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JOHN H. BETHEA. An Investigation of Long-term Sorption Phenomena.  
(under the direction of DR. CASS T. MILLER)

### Abstract

Many of the current attempts at predicting the fate and transport of chemicals in the subsurface rely on several questionable assumptions involving the effects of sorption on solute transport: (1) linear isotherms; (2) instantaneous equilibrium; (3) no competitive effects between cosolutes. For accurate predictions to be made, the impact of these phenomena must be understood.

Sorption rate and equilibrium experiments were conducted in completely mixed batch reactors for single and bisolute systems of naphthalene and phenanthrene on a native and pulverized version of a subsurface material. In the bisolute system, the concentration of naphthalene was varied while the concentration of phenanthrene was kept constant. Isotherms were best fit with a nonlinear Freundlich model. A suppression of the sorption of naphthalene was observed in the presence of phenanthrene in isotherm data. However, these effects were not evident in rate data. A significant amount of sorption continued over the duration of the 3 month study. Pulverizing the subsurface material resulted in an increased rate of sorption followed by a gradual approach to convergence of the sorption on the pulverized and native material.

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## List of Symbols

$A, B, C, D$  = empirical regression coefficients  
 $b$  = Langmuir isotherm enthalpy constant ( $L^3/M$ )  
 $C$  = solute concentration in solution ( $M/L^3$ )  
 $C_{di}$  = aqueous phase solute concentration (data) ( $M/L^3$ )  
 $C_e$  = solute concentration in solution ( $M/L^3$ )  
 $C_{m,i}$  = aqueous phase solute concentration (model) ( $M/L^3$ )  
 $C_m$  = aqueous phase solute concentration (model) ( $M/L^3$ )  
 $C_0$  = initial aqueous phase solute concentration ( $M/L^3$ )  
 $CI$  = constant of integration determined from initial conditions ( $M$ )  
 $f_{io}$  = mass fraction of inorganic sorbing phase (-)  
 $f_{oc}$  = fraction of organic carbon in the sorbent (-)  
 $k$  = first order rate constant ( $1/T$ )  
 $K_f$  = Freundlich capacity coefficient ( $(L^3/M)^n$ )  
 $K_p$  = sorption partition coefficient ( $L^3/M$ )  
 $K_{oc}$  = organic carbon partition coefficient ( $L^3/M$ )  
 $K_{ow}$  = octanol - water partition coefficient (-)  
 $K_r$  = reactor partition coefficient ( $L^3/reactor$ )  
 $K_s$  = specific surface adsorption coefficient ( $L$ )  
 $M$  = mass of sorbent ( $M$ )  
 $M_s$  = mass of solids in system ( $M$ )  
 $Mq$  = mass in solid phase ( $M/M$ )  
 $n$  = Freundlich exponent (-)  
 $n_p$  = number of data points  
 $q$  = solute concentration on solid phase ( $M/M$ )  
 $q_e$  = solute concentration on solid phase ( $M/M$ )  
 $q_i$  = solid concentration (data) ( $M/M$ )  
 $q_i'$  = solid concentration phase (model) ( $M/M$ )  
 $Q^0$  = Langmuir isotherm capacity constant ( $M/M$ )  
 $S$  = aqueous solubility ( $M/L^3$ )  
 $S_s$  = specific surface area of inorganic sorbing phase ( $L^2/M$ )  
 $t$  = time ( $T$ )  
 $V$  = volume of solution ( $L^3$ )  
 $w_i$  = weighting function = average of replicates / variance of replicates

### GREEK

$\alpha_0, \alpha_1, \alpha_2, \beta_1, \beta_2$  = fitting parameters  
 $\nu$  = degrees of freedom ( $n_p - 2$ )  
 $\Gamma(C)$  = source / sink term



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## **1 Introduction**

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### **1.1 Background**

Twenty-five years ago, intensive groundwater monitoring efforts were rare. Increasing public awareness and the formation of environmental government organizations and environmental legislation have forced many environmental issues to be addressed. The current focus on environmental problems has illuminated our lack of understanding of many of the processes that govern a contaminant once released, as well as our need for better tools for predicting the fate, and planning the mitigation of environmental pollutants.

Groundwater is the drinking water source for more than 40% of the people in the United States (McCarty et al., 1981). Any threat to the purity of groundwater is a legitimate threat to the public safety of a large portion of the population. Due to the low solubilities of many of the immiscible organic compounds commonly found in regions of subsurface contamination, small quantities of pollutant can contaminate large volumes of water, even at concentrations near solubility. Many of these compounds are very toxic (Lee et al., 1981; National Research Council, 1983), so that even very low concentrations are cause for concern. Legislated maximum contaminant levels for many compounds are in the parts per billion range, or even zero. These factors make even small periodic releases a threat. When it is recognized that common facilities such as gasoline stations are potential sources of groundwater contamination, through accidental spillage and

leaking tanks, pumps, and supply lines, the magnitude of the potential for subsurface contamination comes into focus.

Upon release to the subsurface, a chemical distributes itself among the non-aqueous phase liquid (NAPL), aqueous, gas, and sorbed, or solid, phases. The biological, chemical, and physical processes that affect a chemical in the subsurface proceed differently in each phase. Further, environmental factors such as pH, temperature, organic carbon, and dissolved oxygen concentrations influence the fate of the chemical. The dominating process at a given site is dependent upon site characteristics and properties of the contaminant itself, such as solubility, biodegradability, and volatility.

Sorption is often a significant process affecting the fate and transport of a chemical in the subsurface. Sorption involves the transfer of a chemical to a solid phase, in this case subsurface solid material, due to a chemical's preference for either the solid phase surfaces or the organic carbon associated with soil particles. In a flowing groundwater system, sorption causes an apparent retardation of the chemical transport relative to groundwater flow. In addition to altering transport behavior, sorption also influences other processes. Biodegradation and chemical reactions proceed much more slowly, if at all, when the chemical is sorbed (Steen et al., 1980; Ogram et al., 1985). This is because small soil pores are often inaccessible to soil bacteria (Casida, 1971; Cary and Hayden, 1973).

The factors that most strongly affect sorption are the hydrophobicity and solubility of a chemical, and the organic carbon content of a soil. In soils containing very little organic carbon, the mineral surface area is an important factor. In order to predict the fate and transport of a subsurface contaminant confidently and accurately, a thorough understanding must be gained of both the total amount of sorption that will occur at equilibrium, and the rate at which this equilibrium is approached.

Many current efforts to include sorption in computer models for the prediction of contaminant transport rely on several assumptions that are questionably applied. The local equilibrium assumption (LEA) is often utilized. The LEA assumes that the sorption

process is rapid relative to groundwater flow, and that sorption equilibrium is linear and reversible. In regions of low concentration and slow groundwater flow these assumptions may hold true. However, instances have been documented, at both the laboratory and field scale, in which the assumption of rapid equilibration does not hold true (Harrison and Barker, 1987; Bahr, 1989; Brusseau and Rao, 1989a,b; Brusseau et al., 1989c; Ball and Roberts, 1991a,b). Nonlinear isotherms have also been frequently observed (Weber, 1986; McGinley et al., 1993; Farrell and Reinhard, 1994). Increasingly, researchers are reporting equilibrium times of months or years, rather than the hours or days regularly reported in the past (Miller and Weber, 1986; Steinberg et al., 1987; Ball, 1989; Ball and Roberts, 1991a,b). This also calls into question the large body of sorption equilibrium data obtained during very short equilibration periods.

Adding to the complexity, many cases of subsurface contamination contain multiple organic chemicals and solvents of unknown origin, quantity, age and composition. Even when the sources and compounds can be accurately defined, the presence of multiple compounds can influence sorption. It has been demonstrated that the presence of miscible solvents can significantly decrease sorptive uptake by soils (Nkedi-Kizza et al., 1985; Rao et al., 1985; Rao et al., 1990). Also, several researchers have reported competitive effects between solutes (Crittenden et al., 1985; Abdul and Gibson, 1986; Coates and Elzerman, 1986; Pignatello, 1990; McGinley et al., 1993), while others have reported none (Karickhoff, 1979; Chiou et al., 1983; Chiou, 1985).

Clearly, further knowledge is still needed concerning how much a particular chemical is sorbed by a specific soil, over what time length, and how the sorption process is affected by the presence of other chemicals.

## 1.2 Research Objectives

The issues of sorption equilibrium nonlinearity, competition among solutes, and the time required for the sorption process to reach equilibrium remain unresolved. This study examines the long-term sorption behavior of nonpolar organic chemicals to a sample subsurface material. Experiments focus on:

- (1) the sorption isotherm linearity, and changes in linearity over time;
- (2) the possibility of competitive effects between solutes;
- (3) the final sorption equilibrium, and the rate at which that equilibrium is approached;
- (4) the use of a pulverized version of the subsurface material as a rapid predictor of long-term sorption.

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## **2 Theory**

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### **2.1 Sorption Processes**

Sorption refers to the combination of two processes, adsorption and absorption. Adsorption is a surface related phenomenon, in which mass is transferred from solution to the interface of the solution and another phase, usually solid, by electrical, physical, and chemical forces. Absorption is the mass transfer from solution into another phase due to the preference of a compound for the other phase. In soil systems this other phase is organic carbon present in the soil. This process can be likened to the partitioning of a dissolved chemical into an organic solvent. Due to the small scale at which adsorption and absorption occur, they can be very difficult to differentiate and the term sorption is usually used to refer to the combination of both processes.

#### **Partitioning to Organic Carbon**

The tendency for hydrophobic sorption to occur is driven by the hydrophobic nature of the solute (Chiou, 1989), an entropy related process. Polar water molecules can be very resistant to the solvation of nonpolar organic molecules. The presence of nonpolar organic solute molecules forces the water molecules in the region surrounding the solute molecules to assume a more structured arrangement (Goring and Thompson, 1972). Because these compounds increase the ordering of water molecules, and decrease surface tension, solute molecules will be driven to the solid-liquid interface as the water

attempts to reduce free surface energy, where they will sorb. This can occur at concentrations well below solubility (Weber et al., 1991).

### **Adsorption to Mineral Surfaces**

The sorption of organic compounds to mineral surfaces is driven by a compound's affinity for specific sites due to physical, chemical, and electrical forces. This is an enthalpic process resulting from specific interactions between the sorbate and sorbent. Adsorption will occur when the bond between the adsorbent and adsorbate are favorable to the bond between solvent and solute.

Physical adsorption occurs most often due to dipole moments between the sorbate and sorbent. These dipole moments can be permanent, induced by a permanent dipole or charged site, or the result of synchronized dipoles of oscillating charges, called London-van der Waals forces. Hydrogen bonding and  $\pi$ -bonding are two additional causes of physical sorption.

Attraction to specific sites due to electrical forces can occur for several reasons. Surface imperfections of isomorphous lattice replacements in a mineral structure can yield a charged site (Stumm and Morgan, 1981). Ligand exchange and ion exchange reactions also contribute to adsorption by electrical forces. The pH and ionic strength of the solution and solid are important to these ionic interactions. Chemical sorption is due to a chemical bond between the sorbate and sorbent. This bond is usually covalent (Hassett and Banwart, 1989). New compounds may be formed in this process.

The thermodynamically driven adsorption process yields a corresponding heat of sorption for each specific bond. Stronger bonds yield higher heats of sorption. Generally, chemical bonds are stronger than hydrogen bonds, which are stronger than dipole bonds (Stumm and Morgan, 1981). Dipole-dipole or induced-dipole adsorption are not expected to play a significant role in the adsorption of nonpolar organic molecules.

## Sorption in Natural Systems

Sorption to organic carbon, clays, and metal oxides accounts for the majority of sorption occurring in natural solid-water systems. In most natural systems, hydrophobic sorption, or partitioning to organic carbon, is the dominant sorption process. Only when the organic carbon content is very low ( $<0.1\%$ ) (Schwarzenbach and Westall, 1981), or a very large quantity of clays or metal oxides are present, does the sorption to mineral surfaces become significant. Furthermore, Chiou et al. (1983) suggested that polar water molecules effectively compete for charged mineral surface sites, especially with nonpolar organic chemicals.

A large amount of work has been conducted that demonstrates the importance of organic carbon in determining the sorptive uptake of a soil (Chiou et al., 1979; Karickhoff, 1979; Abdul et al., 1987). The sorptive capacity of many soils has been correlated with the organic carbon content of the soils examined.

$$K_p = f_{oc}K_{oc} \quad (2-1)$$

$K_p$  = sorption partition coefficient ( $L^3/M$ )

$f_{oc}$  = fraction of organic carbon in the sorbent (-)

$K_{oc}$  = organic carbon partition coefficient ( $L^3/M$ )

Correlations of experimental data with equation (2-1) have provided evidence that in many natural systems, organic carbon is the dominant soil characteristic determining the sorptive capacity of a soil. Further evidence supporting the role of organic carbon in sorption are comparisons between the sorptive properties of soils in their natural states and stripped of organic carbon (Miller and Weber, 1986). These experiments have shown a dramatic reduction in the quantity of sorption on the aquifer material after stripping.

The magnitude of the organic carbon partition coefficient has been experimentally linked to both the hydrophobicities and solubilities of nonpolar organic chemicals (Goring and Thompson, 1972; Chiou et al., 1979; Means et al., 1980; Karickhoff et al., 1981). The correlations are reported to fit regressions similar to those in equations (2-2) and (2-3), suggesting that a solute's tendency to sorb is controlled by the compound's hydrophobicity and solubility.

$$\log(K_{oc}) = A \log(K_{ow}) + B \quad (2-2)$$

$$\log(K_{oc}) = C \log(S) + D \quad (2-3)$$

$K_{ow}$  = octanol - water partition coefficient (-)

$S$  = aqueous solubility (M/L<sup>3</sup>)

$A, B, C, D$  = empirical regression coefficients

To account for sorption beyond that predicted on an organic carbon basis in low carbon soils, a two-site model has been suggested (McCarty et al., 1981; Curtis et al., 1986). It predicts the sorption due to organic carbon as described above, but also includes a mineral sorption component.

$$K_p = f_{oc}K_{oc} + f_{io}S_aK_s \quad (2-4)$$

$f_{io}$  = mass fraction of inorganic sorbing phase (-)

$S_a$  = specific surface area of inorganic sorbing phase (L<sup>2</sup>/M)

$K_s$  = specific surface adsorption coefficient (L)

## **Soil Heterogeneity**

Heterogeneities in soils and aquifer materials have been shown to affect sorption behavior. Experiments conducted by Ball (Ball, 1989; Ball and Roberts, 1991a,b) on size fractions of sand from Borden, Ontario showed significant differences in sorption properties of the various size fractions. The sand from this aquifer was visually homogeneous, and particles were separated by size only, rather than mineral type or geologic origin. Weber and coworkers (Weber et al., 1992) examined the sorption properties of bulk soil and separable mineral fractions. Sorption capacities for a shale fraction were more than two orders of magnitude greater than the capacity of their bulk parent soils. The authors also attribute the commonly observed Freundlich shaped isotherms to contributions from Langmuir type sorption occurring at different strengths and capacities on different soil components. The work conducted by these researchers, as well as others (Karickhoff et al., 1979) suggests that even relatively homogeneous soils can be comprised of soil particles with heterogeneous properties. This also suggests that small variations in the abundance of specific soil fractions may cause large variations in a soil's bulk sorption behavior.

## **2.2 Sorption Equilibrium**

### **Linear Models**

The equilibrium sorption distribution between the aqueous and solid phases are usually displayed by graphing the solid phase concentration versus the aqueous phase concentration. When the relationship is proportionate across the concentration range being examined, the isotherm is a straight line. Linear isotherms have been reported by

many researchers for a wide variety of compounds and soils (Chiou, 1979; Karickhoff, 1979; Abdul and Gibson, 1986). The occurrence of linear isotherms is supported by traditional theory applying to hydrophobic partitioning to organic carbon. No overloading is observed as the solid phase concentration increases. Linear isotherm behavior across wide concentration ranges can be convenient for estimating contaminant transport, especially when estimating by a numerical model. The linear model is commonly represented as the form of equation (2-5).

$$q_e = K_p C_e \quad (2-5)$$

$q_e$  = solute concentration on solid phase (M/M)

$C_e$  = solute concentration in solution (M/L<sup>3</sup>)

### Nonlinear Models

Nonlinear isotherms have been reported in the literature (Weber, 1986; McGinley et al., 1993), especially over wide concentration ranges. Nonlinear isotherms reflect a decrease in sorption capacity as surface loading increases, suggesting sorption may be limited. Nonlinear isotherms are most often modeled by two equations, the Langmuir and Freundlich equations.

The Langmuir equation is represented below, in equation (2-6).

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (2-6)$$

$Q^0$  = Langmuir isotherm capacity constant (M/M)

$b$  = Langmuir isotherm enthalpy constant (L<sup>3</sup>/M)

In the Langmuir equation,  $Q^0$  represents a maximum sorption capacity, and  $b$  is related to the enthalpy of adsorption at a monolayer surface coverage. The Langmuir equation is linear at low concentrations, and often provides a good representation of data in this range. However, at high concentrations a maximum loading is predicted that is not commonly exhibited in laboratory experiments with soil-water systems.

The Freundlich equation often provides a good fit to experimental data, and is widely used. It is often applied at an empirical level, but can be derived from contributions from multiple Langmuir-type isotherms (Adamson, 1990; Weber et al., 1992). The Freundlich model is represented below in equation (2-7).

$$q_e = K_f C_e^n \quad (2-7)$$

$K_f$  = Freundlich capacity coefficient ( $(L^3/M)^n$ )  
 $n$  = Freundlich exponent (-)

In the Freundlich model,  $K$  represents sorption capacity, and  $n$  represents the degree of isotherm nonlinearity. At low concentrations this equation predicts sorption values which may be much higher than those actually observed. This inconsistency with the Freundlich equation can cause numerical tailing when used to estimate transport due to model behavior at low concentrations (Rabideau and Miller, 1994).

The linearity, or lack of linearity, has been frequently used as evidence of a particular sorption mechanism (Chiou, 1979; Karickhoff, 1979). Linear sorption isotherms are often considered to be indicative of partitioning to organic carbon, while isotherms exhibiting a Langmuir shape are considered to be representative of a sorption mechanism with a limited capacity, such as sorption to a limited number of mineral sites. Recently, Spurlock and Biggar (1994) have suggested that the occurrence of nonlinear isotherms may still fit into the framework of traditional partitioning theory. The authors note that

sorption studies with nonionic organic compounds and humic acid have yielded nonlinear isotherms, and that nonlinear dissolution of organic vapors in organic polymers has been reported. They state that linear isotherms are not a prerequisite for partitioning.

### **Multi-solute models**

The often complex chemical composition of sites containing subsurface contamination has encouraged researchers to examine the possibility of competitive sorption effects between multiple species. In situations involving limited sorption capacities, thought to be indicated by nonlinear isotherms, the environment may be even more favorable to competition. In some instances the inhibition of sorption of compounds due to the presence of others has been observed (Crittenden et al., 1985; Abdul and Gibson, 1986; Pignatello, 1990; McGinley et al., 1993). Efforts have been made to quantify these effects and formulate models to predict the amount of competition that can be expected to occur. Several of these models are variations of models used to describe sorption in single-solute systems.

The Langmuir model has been modified to predict sorption in a multi-solute system (Murali and Aylmore, 1983a,b,c). Sorption in a multi-solute system has also been predicted by a modification of the Freundlich equation (Sheindorf et al., 1982). Both models rely upon parameters which must be experimentally obtained. Additionally, in these models no competition would be predicted in: (a) the linear low concentration range of the Langmuir isotherm equation (2-8), or (b) a linear Freundlich isotherm, equation (2-9) with an exponent of 1. Fritz and Shundler (1981) used a modified Freundlich equation for the prediction of competitive sorption isotherms in a bisolute system which allowed for the prediction of competition even with linear single-solute isotherms.

Competitive sorption has also been predicted by the ideal adsorbed solution (IAS) model. The IAS model has strong thermodynamic basis. Single-solute equilibrium

isotherms are determined experimentally and represented by one of the previous single-solute models. The single-solute soil loadings and the reduction in surface tension, or spreading pressure, are then calculated. The prediction of multi-solute equilibrium concentrations are determined by calculating the mole fraction of the sorbed species that would yield a spreading pressure equal to the spreading pressure of the single-solute system (Crittenden et al., 1985).

### 2.3 Rate Theory

In addition to sorption equilibrium in groundwater systems, the rate at which equilibrium is approached is a very important factor affecting contaminant transport. Researchers have observed significant effects of sorption rates on solute transport in porous media at both the field scale (Roberts et al., 1986; Bahr, 1989) and the laboratory scale (Miller and Weber, 1986; Nkedi-Kizza et al., 1989).

In much of the previous sorption work conducted, researchers have concluded that a practical sorption equilibrium was reached in a time scale of hours or days. Samples were analyzed at regular intervals until the change in aqueous phase concentration was less than experimental error. Even in cases where long equilibration times were recognized, experiments were rarely carried out to equilibrium. This has been due to time constraints, experimental problems such as reactor loss and solute degradation over long time periods, as well as an incomplete recognition of the significance of the magnitude of sorption still occurring. Many researchers have recognized sorption processes to proceed very quickly initially, then continue slowly for an indefinite period of time (Cameron and Klute, 1977; Miller and Weber, 1986; Wu and Gschwend, 1986; Weber and Miller, 1988; Brusseau and Rao, 1989a; Ball, 1989). Work by Ball and coworkers (Ball, 1989; Ball and Roberts, 1991a,b) has shown that the magnitude of sorption occurring during this slow uptake period can be very significant if given sufficient time to proceed.

The mass balance of a solute in a completely mixed batch reactor (CMBR) may be expressed as:

$$\frac{dC}{dt} = -\frac{M}{V} \left( \frac{dq}{dt} \right)_{srp} + \left( \frac{dC}{dt} \right)_{rxn} + \Gamma(C) \quad (2-8)$$

C = solute concentration in solution (M/L<sup>3</sup>)

t = time (T)

M = mass of sorbent (M)

V = volume of solution (L<sup>3</sup>)

q = solute concentration on solid phase (M/M)

Γ(C) = source / sink term

For a non-reactive solute with no sources or sinks, the dq/dt term controls the loss of solute from the solution phase. An appropriate model for this term must be found in order to accurately describe the rate of sorption.

The generally accepted rate limiting mechanisms are divided into two classes: chemical nonequilibrium due to slow kinetics of the sorption process and physical nonequilibrium due to mass transfer limitations. Physical limits to the rate of sorption are due to mass transfer limitations and diffusion processes. The immobile layer of water surrounding soil particles can be viewed as a boundary through which solute must pass before sorbing to the soil particle itself. This is most often represented as a first-order process driven by the concentration gradient between the bulk fluid phase and the soil surface.

Researchers have attempted to model the sorption process itself as a first-order reaction. However, the sorption process has frequently been observed to proceed very rapidly at early times, followed by a prolonged slow uptake (Cameron and Klute, 1977; Miller and Weber, 1986; Wu and Gschwend, 1986; Weber and Miller, 1988; Brusseau and

Rao, 1989a; Ball, 1989). In order to capture the sorption behavior accurately at early times, an 'instantaneously sorbed' fraction is often included in the first order model.

The sorption process has also been viewed as two coupled mass transfer steps limiting the rate of sorption. In order to sorb, a solute molecule must first diffuse through an immobile boundary layer of water surrounding the soil particle, then diffuse into the particle. Spherical geometries are assumed for soil particles in this "dual resistance" model in order to reduce the complexity of the problem. The external mass transfer can be sensitive to mixing conditions (Crittenden et al., 1986; Weber and Miller, 1988; Brusseau and Rao, 1989b), and in some instances be insignificant.

Diffusion limited mass transfer can be controlled by several factors. As a solute molecule migrates into the porous structure of a soil particle, its progress can be hindered by the length and tortuosity of the pores (pore diffusion), sorption to the pore walls (surface diffusion), and diffusion through organic matrices (Brusseau and Rao, 1989b; Brusseau et al., 1989c; Szecsody and Bales, 1989). Both pore and surface diffusion models have been used in an effort to describe sorption rates (Rao et al., 1982; Crittenden et al., 1986; Hutzler et al., 1986; Roberts et al., 1987; Wu and Gschwend, 1988).

## **2.4 Previous Experimental Work**

### **Multi-solute**

Competitive sorption effects have been observed on many ionic compounds adsorbing to various sorbents, such as soils, clays, activated carbon, textile fibers and synthetic resins (Martin and Al-Bahrani, 1977; Jossens et al., 1978; Fritz and Schlunder, 1981; Scheindorf et al., 1982). Investigations of competition between nonpolar hydrophobic organic compounds sorbed in soil-water systems is limited. The research that has been conducted has yielded conflicting results. Several researchers have observed no

competitive effects (Karickhoff, 1979; Chiou et al., 1983; Chiou, 1985). Others have observed differences in the sorption of a compound when in the presence of one or more additional solutes (Crittenden, et al., 1985; Abdul and Gibson, 1986; Coates and Elzerman, 1986; Pignatello, 1990; McGinley et al., 1993). The following review of experimental work focusing on competitive effects during sorption is summarized in Table 2.1.

