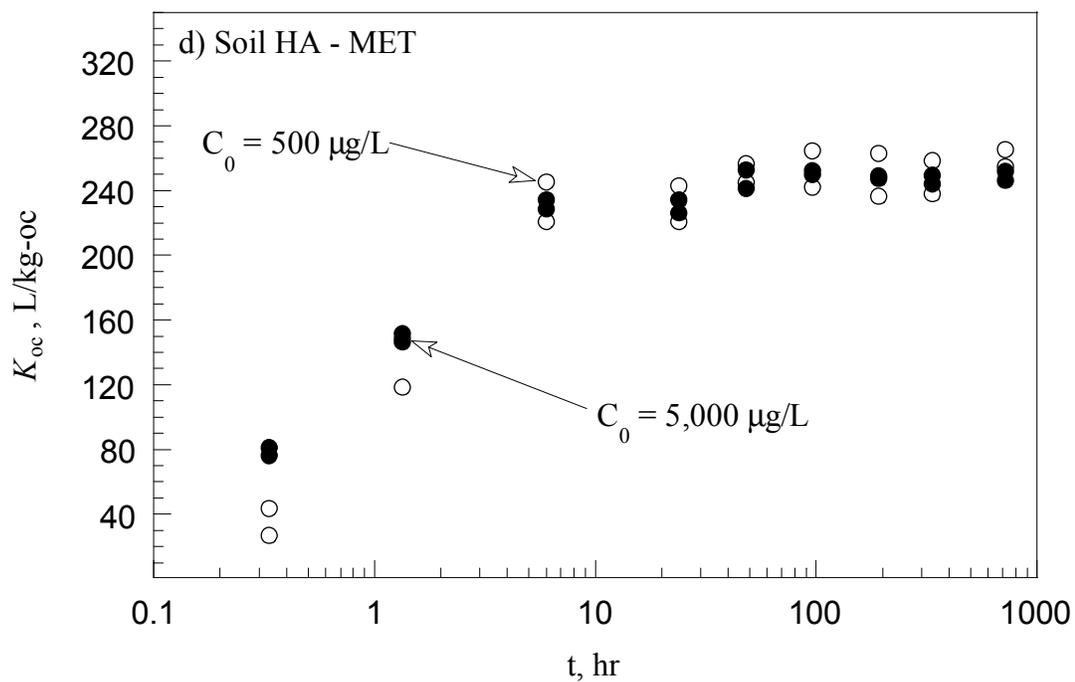
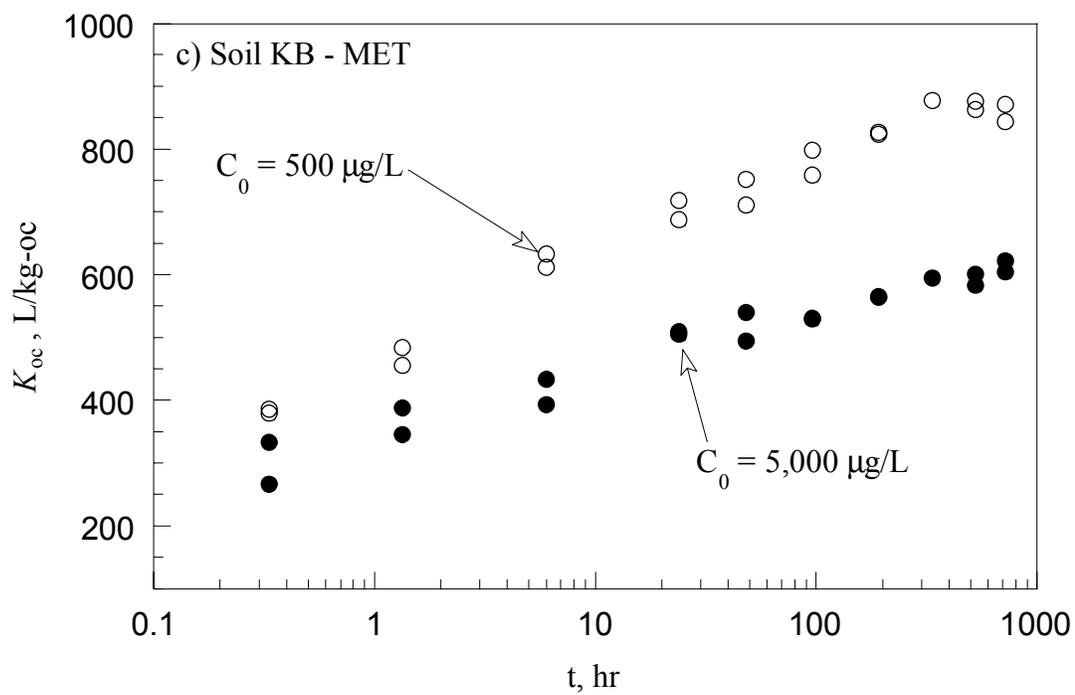


Figure 6.1 contd. c) Soil KB, d) Soil HA.

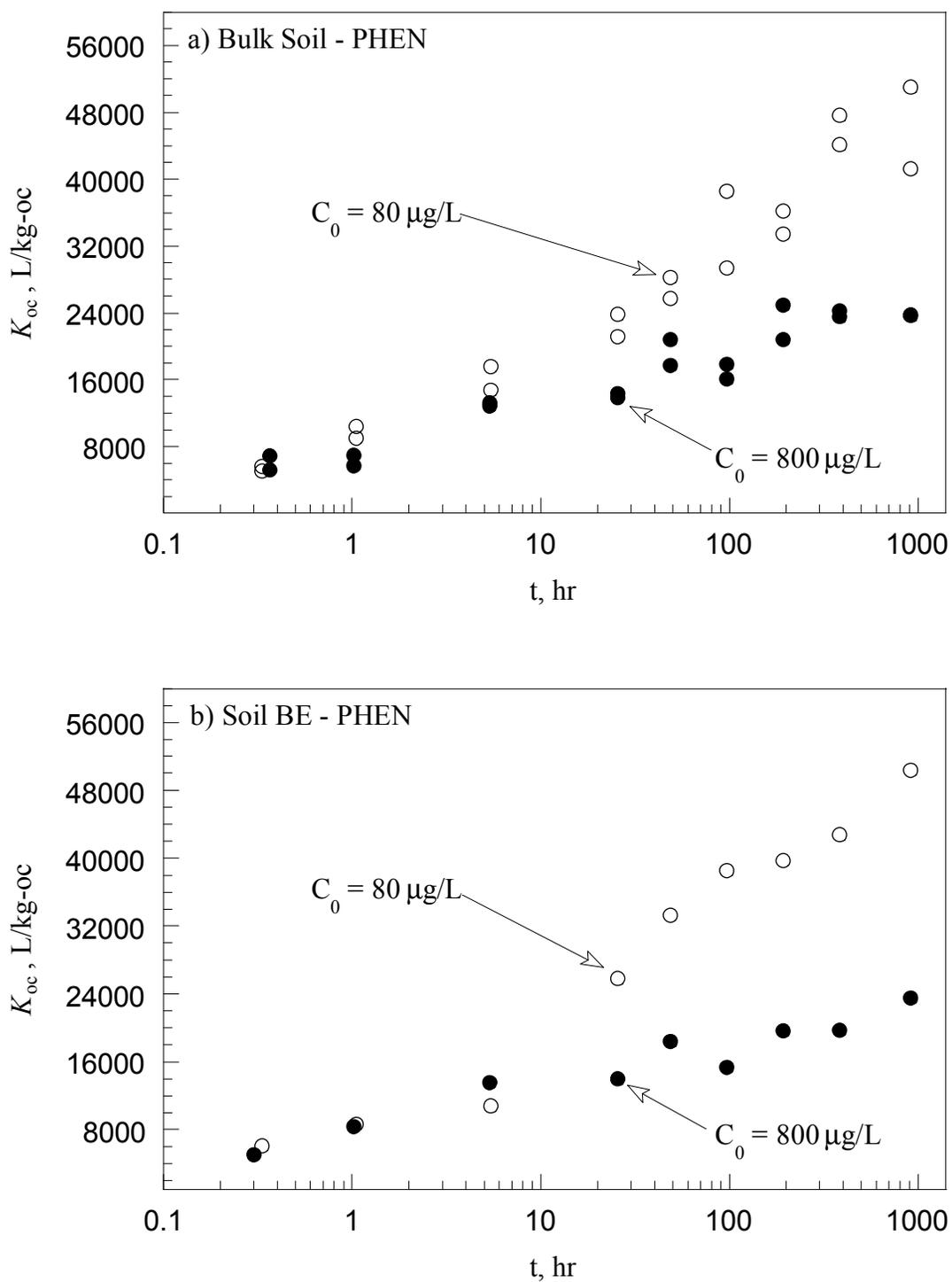


Figure 6.2.  $K_{OC}$  vs.  $t$  graphs for phenanthrene sorption on a) Bulk Soil, b) Soil BE

(continued on next page)

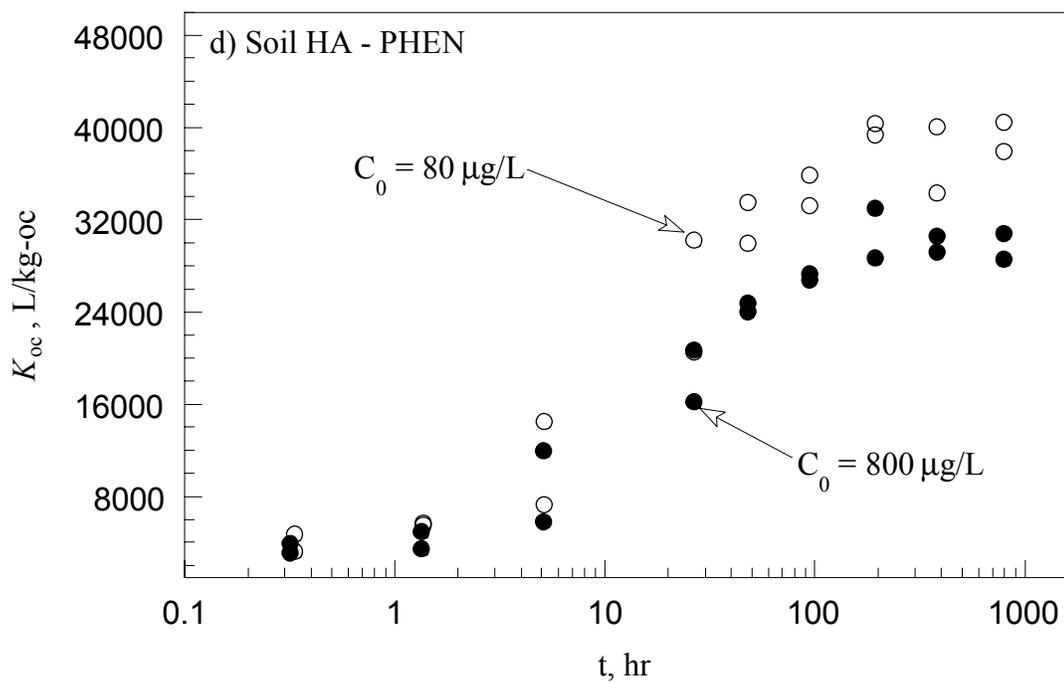
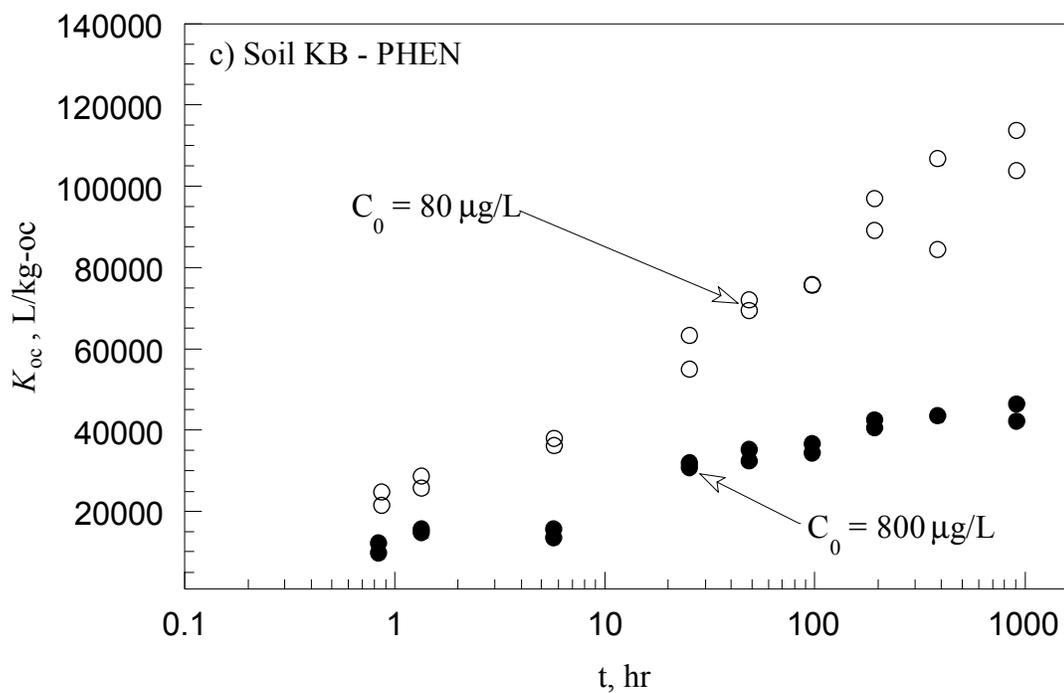


Figure 6.2 contd. c) Soil Kb, d) Soil HA.

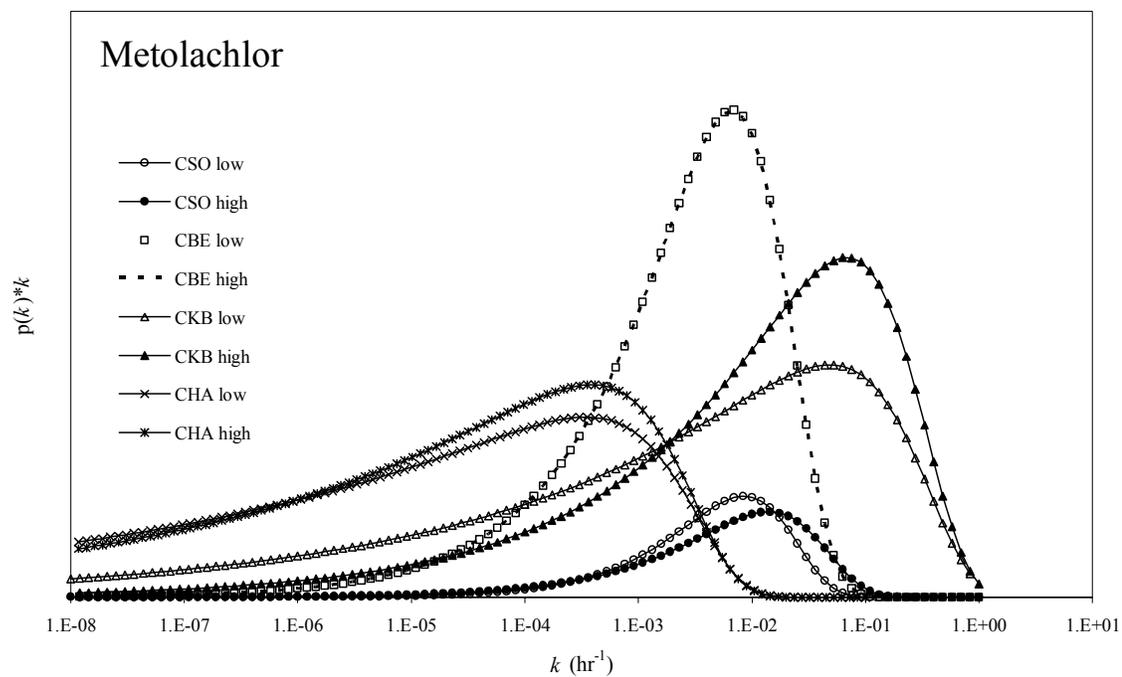


Figure 6.3 The modeled distribution of mass transfer rate coefficients for MET

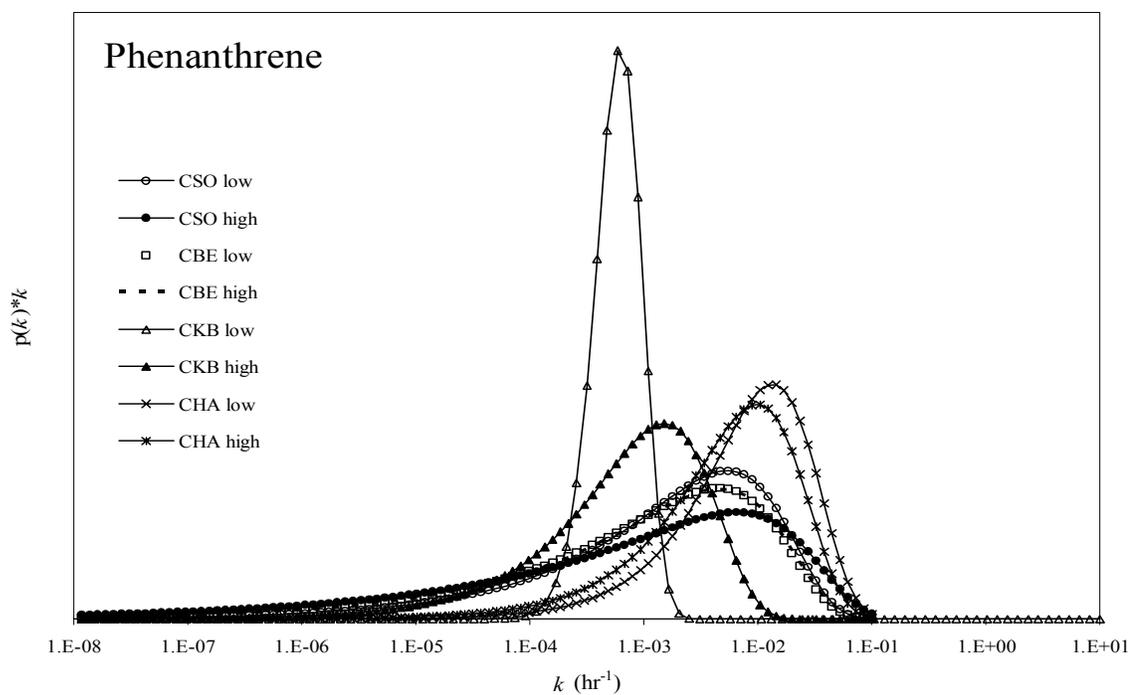


Figure 6.4 The modeled distribution of mass transfer rate coefficients for PHEN

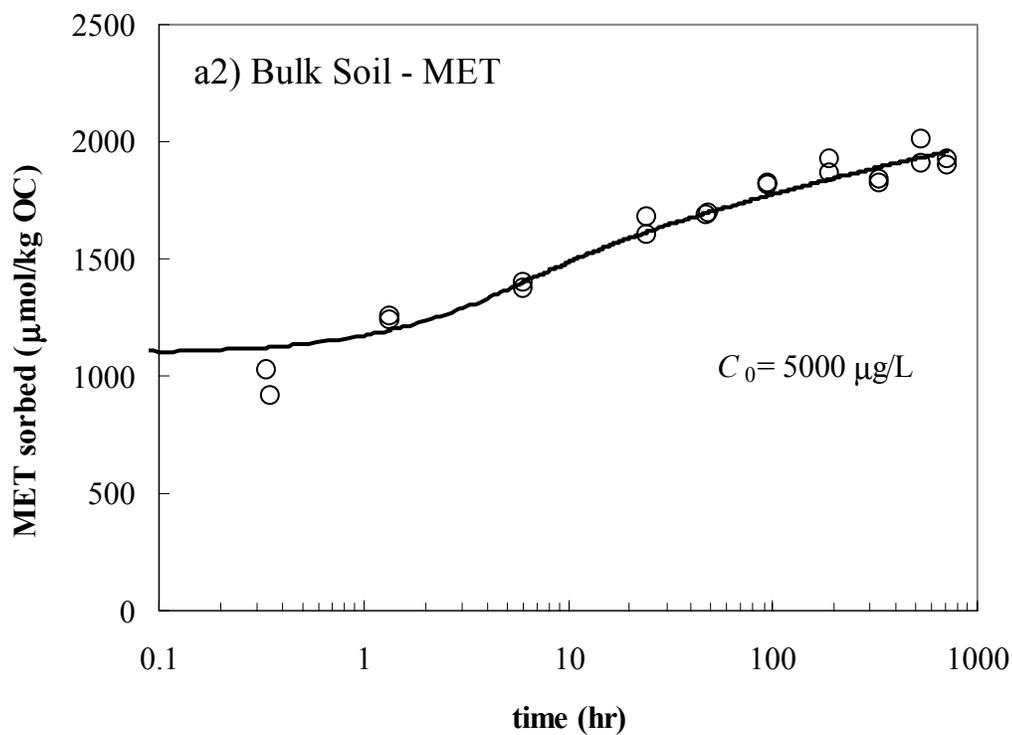
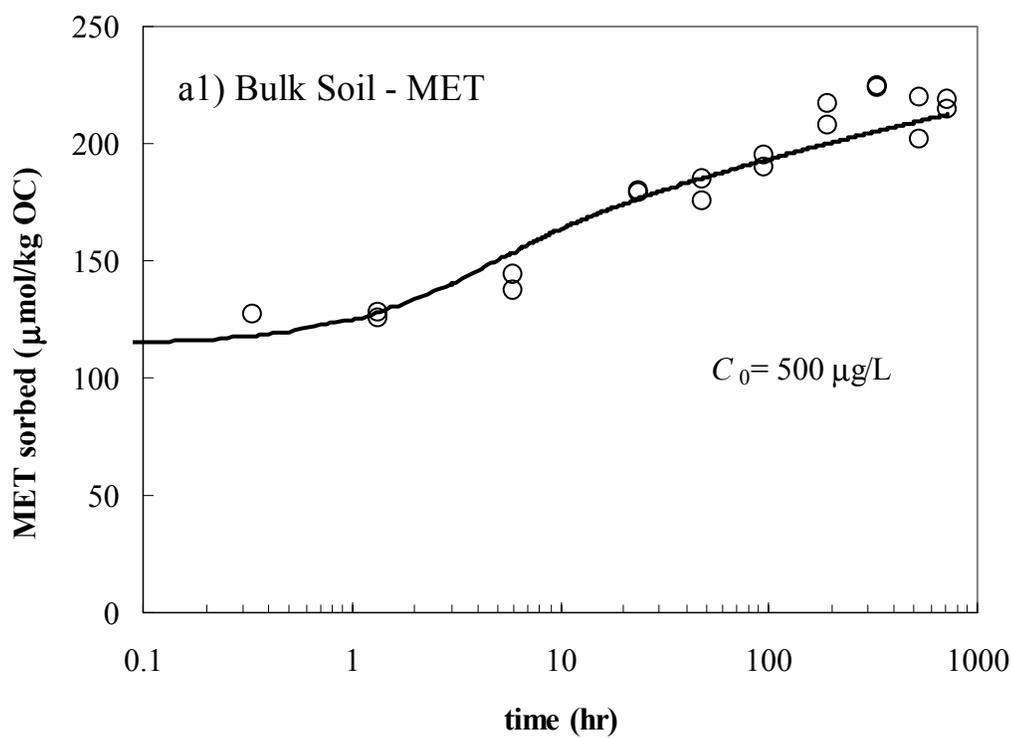


Figure 6.5 Model fits (solid lines) to the rate data (O) for a1) Bulk Soil-MET, low  $C_0$ , a2) Bulk Soil-MET, high  $C_0$  (continued on next page)

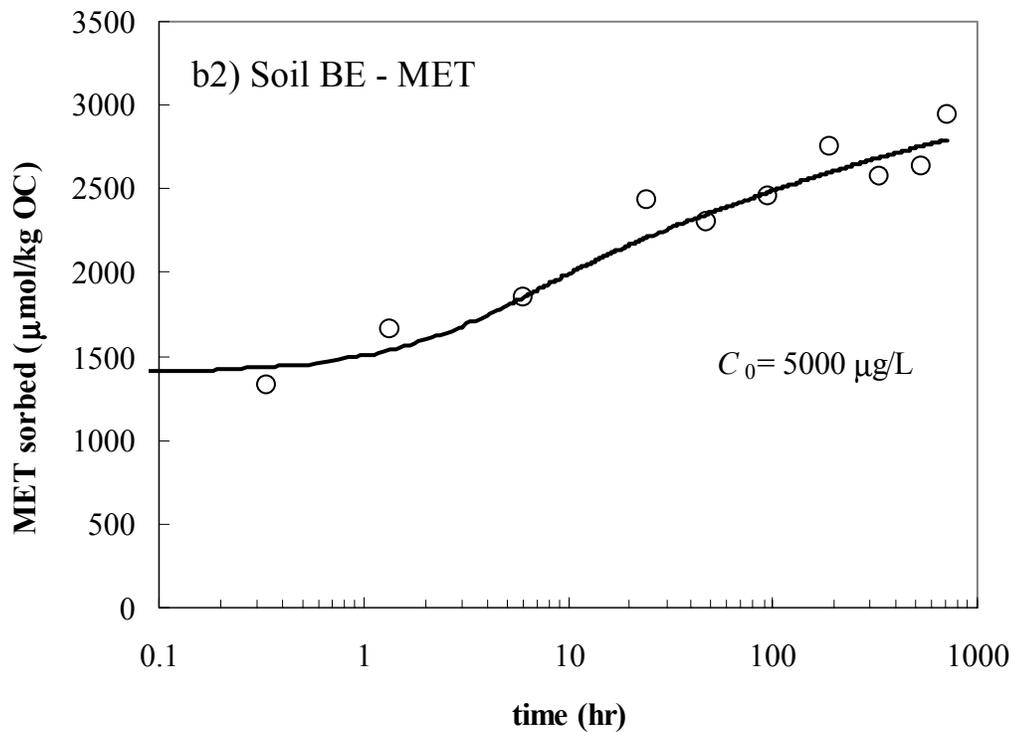
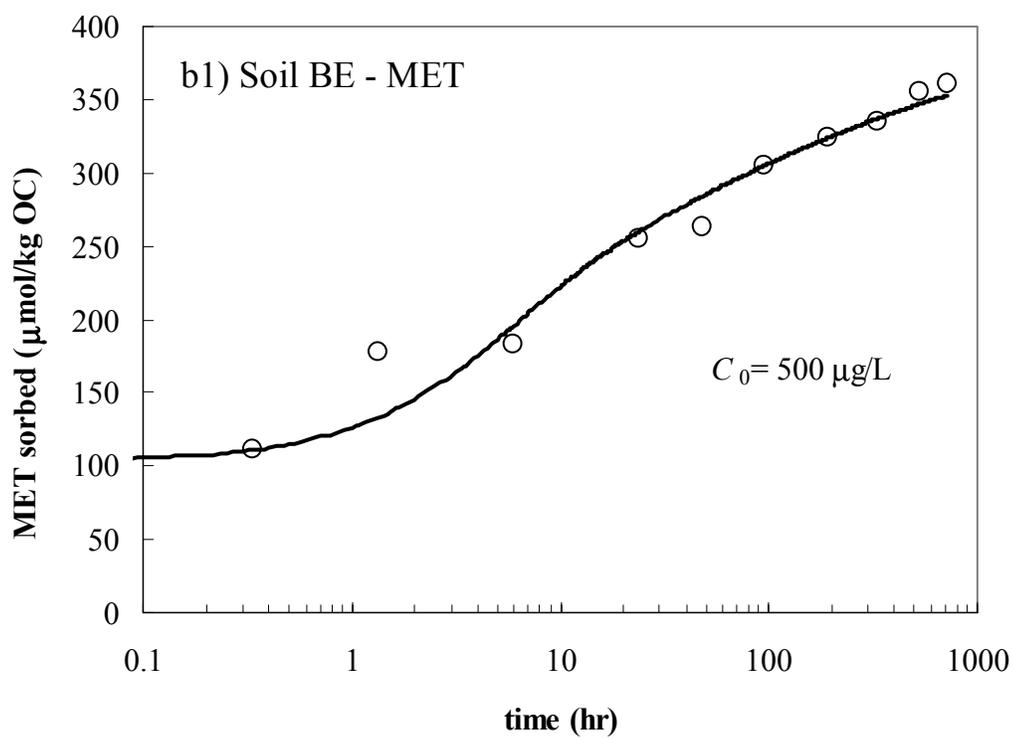