In much of the previous work addressing competitive effects between organic compounds, solutes exhibiting competitive effects in multi-solute systems display nonlinear isotherms in single-solute systems. The constant sorption capacity, in the range examined, suggested by a linear isotherm would not be likely to provide an environment favorable to competition. Karickhoff et al. (1979) conducted batch equilibrium sorption experiments with aromatic hydrocarbons and chlorinated hydrocarbons on pond and river sediments. Linear isotherms were observed over the concentration ranges examined. Phenanthrene and pyrene were sorbed individually and combined to two coarse silt fractions with a high  $f_{oc}$ . No differences in sorption between the single solute and bisolute cases were observed. Similarly, Chiou et al. (1983) investigated the sorption of 1,3-dichlorobenzene and 1,2,4 trichlorobenzene to a silt loam soil with a high  $f_{oc}$ . Linear equilibrium isotherms were observed in all cases studied. No differences between single and bisolute isotherms could be recognized. Abdul and Gibson (1986) conducted equilibrium experiments with six polynuclear aromatic hydrocarbons (PAH's) on a high and low  $f_{oc}$  soil. Linear partitioning was observed for all compounds over the concentration range studied. The sorption of naphthalene and fluorene were suppressed in the presence of a PAH mixture.

Interesting behavior was observed by Chiou (1985) while investigating the roles of soil humus, soil mineral content, soil moisture content and solvent medium on the uptake of parathion and lindane by a silty loam. Single and bisolute equilibrium isotherms were obtained in both soil-water and soil-hexane systems. Linear partitioning and no

competitive effects were observed in the soil-water system, in agreement with earlier work. However, nonlinear partitioning and competition was observed in the soil-hexane system. The researchers hypothesized that the difference was due to preferential sorption of polar water molecules to a mineral component of the soil. In the presence of water, organic phase partitioning was the main sorption mechanism. In the absence of water, organic compounds competed for a limited mineral phase.

While the majority of the competitive effects reported describe suppression of one compound in the presence of another, Coates and Elzerman (1986) reported the opposite. A gaseous purge technique was used to study the sorption and desorption of polychlorinated biphenyl (PCB) congeners on a high  $f_{oc}$  sediment. Equilibrium studies were conducted with both single solutes and mixtures of four congeners. The partition coefficient for 2,4,6,2',4',6'-hexachlorobiphenyl (HCB1) differed by 25% between single solute and multi solute experiments. Desorption rate experiments were conducted with HCB1 in both single solute and multi solute systems. A first order rate model was applied to the desorption data. The desorption model rate parameter differed by 60% between the single and multi solute systems.

Pignatello (1990) conducted sorption experiments with pairs of halogenated aliphatic and aromatic compounds on three sandy loams and a high organic peat soil. Nonlinear partitioning was observed for 1,2-dibromoethane, while linear partitioning was observed for other compounds. A decrease in the sorption of 1,2-dibromoethane was observed in the presence of other nonpolar compounds. Displacement of sorbed 1,2-dibromoethane was also observed upon the addition of a second solute. The researchers noted that competitive effects are greatest between cosolutes with similar surface areas, suggesting that competition is occurring at sites with a preference for a specific molecular size and shape. Additional experiments were carried out with an extracted humic acid solid material. No competition was observed in these experiments, supporting the concept

that multi-solute effects are due to competition for specific sites rather than overloading organic carbon.

McGinley et al. (1993) conducted multi-solute sorption experiments with tetrachloroethylene (TTCE), 1,4-dichlorobenzene (DCB) and trichlorobenzene (TCB) on four soils. Nonlinear isotherms and competition between solutes was observed. The researchers found that soil properties tended to control the nonlinearity of the isotherms. Stronger competitive effects were observed on soils exhibiting more nonlinear isotherms in single solute experiments. An IAS model provided good predictions of the competitive effects observed.

With the exception of Coates and Elzerman (1986) and McGinley et al. (1993), sorption equilibrium was considered to be reached within hours or days. While Coates and Elzerman (1986) and McGinley et al. (1993) allowed up to 150 days and 7-14 days respectively, each concluded that months or years would be required for the systems to reach a true equilibrium. Also, multi-solute systems likely to display competitive effects seem to show some evidence of limited sorption capacity even in the single-solute case.

A general agreement exists that competitive effects are a real phenomenon. Some properties of single solute systems, such as nonlinear isotherms, seem to suggest an improved possibility that competition will be observed in a similar multi-solute system. However, consistent methods for predicting the occurrence and magnitude of competitive effects are not in existence. The occurrence of competitive effects in systems containing solids whose primary sorption mechanism is adsorption to a limited number of sites is conceptually agreeable. However, observations of competition in solids with high organic carbon contents whose likely sorption mechanism would be hydrophobic partitioning does not fit as well with theory. Clearly, additional information is required for this phenomenon to be more fully understood.

**Table 2.1: Previous competitive sorption research**

| Researchers               | Solutes                                                                                                | Sorbents<br>(OC = organic carbon)                            | Equilibration time | Results                                                       |
|---------------------------|--------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|--------------------|---------------------------------------------------------------|
| Karickhoff et al., 1979   | phenanthrene, pyrene                                                                                   | pond and river coarse silt fractions (2.78 and 3.27% OC)     | 24/48 hours        | linear isotherms; no competition                              |
| Chiou et al., 1983        | 1,3-dichlorobenzene, 1,2,4-trichlorobenzene                                                            | silt loam (1.9% OC)                                          | 24 hours           | linear isotherms; no competition                              |
| Chiou et al., 1985        | lindane, parathion                                                                                     | silt loam (1.9% OC)                                          | 24 hours           | results dependent upon solvent                                |
| Abdul and Gibson, 1986    | fluorene, naphthalene, phenanthrene                                                                    | aquifer sample (1.9% OC)                                     | 24 hours           | linear isotherms; competition                                 |
| Coates and Elzerman, 1986 | 2,4,6,2',4',6'-; 2,4,5,2',4',5'-hexachlorobiphenyl; 4,4'-dichlorobiphenyl; 2,6,2',6'-trichlorobiphenyl | sediment (1.21% OC)                                          | 150 days           | linear isotherms; competitive effects                         |
| Pignatello, 1990          | 1,2-dibromoethane in presence of halogenated and aromatic compounds                                    | 3 sandy loams (1.43, 1.81 and 2.21% OC), and peat (44.6% OC) | 24/48 hours        | nonlinear isotherms for solute exhibiting competitive effects |
| McGinley et al., 1993     | tetrachloroethylene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene                                       | 4 subsurface soils (0.15-2.49% OC)                           | 7/14 days          | nonlinear isotherms; competition                              |

## Rate-Limited Sorption

The fact that sorption can continue to occur over time periods of months or years has been recognized by researchers for some time (Hamaker et al., 1966). Experimental evidence of sorption nonequilibrium has been observed in field studies, as well as in column and batch sorption experiments in the laboratory. However, a great deal of experimental work related to sorption has failed to take long sorption equilibration periods into account. Or, when it is considered, it is in an effort to explain experimental data trends after the fact, such as desorption hysteresis and tailing in column studies. A review of the literature has revealed no complete sorption studies that have extended beyond approximately 3 months. Studies that extended for this length of time concluded that, in many cases, sorption is still occurring (Ball, 1989; Ball and Roberts, 1991a,b; Pedit, 1994b). The following review of experimental work focusing on rate-limited sorption is summarized in Table 2.2.

Complementary batch and column sorption studies were conducted by Miller and Weber (Miller and Weber, 1986; 1988; Weber and Miller, 1988) with lindane and nitrobenzene on several aquifer materials. They observed nonlinear isotherms, and sorption rates characterized by an initial fast sorption for a short period of time, followed by an extended period of slow sorption behavior. Dual-resistance and first order paired with instantaneous sorption models provided good fits of the data. Local equilibrium models had difficulty describing the tailing that occurred in the column studies.

An interesting experiment which provided strong evidence supporting the theory of diffusion controlled sorption was conducted by Steinberg et al. (1987) with 1,2-dibromoethane (EDB) on three sandy loam soils. The desorption of EDB was compared on soils that had been allowed to equilibrate with EDB for 24 or 72 hours, and soils that had last been exposed to EDB as long as 19 years previously (referred to as 'native soils'). The quantity of EDB sorbed to the native soils was determined by acetone extraction at 75

° C. Desorption was initiated by either a gas purge technique or solvent extraction. The sorption partition coefficients for the native soils were approximately two orders of magnitude larger than the coefficients for the soils recently exposed to EDB. The native soils were also much more difficult to extract. During a 100 minute desorption purge, all EDB was released from soils recently exposed to EDB, while only 5% was released from the native soils. However, pulverizing the soil greatly increased the release of EDB. Microbial degradation of EDB in the native soils was shown to be greatly reduced compared to degradation in the soils with recently applied EDB, suggesting that much of the EDB was in micropores of the native soil, inaccessible to microorganisms.

At the field scale, Harrison and Barker (1987) conducted complementary laboratory and field experiments investigating the sorption and transport of toluene and chloroform in a soil-sawdust mixture. Significant spreading of elution curves were observed, along with increased sorption at lower flow velocities, suggesting that sorption was not reaching an instantaneous equilibrium.

In an effort to provide evidence supporting intra-particle diffusion as the rate limiting mechanism in the sorption process, Ball and Roberts (Ball, 1989; Ball and Roberts, 1991a,b) investigated the sorption of tetrachloroethene (PCE) and 1,2,4,5-tetrachlorobenzene (TeCB) on Borden Aquifer sand. Batch sorption experiments were conducted on bulk sand, sand size fractions, and pulverized bulk and fractioned sand for periods up to 3 months. The approach to equilibrium was observed to be slowest in the largest particles, followed by the smaller particles and rapid equilibrium in the pulverized samples. These differences were thought to be due to differences in the diffusion path length, roughly proportionate to the diameter of the soil particles. Though the rates were significantly different, the sorption equilibrium was approximately equal in both pulverized and unpulverized samples. Different size fractions exhibited very different sorption properties. It was concluded that diffusion was the rate limiting process. The data was

modeled with a pore diffusion model. For smaller size fractions an 'instantaneously sorbing fraction' had to be assumed to obtain good agreement between data and model.

In an effort to determine the diffusion mechanism responsible for sorption rate limitations, Brusseau et al. (1989c) conducted column experiments in which the flow was interrupted. This interruption technique had been previously used in the field of chemical engineering. In theory, it has the power to determine the differences between rate limitations due to film-diffusion versus intra-particle diffusion. An herbicide labeled 2,4-D was used with a fine sand and silty loam. The results suggested that diffusion through intra-particle organic carbon was responsible for the observed rate limitations. Brusseau (1992) also examined the effects of variations in flowrates on sorption nonequilibrium. Dichlorobenzene, naphthalene, tetrachloroethene, and *p*-xylene were studied in column experiments with three aquifer materials. It was determined that while variations in column flowrates did control the observed nonequilibrium, a simple direct relationship could not be determined, most likely due to time-scale effects.

Also focusing on diffusion as the rate limiting mechanism, Grathwohl and Reinhard (1993) conducted experiments investigating the desorption of trichloroethylene (TCE) from an aquifer material. A gas-purge technique was used to desorb the TCE from both saturated and oven dried versions of the TCE contaminated soil. The desorption from the dried soils proceeded much faster than from the saturated soils. The rate of desorption from the dried soils was dependent upon gas flowrates, while the desorption from saturated soil was independent of flowrates. The authors concluded that desorption is limited by diffusion through water filled pores in the soil. In the dry soil the absence of pore water allowed for a rapid equilibration with the gas phase.

Farrell and Reinhard (1994) conducted sorption column experiments with trichloroethylene (TCE) on unsaturated silica gels and several soils. After equilibration periods of one month on silica gels, the desorption of TCE was observed to continue for months. The silica gels were free of organic carbon, ruling out the possibility of diffusion

through an organic matrix. In particles with equal diameters, but different pore sizes, the particles with smaller pores desorbed more slowly. Heat treating the silica gels to increase the quantity of micropores further decreased the rate of desorption. Longer desorption periods were also observed for systems that exhibited nonlinear sorption isotherms. The authors suggest that micropores strongly trap molecules because of the increased surface area available to individual molecules for sorption in pores with diameters near the diameter of solute molecules. Steric hindrance of solute molecules in the micropores was also thought to reduce the rate of desorption.

In a recent sorption rate modeling effort targeted at addressing the effects of variation in soil particle properties on long-term rate data, Pedit (1994a,b,c) compared the results of single and multiple particle class pore and surface diffusion models to first order rate models with continuously distributed parameters. The author concluded that while best results were obtained with a stochastic, log-normal rate approach model, the work necessary to accurately describe the distributions of soil properties could prove intensive. It was demonstrated that a pore diffusion model with an instantaneously sorbing fraction would provide a reasonable description of the data without the need for as much detail regarding soil characteristics.

Rate-limited sorption is observed with natural subsurface materials in almost every case in which the possibility of rate limitations is considered. A general consensus has been reached that the sorption process is not instantaneous. However, the specific, rate-controlling mechanism has not been identified. Pore diffusion, surface diffusion, diffusion through organic matrices, and diffusion through an immobile aqueous boundary layer have all been offered as the controlling mechanism. Further definition of the specific rate controlling mechanism is required.

Table 2.2: Previous rate-limited research

| Researchers                                             | Solutes                                                           | Sorbents                   | Experiment type                             | Results                                                                                                                        |
|---------------------------------------------------------|-------------------------------------------------------------------|----------------------------|---------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|
| Miller and Weber, 1986, 1988;<br>Weber and Miller, 1988 | lindane, nitrobenzene                                             | aquifer materials          | batch and column sorption                   | extended sorption in batch studies; tailing in columns                                                                         |
| Steinberg et al., 1987                                  | 1,2-dibromoethane                                                 | sandy loam soils           | gas purge and solvent extraction desorption | long equilibrations reduced rate of desorption; pulverizing soil increased rate                                                |
| Harrison and Barker, 1987                               | chloroform, toluene                                               | soil-sawdust mixture       | column and small scale field transport      | tailing in column studies; increased sorption at lower flow velocities; increased sorption during periods of reduced flowrates |
| Ball and Roberts, 1989, 1991a,b                         | tetrachloroethene, 1,2,4,5-tetrachlorobenzene                     | aquifer material           | batch sorption                              | long equilibration periods; increased sorption rates with pulverized samples                                                   |
| Brusseau et al., 1989                                   | herbicide 2,4-D                                                   | fine sand, silty loam      | interrupted column sorption                 | rate limitations likely due to diffusion through organic carbon                                                                |
| Brusseau, 1992                                          | dichlorobenzene, naphthalene, tetrachloroethene, <i>p</i> -xylene | 3 aquifer materials        | column sorption, varied flowrates           | nonequilibrium dependent upon flowrates, but not simply and directly related                                                   |
| Grathwohl and Reinhard, 1993                            | trichloroethylene                                                 | aquifer material           | wet and dry column desorption               | desorption rates limited by pore water                                                                                         |
| Farrell and Reinhard, 1994                              | trichloroethylene                                                 | silica gels and soils      | unsaturated column desorption               | increased microporosity decreases desorption rates                                                                             |
| Pedit, 1994                                             | diuron                                                            | Wagner subsurface material | batch sorption                              | distributed property rate model provided good fit to data                                                                      |

## 2.5 Impacts to Prediction of Contaminant Transport

The common assumptions of sorption isotherm linearity, and rapid equilibration between phases have failed to explain sorption and transport data in many cases. Batch reactor systems have exhibited sorption continuing for periods of months (Ball, 1989; Ball and Roberts, 1991a,b). Significant tailing of solute transport and changes in aqueous solute concentration after the cessation of pumping have been observed in laboratory and field studies (Harrison and Barker, 1987; Bahr, 1989; Brusseau et al., 1989c). Numerical modeling of aquifer restoration has indicated that differences in sorption capacity and nonequilibrium effects can have a significant impact on the estimation of transport of organic compounds (Rabideau and Miller, 1994). The impacts of failing to understand, and account for, the true behavior of chemicals in the subsurface can lead to large errors when estimating the fate of released organic chemicals for purposes such as exposure risk and remediation predictions. Clearly, tenuous assumptions are being made to describe a system that is not yet completely understood.

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### 3 Materials and Methods

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#### 3.1 Introduction

This study focused on two main sorption concepts: (1) the distribution of a chemical between solid and aqueous phases, and (2) the rates at which a final equilibrium distribution was approached. Rate studies defined the mass transfer of solute from the aqueous phase to the solid phase with respect to time at a single concentration, as well as suggested when an equilibrium had been reached. Isotherm studies revealed the distribution between the phases across a wide concentration range at a single point in time. Both rate and isotherm studies were conducted on both a subsurface material in its native state, and a pulverized version of the same material. Two organic compounds were used both individually and combined on both material types. Comparisons of experiments on the pulverized and native versions of the material were also used to predict when the true equilibrium was reached. Bisolute rate and isotherm studies were conducted in an effort to reveal any potential competitive effects between solutes. It should be noted that isotherms are commonly examined once an equilibrium has been reached between the solid and aqueous phases. The contention that equilibrium is not quickly reached is fundamental to this study. Isotherms, or distributions between the solid and aqueous phases, will be compared at points in time that are not intended to represent a state of system equilibrium.

### 3.2 Materials

#### Chemicals

Naphthalene and phenanthrene were chosen as the sorbates for these experiments. Both are nonpolar polycyclic aromatic hydrocarbons (PAH's). Naphthalene is the lighter, more soluble, and more volatile of the two compounds. High performance liquid chromatography (HPLC) grade hexane was used in the aqueous phase extraction process and subsequent gas chromatograph analysis, with hexadecane as an internal standard. The physical and chemical properties of these chemicals, as well as their sources and purities, are listed in Table 3.1.

The aqueous phase in all of the experiments was made with water distilled by a Corning AG-11 still and deionized with a Corning Mega-Pure System DI deionizer. Sodium azide (0.005M) was then added to inhibit any biological degradation of the sorbates within the reactors. Sodium tetraborate decahydrate (0.005M) was added to buffer the system and eliminate any pH effects on sorption. Calcium chloride dihydrate (0.005M) was also added to assist in the phase separation during centrifugation. This buffered solution was then adjusted to a pH of  $8.40 \pm 0.02$  by the addition of hydrochloric acid. The sources and purities of these inorganic chemicals are listed in Table 3.2.

**Table 3.1: Organic chemical properties**

| Chemical                  | aqueous solubility mg/l | log(Kow) | molecular weight | vapor pressure Pa @ 25°C | source  | purity |
|---------------------------|-------------------------|----------|------------------|--------------------------|---------|--------|
| naphthalene <sup>a</sup>  | 32.2                    | 3.29     | 128.18           | 10.80                    | Aldrich | 99+%   |
| phenanthrene <sup>a</sup> | 1.28                    | 4.63     | 178.24           | 0.0187                   | Aldrich | 99.5+% |

<sup>a</sup>quoted, Mackay et al., 1992

**Table 3.2: Inorganic chemical properties**

| <b>Chemical</b>    | <b>use</b>                                | <b>molecular weight</b> | <b>source</b> | <b>purity</b> |
|--------------------|-------------------------------------------|-------------------------|---------------|---------------|
| sodium azide       | biological inhibition                     | 65.01                   | Aldrich       | 99%           |
| sodium tetraborate | buffer                                    | 381.37                  | Aldrich       | 99%           |
| calcium chloride   | particle separation during centrifugation | 147.02                  | Aldrich       | 98+%          |

### **Solid Materials**

The Wagner subsurface material used in all of these experiments was collected approximately 25 meters below ground level in a Michigan gravel pit during October, 1988. The Wagner material was sieved to remove grains larger than 2 mm and allowed to air dry. Nothing further was done to the material used in its native state. The pulverization of the material was accomplished by a tungsten-carbide ball mill (SPEX Industries, Inc.). This process reduced the material visually to the consistency of wheat flour. A summary of the native and pulverized material properties are contained in Table 3.3 and results of particle size analyses are contained in Table 3.4.

It is worth noting that the organic carbon measurements of the native and pulverized materials were significantly different. The organic carbon measurements were obtained by the persulfate oxidation ampule technique on an Oceanographic International Corp. Model 700 TOC analyzer. The organic carbon content of the native material was measured as  $0.043 \pm 0.004\%$ , while the measured organic carbon content of the pulverized material was  $0.22 \pm 0.02\%$ . The difference in organic carbon measurements

was not likely due to contamination by the ball mill. Glass beads in solid form and after pulverization in the ball mill were not significantly different when analyzed for organic carbon content. Other researchers have described large variations in different methods of organic carbon measurement on both the Wagner and other subsurface materials (Powell et al., 1989; Ball et al., 1990; Weber et al., 1992). Likely, pulverizing the solid material makes more organic carbon available to the analytical method. This also supports the theory that significant quantities of organic carbon may exist within the particle, but may not be immediately available to solute molecules for sorption.

**Table 3.3: Sorbent properties**

| <b>Sorbent Property</b>                                  | <b>native Wagner<sup>a</sup></b> | <b>pulverized Wagner</b> |
|----------------------------------------------------------|----------------------------------|--------------------------|
| mean grain size - diameter<br>(mm)                       | 0.48                             | N/A                      |
| grain size uniformity<br>coefficient ( $d_{60}/d_{10}$ ) | 3.00                             | N/A                      |
| percent organic carbon<br>content                        | $0.043 \pm (0.004)\%$            | $0.22 \pm (0.02)\%$      |

<sup>a</sup>Pedit (1994)

**Table 3.4: Particle size distribution - Wagner material**

| sieve range (mm) | mean radius (mm)   | % bulk mass<br>native <sup>a</sup> | % bulk mass<br>pulverized <sup>b</sup> |
|------------------|--------------------|------------------------------------|----------------------------------------|
| 1.40-2.00        | 0.84               | 8.32 ± 1.66                        | 0                                      |
| 1.00-1.40        | 0.59               | 12.16 ± 0.98                       | 0                                      |
| 0.71-1.00        | 0.42               | 13.18 ± 0.18                       | 0                                      |
| 0.50-0.71        | 0.30               | 15.34 ± 0.49                       | 0                                      |
| 0.355-0.50       | 0.21               | 17.33 ± 0.73                       | 0                                      |
| 0.25-0.355       | 0.15               | 16.09 ± 0.58                       | 1.6                                    |
| 0.18-0.25        | 0.11               | 11.97 ± 0.54                       | 6.9                                    |
| 0.125-0.18       | 0.075              | 3.92 ± 0.16                        | 13.3                                   |
| 0.09-0.125       | 0.053              | 1.07 ± 0.02                        | 19.2                                   |
| <0.09            | 0.038 <sup>c</sup> | 0.63 ± 0.06                        | 61.4                                   |

<sup>a</sup>Pedit (1994), mean ± one standard deviation (2 measurements)

<sup>b</sup>single measurement

<sup>c</sup>estimate

### 3.3 Experimental Methods

#### Introduction

All of the experiments were conducted in 40 ml borosilicate glass centrifuge tubes (Kimax) sealed with screw caps and Teflon®-lined septa. All reactors were tumbled continuously to ensure thorough mixing. A single reactor was used for each data point. All data points were repeated in triplicate, and a blank reactor containing no solids was carried along with each triplicate set to estimate loss from the reactors and loss due to sorption to the reactor itself.

Rate studies were conducted at a single concentration. For each experiment, 33 identical reactors containing native material and 21 identical reactors containing pulverized material were prepared. One matching "blank" reactor containing no solids was prepared for each set of three reactors containing material. Three reactors and a blank were removed at a single point in time over a period of three months. Upon removal, the

reactors were immediately centrifuged, extracted, and sampled to determine the concentration of the aqueous phase.

Isotherm studies were conducted across a wide range of concentrations. For each isotherm sampling, three reactors containing solids and a blank were prepared at each of ten concentrations. At a single point in time, three reactors and a blank at each concentration level were centrifuged, extracted, and analyzed to determine the concentration of the aqueous phase.

All blanks were extracted with hexane to estimate possible losses from the reactors as well as sorption to the reactors themselves. Extractions of the solids were also routinely conducted for mass balance purposes. Extractions were conducted by placing 3 ml of hexane (spiked with hexadecane as an internal standard) into the reactor after sampling the aqueous phase. The reactor was then resealed and kept completely mixed for 24 hours for extractions of blank reactors, and 30 days for soil extractions. The hexane phase was then removed and analyzed by gas chromatography.

### **Rate Studies**

The procedures used for preparation of the reactors for rate studies are as follows:

- 1) 1.0 gram of Wagner material was added to a 40 ml Kimax glass centrifuge tube.
- 2) 1.0 ml of the buffer solution described in Section 3.2 was added to the centrifuge tube to pre-wet the Wagner material. The material was allowed to hydrate for 24 hours.
- 3) The reactors were then spiked with approximately 36 ml of the buffer solution containing naphthalene, phenanthrene, or a combination of both. The reactors were filled as near to full as possible to minimize

headspace and possible losses to the gas phase. The reactors were then sealed with screw caps and Teflon®-lined silicone septa and allowed to tumble until sampling.

The solids:solution ratio was chosen in an effort to create a system in which the sorptive uptake of the more weakly sorbing compound was measurable, even at early times, and so that the more strongly sorbing compound would still have a measurable concentration remaining in solution. This constant solids ratio was used in all experiments so that results could be directly compared without concerns of influence from a possible solids concentration effect reported by some researchers (Voice et al., 1983; Voice and Weber, 1985; Mackay and Powers, 1987).

The initial concentrations in the reactors was determined by extracting samples of the solute that was added to the reactors and accounting for the amount of buffer solution used to pre-wet the soil. The solute was sampled by liquid:liquid extraction into hexane and analysis performed by gas chromatography. Six samples were taken to determine the initial concentration for each rate experiment.

All reactors were kept constantly mixed at a temperature of  $22 \pm 2$  degrees Celsius. Bisolute experiments were set up similarly, except both naphthalene and phenanthrene were included in the solute added to the reactors.