Figure 6.5 (contd) b1) Soil BE-MET, low  $C_0$ , b2) Soil BE-MET, high  $C_0$

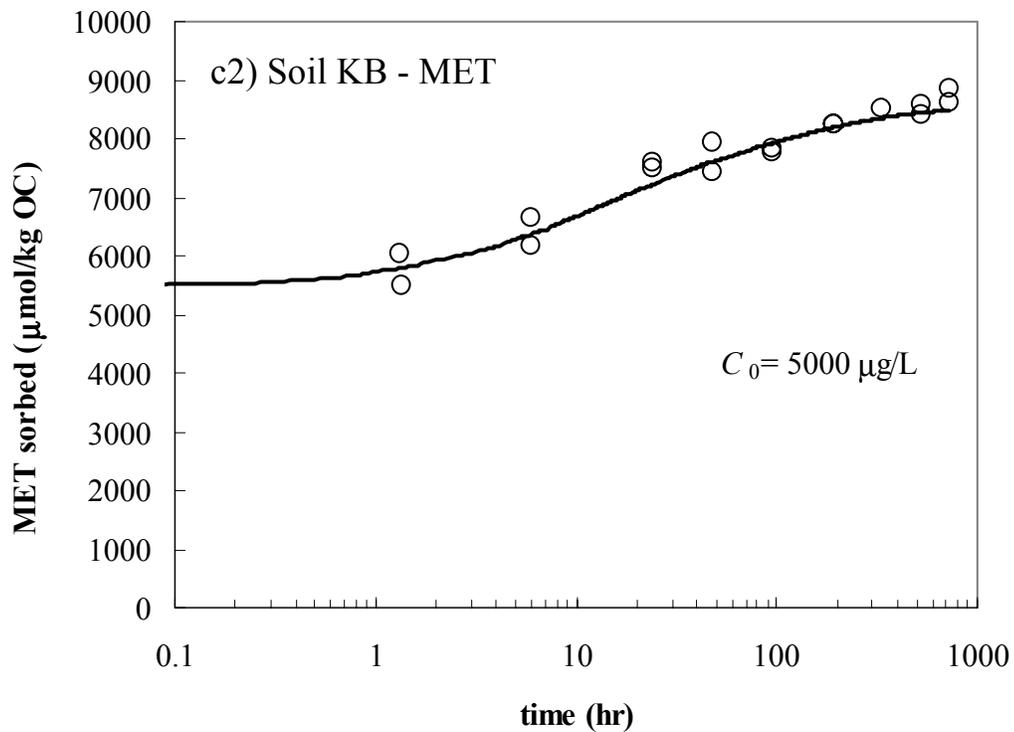
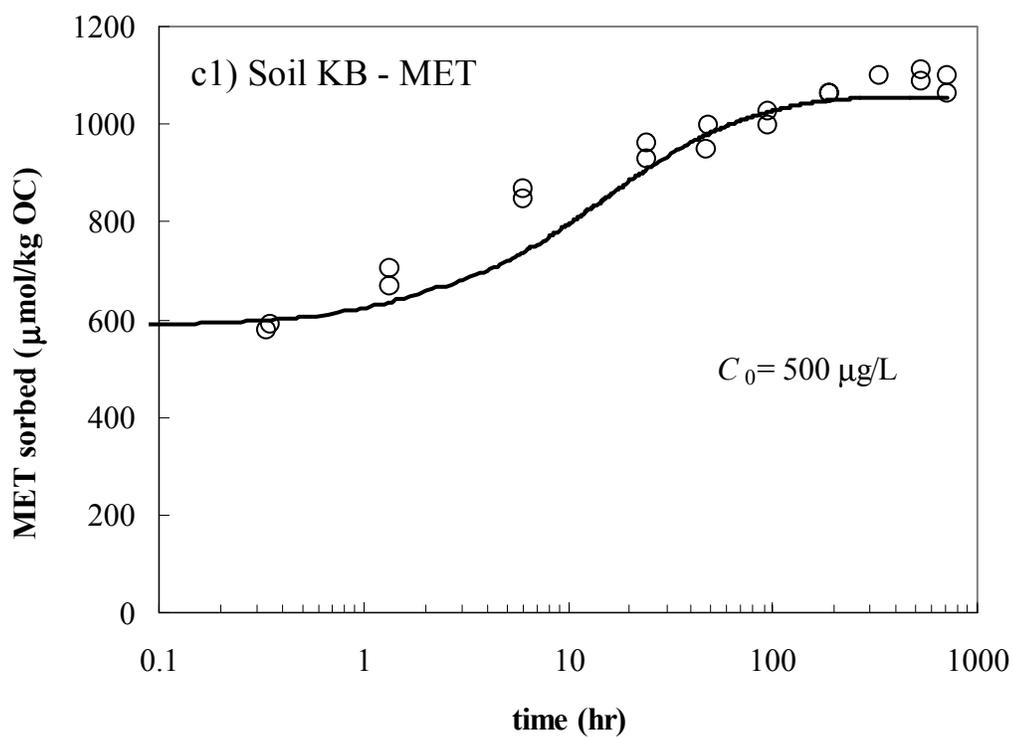


Figure 6.5 (contd) c1) Soil KB-MET, low  $C_0$ , c2) Soil KB-MET, high  $C_0$

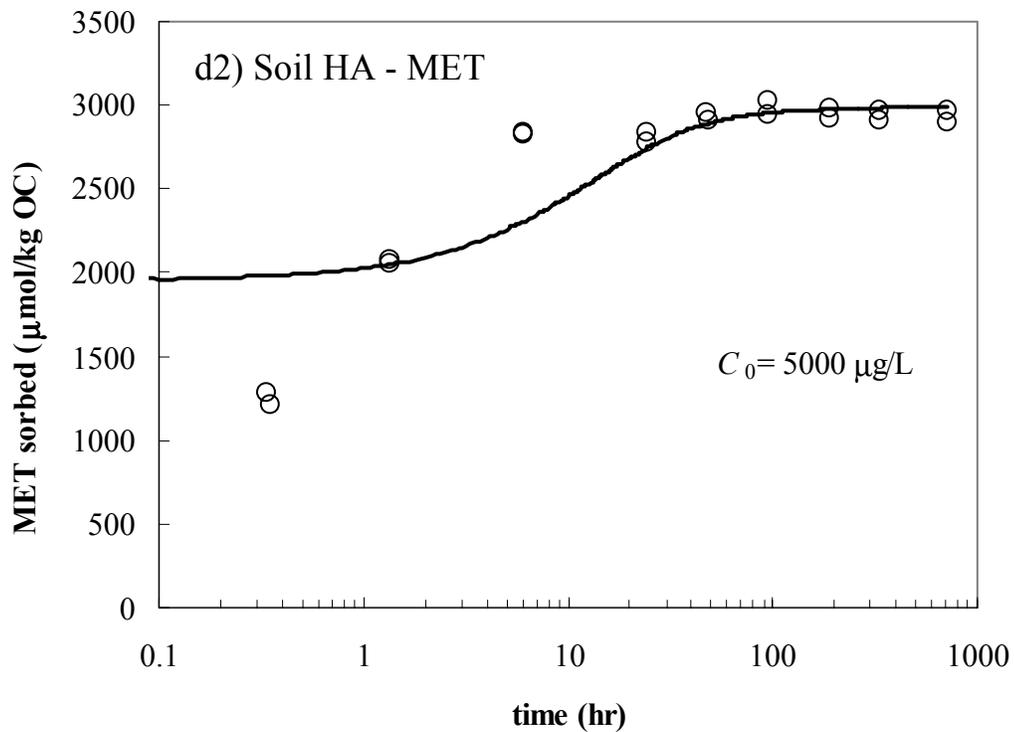
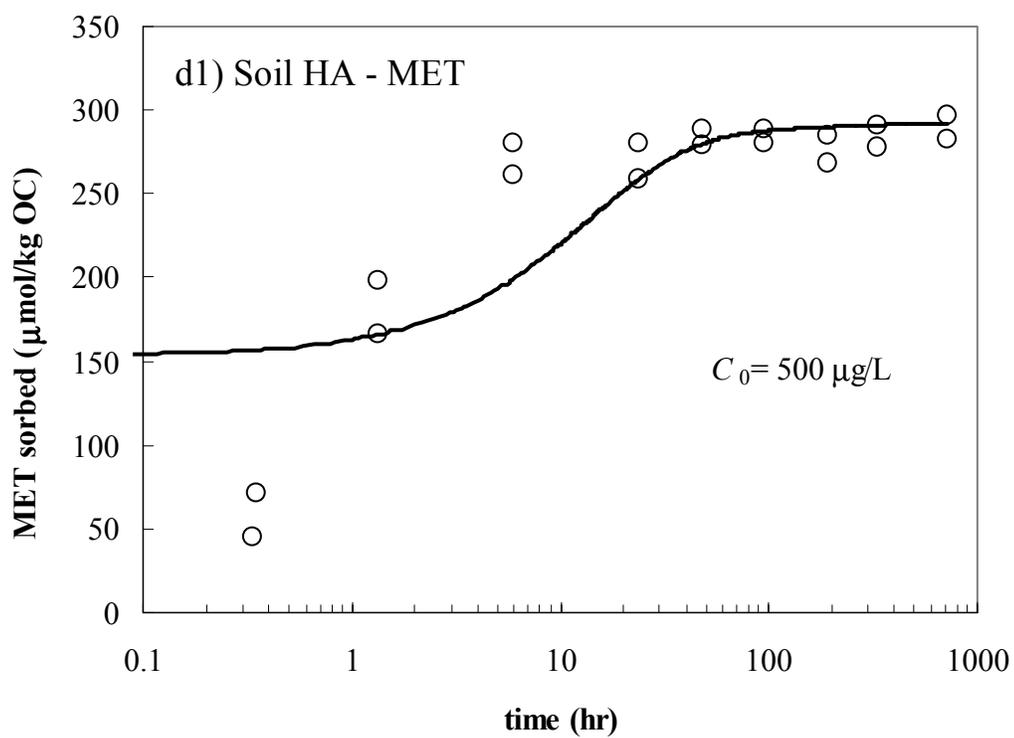


Figure 6.5 (contd) d1) Soil HA-MET, low  $C_0$ , d2) Soil HA-MET, high  $C_0$

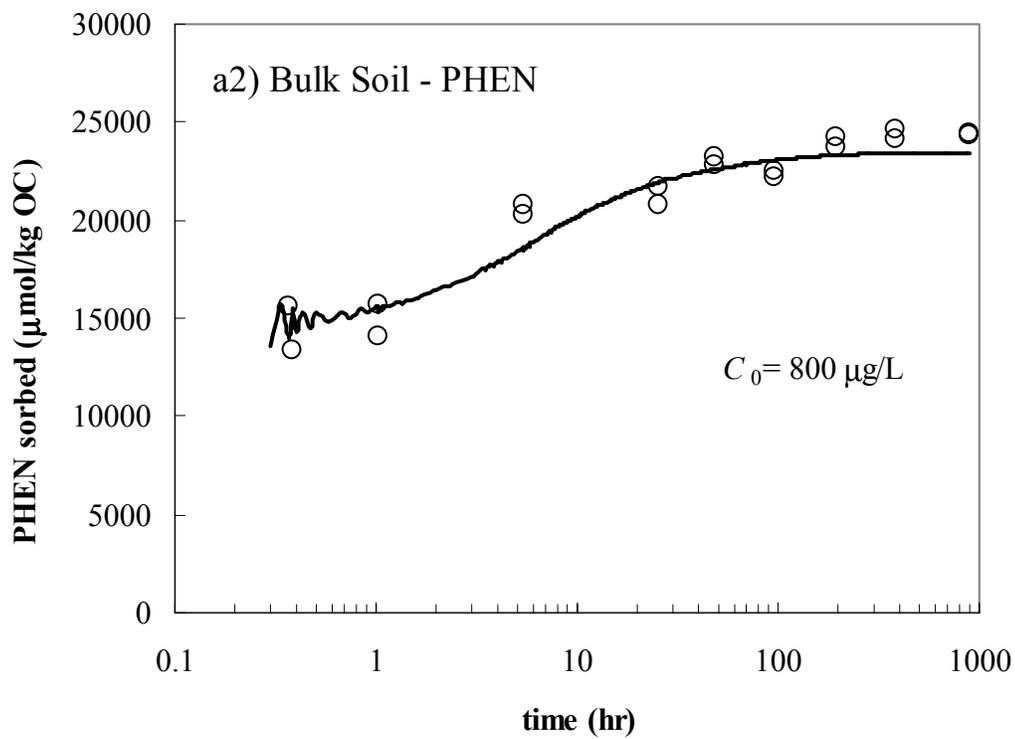
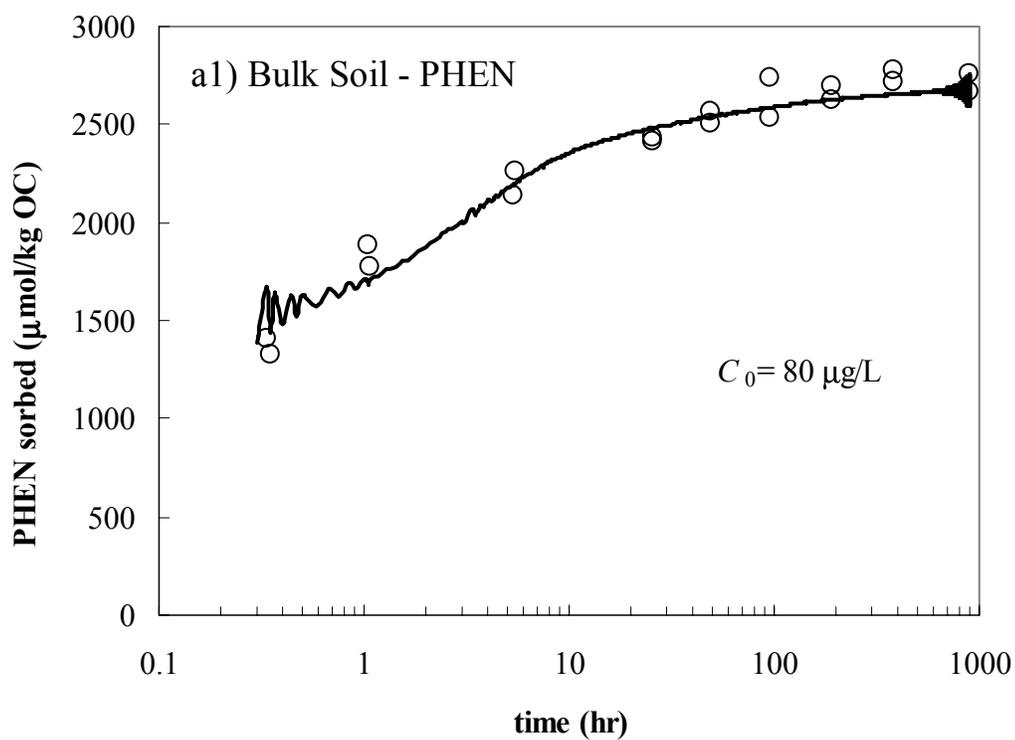