### **Isotherm Studies**

In the isotherm studies the reactors and solids were prepared in the same way as in the rate studies. However, the solute additions were somewhat different. Rather than adding only a single concentration, the concentration of the solute added was varied from near-saturation levels down to approximately 50 µg/l. These variations in concentration were conducted in ten steps and covered at least one order of magnitude. Six samples

were taken at each concentration step during solute addition to determine the initial concentration in the reactors.

All vials from a specific isotherm were sampled at a single point in time. Three replicates and a blank (no solids) reactor were sampled at each of the 10 concentration steps to form an isotherm.

### **Contaminant Spiking**

The solute used for spiking the reactors was prepared by dissolving the compounds of interest into the buffer solution described in section 3.2. The compound was dissolved by adding an excess of the compound to the buffer solution and stirring for several days. The solution was then filtered (1.6  $\mu\text{m}$ , Whatman GF/A) and either used at this concentration or further diluted with the buffer solution. Preparation of the solution used in the bisolute experiments was slightly different. A quantity of buffer solution was saturated with phenanthrene and filtered. Some of this solution was then saturated with naphthalene, and some was set aside to further dilute the naphthalene saturated solution. This was done to maintain a constant background concentration of phenanthrene in the bisolute solutions.

### **Analytical Methods**

Both rate and isotherm studies were carried out for a period of three months. Sampling intervals increased as the experiments progressed. To sample the aqueous phase in each reactor, the reactors were first centrifuged at 1500 RCF for 30 minutes to separate the solid and aqueous phases. Twenty-five ml of the aqueous phase was then removed by pipette and placed into a vial containing 3 ml of hexane spiked with 100 mg/l hexadecane.

The concentration in the hexane was then determined by gas chromatography (GC) analysis by a Hewlett Packard 5890 GC.

The analysis was performed with a J & W Scientific DB-5 capillary column 15 meters in length, with a 0.53 mm inner diameter and 1.5 micron film thickness. The gas chromatograph was equipped with a flame ionization detector (FID), and Hewlett Packard 7673A auto sampler. The results were evaluated by Hewlett Packard 3365 Series II Chemstation software. The injector was set at 250 degrees Celsius, the detector was set at 300 degrees Celsius. The oven temperature was set to 75 degrees Celsius for the initial 0.2 minutes, then ramped to 250 degrees Celsius at 25 deg./min. and held at 250 degrees for 5 minutes. The carrier (He) flowrate was 9 ml/min., and the make-up gas (N<sub>2</sub>) flowrate was 21 ml/min. The FID was supplied with 43 ml/min. H<sub>2</sub>, and 327 ml/min. air.

Each sample was injected twice and the sample concentration was determined from an average of these two values. Hexadecane was used as an internal standard. The ratio of analyte peak area and hexadecane peak area was used to form a multi-point calibration curve, which was fitted with a power function. The standard concentrations bracketed the sample concentrations, and no more than 10 samples were analyzed between sampling a series of standards.

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## 4 Results and Discussion

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### 4.1 Introduction

This study examined two types of sorption data from the systems investigated. First, data addressing the rate of mass transfer from the aqueous phase to the solid phase was examined. Second, sorption isotherms, or distributions between solid and aqueous phases across a wide concentration range at a point in time, were examined. The systems investigated included both naphthalene and phenanthrene individually, and naphthalene with a constant background concentration of phenanthrene. Both native and pulverized versions of subsurface material were used with each solute combination. Collection of some data was prevented by interference from biological degradation in the naphthalene (single solute) system, and excessive sorption in the phenanthrene long-term and pulverized solid systems. Table 4.1 describes the schedule of the collection of rate data, and the schedule of collected isotherm data is tabulated in Table 4.2.

All experiments were conducted at a constant solid:solute ratio so that results could be directly compared without possible influences of solids concentration effect reported by other researchers (Voice et al., 1983; Voice and Weber, 1985; Mackay and Powers, 1987). It has been suggested that variations in the solid:solute ratio can cause variations in the measured sorption due to variations in the concentrations of particles not removed from the aqueous phase during the separation process, or changes in the extent of particle abrasion during mixing.

**Table 4.1: Rate experiment sampling schedule**

| Time<br>(hr) | Single solute |                |                |                | Bisolute       |             |
|--------------|---------------|----------------|----------------|----------------|----------------|-------------|
|              | phenanthrene  |                | naphthalene    |                | naphthalene    | w/ phen.    |
|              | Co=796 µg/l   |                | Co=14,908 µg/l |                | Co=14,581 µg/l | Co=687 µg/l |
|              | native        | pulv.          | native         | pulv.          | native         | pulv.       |
| 4            | X             |                | X              |                | X              |             |
| 8            | X             | X              | X              | X              | X              | X           |
| 16           | X             |                | X              |                | X              |             |
| 24           | X             | X              | X              | X              | X              | X           |
| 48           | X             |                | X              |                | X              |             |
| 96           | X             |                | X              |                | X              |             |
| 168          | X             | X              | X              | X              | X              | X           |
| 336          | X             | X              | X              | X              | X              | X           |
| 720          | X             | X              | X              | X              | X              | X           |
| 1440         | X             | X <sup>a</sup> | X              | X <sup>b</sup> | X              | X           |
| 2160         | X             | X <sup>a</sup> | X <sup>b</sup> | X <sup>b</sup> | X              | X           |

<sup>a</sup>not quantified due to excessive sorption

<sup>b</sup>not quantified due to biological interference

**Table 4.2: Isotherm experiment sampling schedule**

| Time<br>(hr) | Single solute   |                |                   |                | Bisolute          |             |
|--------------|-----------------|----------------|-------------------|----------------|-------------------|-------------|
|              | phenanthrene    |                | naphthalene       |                | naphthalene       | w/ phen.    |
|              | Co=117-922 µg/l |                | Co=77-29,767 µg/l |                | Co=53-29,024 µg/l | Co=687 µg/l |
|              | native          | pulv.          | native            | pulv.          | native            | pulv.       |
| 24           | X               | X              | X                 | X              | X                 | X           |
| 168          | X               |                | X                 |                | X                 |             |
| 720          | X               | X <sup>a</sup> | X                 | X <sup>b</sup> | X                 | X           |
| 2160         | X <sup>a</sup>  | X <sup>a</sup> | X <sup>b</sup>    | X <sup>b</sup> | X                 | X           |

<sup>a</sup>not quantified due to excessive sorption

<sup>b</sup>not quantified due to biological interference

## 4.2 Correction of Isotherm Data

At each sampling time for each system examined, three replicate reactors and one blank (no solids) were sampled. Late in the experiment, consistently increasing losses were noticed from the blank reactors that could only be partially recovered by extraction. It was concluded that these losses were due to volatilization and diffusion through or around the screw cap and Teflon<sup>®</sup> lined septa seal of the reactors. These losses increased over time, and a first order model was fit to the data. The loss coefficients for naphthalene in both the single solute and bisolute system were almost identical, providing further evidence that the losses were systematic and efforts should be made to account for them. An approach similar to that used in Miller and Pedit (1992) was employed to account for the losses. The following corrections were applied to all sorption isotherms. The mass remaining in the blank reactors over time was represented as:

$$\frac{dC}{dt} = -kC \quad (4-1)$$

C = aqueous phase solute concentration (M/L<sup>3</sup>)

k = first order rate constant (1/T)

t = time (T)

The first order loss rate coefficient was found by satisfying:

$$\text{Minimize: } E = \sum_{i=1}^{n_p} [(C_{d,i} - C_{m,i}) / C_{m,i}]^2 \quad (4-2)$$

n<sub>p</sub> = number of data points

C<sub>d,i</sub> = aqueous phase solute concentration (data) (M/L<sup>3</sup>)

C<sub>m,i</sub> = aqueous phase solute concentration (model) (M/L<sup>3</sup>)

Figures 4.1 - 4.3 contain the recoverable blank concentrations fitted with their corresponding first order rate models for phenanthrene, naphthalene (single solute), and naphthalene (bisolute), respectively.

The losses from the reactors made the dynamic system more complex. Since the volatilization was occurring before the system had reached equilibrium, both sorption and desorption may have been occurring at different regions within the particle at the same time, hampering efforts to determine when and if the sorbent reached its true sorption capacity. At the very least, the driving force of the sorption process, the aqueous phase concentration in excess of equilibrium, was being reduced. An empirical model was fit to the rate data:

$$C_m = \alpha_0 + \alpha_1 e^{(-\beta_1 t)} + \alpha_2 e^{(-\beta_2 t)} \quad (4-3)$$

$C_m$  = aqueous phase solute concentration (model) (M/L<sup>3</sup>)

$\alpha_0, \alpha_1, \alpha_2, \beta_1, \beta_2$  = fitting parameters

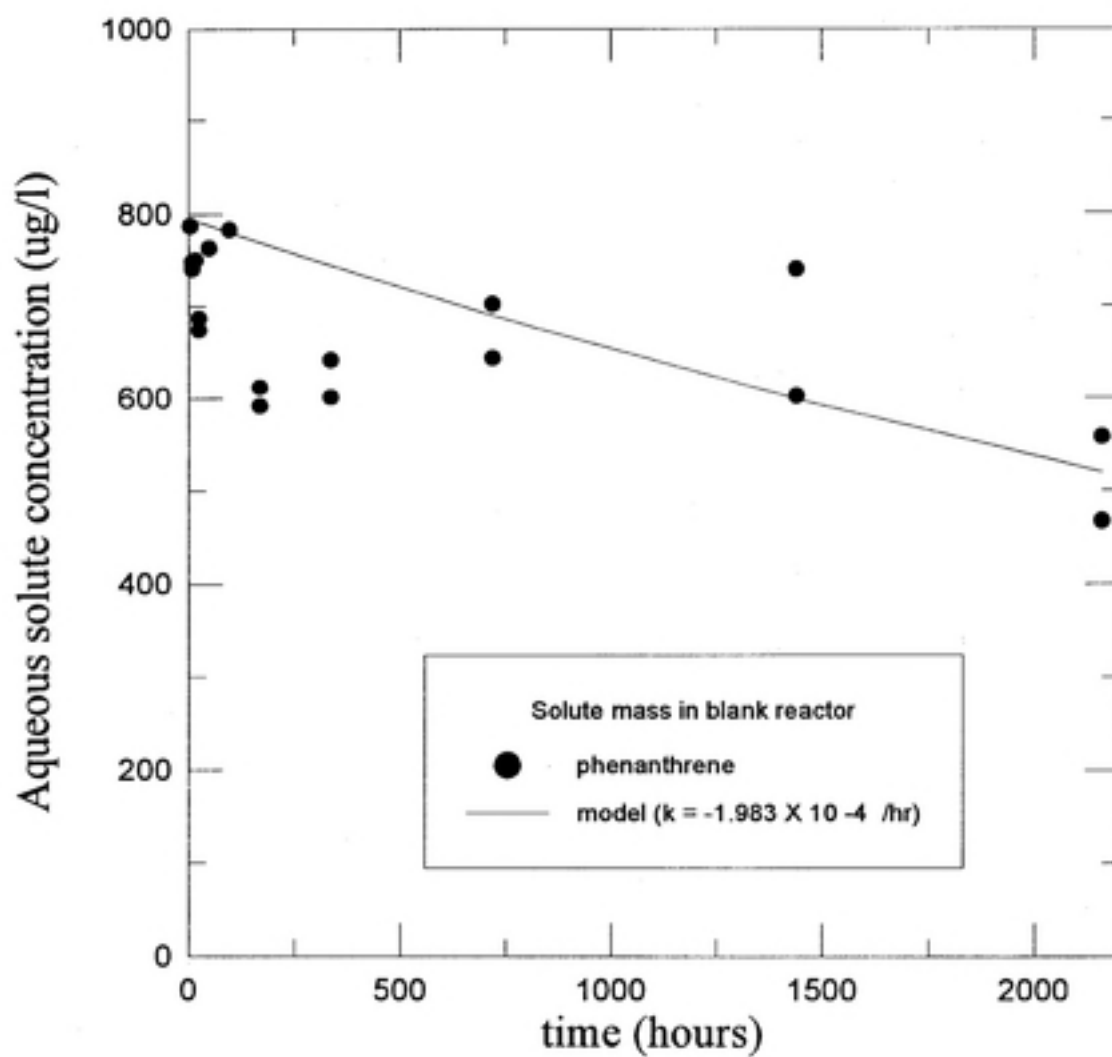
Subject to:  $\alpha_0 = C_0 - \alpha_1 - \alpha_2 \quad (4-4)$

$C_0$  = initial aqueous phase solute concentration (M/L<sup>3</sup>)

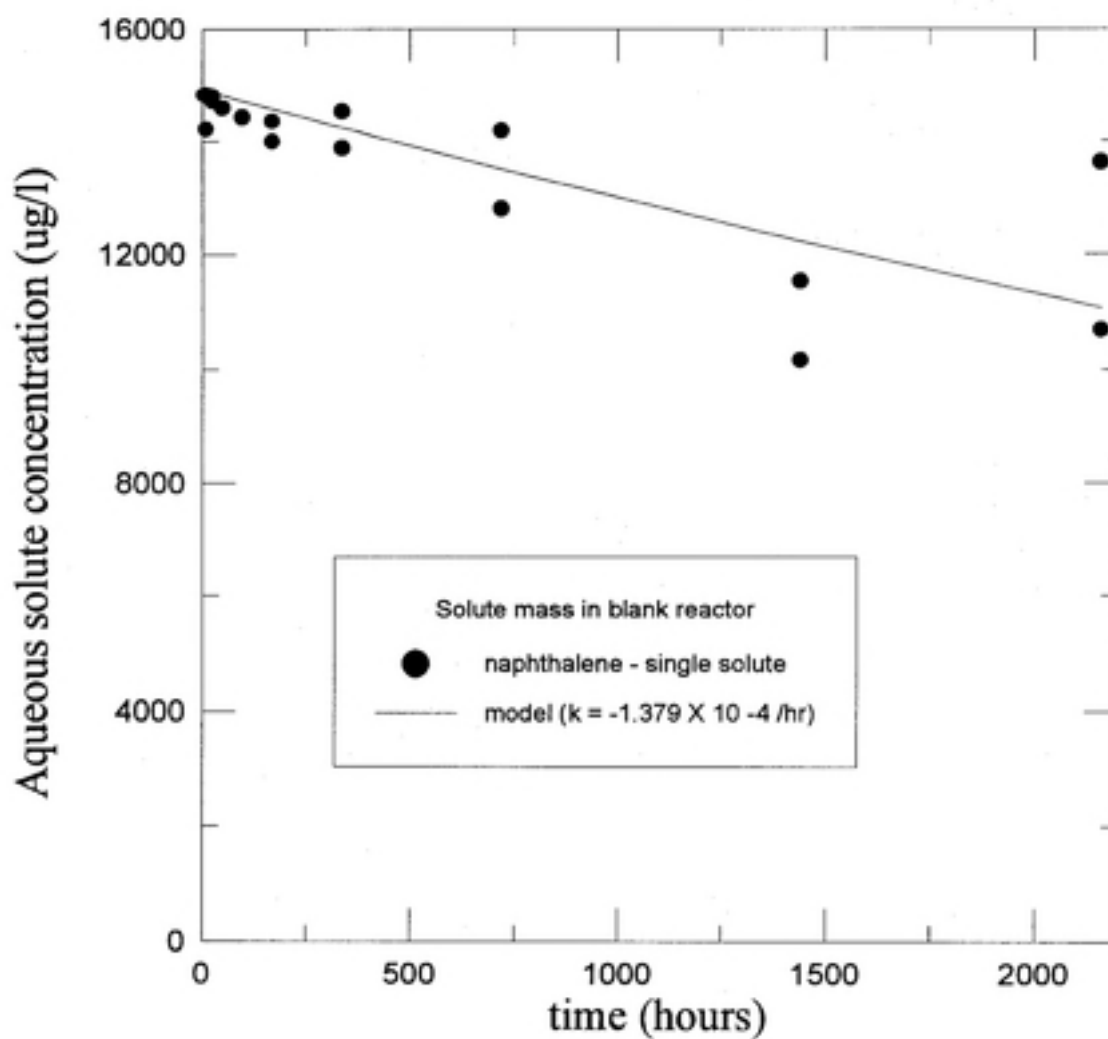
and was solved by minimizing:

$$E = \sum_{i=1}^{np} (C_{m,i} - C_{d,i})^2 \quad (4-5)$$

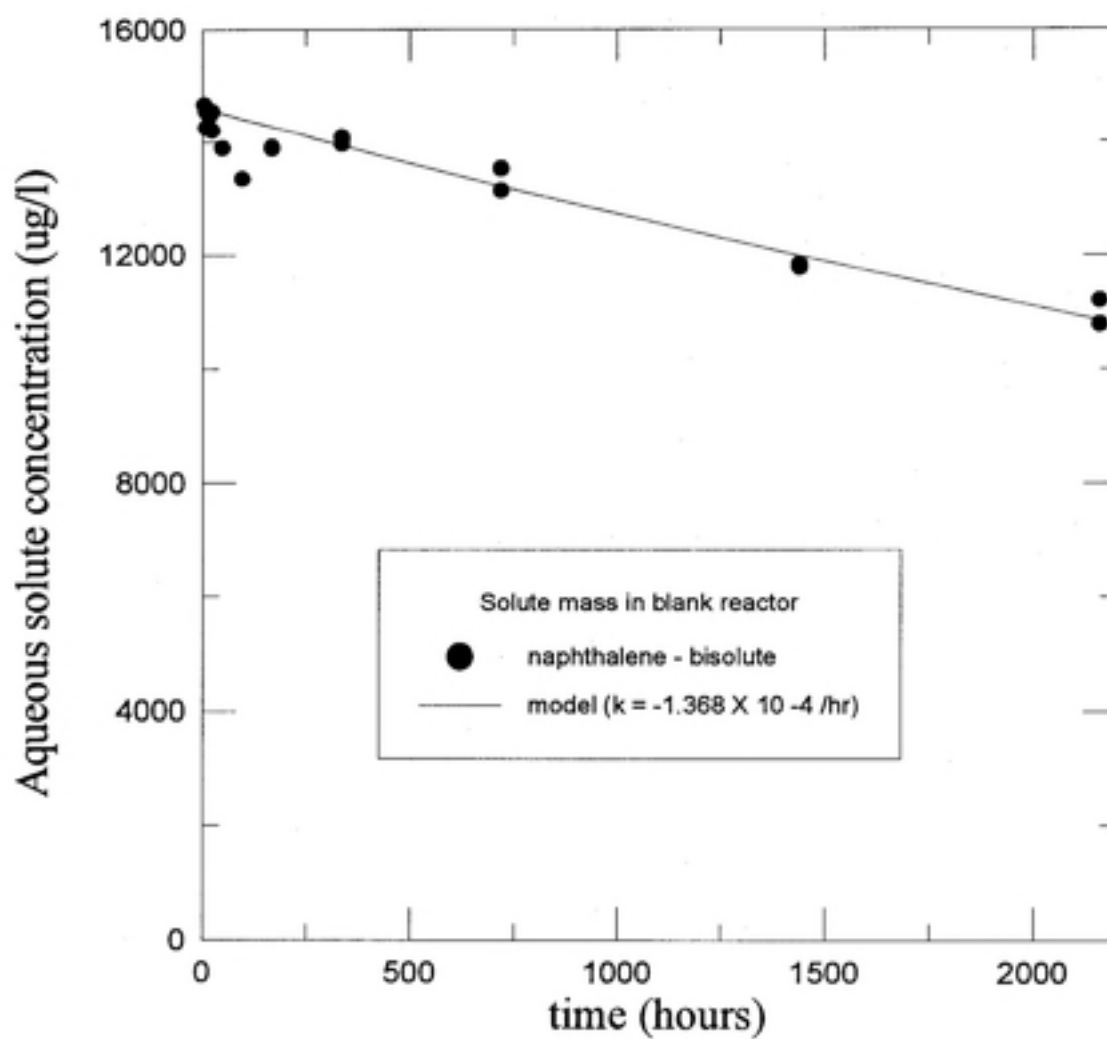
Once an empirical representation of solute loss within the reactor was obtained,



**Figure 4-1:** Phenanthrene (single solute) aqueous phase concentration in blank reactors vs. time



**Figure 4-2:** Naphthalene (single solute) aqueous phase concentration in blank reactors vs. time



**Figure 4-3:** Naphthalene (bisolute) aqueous phase concentration in blank reactors vs. time

solute present in the solid phase could be estimated. Mass of solute present in reactor can be represented as:

$$\frac{dM}{dt} = -kVC \quad (4-6)$$

M = solute mass in system (M)

By substituting C with Equation (4-4):

$$\frac{dM}{dt} = -kV \left[ \alpha_0 + \alpha_1 e^{(-\beta_1 t)} + \alpha_2 e^{(-\beta_2 t)} \right] \quad (4-7)$$

By solving:

$$M = -kV \left[ \alpha_0 t - \frac{\alpha_1}{\beta_1} e^{(-\beta_1 t)} - \frac{\alpha_2}{\beta_2} e^{(-\beta_2 t)} \right] + CI \quad (4-8)$$

CI = constant of integration determined from initial conditions (M)

The mass in the solid phase is then predicted by:

$$M_q = M - CV \quad (4-9)$$

M<sub>q</sub> = mass in solid phase (M/M)

Estimates of the mass present in the system, as well as in the solid phase, led to the consideration that determining the reactor-loss rate coefficient from the mass balances of the reactors with solids might lead to more correct estimates of system dynamics. While the reactors with and without solids are similar, the presence of solids may have had some effect on the completely mixed system. The loss rate coefficient determined from the reactor extraction mass balance data was used in place of the rate coefficients determined from blank (no solids) reactors in the final isotherm corrections. The first-order volatilization rate coefficients determined from both blank reactors and system extractions are tabulated in Table 4.3.

**Table 4.3: Volatilization rate coefficients**

| System                      | k (from blank data) hr <sup>-1</sup> | k (from extraction data) hr <sup>-1</sup> <sup>a</sup> |
|-----------------------------|--------------------------------------|--------------------------------------------------------|
| phenanthrene                | 1.98 X 10 <sup>-4</sup>              | 1.63 X 10 <sup>-4</sup> / no data                      |
| naphthalene (single solute) | 1.38 X 10 <sup>-4</sup>              | 9.83 X 10 <sup>-5</sup> / 1.52 X 10 <sup>-4</sup>      |
| naphthalene (bisolute)      | 1.37 X 10 <sup>-4</sup>              | 1.27 X 10 <sup>-4</sup> / 8.71 X 10 <sup>-5</sup>      |

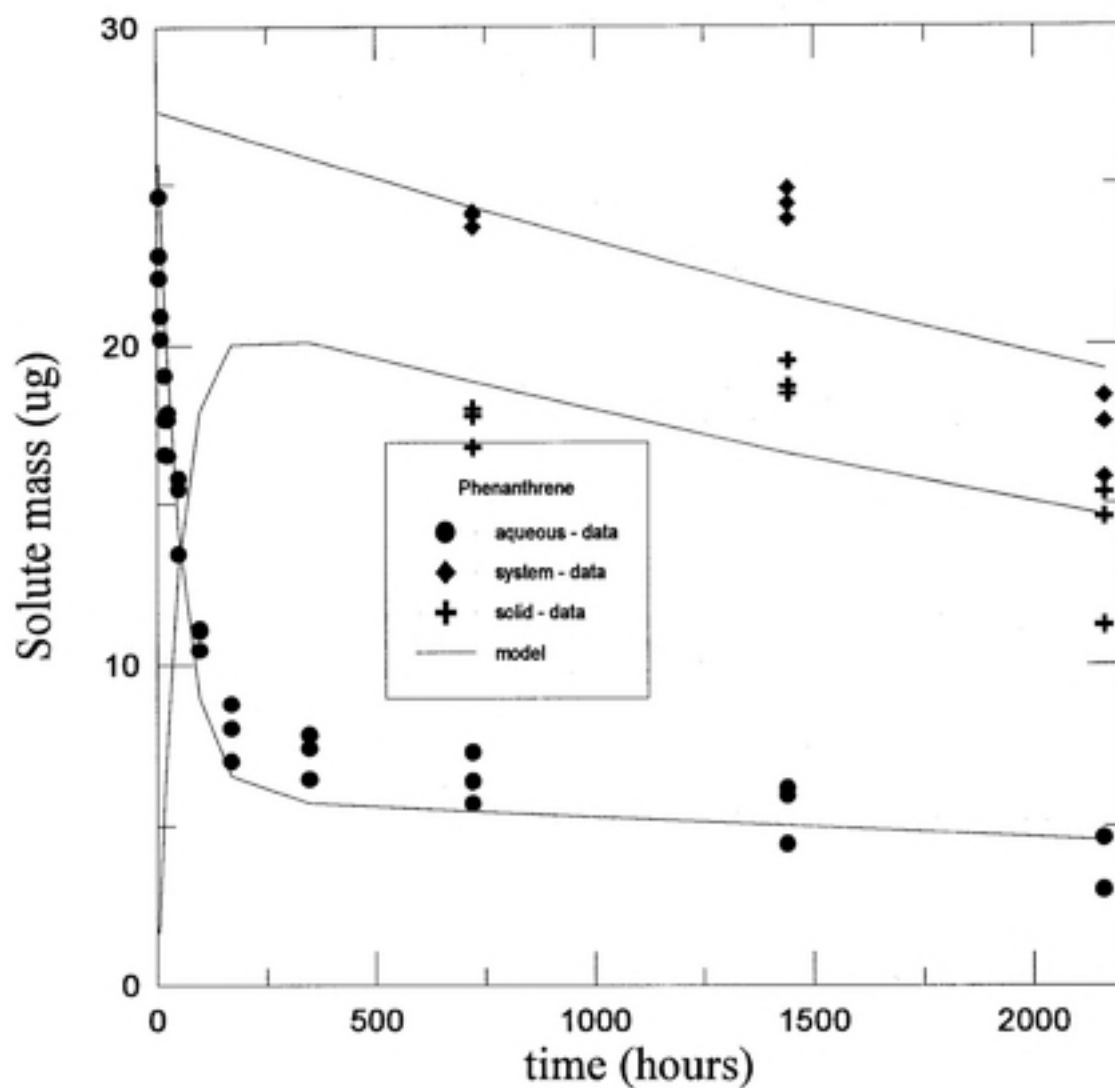
<sup>a</sup>native solids / pulverized solids

A second source of systematic error was also recognized. Consistent differences between blank aqueous phase concentrations and extraction results revealed that a portion of the solute was sorbing to the reactor itself. This fraction of solute was consistent and recoverable by extraction from very early to long-term data. It was concluded that this loss was indeed due to partitioning to the reactor, and was accounted for in all determinations of sorbed concentrations. Table 4.4 summarizes the fractions of solute sorbed to the reactor walls.