Figure 6.6 Model fits (solid lines) to the rate data (O) for a1) Bulk Soil-PHEN, low  $C_0$ , a2) Bulk Soil-PHEN, high  $C_0$  (continued on next page)

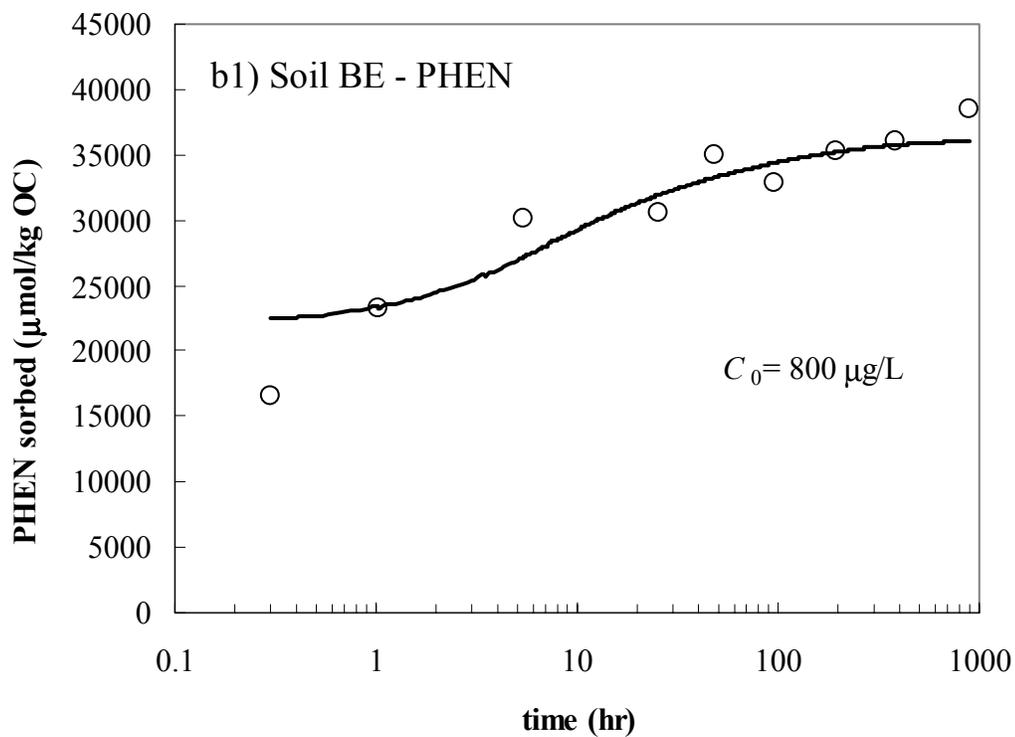
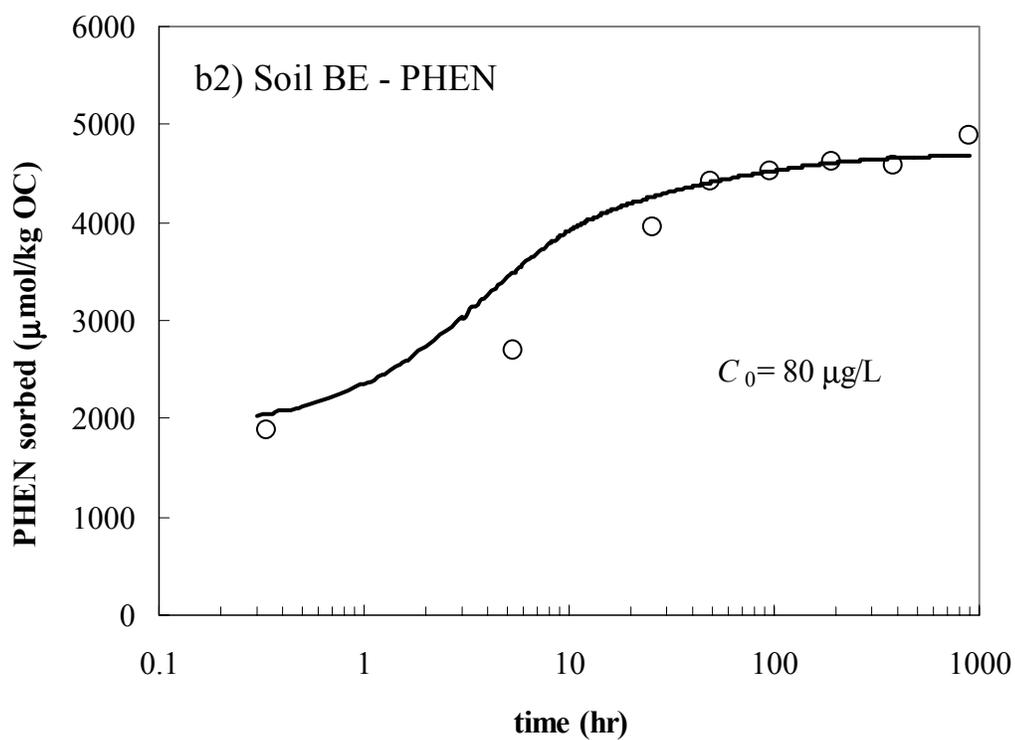


Figure 6.6 (contd) b1) Soil BE-PHEN, low  $C_0$ , b2) Soil BE-PHEN, high  $C_0$

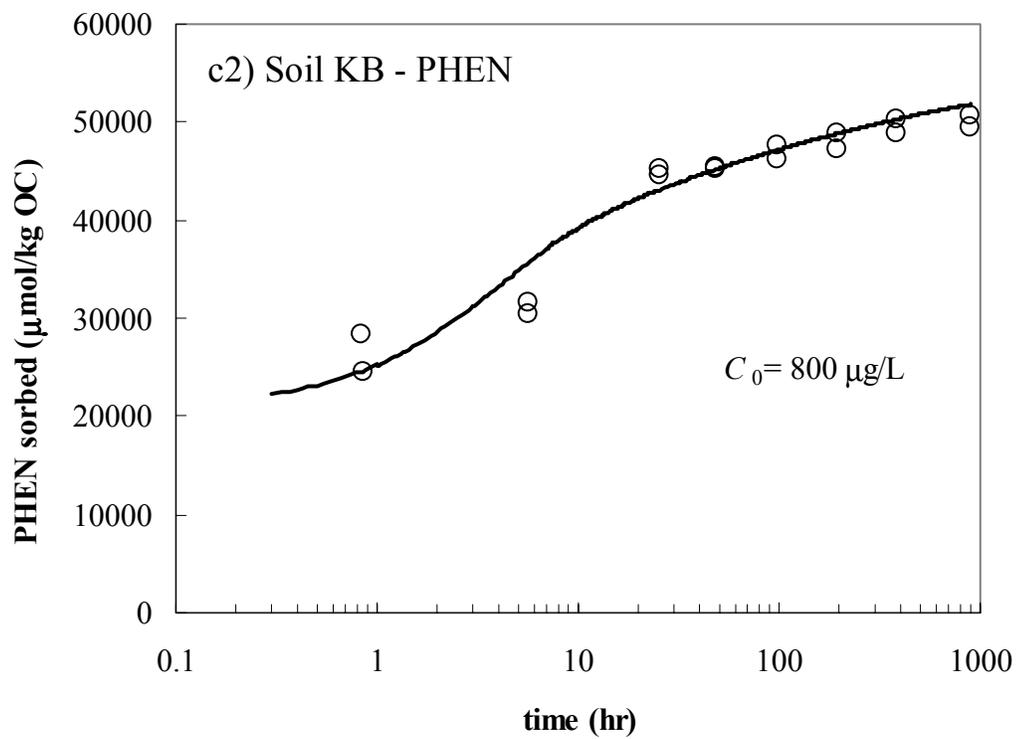
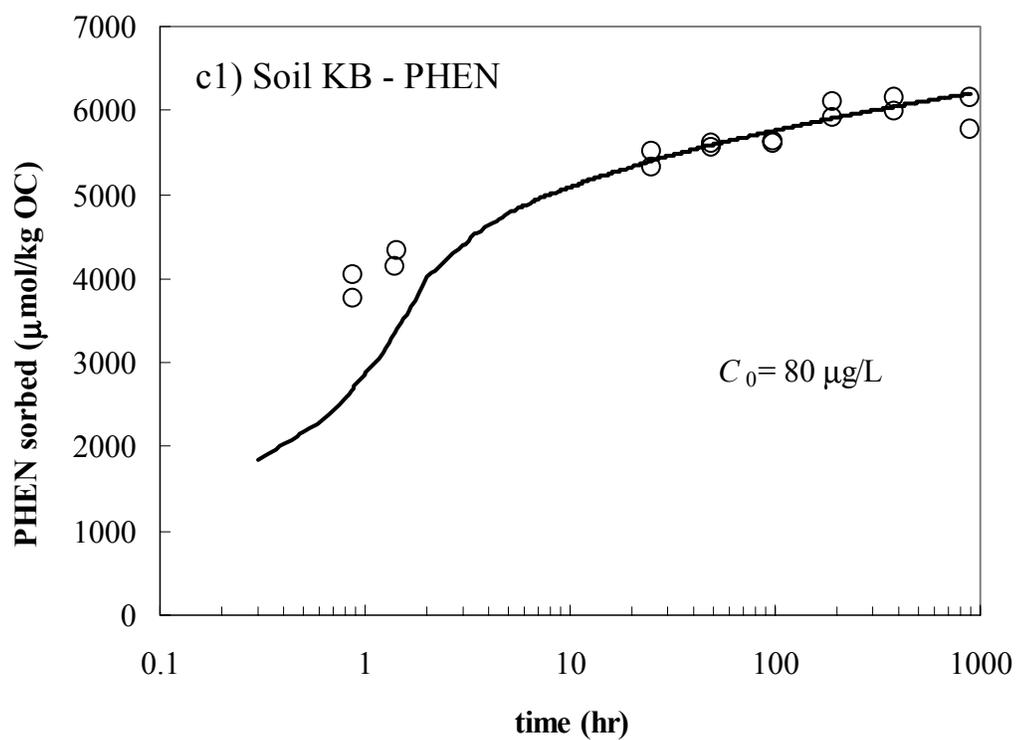


Figure 6.6 (contd) c1) Soil KB-PHEN, low  $C_0$ , c2) Soil KB-PHEN, high  $C_0$

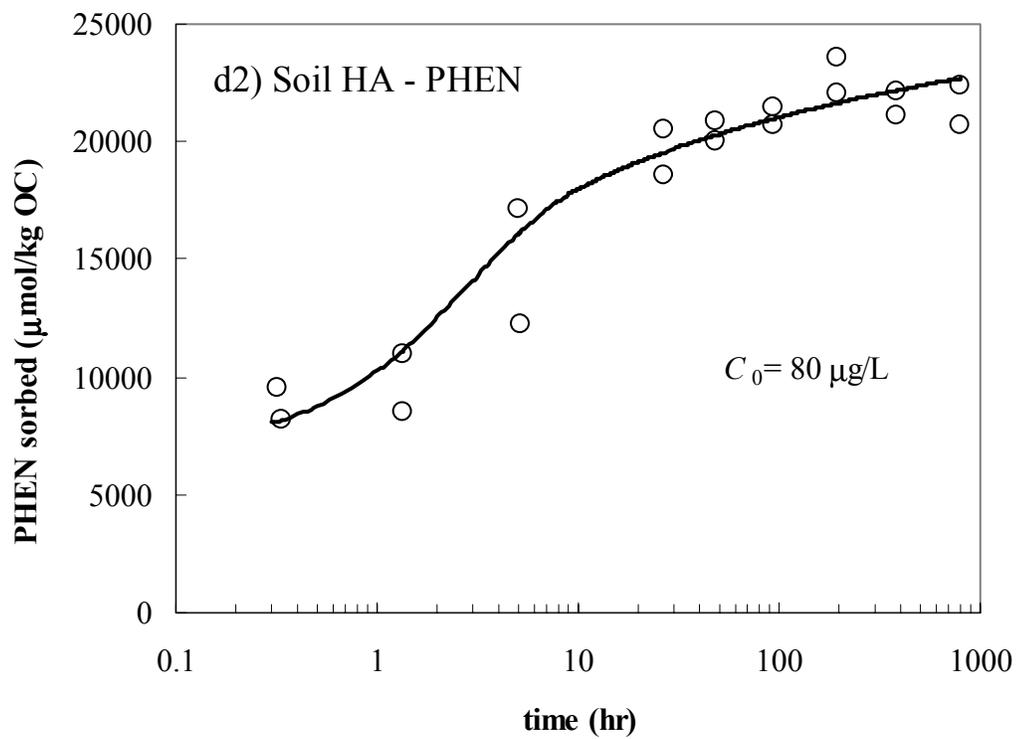
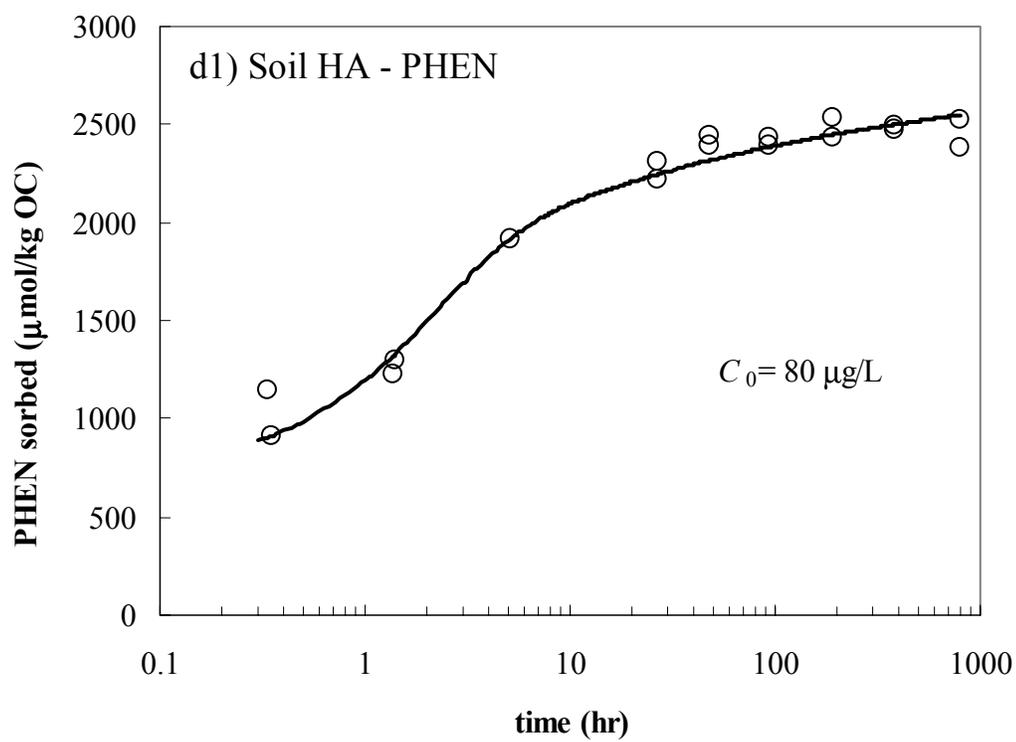