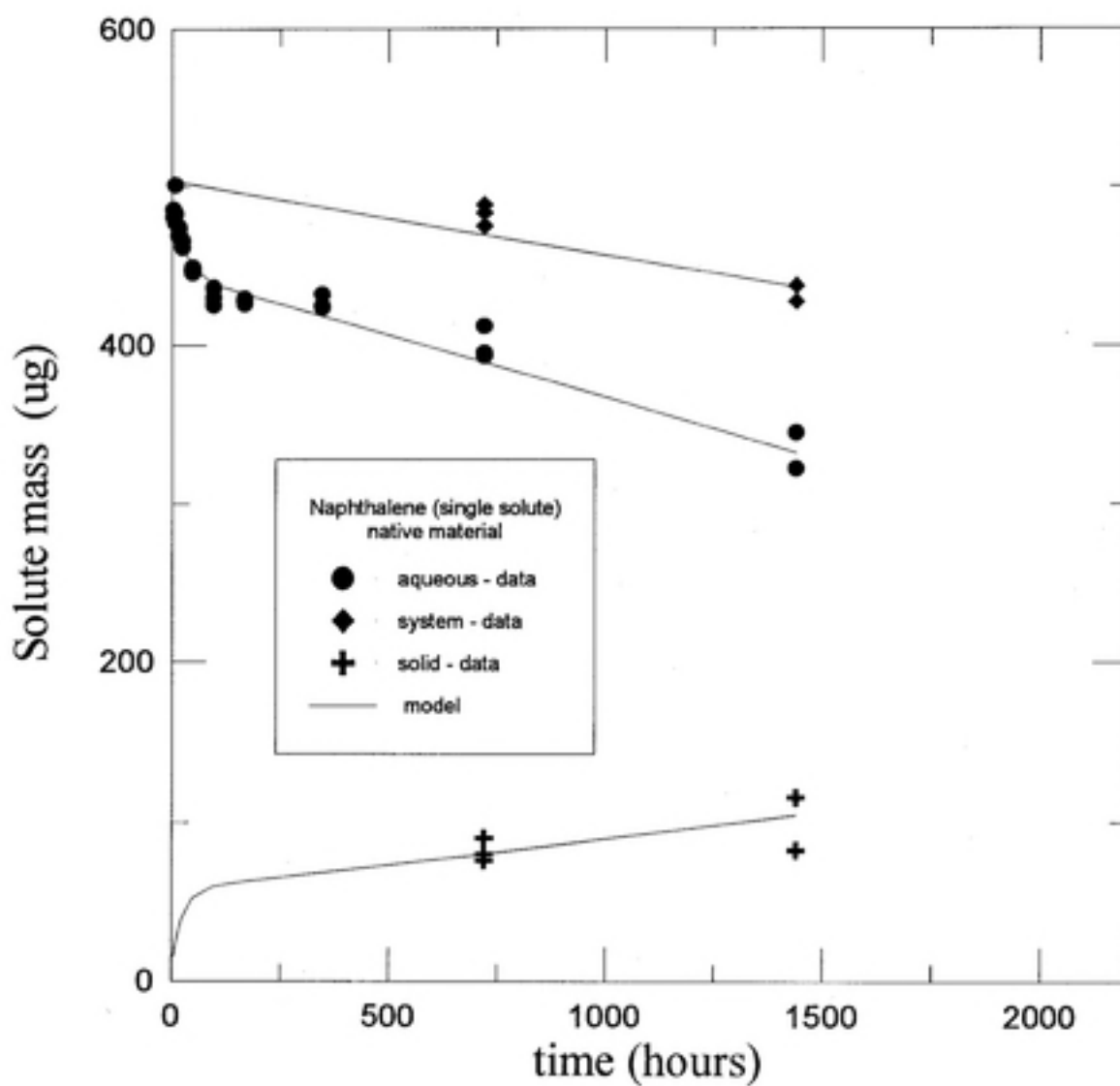
**Table 4.4: Reactor partition coefficients**

| System                      | K <sub>reactor</sub> ± (one standard deviation) L/reactor |
|-----------------------------|-----------------------------------------------------------|
| phenanthrene                | 0.0772 ± (0.0411)                                         |
| naphthalene (single solute) | 0.0326 ± (0.0092)                                         |
| naphthalene (bisolute)      | 0.0325 ± (0.0093)                                         |

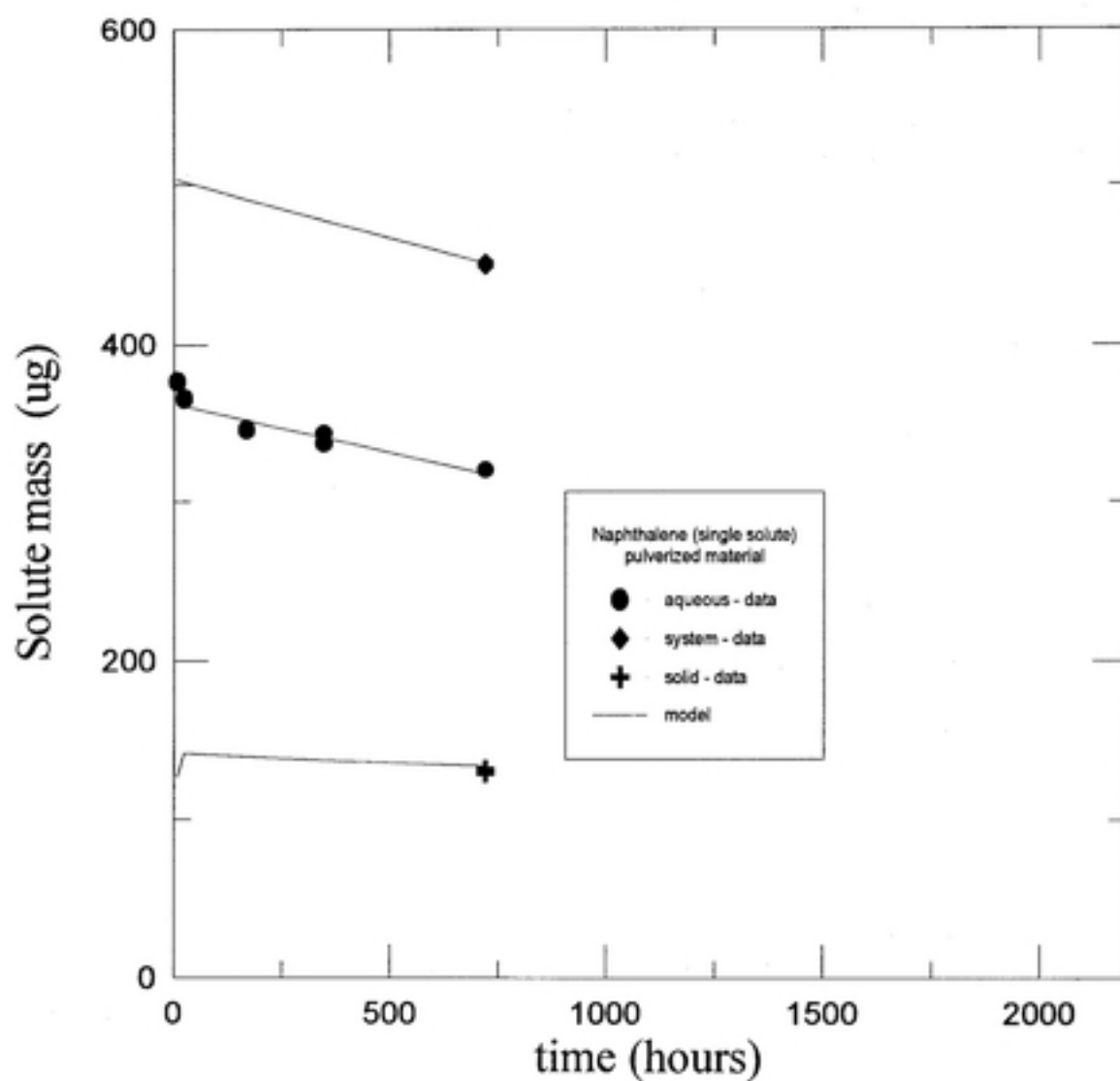
Figures 4.4-4.8 show the experimental data and model predictions for solute mass present in the aqueous and solid phases, as well as within the total system for phenanthrene with native solids, naphthalene (single solute) with native and pulverized solids, and naphthalene (bisolute) with native and pulverized solids, respectively. In the naphthalene (single solute) and naphthalene (bisolute) systems, fits of the data are good, suggesting that the losses from the reactor are being taken into account accurately. In the phenanthrene system, the fit is not as good due to scatter in the data. However, the exhibited trends of mass transfer appear to be reasonably well estimated and should be



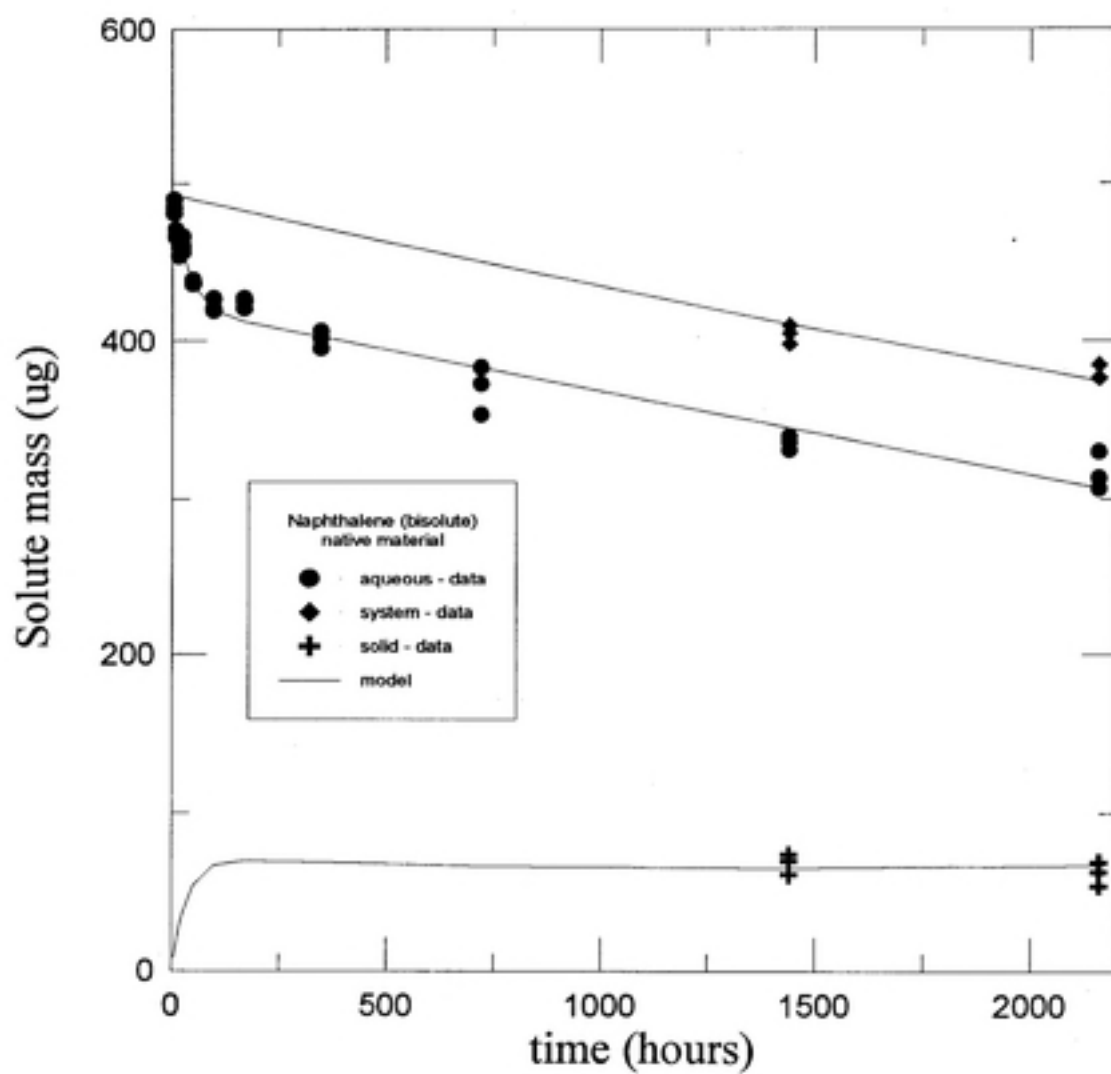
**Figure 4-4:** Mass of phenanthrene (single solute) in system phases from data and model - native material



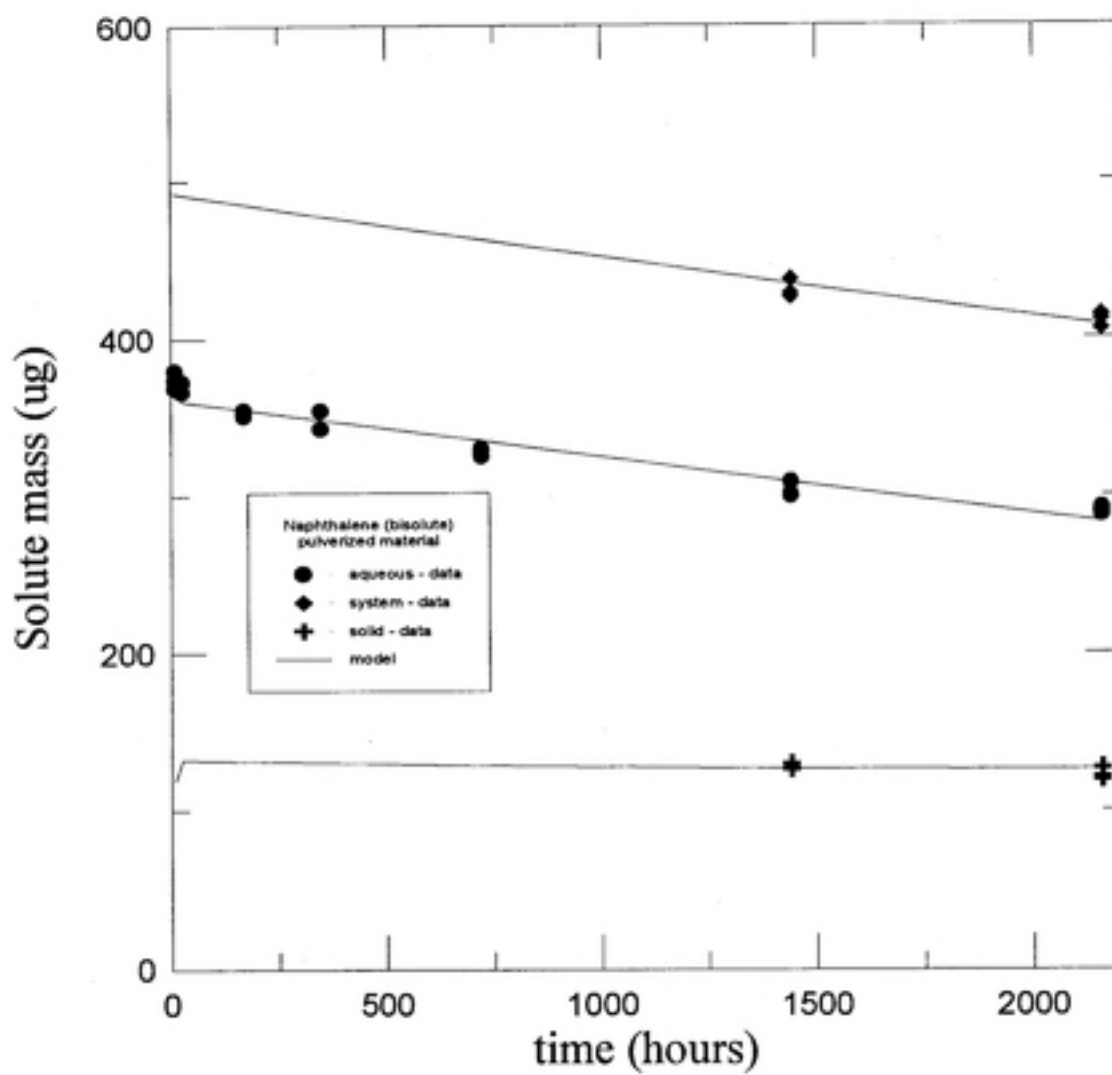
**Figure 4-5:** Mass of naphthalene (single solute) in system phases from data and model - native material



**Figure 4-6:** Mass of naphthalene (single solute) in system phases from data and model - pulverized material



**Figure 4-7:** Mass of naphthalene (bislute) in system phases from data and model - native material



**Figure 4-8:** Mass of naphthalene (bisolute) in system phases from data and model - pulverized material

expected to aid in the estimation of true solid phase concentrations. The information gained through accounting for losses to the reactors was applied to the isotherm data as follows:

$$q = (M - CV - K_r VC) / M_s \quad (4-10)$$

$q$  = solid phase solute concentration (M/M)

$K_r$  = reactor partition coefficient (L<sup>3</sup>/reactor)

$M_s$  = mass of solids in system (M)

### 4.3 Results

#### 4.3.1 Sorption rates

##### Single-solute

Figures 4.9 and 4.10 display the fractional aqueous phase solute concentrations versus time for phenanthrene and naphthalene, respectively. Clearly, phenanthrene sorbed much more strongly than naphthalene. Within days, the aqueous concentration of phenanthrene had decreased to approximately one third of its original value. The pulverized material reduced the aqueous concentration of phenanthrene to a couple percent of its original value prior to the first sampling period at 8 hours. The aqueous phase concentrations of phenanthrene in the system containing a pulverized version of the subsurface material remained very low through 1 month. After 1 month the aqueous phase was below detection limits, preventing quantification of the sorption.

The naphthalene (single solute) system exhibited similar behavior. However, as expected, the magnitude of sorption was not nearly as great. The native material displayed a rapid initial uptake followed by a sustained slow uptake. Meanwhile, the

pulverized material displayed much stronger sorption initially, but the subsequent sorption occurring over an extended period of time was not as significant as in the native material.

#### Multi-solute

The set of rate data for the naphthalene (bisolute) system is the most complete (Figure 4.11). The general rate behavior is very similar to the sorption observed in the single-solute system. However, sorption to both native and pulverized samples is tracked to 3 months. An approach to convergence is observed for the native and pulverized solid systems near the later sampling times.

### **4.3.2 Sorption isotherms**

#### Single-solute

The phenanthrene isotherms show a larger degree of variability than the other systems. However, a general trend in agreement with the rate data can be observed. Isotherms on the native material compared at 1 day, 7 days and 1 month reveal an increase in sorption that is most rapid at early times (Figure 4.12). A comparison of isotherms on native and pulverized solid samples at 1 day (Figure 4.13) reflects the very significant difference in the magnitude of sorption at early times due to the pulverization process previously observed in the rate data.

An examination of the naphthalene (single-solute) isotherms reveals similar characteristics. The mass transfer from the aqueous to the solid phase is most rapid at early times, and the pulverization process significantly increases the sorption capacity of the solid phase at early times (Figures 4.14 and 4.15).

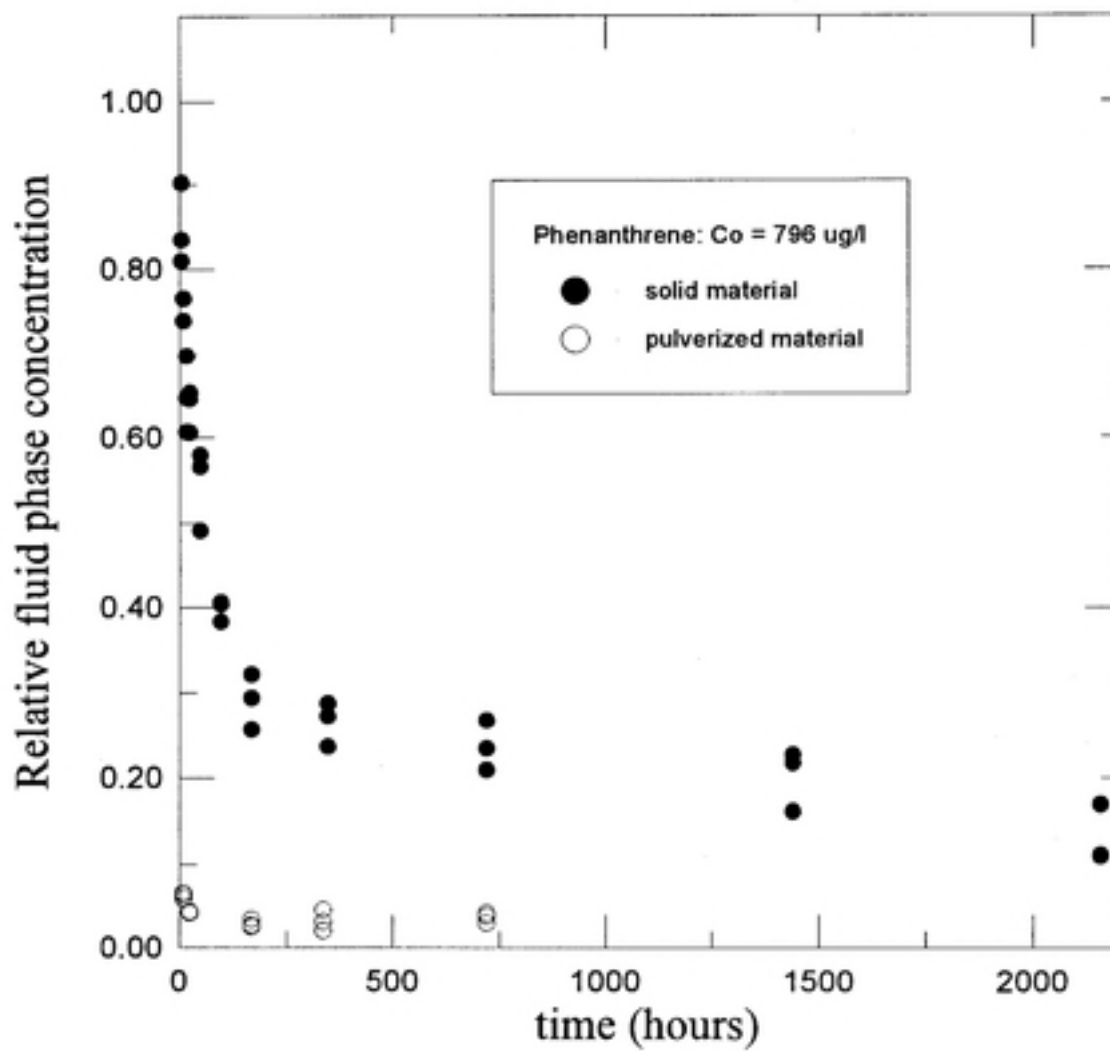


Figure 4-9: Relative phenanthrene (single solute) fluid phase concentration vs. time

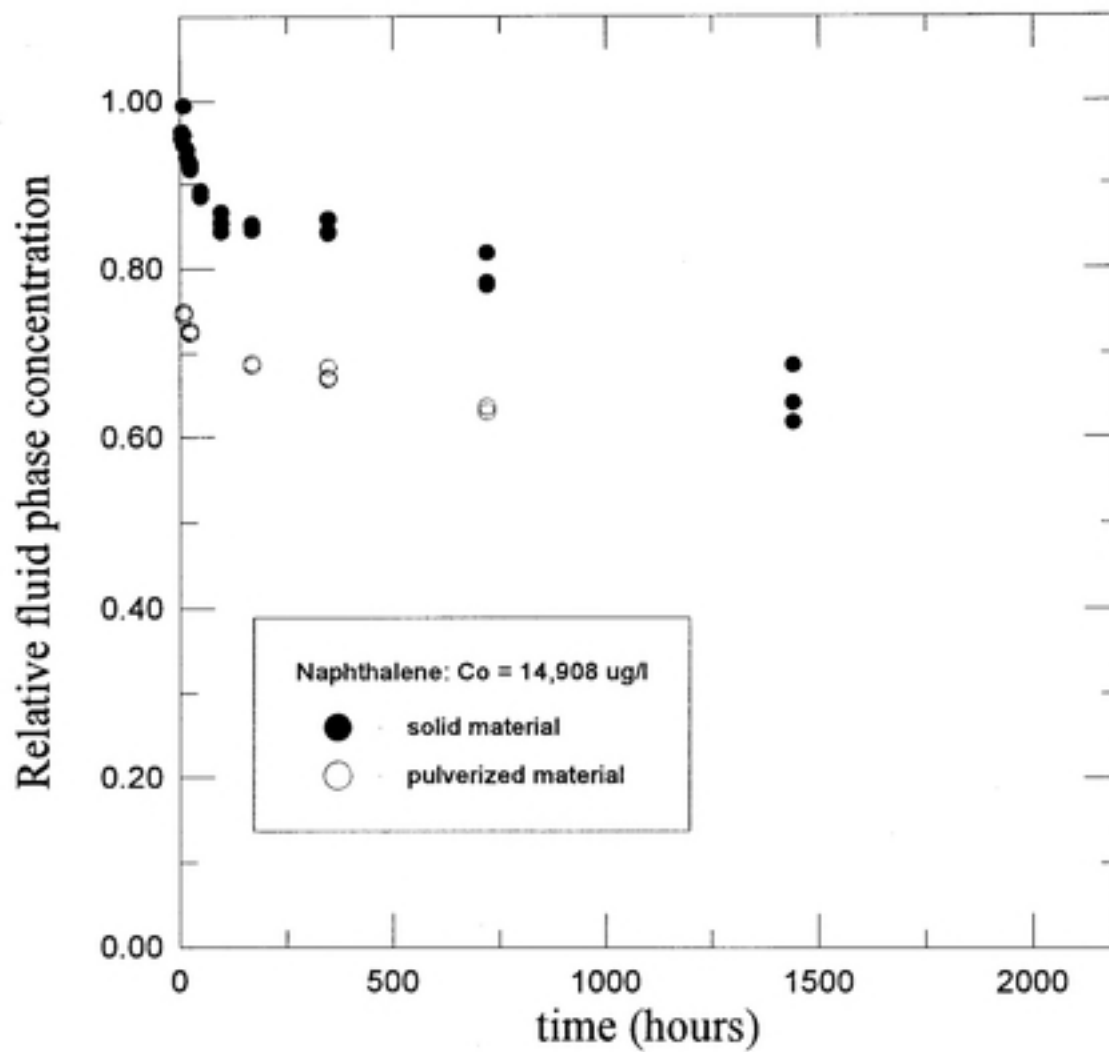


Figure 4-10: Relative naphthalene (single solute) fluid phase concentration vs. time

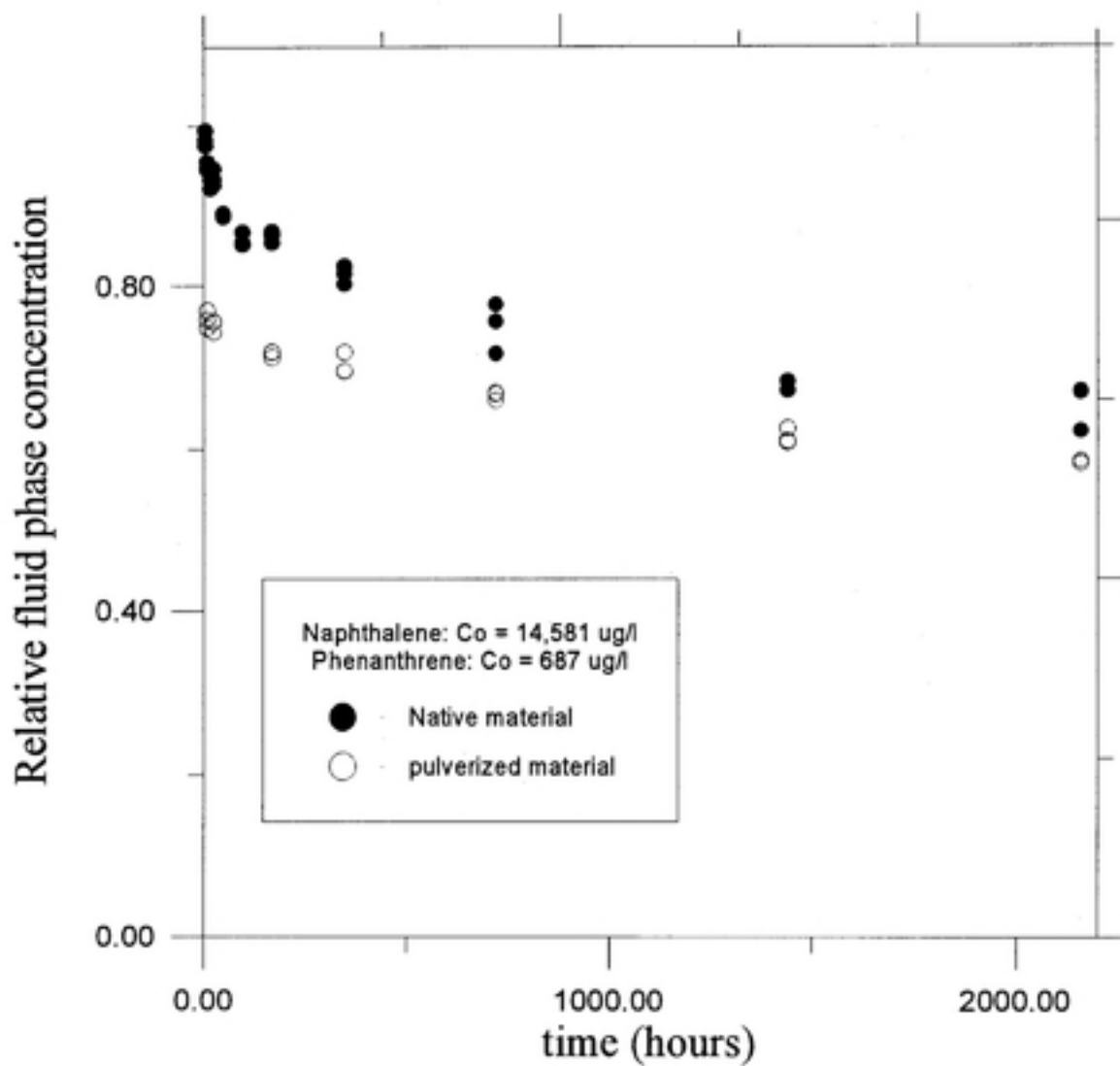
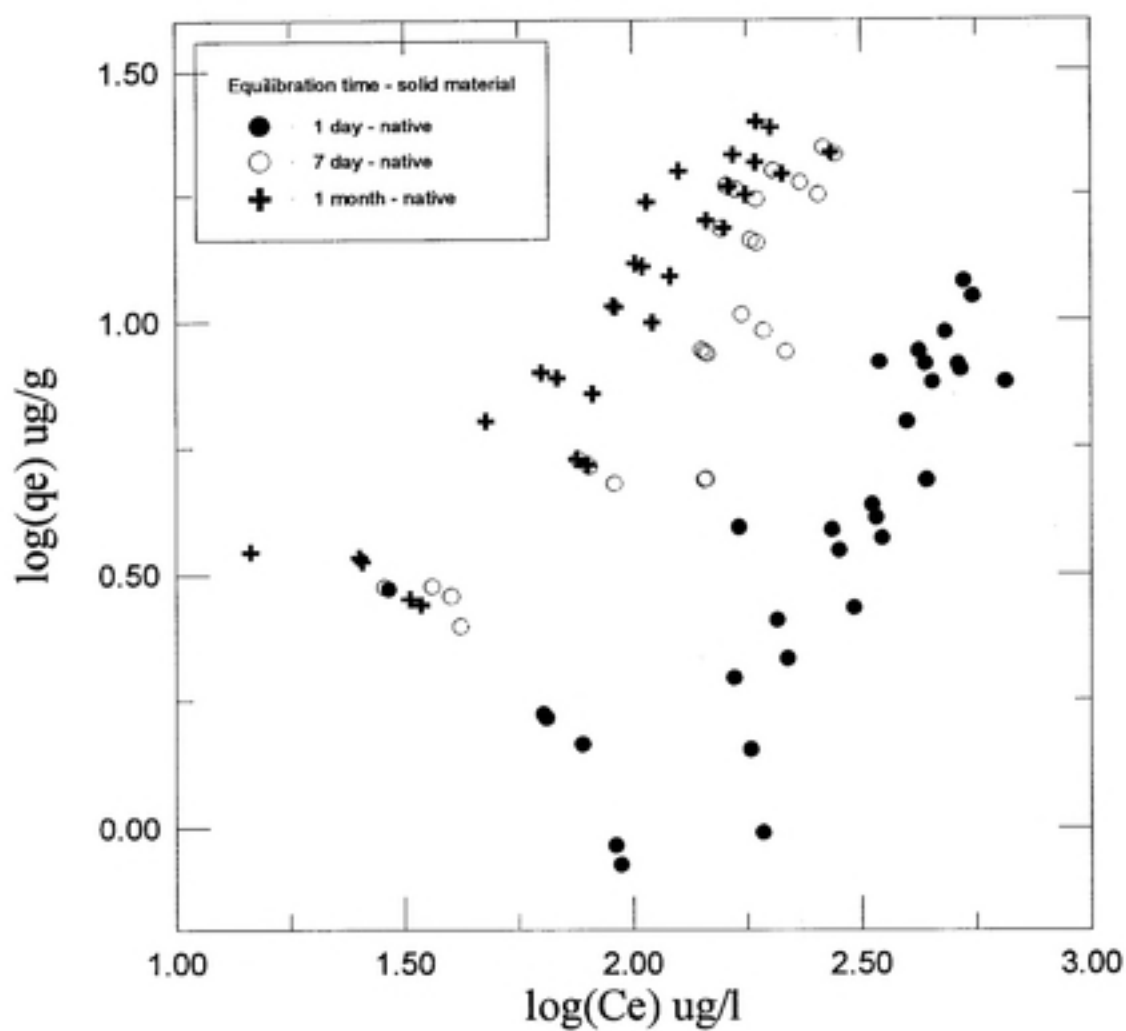
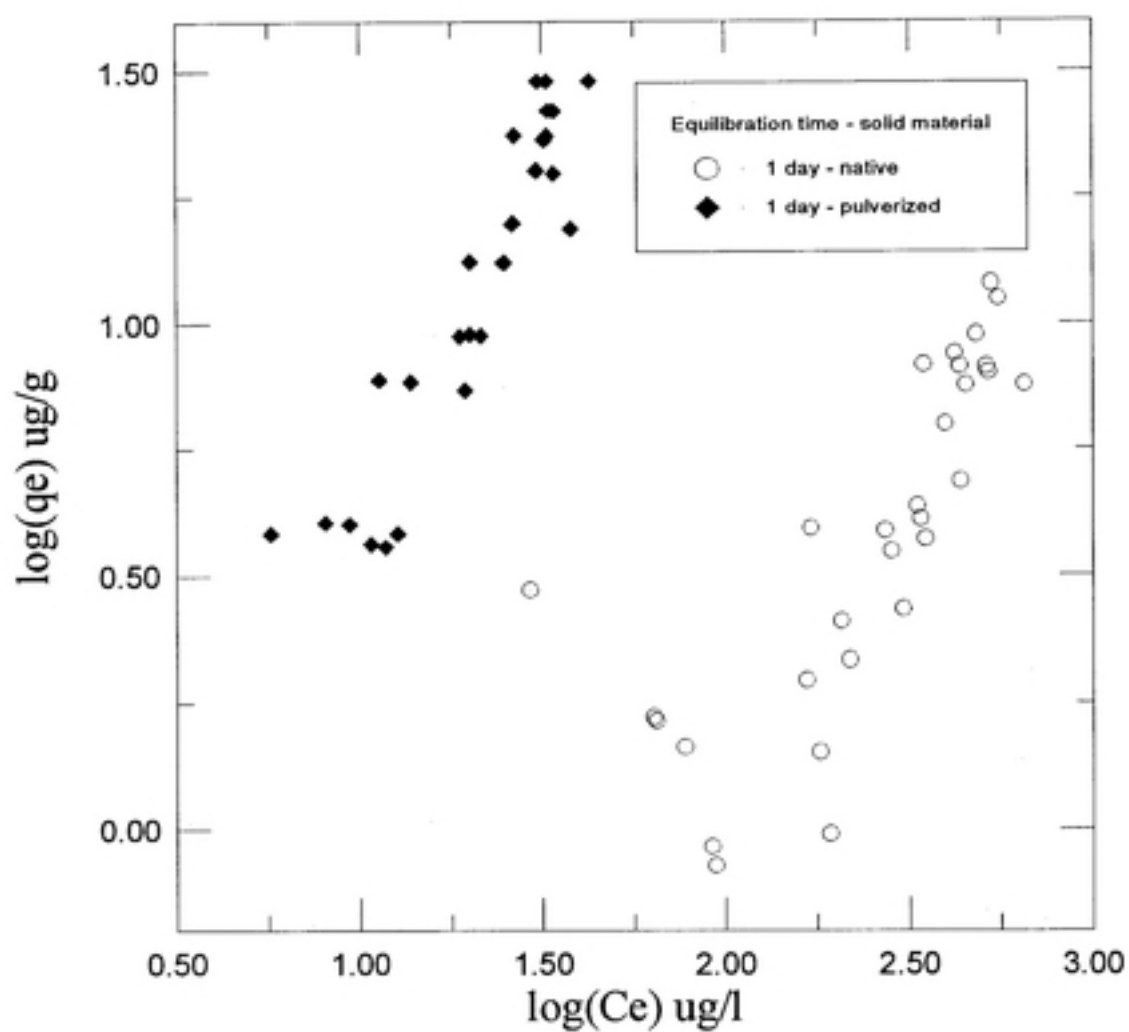
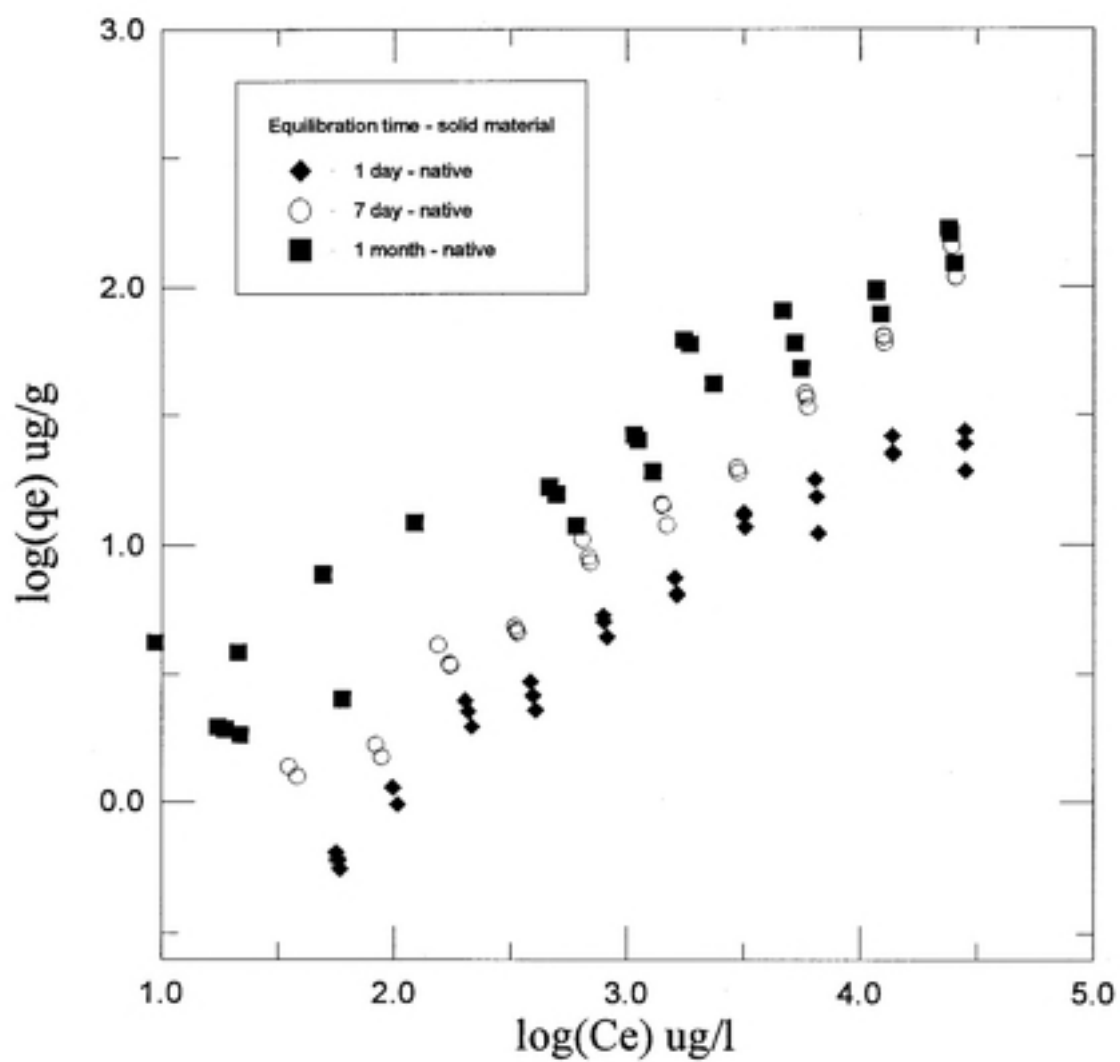


Figure 4-11: Relative naphthalene (bislute) fluid phase concentration vs. time

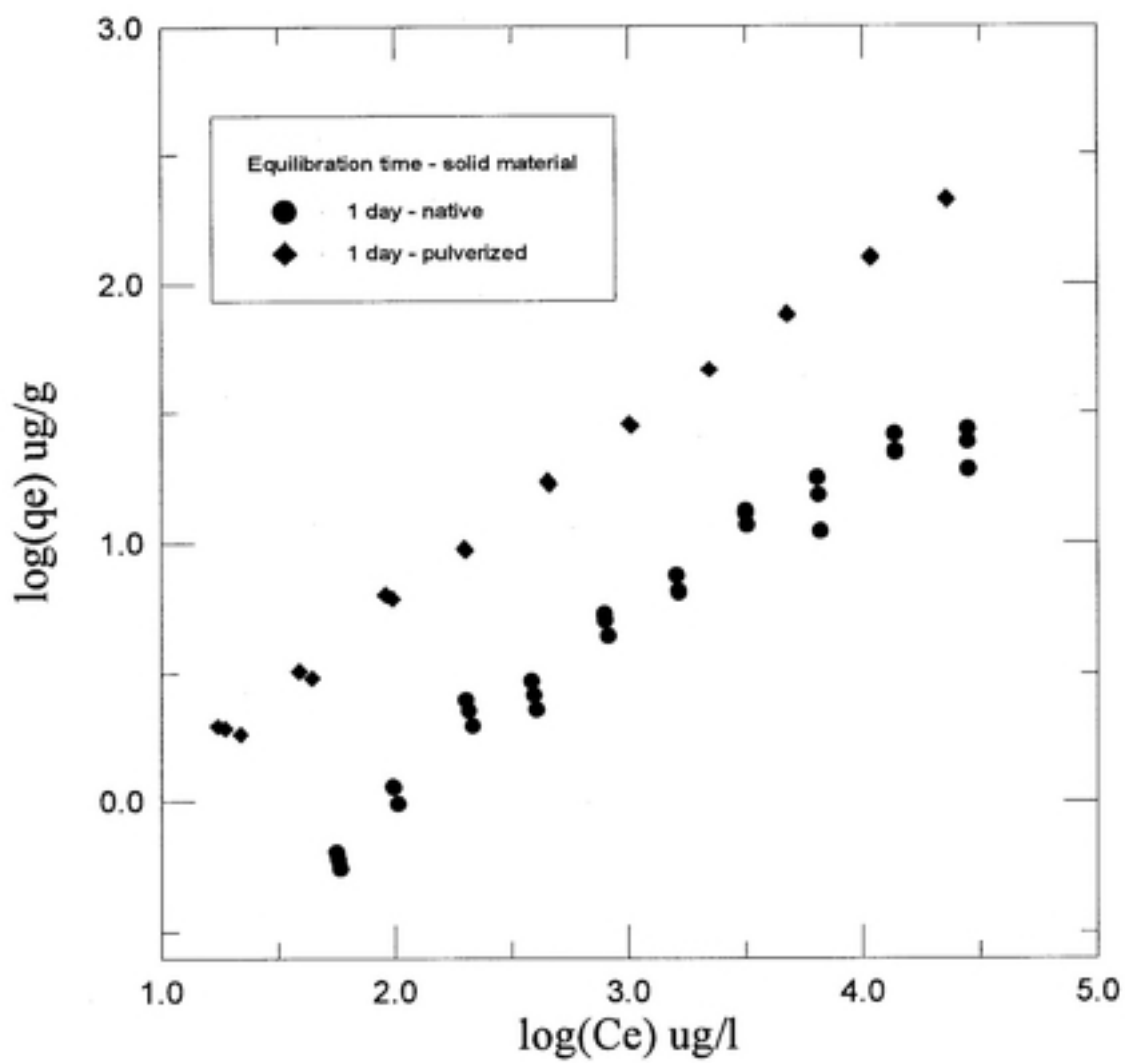




**Figure 4-13:** Phenanthrene (single solute) isotherms at 1 day on native and pulverized material



**Figure 4-14:** Naphthalene (single solute) isotherms on native material at 1 day, 7 days, and 1 month



**Figure 4-15:** Naphthalene (single solute) isotherms at 1 day on native and pulverized material

### Multi-solute

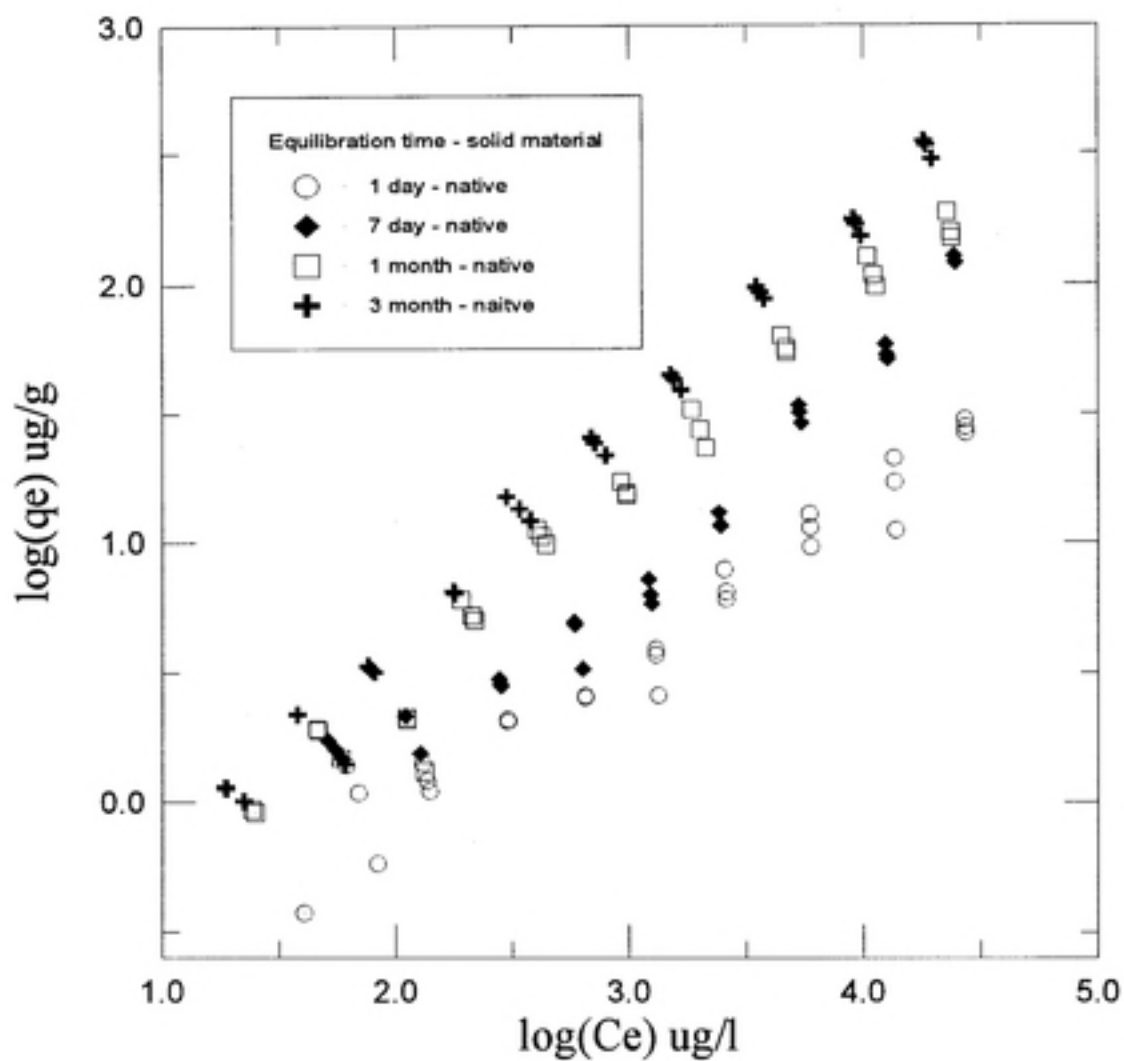
The additional data available in the naphthalene (bisolute) data set allows a clearer view of the isotherm progression over time in both the native and pulverized solid systems (Figures 4.16 and 4.17). It is also evident that the solid phase concentration of the native material at 3 months is approximately an order of magnitude greater than it is at 1 day. A comparison of isotherms on the native and pulverized samples at 1 day and 3 months reveals that while pulverizing the sample greatly increases the sorption at early times, by 3 months the native and pulverized isotherms have nearly converged, suggesting that while pulverizing the solid material increases the rate of sorption, it does not necessarily increase the magnitude of sorption observed as equilibrium is approached (Figure 4.18).