Figure 6.6 (contd) d1) Soil HA-PHEN, low  $C_0$ , d2) Soil HA-PHEN, high  $C_0$

## **CHAPTER 7: EFFECT OF INORGANIC COATINGS ON THE SORPTION OF PHENANTHRENE BY KB**

### **Overview**

This Chapter investigates the effects of calcite ( $\text{CaCO}_3$ ) and ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) coatings on the equilibrium sorption of Phenanthrene on Chelsea Soil KB and Illinois # 6 Coal. Two concentration levels of  $\text{CaCO}_3$  and three concentration level of  $\text{Fe}(\text{OH})_3$  were coated on the KB and one concentration level of  $\text{CaCO}_3$  and  $\text{Fe}(\text{OH})_3$  were coated on the Coal. The obtained isotherm data was fit to the Freundlich model; the Freundlich parameters are presented and discussed and the isotherms are presented in both nonlinear and linearized logarithmic form. A comparison of these parameters with those observed for PHEN for other condensed carbon sorbents is presented along with the results that indicate that both calcite and ferric hydroxide cause a decrease in sorption capacity of KB and Coal.

### **7.1 Rationale and Objectives**

In previous chapters isolated KB fraction from Chelsea Soil and Pahokee Peat were used for sorption equilibrium and/or rate studies. In Chapter 4, it was found that the sum of contribution of isolated Bulk Soil components exceeded the observed sorption to the Bulk Soil. The observed organic carbon normalized sorption capacity for isolates Soil KB was much higher than other soil components. Since hot acid treatment is use to dissolve the minerals in the isolation of KB, its sorption surfaces become cleaner and fully exposed to the incoming sorbents. In the dynamic structure of soil aggregates in the

environment, small inorganic and organic molecules are continuously associated with KB. Encapsulation and blocking of KB pores with such materials is likely to dramatically affect its sorption behavior and measured sorption coefficients. The major objective of this chapter was to demonstrate that inorganic coatings on KB might be one of the causes of its diminished sorption capacity when present in soil aggregates, as was hypothesized from sorption equilibrium experiments of Chapter 4. Although Chapter 4 discussed the equilibrium sorption of pesticides, our group found similar reduction in sorption capacity of KB and BC for Phenanthrene (PHEN). PHEN was used as a probe for experiments in this Chapter due to its purely hydrophobic interactions with KB, thus making it a molecule of choice for the conceptual demonstration attempted here. Also, PHEN was used due to the well-documented high sorption capacity of KB for PHEN, which would make any decrease in sorption capacity due to inorganic coatings more observable. Also previous studies exist that suggest a decrease in sorption capacity of the condensed carbon fractions for PHEN due to addition of small biopolymer and humic molecules (Cornelissen et al., 2006; Jonker et al., 2004), thus serving as a comparison for the effect of inorganic molecules on KB sorption. Illinois #6 Coal, a bituminous coal, was used as another high porosity condensed carbon fraction to validate the observed results.

## **7.2 Experiments and Data Analysis**

The detailed procedure used for preparing the coated samples was presented in Chapter 3. The treatment yielded 5 coated KB samples and 2 coated coal samples as shown in Table 7.1 below. Equilibrium sorption experiments were performed with PHEN for all the samples using the procedures described in Chapter 3, Section 3.3. The obtained

data were fit to the linearized Freundlich Model (equation 2.4) to obtain the  $\log K_F$  and  $n$  parameters.

### 7.3 Results and Discussion

*Reduction in  $\log K_F$ :* The sorption isotherms for the Original KB and the calcite and iron hydroxide coated KB are shown in Figures 7.1 and 7.2 and for the Original and coated Coal samples are shown in Figure 7.3. The obtained Freundlich isotherm parameters  $n$  and  $\log K_F$ , along with the standard errors of estimate and  $R^2$  of the fits are presented in Table 7.2. A general increase in values or decrease in isotherm nonlinearity is observed with increasing concentration level of Ca coatings in KB. The Ca and Fe coatings on Coal also seemed to increase the  $n$  values. This trend was however not observed for the Fe coating on KB. The isotherms in Figures 7.1, 7.2 and 7.3 and the  $\log K_F$  values in Table 7.2 indicate that isotherm sorption capacity (represented by  $\log K_F$ ) is significantly lower for the coated samples compared to the original samples. The values of  $\log K_F$  for the coated KB samples are 4 - 10% lower than uncoated KB, which translates to a 37 - 69% decrease in the  $K_F$  values of the sorbents. Similarly, a 3 and 9% decrease in  $\log K_F$  values or 30 and 68% decrease in sorption capacities of Coal is observed with the addition of Fe and Ca coatings respectively. The decrease in  $\log K_F$  values is dependent on the concentration level of coated Ca, with the sorption capacity decreasing 55% for level 1 of Ca coating and 69% for level 2 of Ca coating. The level 1 of Fe coating seemed to have no effect on the sorption capacity of KB, while the levels 2 and 3 decreased the sorption capacity to the same extent (37%).

The above results clearly indicate that inorganic coatings on KB can significantly reduce its sorption capacity. A previous study has indicated that small lipid-like organic molecules can cause a decrease in the total surface area of wood charcoal particles measured by N<sub>2</sub> BET (Kwon and Pignatello, 2005). Also, the native organic compounds in Black Carbon (BC) and molecules of the amorphous carbon itself (FAs and HAs) have been proposed to exhibit sorption competition with the incoming PHEN, thereby reducing the BC sorption capacity (Cornelissen et al., 2006; Jonker et al., 2004). Sorption capacity of activated carbon for trichloroethylene (TCE) has been found to be reduced due to blocking of its pores by humic substances, a phenomenon known as “fouling” (Kilduff and Wigton, 1999; Carter and Weber, 1994). Wang et al. (1998) also reported the reduced sorption capacity of activated carbon for atrazine due to background dissolved organic matter. However, as noted by Cornelissen et al. (2005) this reduction in sorption capacity has been observed only for BC and coal. They suggested that kerogen should show similar attenuation in sorption capacity due to its markedly similar properties with BC and coal. This study shows, apparently for the first time, that small inorganic molecules that are minor components of soils can attenuate the sorption capacity of KB and Coal.

Since the sorption of PHEN to mineral surfaces and amorphous organic carbon has been shown to be fast and linear, we suggest that it is unlikely that either of these soil components will reduce the sorption capacity of KB. The amorphous organic carbon and smaller biopolymer molecules present in the soil provide a solvent-like phase for the absorption and dissolution of HOCs such as PHEN and thus should not in theory cause any blockage of the KB pores. In fact, Cornelissen et al. (2006) reported that precipitated

HA on BC had no effect on its sorption capacity for dehydrated PHEN, while competition with added PAHs did reduce the sorption capacity of BC. The observed attenuation reported in Chapter 4 can thus be attributed to the presence of coating of small inorganic molecules on the KB in soil aggregates. This conclusion is supported by the fact that sorption capacity attenuation of KB increases with increased loadings of Ca. The lack of sorption capacity attenuation for the level 1 of Fe and the similar attenuation of sorption capacity of KB with level 2 and 3 of Fe indicates that probably minimum and maximum levels of loading exist below which the inorganic coating is not sufficient to cause pore blockage in KB or above which no further pore blockage is possible.

*Effect of Initial Aqueous Phase Concentration:* Table 7.2 also shows the calculated single point  $K_{OC}$  values for three different equilibrium aqueous phase concentrations, that translate into three levels of initial aqueous phase concentrations, are one order of magnitude different from each other. As pointed out in Chapter 4,  $K_{OC}$  values calculated at lower concentration are larger than  $K_{OC}$  values at higher concentration, as a result of isotherm nonlinearity. A comparison of the  $K_{OC}$  values for the coated samples and KB at the same  $C_e/C_s$  level indicate that reduction in sorption capacity is not significantly affected by initial aqueous phase concentration. For example, at a  $C_e/C_s = 0.5$ , level 1 of Ca coating causes a 48% decrease in the  $K_{OC}$  value of KB, while at  $C_e/C_s = 0.005$ , the same loading of Ca causes a similar reduction of 52%. This result is to be expected because of similar degree of isotherm nonlinearity, i.e., similar  $n$  values for KB and coated KB isotherms; thus  $K_{OC}$  values for KB and coated KB samples increase to a similar extent at lower concentrations. Similarly, the decrease in  $K_{OC}$  values for coated

coal samples is approximately the same across different  $C_e/C_s$ , although for a single sorbent, there is a larger difference in the  $K_{OC}$  values of uncoated coal across different  $C_e/C_s$  values owing to its extremely nonlinear isotherm ( $0.528 < n < 0.547$ ).

#### **7.4 Summary and Implications**

The results from experiments in this Chapter indicate that inorganic coatings might significantly attenuate the sorption capacity of KB and coal for HOCs such as PHEN. It is reasonable to assume that such coatings will also affect the sorption of pesticides. However, since the pesticides molecules are bigger and slightly more polar than PHEN, sorption capacity attenuation of the extent similar to PHEN might not be observable for pesticides, since the pesticide molecules are not able to access the smallest nanopores of the KB like PHEN. Nevertheless, even a smaller degree of attenuation in sorption capacity of KB (an attenuation of 30% on average was observed for the herbicides atrazine, metolachlor and napropamide in Chapter 4) will have an impact on the overall sorption capacity of the soil, given the dominance of KB in sorption of herbicides. The overall scenario for pesticide sorption suggested by this study is that while assuming that SOM consists entirely of amorphous organic matter will underestimate its sorption capacity, estimates of sorption capacities of soil based on their amorphous and condensed organic matter contents using their isolated sorption properties may overestimate their sorption capacities. This observation is also important for remediation strategies that use activated carbon and other forms of black carbon for sorption and sequestration of organic pollutants.

Table 7.1 Description of coating treatments used to achieve the coated samples

Sorbent	Coating	Treatment
KB	–	pH > 8.3
Ca1KB	CaCO <sub>3</sub> – level 1	0.1M CaCl <sub>2</sub> , 0.2 M NaHCO <sub>3</sub> , pH > 8.3
Ca2KB	CaCO <sub>3</sub> – level 2	0.2M CaCl <sub>2</sub> , 0.4 M NaHCO <sub>3</sub> , pH > 8.3
Fe1KB	Fe(OH) <sub>3</sub> – level 1	0.01M FeCl <sub>3</sub> , pH > 8.0
Fe2KB	Fe(OH) <sub>3</sub> – level 2	0.05M FeCl <sub>3</sub> , pH > 8.0
Fe3KB	Fe(OH) <sub>3</sub> – level 3	0.1M FeCl <sub>3</sub> , pH > 8.0
Illinois #6 Coal	–	–
Ca1Coal	CaCO <sub>3</sub> – level 1	0.1M CaCl <sub>2</sub> , 0.2 M NaHCO <sub>3</sub> , pH > 8.3
Fe2Coal	Fe(OH) <sub>3</sub> – level 2	0.05M FeCl <sub>3</sub> , pH > 8.0

Table 7.2 Freundlich sorption isotherm parameters and single point  $K_{OC}$  values at three different aqueous phase concentrations for sorption of phenanthrene on coated samples

Original Sorbent	Coated Sorbent	$n$	$\log K_F$ ( $\mu\text{g}/\text{kg}/(\mu\text{g}/\text{L})^n$ )	N	$R^2$	$C_d/C_s^a = 0.005$	$C_d/C_s = 0.05$	$C_d/C_s = 0.5$
KB	Ca1KB	0.762 (0.020) <sup>b</sup>	4.487 (0.043) <sup>b</sup>	14	0.991	64781	37450	21650
	Ca2KB	0.782 (0.023)	4.318 (0.050)	14	0.989	45564	27582	16696
	Fe1KB	0.731 (0.021)	4.839 (0.042)	14	0.989	137517	74021	39843
	Fe2KB	0.733 (0.025)	4.629 (0.053)	14	0.985	85109	46023	24887
	Fe3KB	0.685 (0.029)	4.630 (0.061)	14	0.978	78004	37767	18286
	KB	0.742 (0.017)	4.831 (0.033)	14	0.993	137803	76078	42001
Coal	Ca1Coal	0.547 (0.027)	5.070 (0.060)	12	0.974	64900	22901	8070
	Fe2Coal	0.532 (0.021)	5.412 (0.044)	6	0.992	138901	47283	16096
	Coal	0.528 (0.011)	5.567 (0.022)	12	0.995	197000	66446	22411

<sup>a</sup> $C_s$  (Phenanthrene) = 1.29 mg/L, <sup>b</sup>standard error of estimate