## **4.4 Discussion**

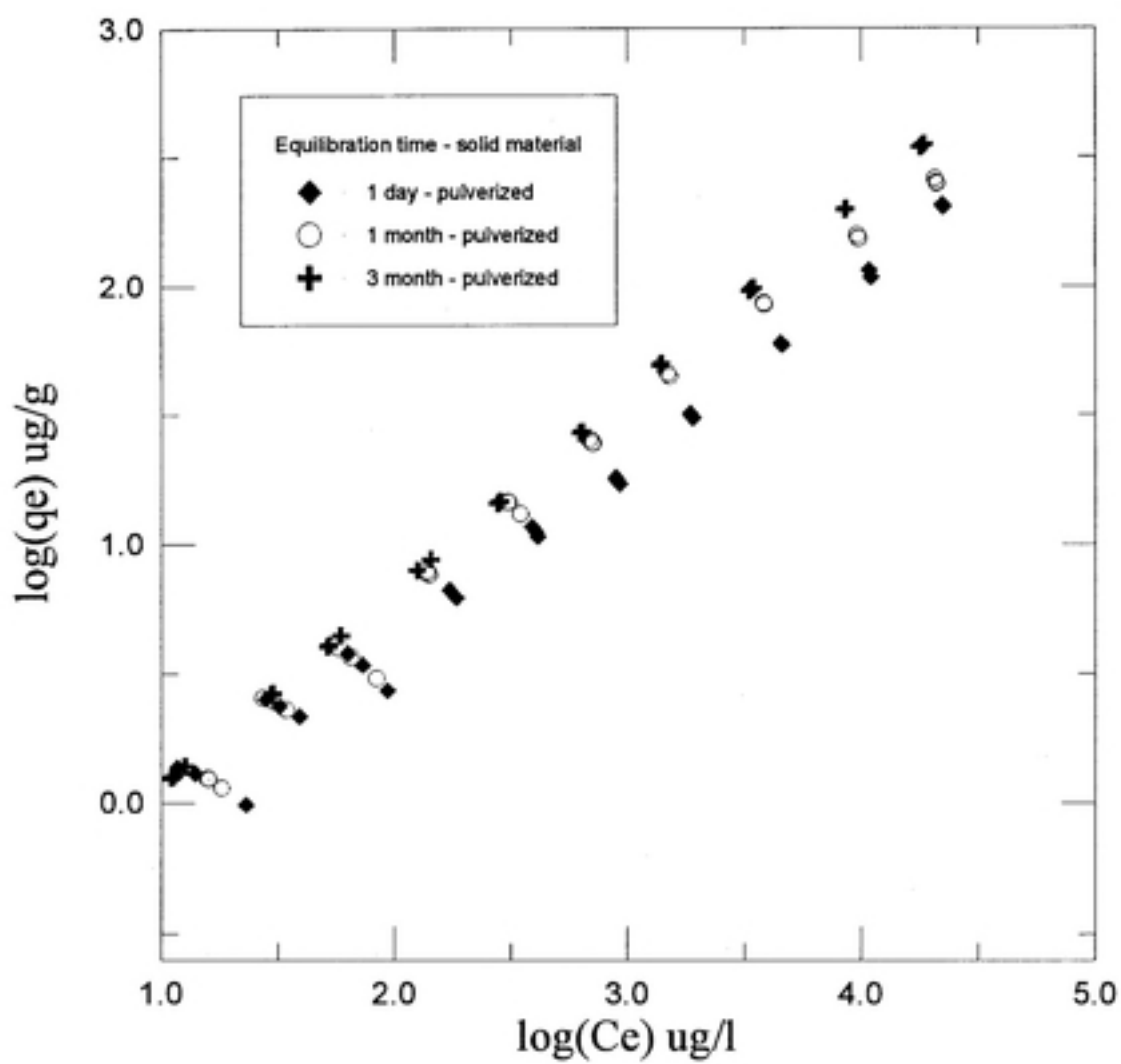
### **4.4.1 Sorption rates**

#### Single-solute

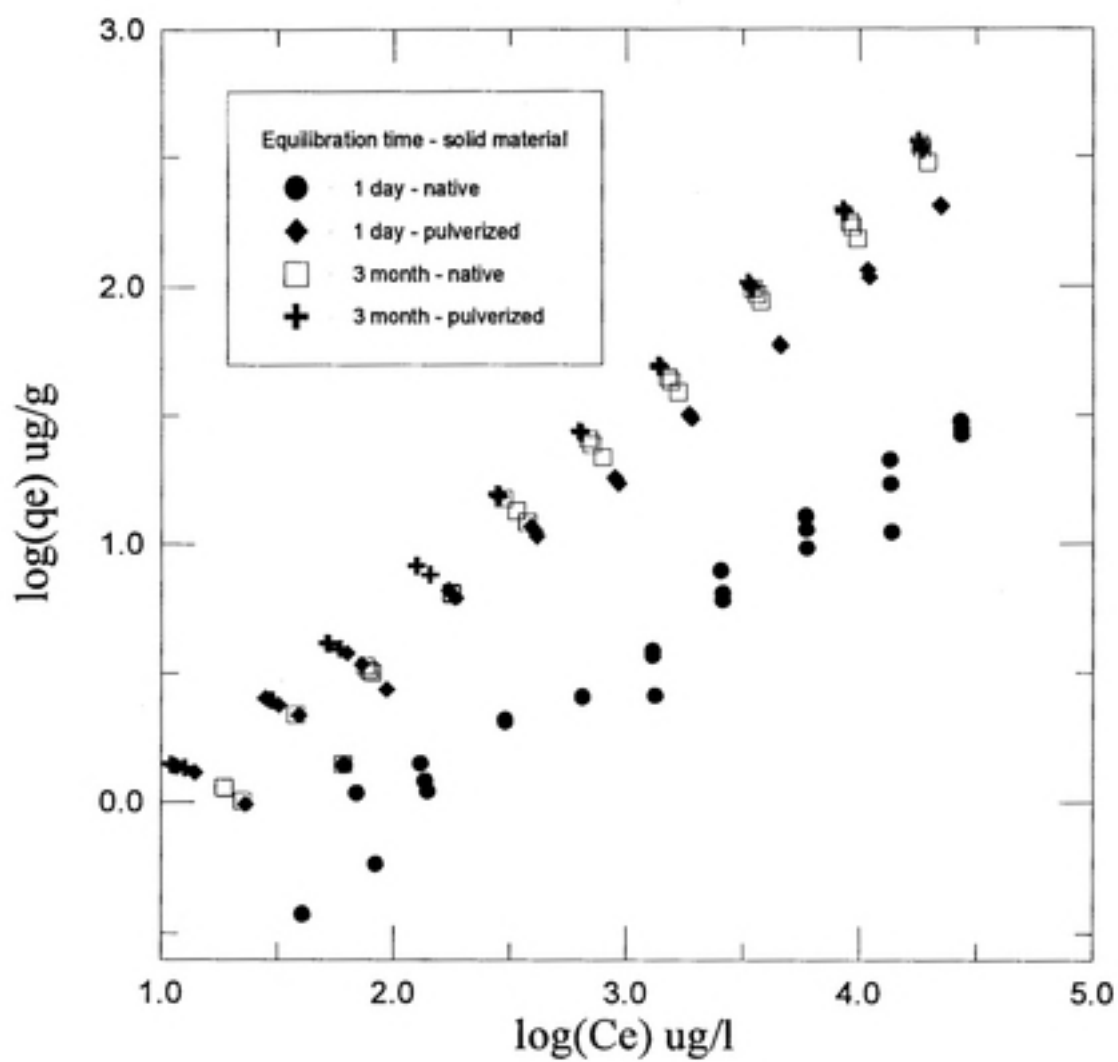
One would expect phenanthrene, which has an octanol-water partition coefficient an order of magnitude larger (Table 3.1), and is less soluble than naphthalene, to sorb much more strongly to the solid material. This behavior is evident in these experiments. In a diffusion limited sorption process, more strongly sorbing compounds would be expected to exhibit a slower approach to equilibrium due to greater retardation of intra-particle diffusion caused by increased sorption to pore walls or intra-particle organic carbon. Losses from the reactors, described in more detail in section 4.2, have complicated the task of determining which losses from the aqueous phase are due to



**Figure 4-16:** Naphthalene (bisolute) isotherms on native material at 1 day, 7 days, 1 month, and 3 months



**Figure 4-17:** Naphthalene (bisolute) isotherms on pulverized material at 1 day, 1 month, and 3 months



**Figure 4-18:** Naphthalene (bisolute) isotherms at 1 day and 3 months on native and pulverized material

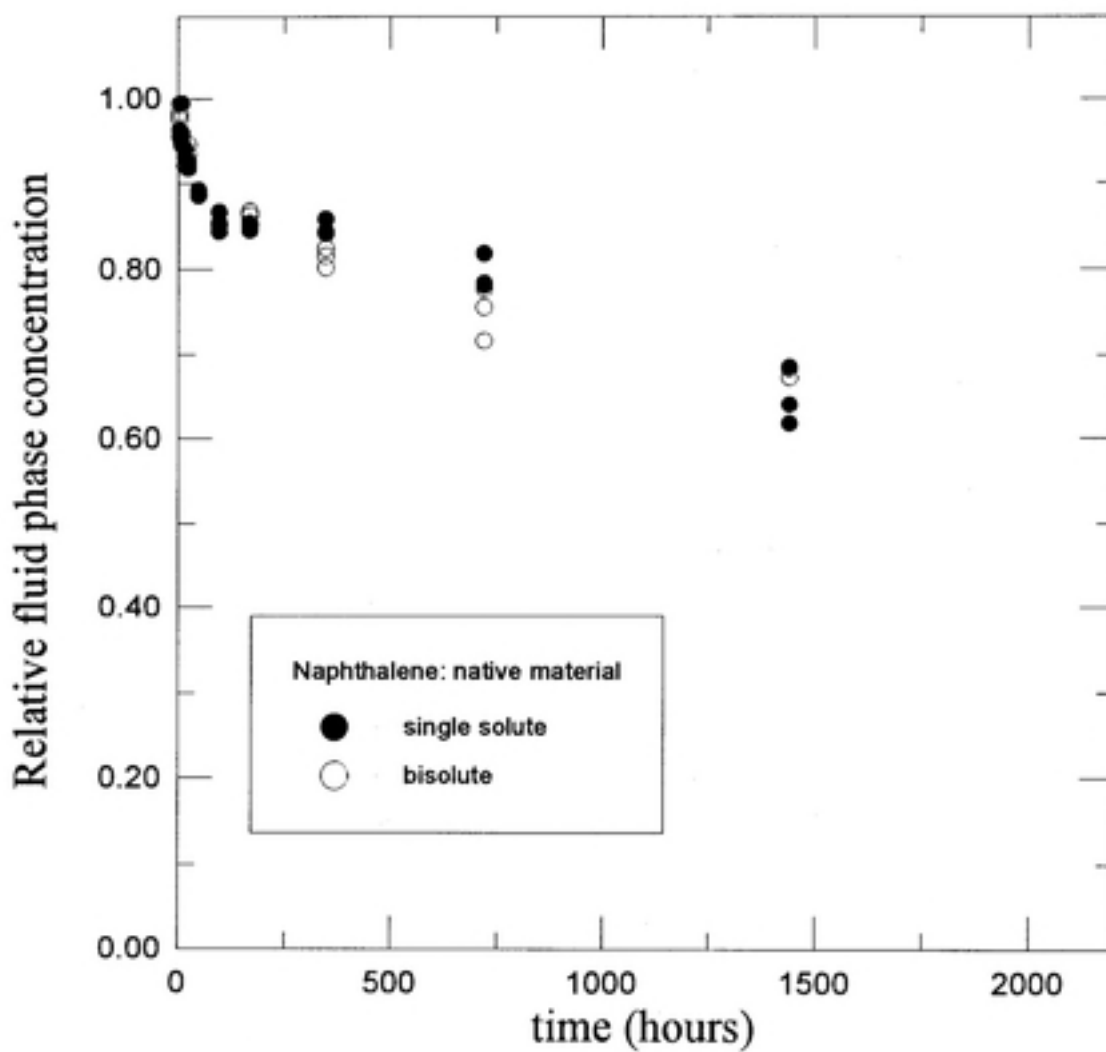
sorption, and which losses are due to other processes. The data does not give a clear indication of the sorption rate differences between naphthalene and phenanthrene, or at what time period the single solute systems have finally reached equilibrium (Figures 4.9 and 4.10).

Assuming diffusion is the rate limiting process, longer diffusion paths would require more time to be traversed. Reduction in particle size should have the effect of reducing diffusion path lengths and increasing the rate of attainment of equilibrium. In the work by Ball and coworkers (Ball, 1989; Ball and Roberts, 1991a,b), a low organic carbon aquifer material (from Borden, Ontario) was pulverized in a shatterbox so that 98% of soil particles were smaller than 0.040 mm in diameter. The solutes used in this study were tetrachloroethene (PCE), and 1,2,4,5-tetrachlorobenzene (TeCB). The log of their octanol-water partition coefficients are 2.7 and 4.5, respectively. Pulverization of the samples greatly increased the rate of approach to equilibrium for both compounds. However, TeCB, the more strongly sorbing compound took much longer to reach equilibrium than PCE. Even on pulverized samples, while PCE reached equilibrium after several days, TeCB required 30 to 60 days. This decrease in the rate of the more strongly sorbing compound was likely due to a reduced apparent rate of diffusion caused by increased sorption to pore walls. In this study, the increase in uptake due to pulverizing the solid material is seen in the single solute systems. However, only the bisolute system yielded data through 3 months for both the native and solid material systems. The sorption occurring in both systems appears to be converging at later times, suggesting that only the rates, rather than the sorption capacities, are changed by the pulverization process.

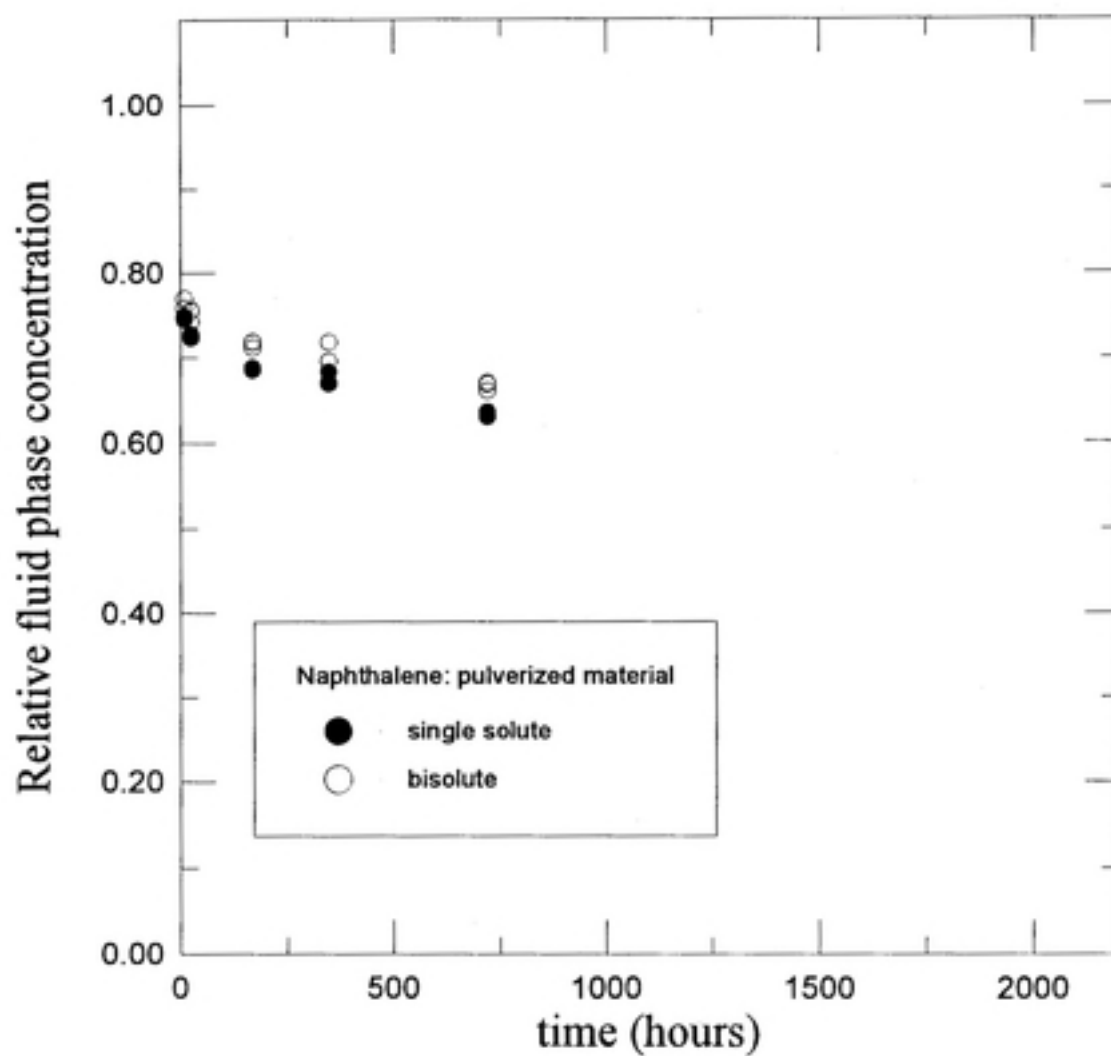
### Multi-solute

The sorption occurring due to both the native and pulverized samples in the bisolute system (Figure 4.11) appear to be approaching convergence at extended time periods, suggesting that equilibrium is being approached and that the mass of solute sorbed at equilibrium may not be significantly changed by pulverizing the soil, as suggested by other researchers (Ball, 1989; Ball and Roberts, 1991a,b). However, the rate at which this equilibrium is approached is much more rapid in the cases involving pulverized material samples. Because the main difference between the native and pulverized solid materials is particle diameter, this initial increase in sorption due to the pulverization of the solid material accompanied by an eventual approach to convergence of the native and pulverized samples supports diffusion as the mechanism limiting the approach to equilibrium.

The rate data were examined for evidence of competitive effects during the sorption process. The naphthalene single solute and bisolute rate data were normalized by the initial concentrations in order to compare the data directly. Figure 4.19 contains the rate data for the native soil through 2 months, and Figure 4.20 contains the rate data for the pulverized soil through 1 month. If competition were occurring, one would expect a decrease in the amount of sorbed naphthalene as in the presence of the more strongly sorbing phenanthrene. Differences between the systems are not evident in the native solids system. The systems containing pulverized solids show some suppression of the sorption of naphthalene in the presence of phenanthrene. Even in systems where differences are seen in the rate data between single and bisolute systems, these data alone are not sufficient to conclude that competitive effects will be observed in the final equilibrium results. While this is one possibility, it is also possible that the competitive effect observed here is a transient phenomenon due to influences from the additional solute.



**Figure 4-19:** Relative naphthalene (single and bisolute) fluid phase concentration vs. time on native material



**Figure 4-20:** Relative naphthalene (single and bisolute) fluid phase concentrations vs. time on pulverized material

#### 4.4.2 Sorption isotherms

The linear, Langmuir and Freundlich isotherm models described in Chapter 2 were fitted to all of the isotherms and compared for accuracy of fit. Because the experiments were designed so that the results would be approximately evenly spaced in log-log format for ease of comparison across wide concentration ranges, determining isotherm parameters by minimizing the squared error, or squared relative error, would have biased the results toward the lower concentrations. A weighted least squares method was employed in which more emphasis was placed upon the data that exhibited less relative variance.

$$\text{Minimize: } MSWE = \frac{1}{v} \sum_{i=1}^{n_p} (q_i - q_i')^2 w_i \quad (4-11)$$

$n_p$  = number of data points

$v$  = degrees of freedom ( $n_p - 2$ )

$w_i$  = weighting function = average of replicates / variance of replicates

$q_i$  = solid phase concentration (data) (M/M)

$q_i'$  = solid phase concentration (model) (M/M)

This method most strongly weights the results from the replicates that most strongly duplicate one another. This method is applied upon the assumption that the variance of replicates is proportionate to their magnitudes.

The results from this fitting procedure are contained in Table 4.5. Because of the weighting procedure used, the mean squared weighted error can only be used for comparison purposes within an experimental set. However, this error is consistently lowest when the isotherm data is represented by the Freundlich model. In addition to fitting the data better than the other two models tested, the Freundlich model offers some additional advantages. The Freundlich equation can be linearized by log transforming the

Table 4.5: Fitted isotherm parameters for linear, Langmuir and Freundlich models

| Experiment Description |                   |            |                            | Linear Model          |         | Langmuir Model |                       |        | Freundlich Model          |      |        |
|------------------------|-------------------|------------|----------------------------|-----------------------|---------|----------------|-----------------------|--------|---------------------------|------|--------|
| Primary Solute         | Background Solute | Solid      | Equilibrium Period (hours) | $K_p$ (L/g)           | MSWE    | $Q^o$ (ug/g)   | $b$ (L/ug)            | MSW E  | $K_f$ (L/ug) <sup>n</sup> | n    | MSWE   |
| phenanthrene           |                   | native     | 24                         | $1.53 \times 10^{-2}$ | 23      | 9021.5         | $1.69 \times 10^{-6}$ | 23     | 0.920                     | 0.30 | 56     |
| phenanthrene           |                   | native     | 168                        | $3.69 \times 10^{-2}$ | 5438    | 9288.8         | $3.97 \times 10^{-6}$ | 5666   | $5.14 \times 10^{-5}$     | 2.31 | 4217   |
| phenanthrene           |                   | native     | 720                        | $1.14 \times 10^{-1}$ | 182     | 80.8           | $1.69 \times 10^{-3}$ | 135    | 0.198                     | 0.88 | 136    |
| phenanthrene           |                   | pulverized | 24                         | $8.27 \times 10^{-1}$ | 1044482 | 51.3           | $3.85 \times 10^{-2}$ | 586281 | 6.167                     | 0.44 | 634628 |
| naphthalene            |                   | native     | 24                         | $1.61 \times 10^{-3}$ | 297     | 28.9           | $2.41 \times 10^{-4}$ | 20     | 0.106                     | 0.56 | 48     |
| naphthalene            |                   | native     | 168                        | $5.35 \times 10^{-3}$ | 555     | 145.3          | $5.90 \times 10^{-5}$ | 270    | 0.060                     | 0.73 | 78     |
| naphthalene            |                   | native     | 720                        | $7.17 \times 10^{-3}$ | 282     | 157.2          | $1.59 \times 10^{-4}$ | 118    | 0.495                     | 0.56 | 85     |
| naphthalene            |                   | pulverized | 24                         | $1.90 \times 10^{-2}$ | 295248  | 291.6          | $8.59 \times 10^{-5}$ | 8869   | 0.328                     | 0.64 | 166    |
| naphthalene            | phenanthrene      | native     | 24                         | $2.00 \times 10^{-3}$ | 2927    | 35.0           | $1.24 \times 10^{-4}$ | 162    | 0.045                     | 0.63 | 55     |
| naphthalene            | phenanthrene      | native     | 168                        | $5.06 \times 10^{-3}$ | 181     | 4783.5         | $1.08 \times 10^{-6}$ | 187    | 0.010                     | 0.93 | 163    |
| naphthalene            | phenanthrene      | native     | 720                        | $9.24 \times 10^{-3}$ | 565     | 240.3          | $7.89 \times 10^{-5}$ | 136    | 0.099                     | 0.74 | 79     |
| naphthalene            | phenanthrene      | native     | 2160                       | $2.37 \times 10^{-2}$ | 3045    | 491.4          | $7.20 \times 10^{-5}$ | 438    | 0.084                     | 0.84 | 201    |
| naphthalene            | phenanthrene      | pulverized | 24                         | $9.80 \times 10^{-3}$ | 4805    | 481.0          | $3.23 \times 10^{-5}$ | 861    | 0.100                     | 0.76 | 158    |
| naphthalene            | phenanthrene      | pulverized | 720                        | $1.87 \times 10^{-2}$ | 33590   | 384.4          | $7.56 \times 10^{-5}$ | 2301   | 0.331                     | 0.67 | 415    |
| naphthalene            | phenanthrene      | pulverized | 2160                       | $2.80 \times 10^{-2}$ | 37228   | 386.1          | $1.22 \times 10^{-4}$ | 9247   | 0.191                     | 0.77 | 309    |

data. The Freundlich parameters can be found by performing a linear regression through the logged data. This method of determining the Freundlich parameters distributes the error uniformly, appropriate with the assumption that the variance in the solid phase concentration is proportionate to the solid phase concentration (Bowman et al., 1984). Freundlich isotherm parameters were determined for all isotherms by this method. Table 4.6 summarizes the results of these fits, as well as the mean square error and the coefficients of determination of the linear regressions performed on the log transformed data.

The variance of the replicates is much smaller in the isotherms conducted on pulverized material. This suggests heterogeneity in the soil is eliminated when the soil is pulverized and mixed.

The linearity of the sorption isotherms, represented by the Freundlich exponent  $n$ , shows a weak tendency to increase over time. As the shape of the isotherm model becomes more linear,  $n$  approaches one. However, there are several exceptions to this trend that make conclusions regarding changes in the isotherm nonlinearity difficult.