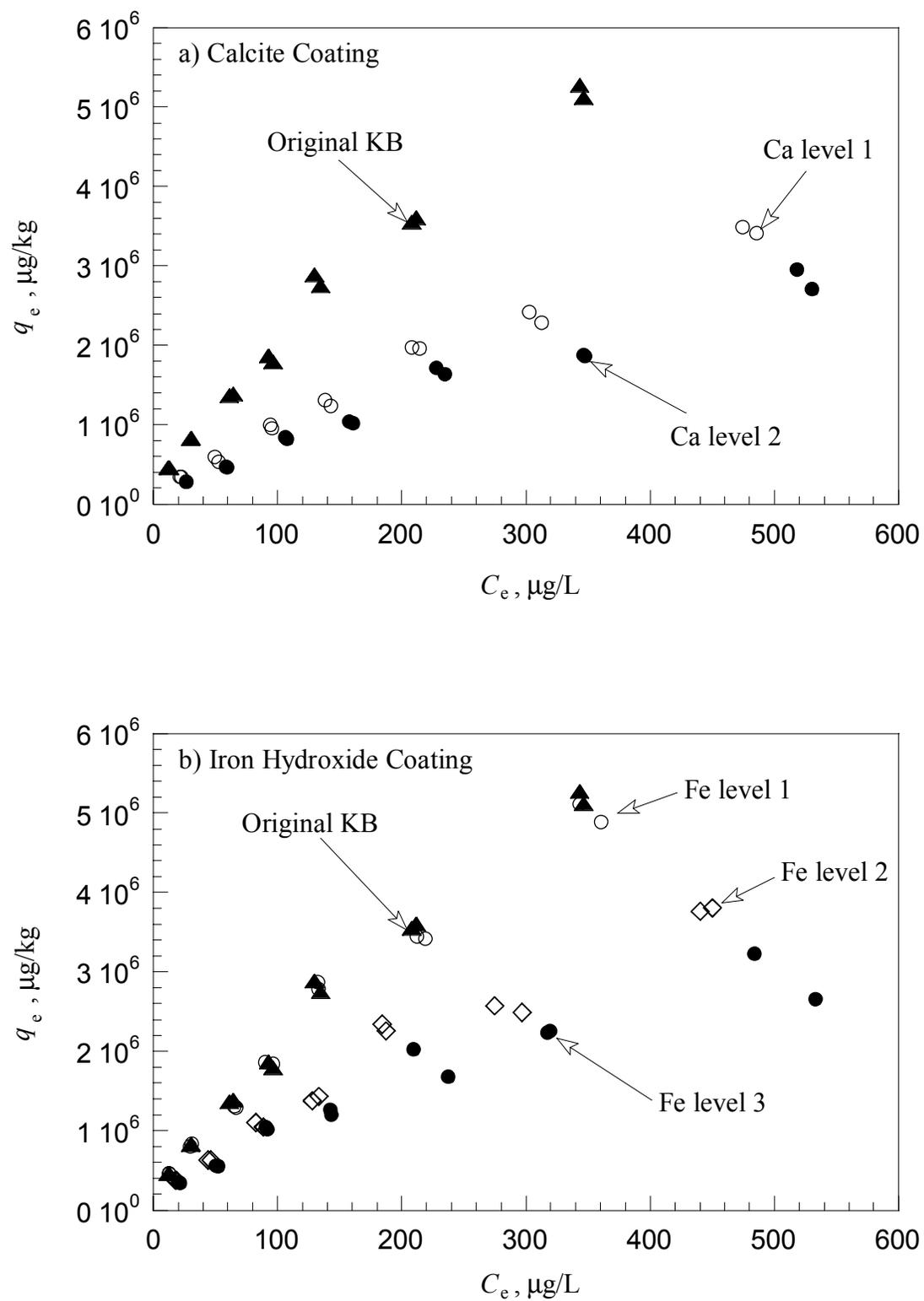


Figure 7.1 Sorption Isotherms for Original KB and a) two levels of calcite coating and b) three levels of iron hydroxide coating.

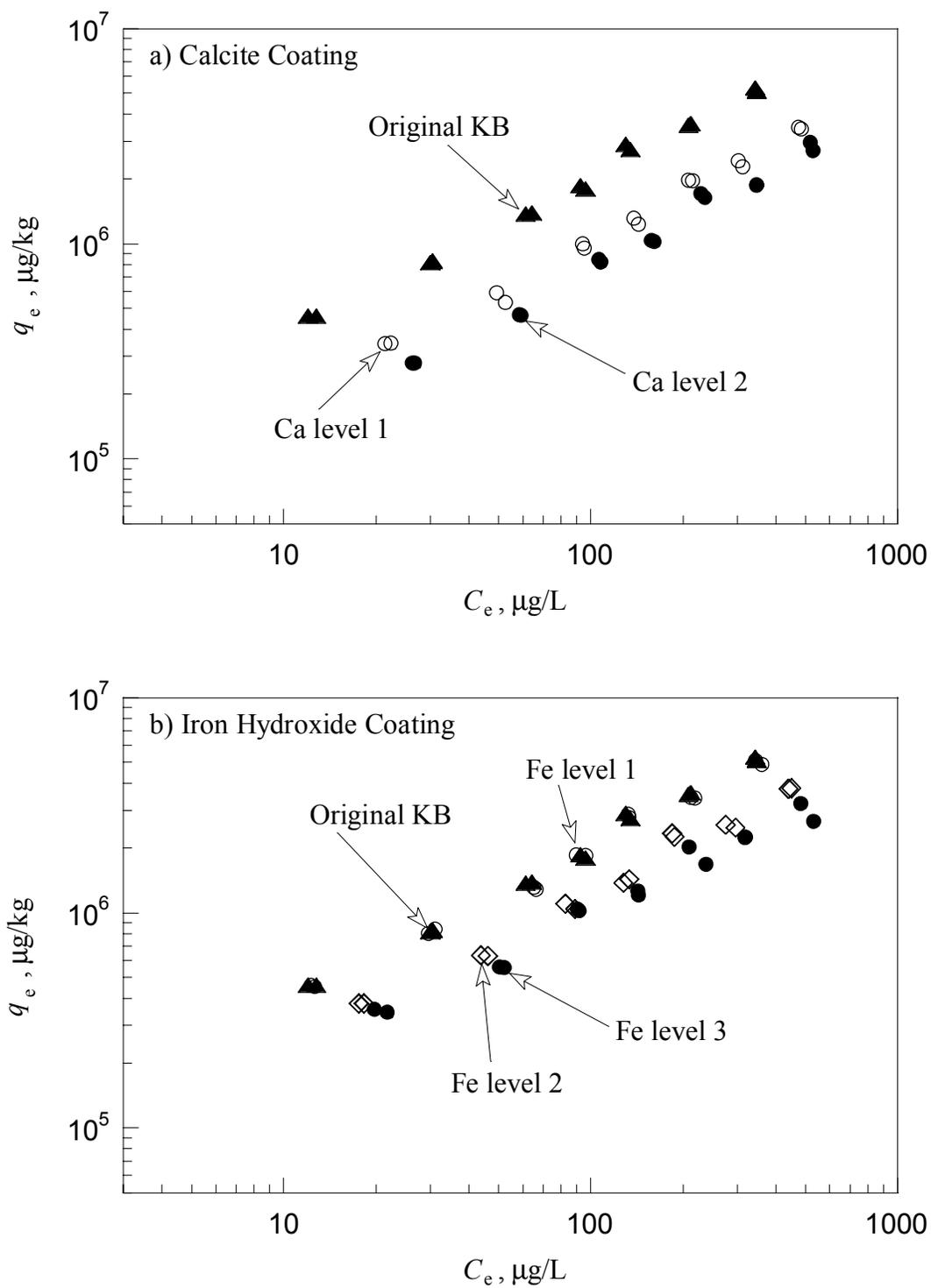


Figure 7.2 Linearized Sorption Isotherms for Original KB and a) two levels of  $\text{CaCO}_3$  calcite coating and b) three levels of iron hydroxide coating.

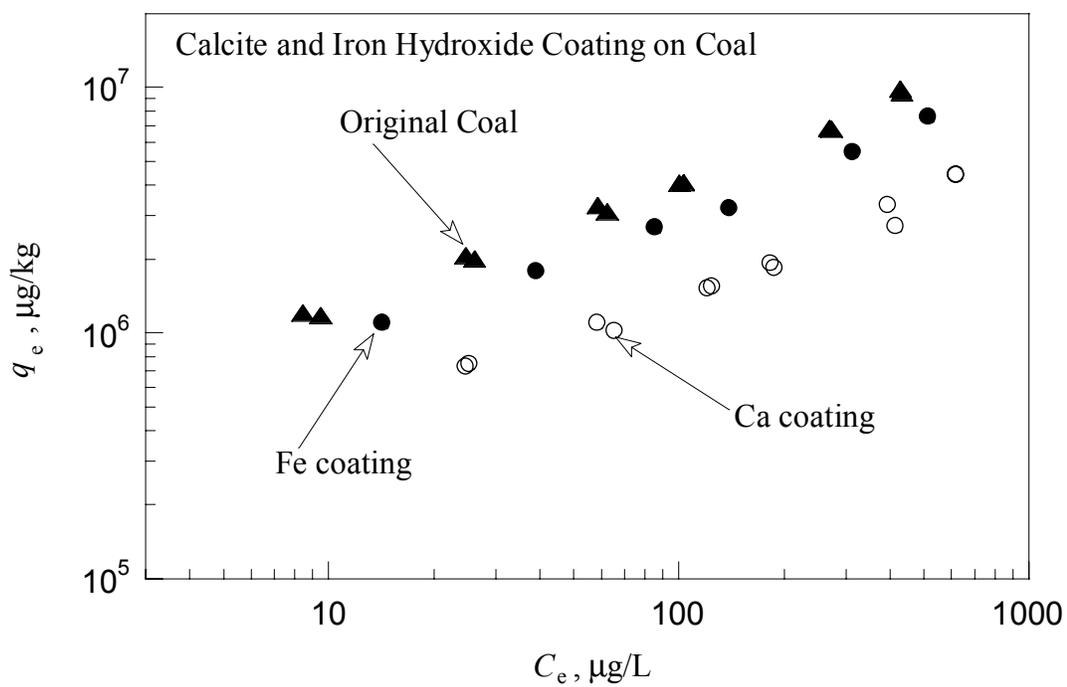
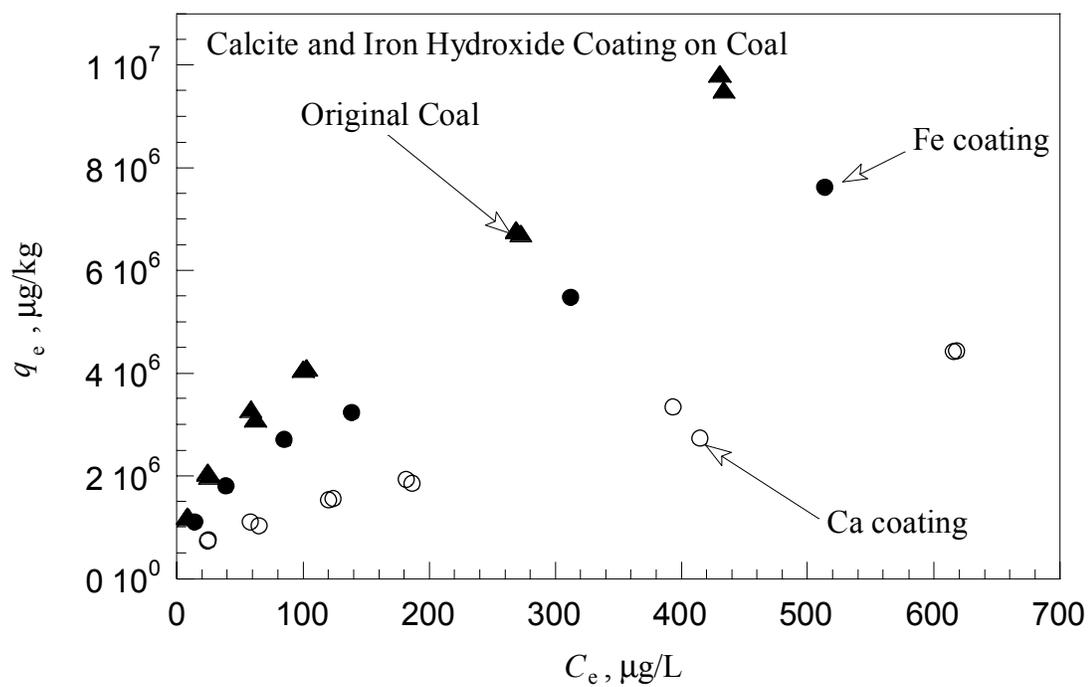


Figure 7.1 Sorption Isotherms for Original Coal, Calcite coated Coal and Iron Hydroxide coated Coal (above), linearized isotherms (below)

## CHAPTER 8: CONCLUSIONS, IMPLICATIONS AND RECOMMENDATIONS

### 8.1 Conclusions

The experiments in this dissertation provide evidence of herbicide sorption behavior in soils that are either similar to HOCs such as PAHs or different from them.

These are summarized below:

- 1) It was found that similar to PAHs, herbicides exhibited nonlinear isotherms, with the nonlinearity index being close to unity for HA fractions.
- 2) Organic carbon normalized uptake ratios ( $K_{OC}$ ) for the herbicides were found to be dependent on the initial aqueous concentration of the herbicides, which is essentially a consequence of isotherm non linearity.
- 3) Similar to PAHs, hydrophobic interactions seemed to dominate the sorption of herbicides to the Bulk Soil and its fractions, as evident from the highest sorption capacity of all sorbents for NAP, the herbicide with highest octanol water partition coefficient.
- 4) The isolated KB fraction was found to have a strong sorption affinity for the herbicides, compared to other sorbents as observed for PAHs.
- 5) The super-sorbent property of Soil KB was diminished when it existed as an aggregate in Bulk Soil suggesting reduced access of solute molecules to KB aggregated within soil matrices. This phenomenon was also observed by our group for the PAH PHEN and estrogen compounds.
- 6) No significant hysteresis was observed for the KB fraction for the herbicides, in contrast to strong sorption desorption hysteresis shown for the sorption of PHEN

to condensed organic matter rich soils.

- 7) any of the sorbents for MET and NAP. For ATZ, hysteresis was statistically significant only for the Bulk Peat, Bulk Soil and their BE fractions.
- 8) Specific binding or chemisorption was observed for sorption of ATZ on the Bulk Soil and its BE fraction in contrast to PHEN for which no hysteresis for the Bulk Chelsea Soil or its BE fraction was observed.
- 9) Sorption rate of the herbicide MET and PHEN were found to be dependent on initial aqueous solute concentration, with the higher initial concentration exhibiting higher rate of sorption.
- 10) Sorption rate for MET and PHEN was found to be fastest for the HA fraction; sorption rate of MET n HA was faster than PHEN.
- 11) Sorption rate of MET and PHEN on KB fraction was found to be slow; apparent equilibrium was not achieved within the 30 d reaction time.

## **8.2 Implications**

ATZ, MET and NAP are herbicides belonging to three different chemical classes and are among the most frequently detected pesticides in the U.S. surface and ground waters (Barbash et al., 2001; Larson et al., 1999). All are used pre or post-emergence for broad leaf and grass weed control. ATZ is a known endocrine disruptor and its use has been banned in many European countries (Kettles et al., 1997; Hayes et al., 2006). The potential carcinogen label given to MET in 1991 was removed by the EPA following lack of evidence regarding it. MET (with ATZ) and napropamide are widely used in pesticide formulations (Hayes et al., 2006; Rim et al., 2005) and mixtures such as these have been

shown to cause increased endocrine disruption in amphibians than the individual herbicides (Hayes et al., 2006). Notwithstanding the 2006 USEPA decision for continued usage of ATZ (Sherman, 2006), the usage of other herbicides such as MET and NAP may become more important if atrazine is phased out in the U.S. in near future.

The non linear isotherms and high sorption capacity of the isolated KB fraction observed for these herbicides in sorption equilibrium experiments points out the inaccuracies of employing simplistic linear partitioning models for predicting existing herbicide concentrations in the environment. Use of empirical data from non linear models such as the Freundlich model can help in obtaining more realistic environmental concentrations of herbicides. This study cautions that while soils cannot be considered to be consisting of amorphous humic matter alone and the presence of KB greatly enhances sorption capacities of soils, the determination of HA and KB content of a soil cannot be solely utilized to predict soil sorption capacities. The complex aggregation structure of soils and the attenuation of KB sorption capacity in soils need to be assessed and incorporated into fate and transport models.

This study indicates that in general, herbicides do not exhibit hysteresis linked to entrapment, condensation and constriction of molecules inside the KB matrix since the molecules are much larger than the observed interlayer distances of KB. Herbicides may however show specific binding such as chemisorption that could cause the desorption step to appear hysteretic. In general, the low or insignificant hysteresis observed for the herbicides indicates that a larger fraction of an herbicide would be present in the aqueous phase rather than bound to soils in comparison to PAHs, as evidenced by the herbicides'

detection frequency in ground and surface waters (Barbash et al., 2001; Larson et al., 1999).

Given that apparent sorption equilibrium is not reached within the 30 d time period of this experiment, the runoff and leachate concentrations of pesticides could be several times higher than equilibrium predicted values in case of flash storm events that happen right after pesticide application. This non attainment of equilibrium is caused by slow sorption of the herbicides to KB, as the sorption rates of herbicides on HA fraction were observed to be fast. In most environmental scenarios, therefore, a fate and transport modeler is looking at non-equilibrium conditions with respect to sorption of herbicides to soils and actual concentrations in ground water could be higher than those predicted by equilibrium sorption constants.

### **8.3 Recommendations for Future Work**

Future directions of research to be points out from include the evaluation of desorption rate phenomena with pesticides which can give further evidence of mass transfer limitations and specific interactions during the sorption desorption process. For a further understanding of mechanisms of pesticide interactions with various soils components, microscopic and spectrometric study of sorption phenomena of herbicides that can reveal the exact binding sites would be the direction to follow in future. For example, spectroscopic studies can help identify specific molecules bound to mineral, amorphous or condensed carbon sites. The investigation of sorption equilibrium and rate for a wide variety of pesticides can help generalize observations made in this study and possibly help in the development of simultaneous multi-parameter LFERs be developed

that account for all the domains and interactions in soils. Another interesting dimension would be to explore the possibility of developing three dimensional aggregation models for soils, that can help pin point the exact pathways and resistances in the way of pesticide sorption into and desorption out of soils.

### Appendix A: Sample spreadsheet for Rate Data Modeling

Table A1. Initial conditions and model parameters for modeling metolachlor sorption on Bulk Soil

System Properties		Model Parameters
TOC (%) =	5.29%	fraction ( $f$ ) = 0.281
$S_0$ (Initial solid phase concentration) =	0	$\alpha$ = 0.736
$K_{oc}$ =	295 $\mu\text{M}/\text{kg-OC}$	$\beta$ = 86.000
$n$ (number of compartments) =	100	min $k$ 1.00E-08 $\log(k)$ -8
mass of sorbent	1.000 g	max $k$ 1 $\log(k)$ 0
volume of aqueous solution =	13.00 mL	mean $k$ 8.6E-03
$C_0$ (Initial aqueous phase concentration) =	1.842 $\mu\text{M}$	Gamma (alpha) 1.2440
		error (%) 2.94

Table A2. Generating the probability distribution for mass transfer rate coefficients

Gamma function						
$\log(k)$	k	P(k)		n	$k \cdot p(k)$	P(k), cumulative
-8	1.00E-08	2.75E+03	2.75E-05			0.000
-7.92	1.20E-08	2.62E+03	5.292E-06	1	0.000	0.000
-7.84	1.45E-08	2.49E+03	6.061E-06	2	0.000	0.000
-7.76	1.74E-08	2.37E+03	6.942E-06	3	0.000	0.000
-7.68	2.09E-08	2.26E+03	7.95E-06	4	0.000	0.000
-7.6	2.51E-08	2.15E+03	9.105E-06	5	0.000	0.000
-7.52	3.02E-08	2.05E+03	1.043E-05	6	0.000	0.000
-7.44	3.63E-08	1.96E+03	1.194E-05	7	0.000	0.000
-7.36	4.37E-08	1.86E+03	1.368E-05	8	0.000	0.000
-7.28	5.25E-08	1.77E+03	1.566E-05	9	0.000	0.000
-7.2	6.31E-08	1.69E+03	1.794E-05	10	0.000	0.000
-7.12	7.59E-08	1.61E+03	2.055E-05	11	0.000	0.000
-7.04	9.12E-08	1.53E+03	2.353E-05	12	0.000	0.000
-6.96	1.10E-07	1.46E+03	2.695E-05	13	0.000	0.000
-6.88	1.32E-07	1.39E+03	3.086E-05	14	0.000	0.000
-6.8	1.58E-07	1.33E+03	3.535E-05	15	0.000	0.000
-6.72	1.91E-07	1.26E+03	4.048E-05	16	0.000	0.000
-6.64	2.29E-07	1.20E+03	4.636E-05	17	0.000	0.000
-6.56	2.75E-07	1.15E+03	5.31E-05	18	0.000	0.000
-6.48	3.31E-07	1.09E+03	6.081E-05	19	0.000	0.000
-6.4	3.98E-07	1.04E+03	6.965E-05	20	0.000	0.001
-6.32	4.79E-07	9.91E+02	7.976E-05	21	0.000	0.001
-6.24	5.75E-07	9.44E+02	9.135E-05	22	0.001	0.001
-6.16	6.92E-07	8.99E+02	0.0001046	23	0.001	0.001
-6.08	8.32E-07	8.56E+02	0.0001198	24	0.001	0.001
-6	1.00E-06	8.16E+02	0.0001372	25	0.001	0.001
-5.92	1.20E-06	7.77E+02	0.0001571	26	0.001	0.001
-5.84	1.45E-06	7.40E+02	0.00018	27	0.001	0.001
-5.76	1.74E-06	7.05E+02	0.0002061	28	0.001	0.002
-5.68	2.09E-06	6.72E+02	0.000236	29	0.001	0.002
-5.6	2.51E-06	6.40E+02	0.0002703	30	0.002	0.002
-5.52	3.02E-06	6.09E+02	0.0003096	31	0.002	0.002
-5.44	3.63E-06	5.80E+02	0.0003545	32	0.002	0.003
-5.36	4.37E-06	5.53E+02	0.000406	33	0.002	0.003
-5.28	5.25E-06	5.27E+02	0.000465	34	0.003	0.004
-5.2	6.31E-06	5.02E+02	0.0005325	35	0.003	0.004
-5.12	7.59E-06	4.78E+02	0.0006098	36	0.003	0.005
-5.04	9.12E-06	4.55E+02	0.0006982	37	0.004	0.005
-4.96	1.10E-05	4.33E+02	0.0007996	38	0.004	0.006

-4.88	1.32E-05	4.13E+02	0.0009155	39	0.005	0.007
-4.8	1.58E-05	3.93E+02	0.0010483	40	0.006	0.008
-4.72	1.91E-05	3.74E+02	0.0012002	41	0.007	0.009
-4.64	2.29E-05	3.57E+02	0.0013741	42	0.008	0.011
-4.56	2.75E-05	3.40E+02	0.0015731	43	0.009	0.012
-4.48	3.31E-05	3.23E+02	0.0018008	44	0.010	0.014
-4.4	3.98E-05	3.08E+02	0.0020612	45	0.012	0.016
-4.32	4.79E-05	2.93E+02	0.002359	46	0.013	0.019
-4.24	5.75E-05	2.79E+02	0.0026995	47	0.015	0.021
-4.16	6.92E-05	2.65E+02	0.0030886	48	0.017	0.024
-4.08	8.32E-05	2.52E+02	0.003533	49	0.020	0.028
-4	1.00E-04	2.40E+02	0.0040404	50	0.023	0.032
-3.92	1.20E-04	2.28E+02	0.0046193	51	0.026	0.037
-3.84	1.45E-04	2.17E+02	0.0052793	52	0.029	0.042
-3.76	1.74E-04	2.06E+02	0.006031	53	0.034	0.048
-3.68	2.09E-04	1.96E+02	0.0068863	54	0.038	0.055
-3.6	2.51E-04	1.86E+02	0.0078581	55	0.044	0.063
-3.52	3.02E-04	1.76E+02	0.0089604	56	0.050	0.072
-3.44	3.63E-04	1.67E+02	0.0102083	57	0.057	0.082
-3.36	4.37E-04	1.58E+02	0.0116177	58	0.065	0.093
-3.28	5.25E-04	1.50E+02	0.0132047	59	0.074	0.107
-3.2	6.31E-04	1.41E+02	0.0149856	60	0.084	0.122
-3.12	7.59E-04	1.33E+02	0.0169752	61	0.095	0.139
-3.04	9.12E-04	1.25E+02	0.0191864	62	0.108	0.158
-2.96	1.10E-03	1.17E+02	0.0216277	63	0.122	0.179
-2.88	1.32E-03	1.10E+02	0.0243017	64	0.137	0.204
-2.8	1.58E-03	1.02E+02	0.0272011	65	0.154	0.231
-2.72	1.91E-03	9.45E+01	0.0303055	66	0.172	0.261
-2.64	2.29E-03	8.71E+01	0.0335765	67	0.191	0.295
-2.56	2.75E-03	7.97E+01	0.0369519	68	0.210	0.332
-2.48	3.31E-03	7.24E+01	0.0403403	69	0.231	0.372
-2.4	3.98E-03	6.51E+01	0.0436146	70	0.251	0.416
-2.32	4.79E-03	5.79E+01	0.0466086	71	0.270	0.462
-2.24	5.75E-03	5.07E+01	0.0491152	72	0.286	0.511
-2.16	6.92E-03	4.37E+01	0.0508924	73	0.299	0.562
-2.08	8.32E-03	3.69E+01	0.0516771	74	0.307	0.614
-2	1.00E-02	3.04E+01	0.0512119	75	0.309	0.665
-1.92	1.20E-02	2.44E+01	0.0492873	76	0.302	0.715
-1.84	1.45E-02	1.88E+01	0.0457951	77	0.286	0.760
-1.76	1.74E-02	1.40E+01	0.0407881	78	0.261	0.801
-1.68	2.09E-02	9.82E+00	0.0345271	79	0.227	0.836
-1.6	2.51E-02	6.51E+00	0.0274938	80	0.188	0.863
-1.52	3.02E-02	4.00E+00	0.0203416	81	0.145	0.883

-1.44	3.63E-02	2.26E+00	0.013777	82	0.104	0.897
-1.36	4.37E-02	1.14E+00	0.0083903	83	0.068	0.906
-1.28	5.25E-02	5.09E-01	0.004497	84	0.040	0.910
-1.2	6.31E-02	1.95E-01	0.0020671	85	0.020	0.912
-1.12	7.59E-02	6.19E-02	0.00079	86	0.009	0.913
-1.04	9.12E-02	1.58E-02	0.0002418	87	0.003	0.913
-0.96	1.10E-01	3.07E-03	5.668E-05	88	0.001	0.913
-0.88	1.32E-01	4.35E-04	9.638E-06	89	0.000	0.913
-0.8	1.58E-01	4.18E-05	1.114E-06	90	0.000	0.913
-0.72	1.91E-01	2.53E-06	8.103E-08	91	0.000	0.913
-0.64	2.29E-01	8.75E-08	3.374E-09	92	0.000	0.913
-0.56	2.75E-01	1.55E-09	7.184E-11	93	0.000	0.913
-0.48	3.31E-01	1.23E-11	6.833E-13	94	0.000	0.913
-0.4	3.98E-01	3.68E-14	2.466E-15	95	0.000	0.913
-0.32	4.79E-01	3.45E-17	2.776E-18	96	0.000	0.913
-0.24	5.75E-01	7.96E-21	7.702E-22	97	0.000	0.913
-0.16	6.92E-01	3.41E-25	3.966E-26	98	0.000	0.913
-0.08	8.32E-01	1.93E-30	2.697E-31	99	0.000	0.913
0	1.00E+00	9.56E-37	1.608E-37	100	0.000	0.913

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Table A4. Raw data used for modeling – solid phase concentration  $q(t)$  vs. time ( $t$ )