It has been suggested that while nonlinear models may best describe isotherms across a wide range in concentration, a linear model may be satisfactory at low concentrations (Weber et al., 1991). Linear regressions were performed on the naphthalene single-solute and bisolute data (not log transformed) with aqueous phase concentrations below 1 mg/l. Table 4.7 summarizes these results. The best regressions were observed on the pulverized samples, reflecting the decrease in heterogeneity achieved during the pulverization process. In general, the data continued to exhibit some nonlinear behavior. The regressions with poorer fits appeared to be due to curvature of the isotherm rather than scatter of data. A representative partial isotherm is supplied in Figure 4.21. However, for estimates over a narrow concentration range, a linear estimation may prove acceptable. The progression of the estimated linear isotherm

Table 4.6: Freundlich isotherm parameters fitted by linear regression of log transformed isotherms

| Primary Solute | Background Solute | Solid      | Equilibration Period (hours) | $K_f$ | 95% confidence interval | n    | 95% confidence interval | RMSE  | $r^2$ |
|----------------|-------------------|------------|------------------------------|-------|-------------------------|------|-------------------------|-------|-------|
| phenanthrene   |                   | native     | 24                           | 0.051 | 0.013,0.201             | 0.78 | 0.53,1.03               | 0.049 | 0.60  |
| phenanthrene   |                   | native     | 168                          | 0.080 | 0.028,0.228             | 0.97 | 0.76,1.18               | 0.021 | 0.79  |
| phenanthrene   |                   | native     | 720                          | 0.181 | 0.096,0.341             | 0.89 | 0.75,1.03               | 0.013 | 0.87  |
| phenanthrene   |                   | pulverized | 24                           | 0.233 | 0.124,0.437             | 1.30 | 1.09,1.50               | 0.015 | 0.86  |
| naphthalene    |                   | native     | 24                           | 0.073 | 0.052,0.104             | 0.60 | 0.55,0.65               | 0.012 | 0.96  |
| naphthalene    |                   | native     | 168                          | 0.076 | 0.054,0.107             | 0.72 | 0.67,0.76               | 0.011 | 0.97  |
| naphthalene    |                   | native     | 720                          | 0.554 | 0.357,0.861             | 0.55 | 0.49,0.61               | 0.028 | 0.93  |
| naphthalene    |                   | pulverized | 24                           | 0.290 | 0.271,0.311             | 0.66 | 0.65,0.67               | 0.001 | 1.00  |
| naphthalene    | phenanthrene      | native     | 24                           | 0.066 | 0.045,0.097             | 0.58 | 0.53,0.63               | 0.013 | 0.96  |
| naphthalene    | phenanthrene      | native     | 168                          | 0.073 | 0.048,0.0111            | 0.69 | 0.63,0.75               | 0.021 | 0.96  |
| naphthalene    | phenanthrene      | native     | 720                          | 0.074 | 0.053,0.103             | 0.78 | 0.73,0.83               | 0.013 | 0.98  |
| naphthalene    | phenanthrene      | native     | 2160                         | 0.087 | 0.069,0.108             | 0.84 | 0.069,0.108             | 0.006 | 0.99  |
| naphthalene    | phenanthrene      | pulverized | 24                           | 0.184 | 0.153,0.222             | 0.69 | 0.66,0.71               | 0.006 | 0.99  |
| naphthalene    | phenanthrene      | pulverized | 720                          | 0.177 | 0.151,0.207             | 0.74 | 0.72,0.77               | 0.004 | 0.99  |
| naphthalene    | phenanthrene      | pulverized | 2160                         | 0.200 | 0.188,0.213             | 0.76 | 0.75,0.77               | 0.001 | 1.00  |

**Table 4.7: Linear regression of low concentration isotherm data**

| Primary solute | Background solute | Solid      | Equilibration period (hours) | $K_p$ (slope)         | RMSE  | $r^2$ | number of data points |
|----------------|-------------------|------------|------------------------------|-----------------------|-------|-------|-----------------------|
| naphthalene    |                   | native     | 24                           | $6.55 \times 10^{-3}$ | 0.319 | 0.87  | 15                    |
| naphthalene    |                   | native     | 168                          | $1.43 \times 10^{-2}$ | 0.881 | 0.91  | 15                    |
| naphthalene    |                   | native     | 720                          | $2.93 \times 10^{-2}$ | 19.2  | 0.43  | 12                    |
| naphthalene    |                   | pulverized | 24                           | $4.04 \times 10^{-2}$ | 2.94  | 0.91  | 15                    |
| naphthalene    | phenanthrene      | native     | 24                           | $4.79 \times 10^{-3}$ | 0.427 | 0.21  | 12                    |
| naphthalene    | phenanthrene      | native     | 168                          | $8.10 \times 10^{-3}$ | 0.940 | 0.47  | 15                    |
| naphthalene    | phenanthrene      | native     | 720                          | $1.83 \times 10^{-2}$ | 3.29  | 0.90  | 18                    |
| naphthalene    | phenanthrene      | native     | 2160                         | $3.40 \times 10^{-2}$ | 3.92  | 0.95  | 18                    |
| naphthalene    | phenanthrene      | pulverized | 24                           | $2.15 \times 10^{-2}$ | 4.43  | 0.88  | 18                    |
| naphthalene    | phenanthrene      | pulverized | 720                          | $3.78 \times 10^{-2}$ | 3.29  | 0.96  | 18                    |
| naphthalene    | phenanthrene      | pulverized | 2160                         | $4.57 \times 10^{-2}$ | 3.12  | 0.97  | 18                    |

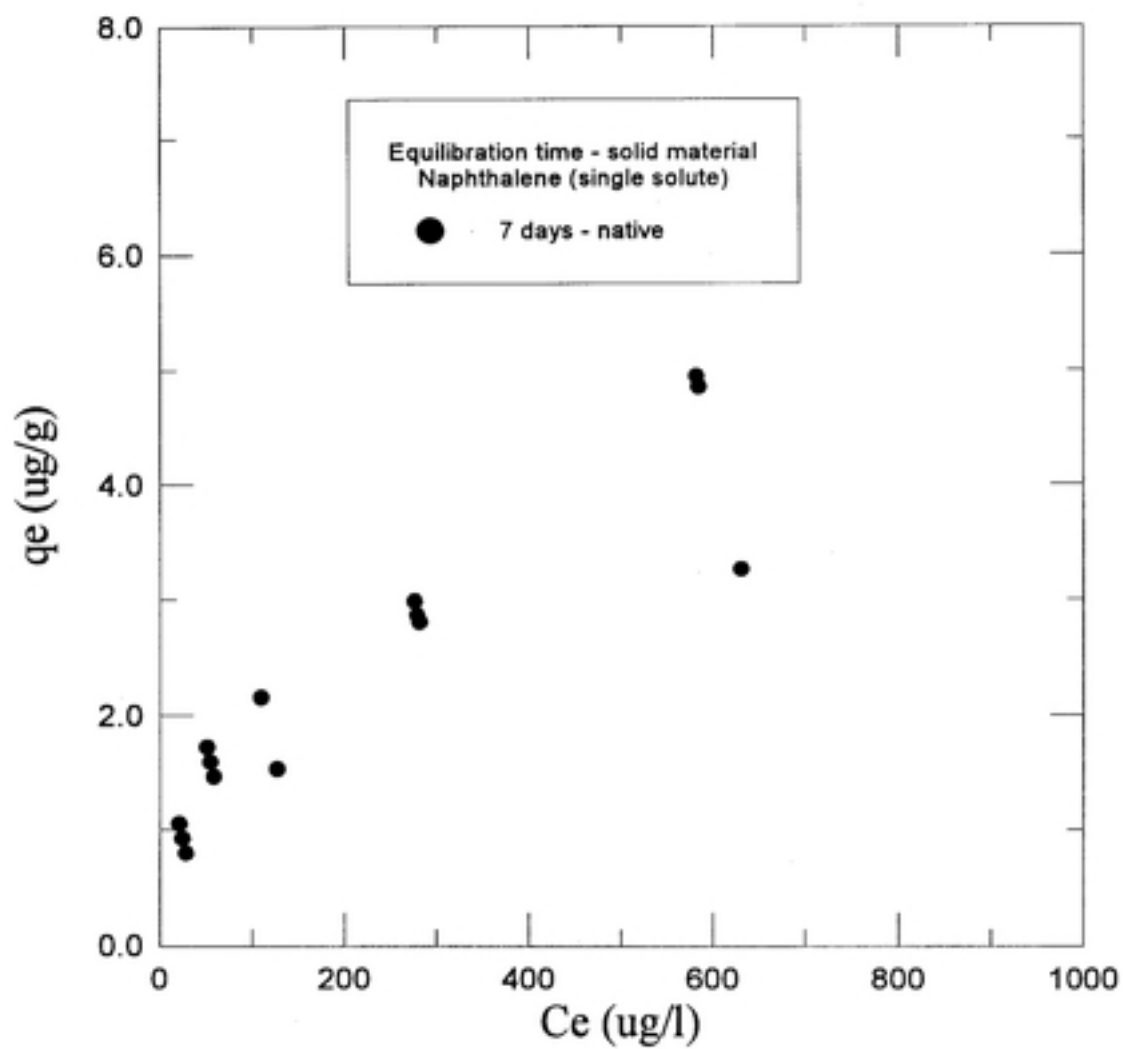


Figure 4-21: Representative lower-concentration portion of isotherm

parameter ( $K_p$ ) over time is clear in the tabulated data, reflecting the continuation of sorption over the period of the 3 month study.

The bulk of the data in the literature pertaining to sorption has been collected from systems assumed to be at an equilibrium within a matter of hours or days. The observed continuation of the sorption process suggests that the magnitude of sorption in much of this reported data is underestimated (Ball, 1989; Ball and Roberts, 1991a,b). Procedures to predict the extent of sorption based on this data, using chemical properties and the fraction of organic carbon present in the solids, have been developed (Equations 2.1-2.3). Equations 2.1 and 2.2 were used to compare the predicted sorption based on methods and values reported in the literature to the results observed in this study. Table 4.8 contains the parameters used to calculate the predicted sorption, and Figure 4.22 displays this prediction with some of the data collected in this study. Clearly, the extent of sorption is being underestimated by this prediction. Even if a better estimate had been provided at 1 day, it would have become less accurate as the sorption process continued to proceed because the sorption had not reached an equilibrium at this time.

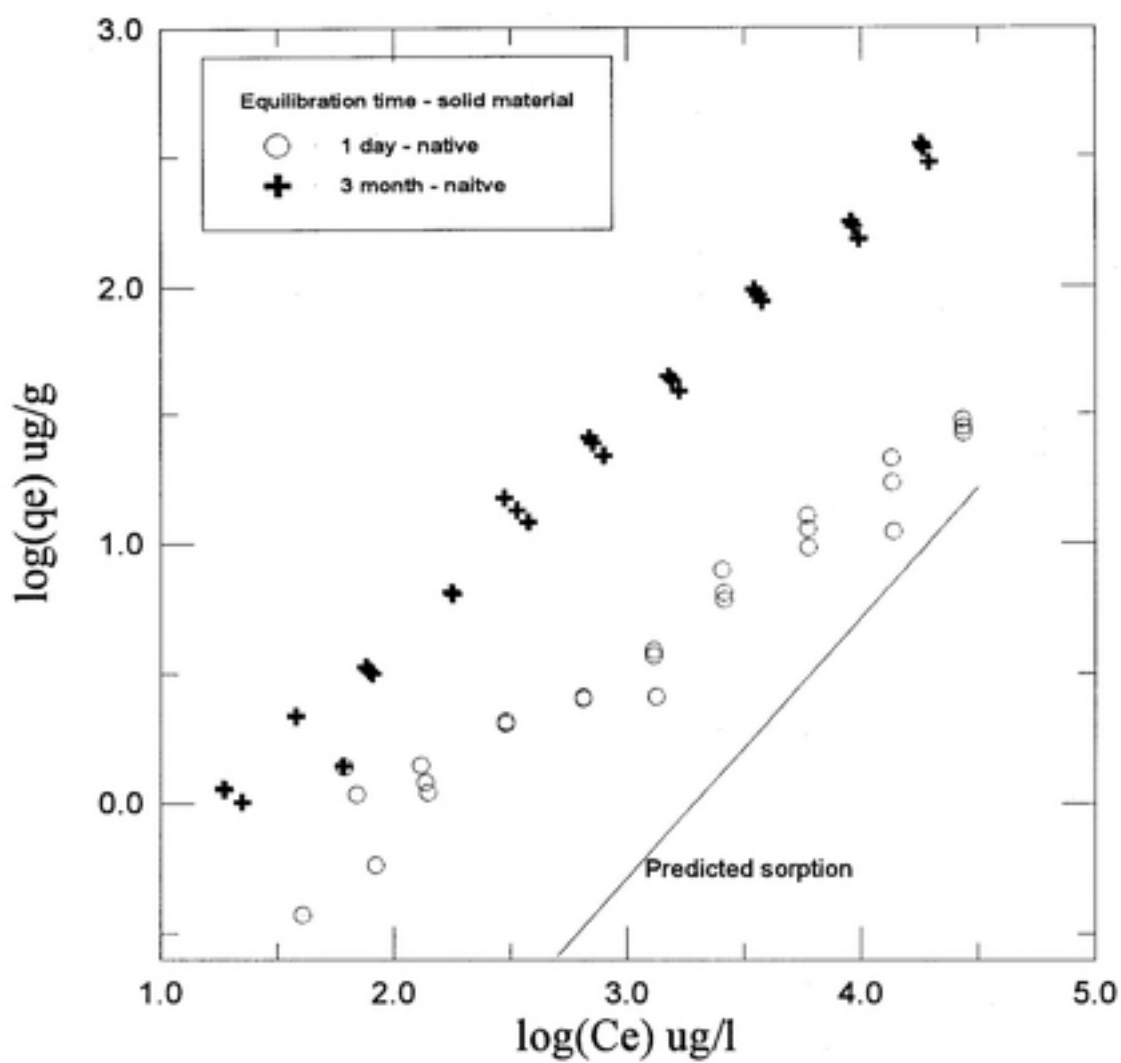
**Table 4.8: Sorption estimates from literature correlation**

| Solute       | a <sup>a</sup> | b <sup>a</sup> | $K_{oc}$ L/g | $K_{p(native)}$ L/g |
|--------------|----------------|----------------|--------------|---------------------|
| naphthalene  | 1.00           | -0.21          | 1.202        | 0.000517            |
| phenanthrene |                |                | 26.303       | 0.0113              |

<sup>a</sup>Schwartzbach and Westall, 1984

#### Single-solute

The additional sorption occurring over time indicate that the sorption process is strongly rate limited. This behavior is evident in both of the single solute systems with native solids (Figures 4.12, 4.14). The increased rate of uptake evident in comparisons of isotherms at one day on native and pulverized solid samples suggests that the rate limiting



**Figure 4-22:** Naphthalene (bisolute) isotherm on native material at 1 day and 3 months with prediction of sorption from reported correlations

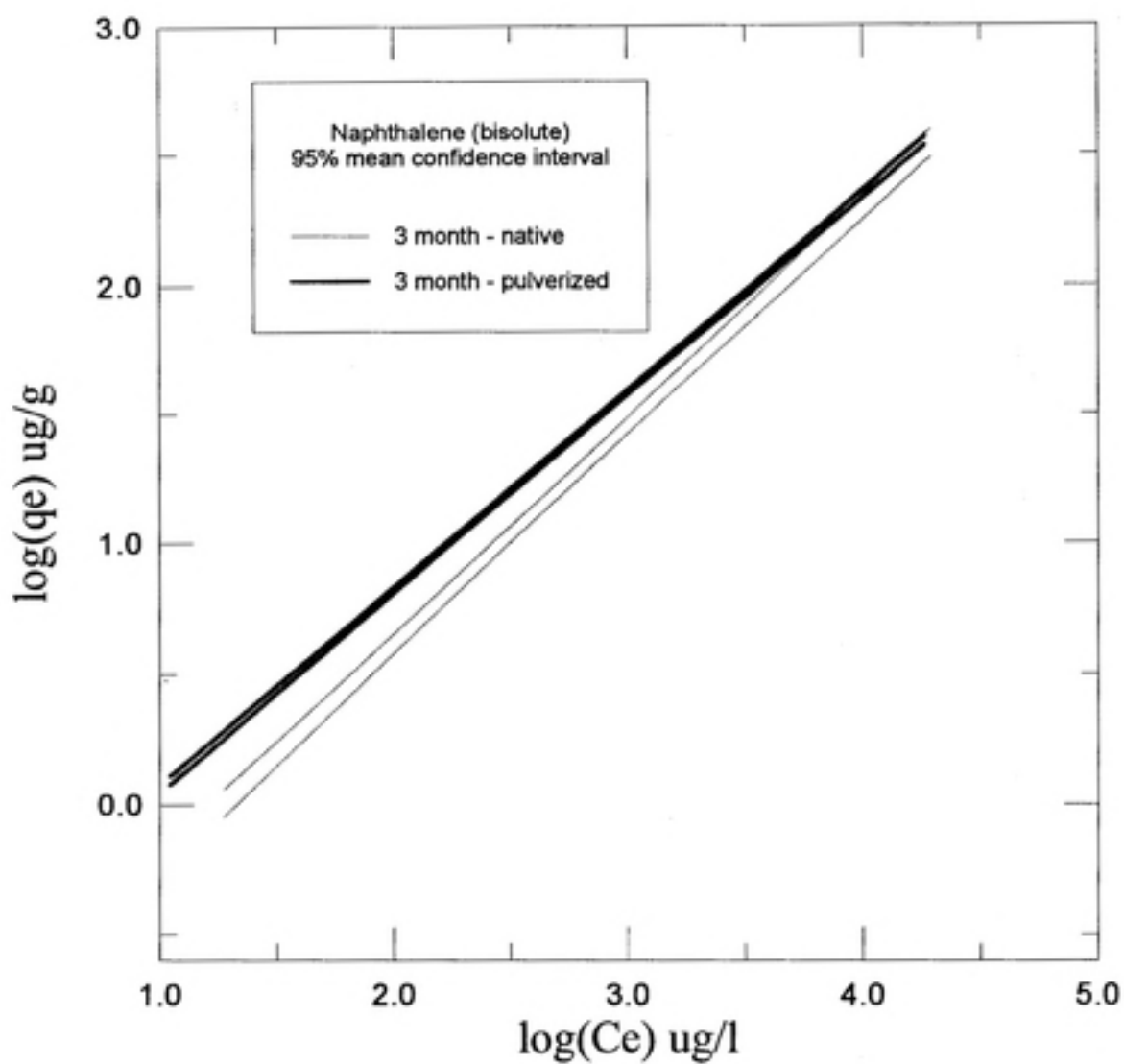
mechanism may be a diffusion process. As the diffusion path length is reduced, the rate of approach to equilibrium is increased (Figures 4.13, 4.15).

#### Multi-solute

Figure 4.16 displays the progression of naphthalene (bisolute) isotherms from 1 day through 3 months on the native material. Figure 4.17 shows the progression of naphthalene (bisolute) isotherms from 1 day through 3 months on the pulverized material. In both cases note that while the sample intervals between the first couple isotherms are shorter, the differences in sorption are greater than between later isotherms. In both cases the general pattern of a long approach to a final equilibrium is suggested. Figure 4.18 compares the differences between pulverized and native soil isotherms at 1 day and 3 months in the same naphthalene (bisolute) system. The differences between the pulverized and native material isotherms at 1 day are very significant. However, by 3 months the pulverized and native samples show similar sorptive uptakes. Convergence of the pulverized and native sorption isotherms was examined statistically by plotting 95% confidence intervals of the slopes of the respective Freundlich fits. A continuous overlap of the confidence interval would suggest that the isotherms are statistically equivalent.

Figure 4.23 displays the 95% confidence intervals of the means of the isotherms. This method indicates that although the isotherms are close, they have not converged. If the isotherms will truly converge, a longer equilibration time is needed.

An identical procedure was used to examine the similarity of the naphthalene single solute and bisolute isotherms. As might be expected, a decrease in the sorption of naphthalene when in the presence of phenanthrene is observed. Single solute and bisolute isotherms at 1 day, and 1 month conducted on native material were compared, as were isotherms at 1 day conducted on pulverized material (Figures 4.24-4.26). The 95% confidence intervals of the paired isotherms are plotted in Figures 4.27-4.29. None of the



**Figure 4-23:** Ninety-five percent confidence interval for naphthalene (bislute) isotherm at 3 months on native and pulverized material

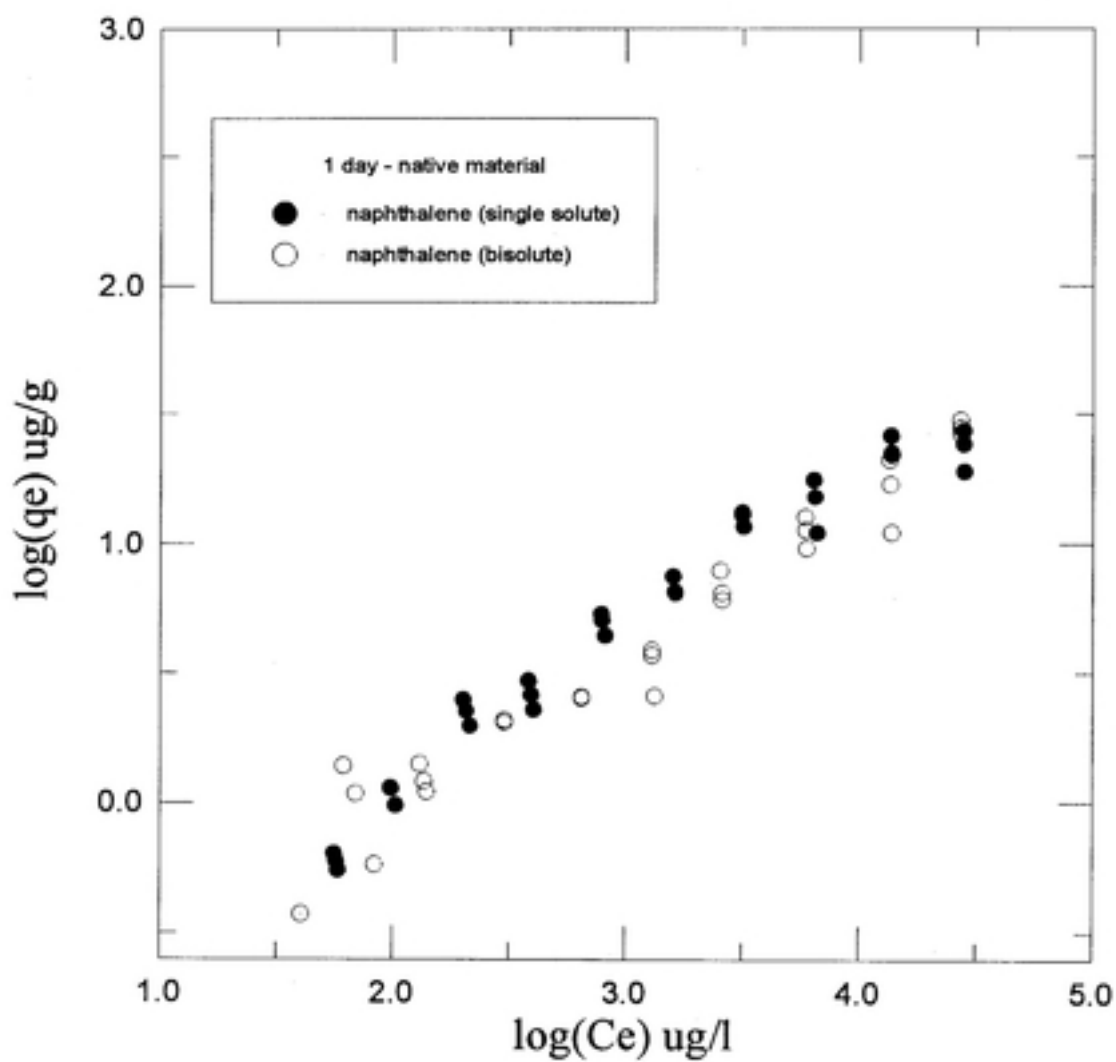


Figure 4-24: Naphthalene (single and bisolute) isotherms on native material at 1 day

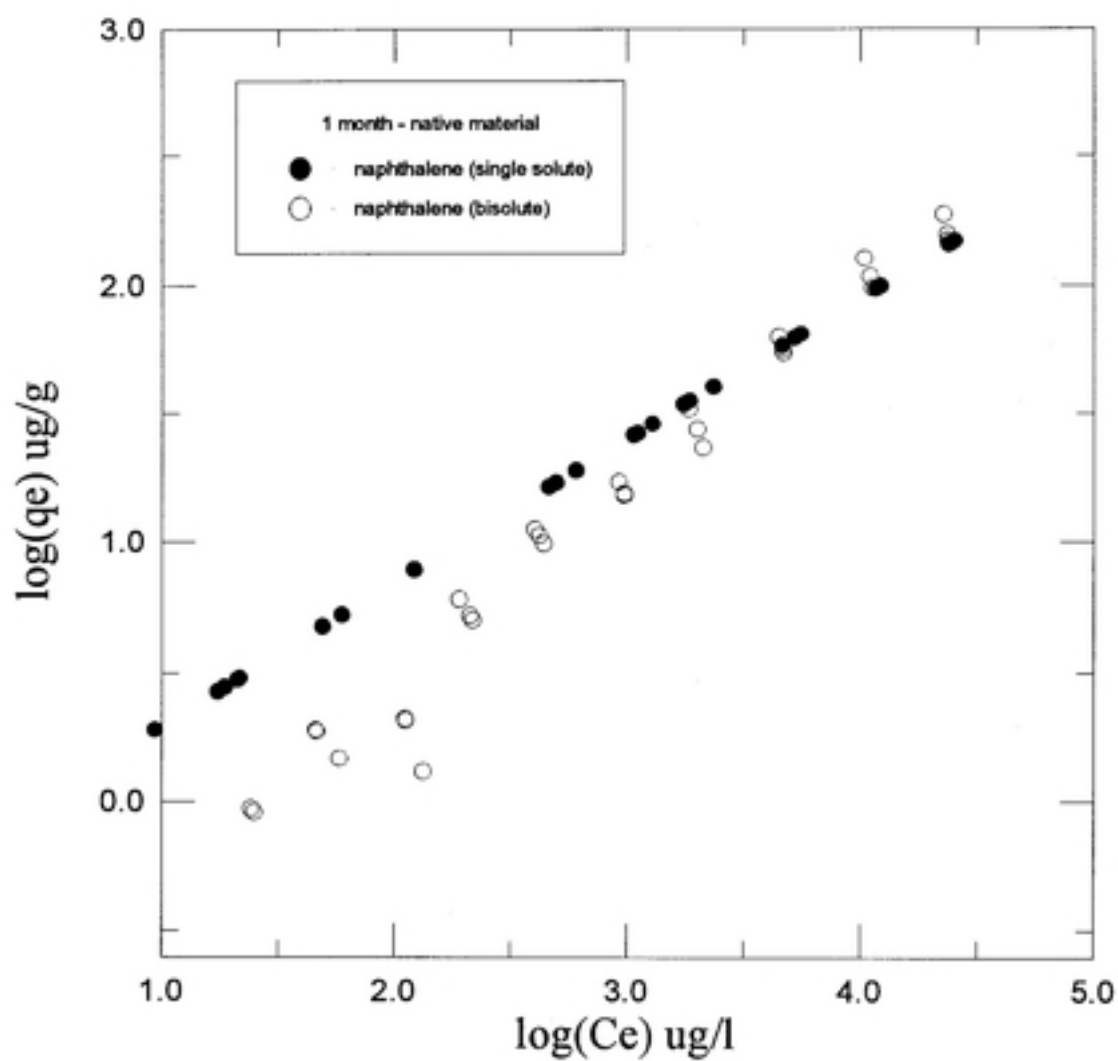


Figure 4-25: Naphthalene (single and bisolute) isotherms on native material at 1 month