Conc. Level	Time min	Bulk Soil with initial aqueous phase concentration = 500 $\mu\text{g/L}$									
		$C(t)$ $\mu\text{g/L}$	$\mu\text{M}$	$q(t)$ $\mu\text{g/g}$	$q(t)$ $\mu\text{g/kg}$	$q(t)$ $\mu\text{mol/kg}$	$q(t)$ $\mu\text{mol/kgOC}$	$K_D$	$K_{oc}(t)$ L/g	$K_{oc}(t)$ L/kg	
1.000	20.000	343.676	1.210	1.908	1907.516	6.717	126.968	0.006	0.105	104.921	
1.000	80.000	339.943	1.197	1.924	1923.644	6.773	128.041	0.006	0.107	106.970	
1.000	81.000	348.119	1.226	1.890	1889.894	6.655	125.795	0.005	0.103	102.625	
1.000	360.000	324.617	1.143	2.059	2058.543	7.248	137.021	0.006	0.120	119.876	
1.000	361.000	325.309	1.145	2.160	2159.602	7.604	143.747	0.007	0.125	125.494	
1.000	1440.000	267.968	0.944	2.687	2687.293	9.462	178.871	0.010	0.190	189.573	
1.000	1441.000	271.722	0.957	2.701	2700.795	9.510	179.770	0.010	0.188	187.893	
1.000	2880.000	282.202	0.994	2.630	2630.320	9.262	175.079	0.009	0.176	176.195	
1.000	2881.000	267.330	0.941	2.778	2778.303	9.783	184.929	0.010	0.196	196.461	
1.000	5760.000	245.709	0.865	2.847	2847.186	10.025	189.514	0.012	0.219	219.048	
1.000	5761.000	248.013	0.873	2.927	2927.064	10.307	194.831	0.012	0.223	223.102	
1.000	11520.000	224.285	0.790	3.255	3254.981	11.461	216.658	0.015	0.274	274.342	
1.000	11521.000	230.794	0.813	3.114	3114.401	10.966	207.301	0.013	0.255	255.091	
1.000	20160.000	213.378	0.751	3.357	3356.667	11.819	223.426	0.016	0.297	297.374	
1.000	20161.000	222.792	0.784	3.370	3369.845	11.866	224.303	0.015	0.286	285.926	
1.000	31680.000	243.033	0.856	3.036	3036.019	10.690	202.083	0.012	0.236	236.147	
1.000	31681.000	230.226	0.811	3.298	3297.711	11.612	219.502	0.014	0.271	270.772	
1.000	43200.000	206.014	0.725	3.226	3225.880	11.359	214.721	0.016	0.296	296.003	
1.000	43201.000	211.408	0.744	3.283	3283.350	11.561	218.546	0.016	0.294	293.589	

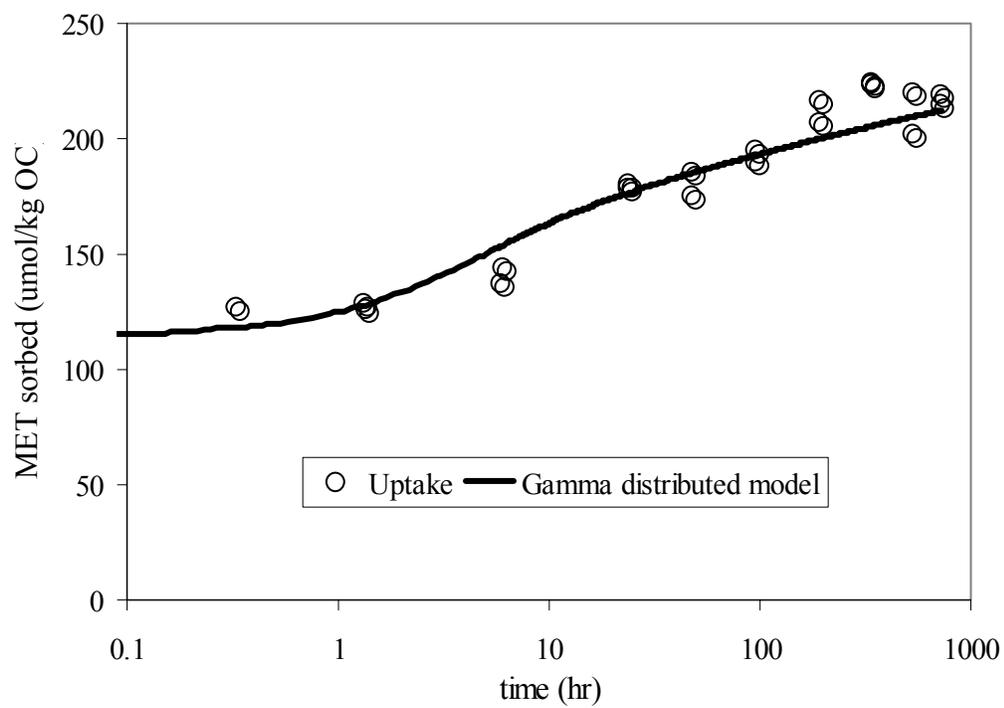
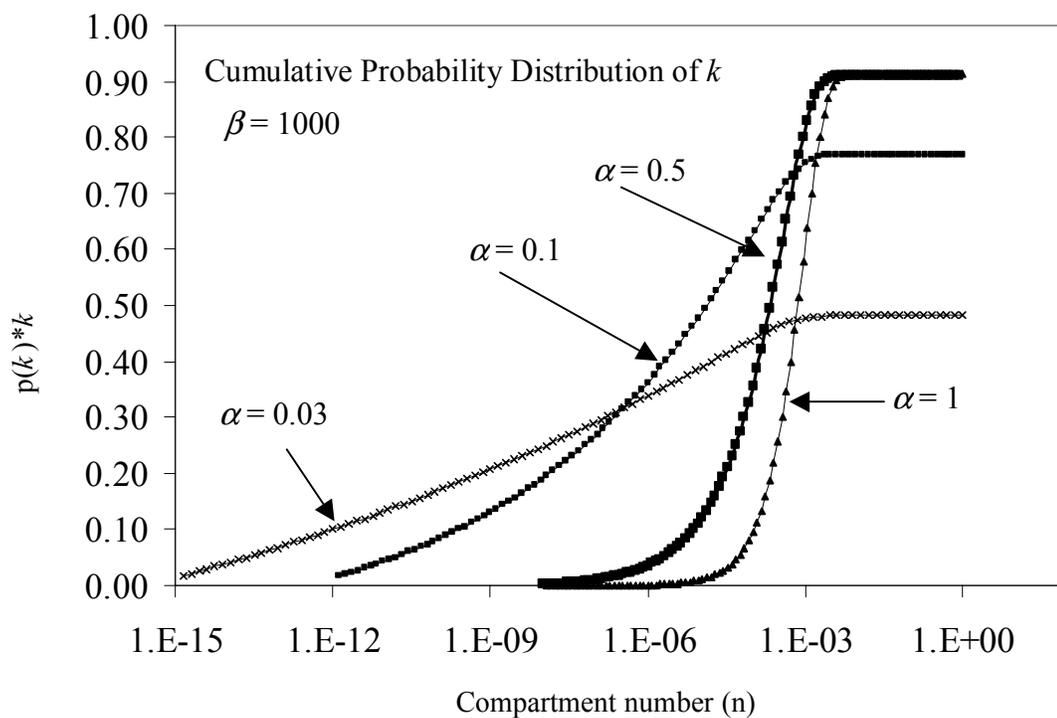
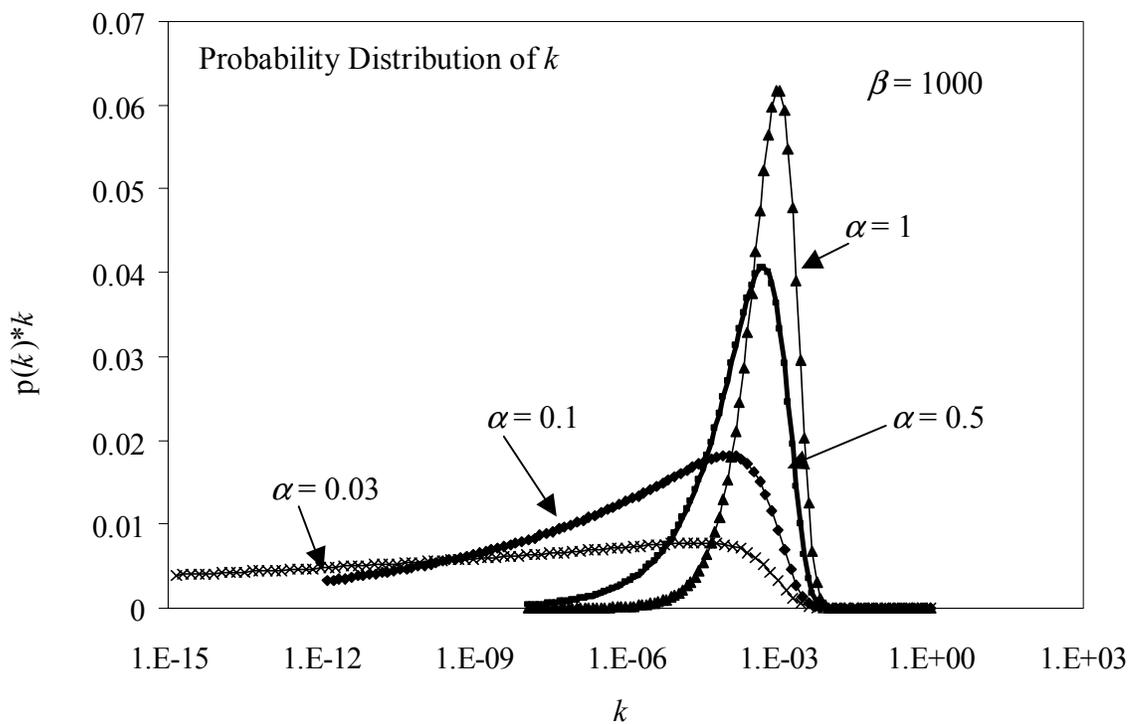
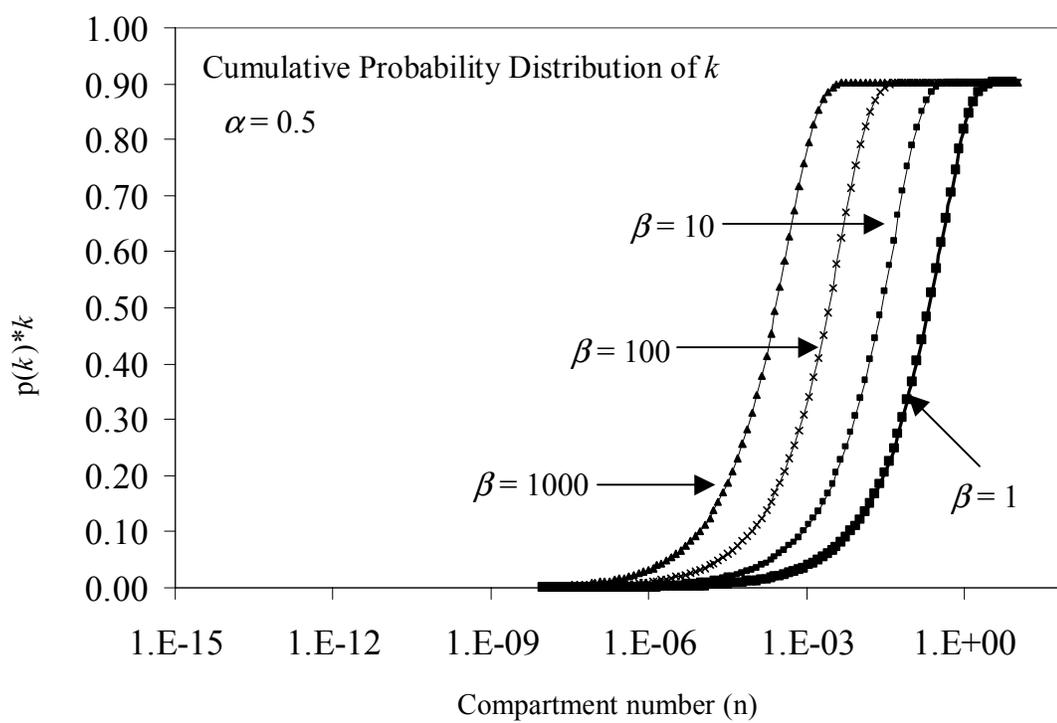
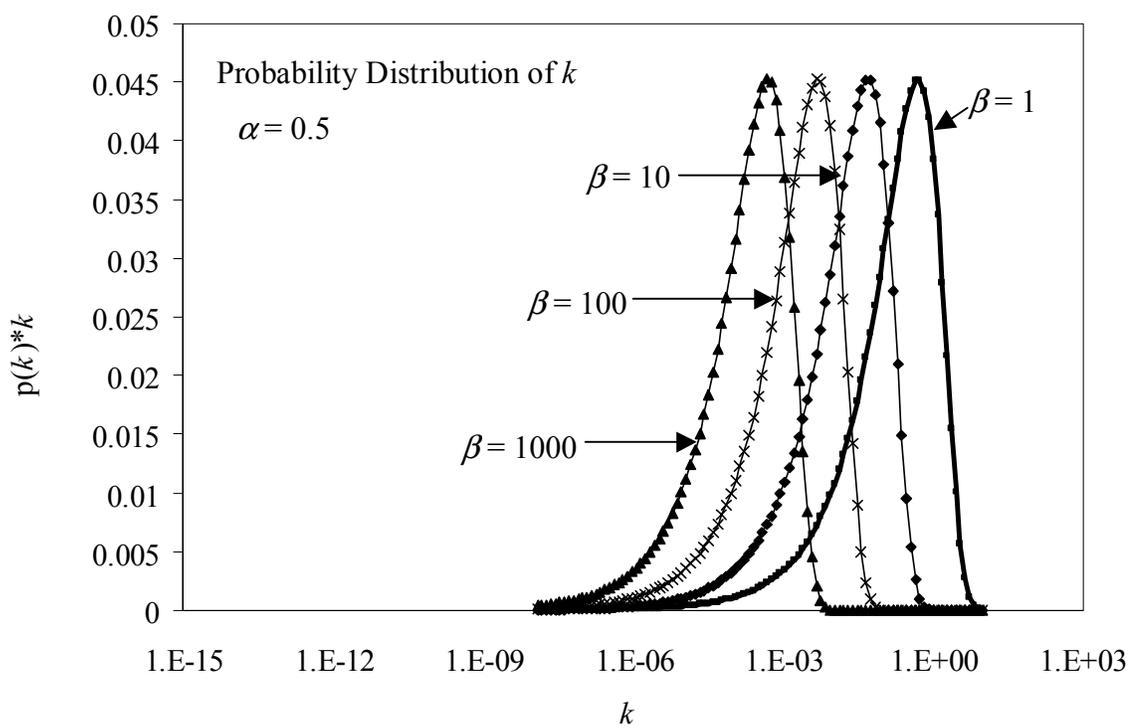


Figure A1. Obtained model fit to the rate data.

**Appendix B: Effect of changes in parameters  $\alpha$  and  $\beta$  on probability density function used in rate data modeling**





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