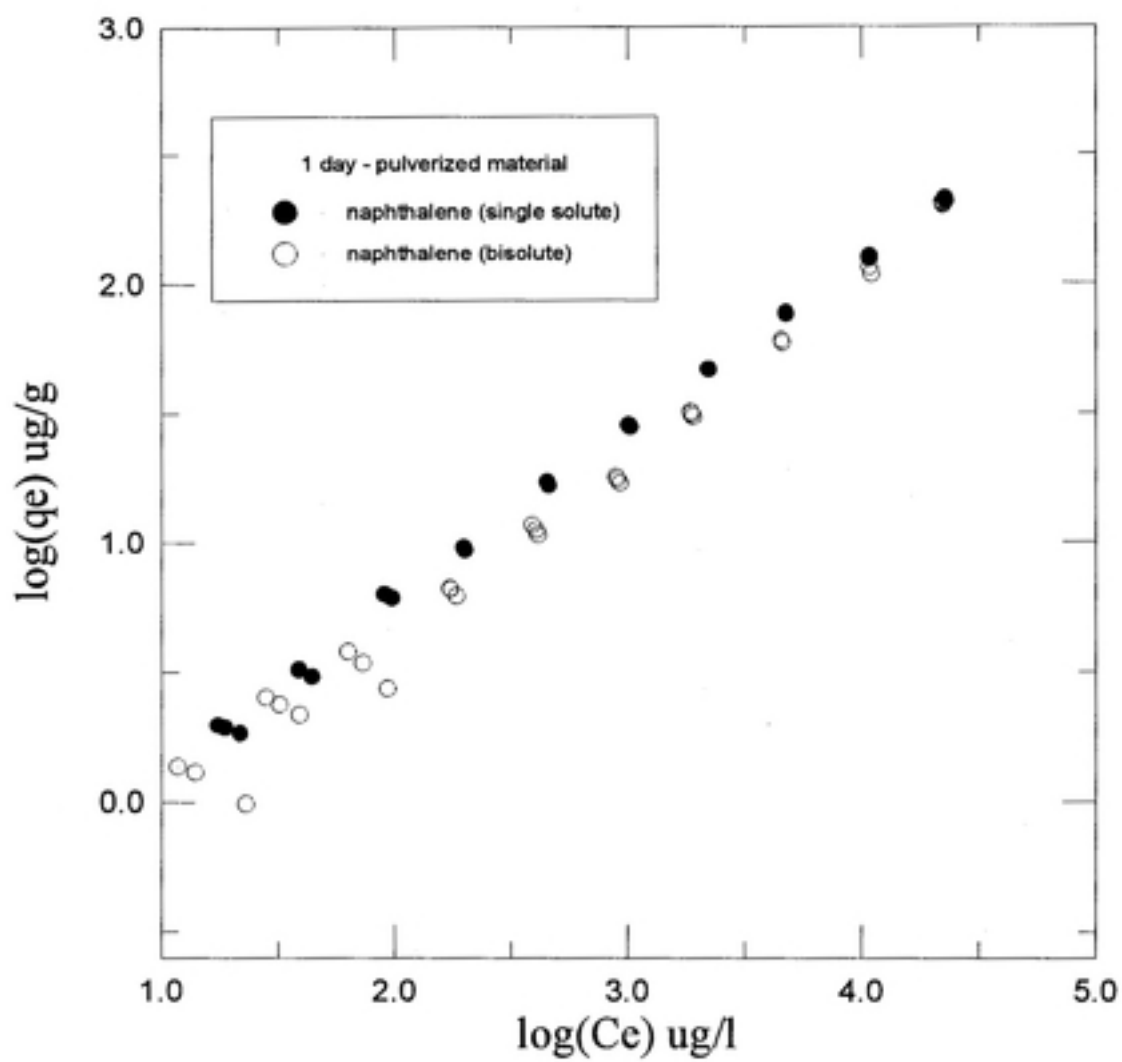
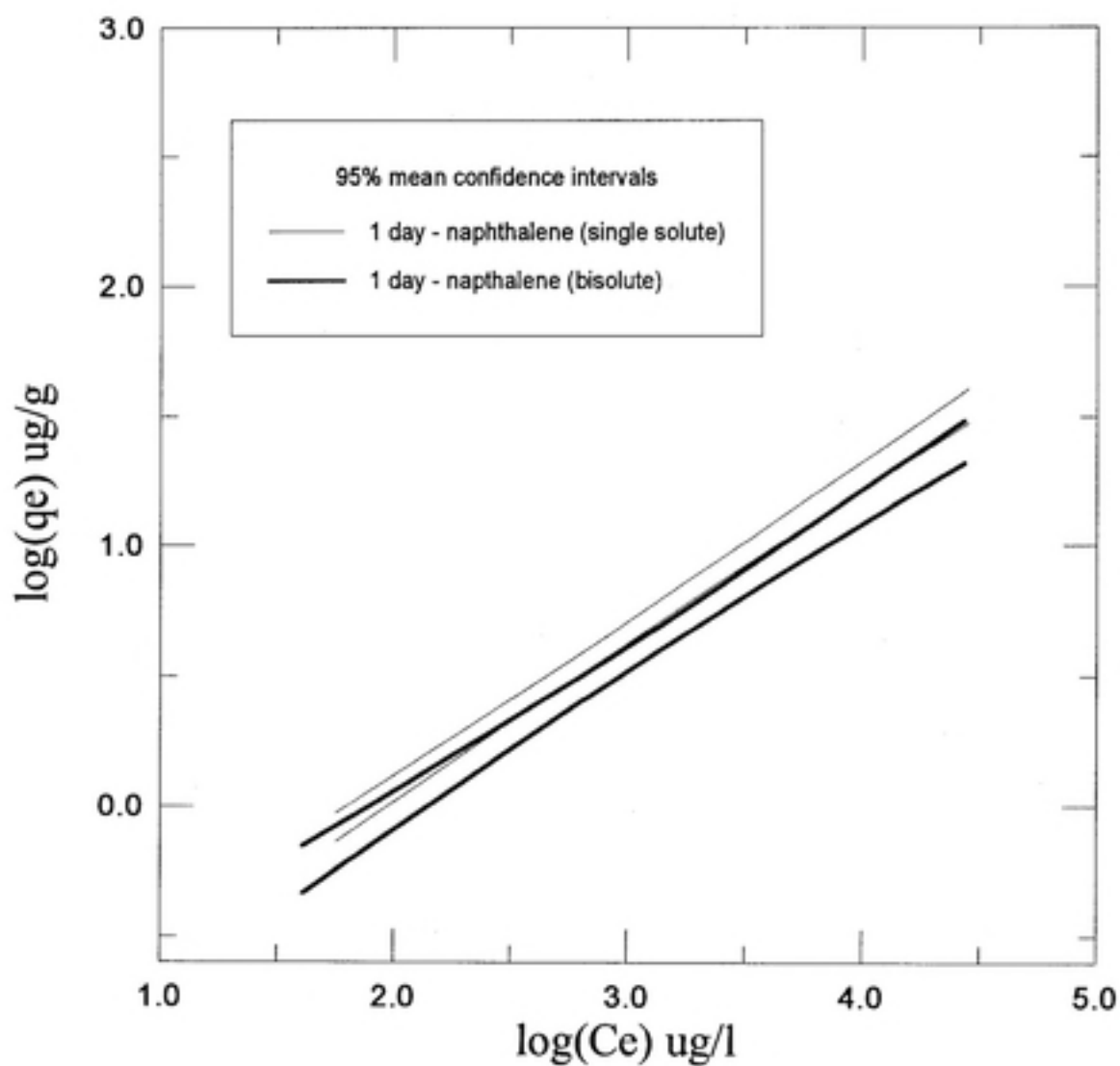
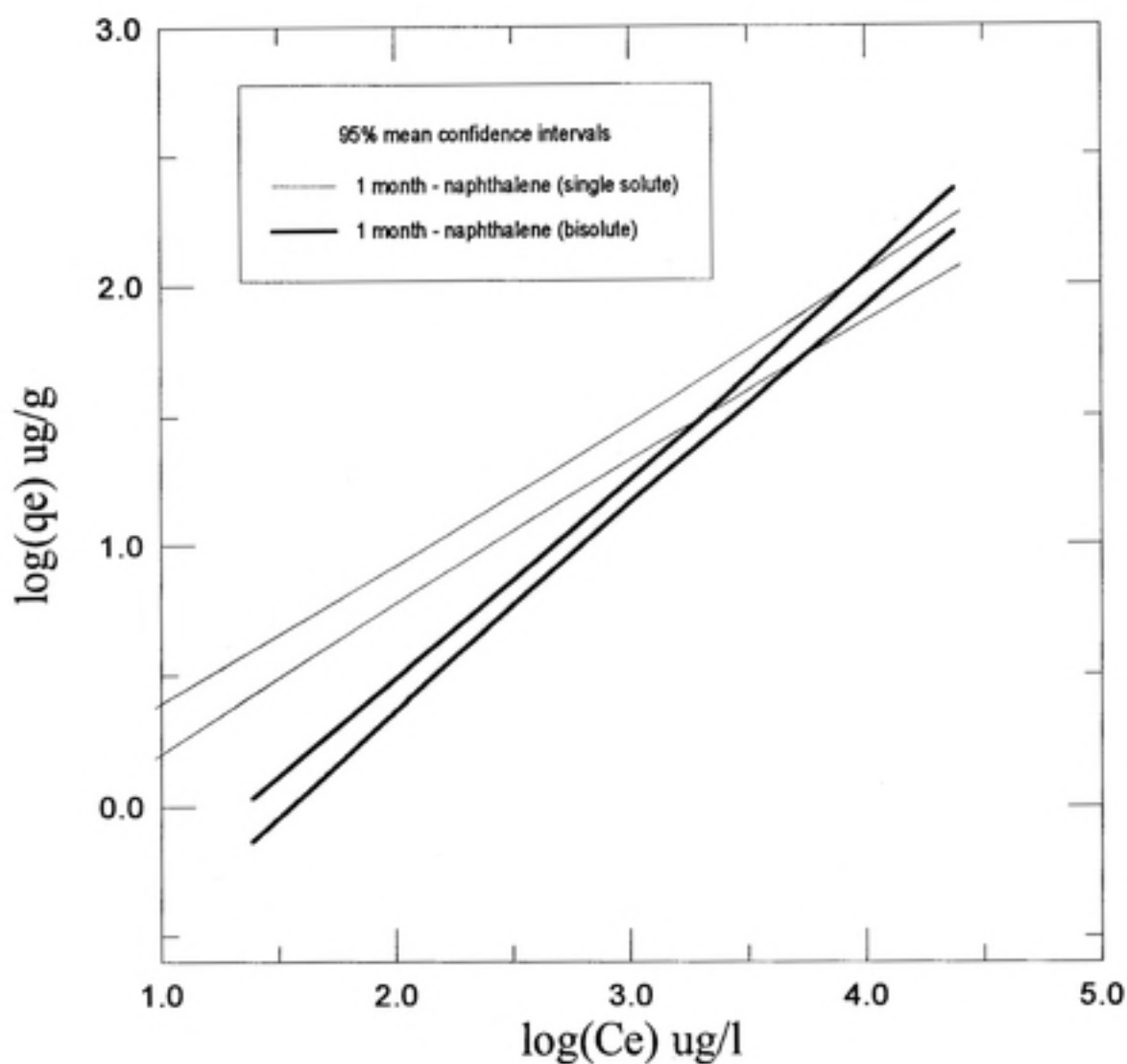


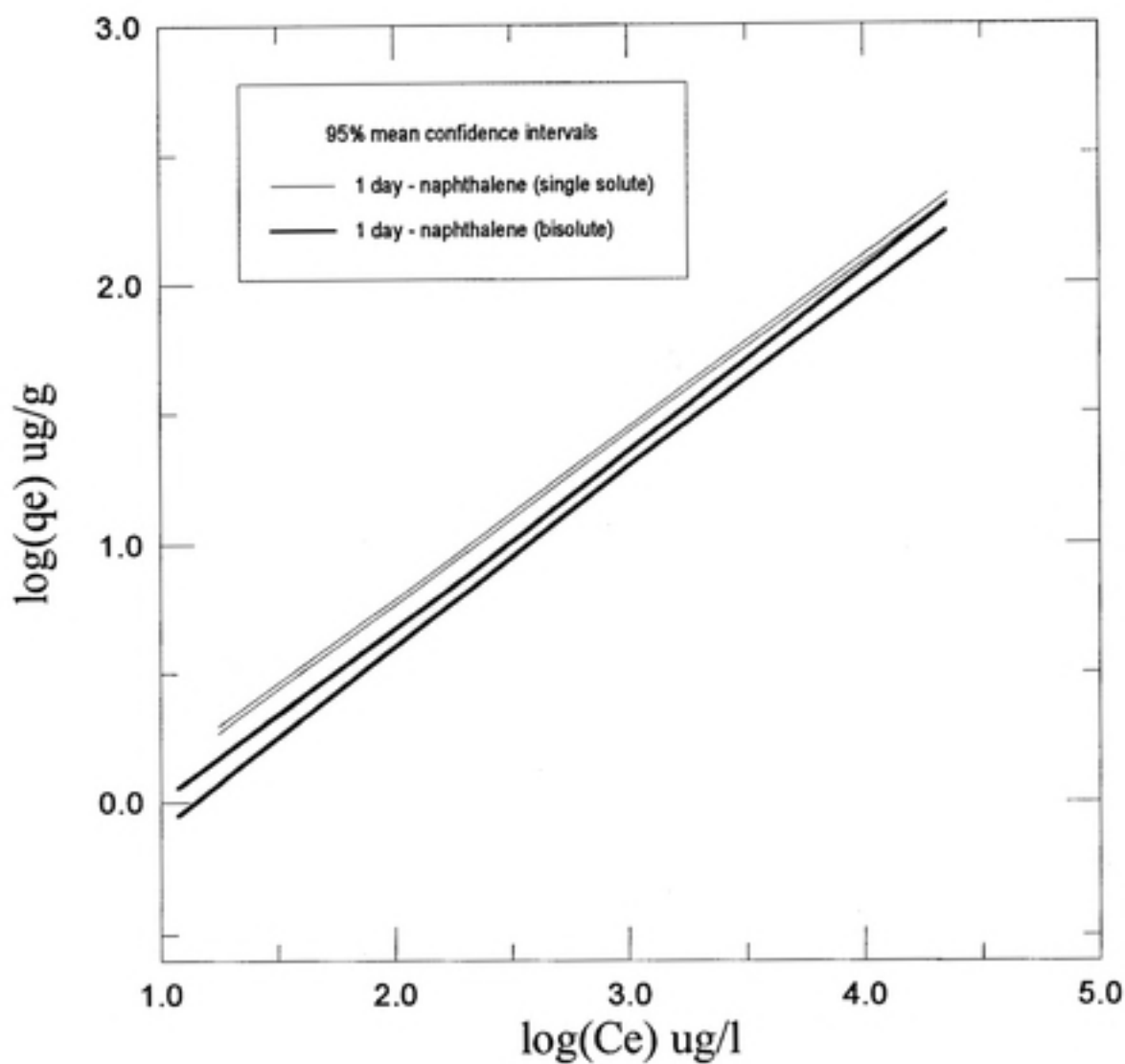
Figure 4-26: Naphthalene (single and bisolute) isotherms on pulverized material at 1 day



**Figure 4-27:** Ninety-five percent confidence interval for naphthalene (single and bisolute) isotherm at 1 day on native material



**Figure 4-28:** Ninety-five percent confidence interval for naphthalene (single and bisolute) isotherm at 1 month on native material



**Figure 4-29:** Ninety-five percent confidence interval for naphthalene (single and bisolute) isotherm at 1 day on pulverized material

paired isotherms met the criteria to be considered equivalent, although the native material systems were very close at 1 day. While competitive effects appear statistically significant, the magnitude of the difference in sorption is small compared to the difference encountered when comparing sorption isotherms with equilibration times of 1 day and several months. In this system, nonequilibrium effects would likely have a greater impact on the solute transport behavior than competitive effects.

#### **4.5 Impacts to the Understanding and Prediction of Contaminant Transport**

Numerical modeling of contaminant transport in the subsurface has been the subject of research (Rabideau and Miller, 1994). The functional goal is to be able to predict how far and how fast a chemical will travel so that estimates such as who will be affected and how much time and effort are required to clean an aquifer can be made. In order to accurately predict the movement of a chemical species, its behavior must be understood and translated into a mathematical format. The sorption process often has a significant influence on the transport process. As a chemical sorbs, its apparent migration relative to the groundwater flow is retarded. In order to accurately predict this influence, the following must be known: (1) how much is sorbed at a given concentration; (2) at what rate is this equilibrium reached; (3) does this behavior vary with concentration; (4) is this behavior altered by the presence of other chemicals; (5) is it reversible. This study addresses the first 4 issues.

Common assumptions utilized in the prediction of subsurface contaminant transport include:

- (1) linear isotherms
- (2) instantaneous equilibrium
- (3) no competitive effects between cosolutes
- (4) complete reversibility of the sorption process

This study has provided additional evidence that these assumptions are not always true. In this study the following were observed:

- (1) nonlinear isotherms, even at low concentrations
- (2) long equilibration times
- (3) competitive effects between solutes

These effects suggest that true behavior of a chemical in the subsurface could be expected to deviate from predictions based on the assumptions of linear isotherms, instantaneous equilibrium, and no competitive effects in the following manner:

nonlinear isotherms: A nonlinear isotherm (concave down) suggests that sorption is stronger at lower concentrations. This would mean that a chemical would be more resistant to desorption at lower concentrations. Since health limits for many compounds are often extremely low, a significant amount of additional effort may be required to reduce concentrations to safe levels. Also, as a contaminant plume migrates, isotherm nonlinearities would likely increase any tailing effects.

long equilibration period: The magnitude of the sorption was much greater at 3 months than at 1 day. This makes much of the reported sorption equilibrium data based on short equilibration times suspect. Significantly more sorption is likely to occur than previously reported. Less of the chemical would be free be available for biodegradation and volatilization. Diffusion into the sorbing particles is likely the rate limiting mechanism. Desorption, which would require diffusion out of the solid particles, should be comparably limited. This would result in increased tailing of migrating plumes and an increase in the time and effort to reduce the concentration of a chemical in the subsurface. Additionally, if a pump and treat system is being utilized, aqueous concentrations may even increase in an aquifer after the cessation of pumping as the chemical continues to desorb.

competitive effects: While the effects noted in this study did not appear large, locations such as landfills may have systems which are much more complex and may exhibit increased competitive behavior. The reduction in sorption caused by competition with another compound would increase the apparent rate of transport of a chemical by decreasing the retardation due to sorption.

#### **4.6 Prevention of Microbial Degradation and Volatile Losses**

Two significant problems were recognized while this study was in progress. In all reactors, solute mass was slowly being lost. Some of the reactors containing soil also sustained complete loss of all reactor solute, most likely due to microbial degradation. This section suggests measures to be incorporated in future studies to prevent similar difficulties.

##### **4.6.1 Microbial Degradation**

All of the reactors in this study exhibited a small loss to volatilization that progressed with time. Some reactors containing solids, however, exhibited complete solute loss. These losses never occurred prior to 1 month after the initiation of the experiment. Subsequent extractions of the solid phases of these reactors revealed that no solute was present in the solid phase. Sodium azide was used as a biological inhibitor in this study at a concentration of 0.005 M. The losses encountered suggest that sodium azide: (1) was not present in sufficient concentration, (2) was not sufficiently toxic to the degrading organism, or (3) did not provide a sufficient residual.

An additional study was performed to evaluate the effect of alternative methods of microbial inhibition on the sorption properties of the system studied. The two alternatives considered were: (1) autoclaving the solids, reactors and experimental equipment for 2

hours, and filtering all solutes with a 0.2  $\mu\text{m}$  filter (Gelman), and (2) using mercuric chloride (Fisher) in place of sodium azide. These methods were chosen based on preliminary work by Ball (1989) and personal communication with Professors Michael Aitken (Department of Environmental Sciences and Engineering, UNC-Chapel Hill) and Hans Paerl (Institute of Marine Sciences, UNC-Morehead City). Mercuric chloride is easier to implement and provides a persistent residual, but safety and disposal concerns are greater than for autoclaving.

A batch reactor sorption experiment was conducted in which three sets of reactors were set up at approximately the same concentration. The experiment was set up similarly to the large experiment described in Chapter 3. The two differences were: (1) different methods of biological inhibition were used, and (2) flame sealed glass ampules (Wheaton, 20 ml) were used as the system reactors. One set was treated with sodium azide as in the larger study, to be used as a control. The second set contained autoclaved soil, and all solute was filtered with a 0.2  $\mu\text{m}$  filter and handled with autoclaved experimental equipment. The third set contained mercuric chloride at a concentration of 100 mg/l, in place of sodium azide.

A partition coefficient was calculated for each experimental subset and can be seen in Table 4.9. Neither of the methods investigated caused sorption to differ significantly at the concentration examined at an equilibration period of 7 days. It should be noted that while investigating similar procedures for inhibiting microbial activity, Ball (1989) observed some differences in sorption properties in the presence of mercuric chloride after 3 days of equilibration. These differences had disappeared prior to samplings at 10 and 30 days of equilibration and were attributed to pH effects from the addition of mercuric chloride. This experiment was not conducted for a sufficient time to evaluate the effectiveness of the methods of biological inhibition. Its purpose was to evaluate possible effects on sorption from these alternative methods. Long term experiments would be required for a true evaluation of the effectiveness of these alternative methods.

**Table 4.9: Partition coefficients of experiments implementing alternative methods of biological inhibition**

| Method of biological inhibition      | partition coefficient: $K_d \pm (95\% \text{ CI})$ | number of samples |
|--------------------------------------|----------------------------------------------------|-------------------|
| autoclave / 0.2 $\mu\text{m}$ filter | $7.07 \times 10^{-3} \pm (6.11 \times 10^{-4})$    | 4                 |
| sodium azide                         | $7.34 \times 10^{-3} \pm (3.53 \times 10^{-4})$    | 11                |
| mercuric chloride, 100mg/l           | $7.21 \times 10^{-3} \pm (2.57 \times 10^{-4})$    | 12                |

#### 4.6.2 Volatilization

Other researchers have experienced similar losses from glass centrifuge tubes with screw on caps and Teflon<sup>®</sup> liners (Curtis, 1986; Lion et al., 1990; Weber et al., 1992). It has been suggested that volatile compounds can diffuse through or around the liner and escape from the reactor. Flame-sealed glass ampules, though more labor intensive and impossible to reuse, appear to offer the best protection against losses such as those encountered in this study. Since the system is completely enclosed in borosilicate glass, the only obvious way for volatile losses to occur from such a reactor would be during set-up prior to sealing the ampule, or during sampling, when the ampule is opened. An experiment was conducted to evaluate the feasibility of setting up and sampling with flame sealed ampules without solute loss. Glass ampules (Wheaton, 20 ml) were loaded with 20 ml of distilled water saturated with naphthalene. After one day of equilibration, the ampules were placed inside a 250 ml glass jar with a Teflon<sup>®</sup> lined screw cap with 5 ml of hexane. After sealing the large jar with the ampule and hexane inside, the ampule was then broken by shaking the jar. After tumbling for 2 hours, the jar was then opened and

the hexane phase was sampled and analyzed by gas chromatography in a manner similar to that described in chapter 3. Admittedly, this method is somewhat crude. Other researchers have conducted extractions in a similar manner, the exception being the use of a custom stainless steel chamber for breaking the ampules and performing the extractions. Mass balance results suggest that no solute was lost during the loading and sealing process. The average mass recovered from five samples was 103.62%, with a 95% confidence interval of 5.53%. Flame sealed ampules appear to be a suitable alternative to other methods for restricting system losses due to volatility over long periods of time.

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## 5 Conclusions and Recommendations

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### 5.1 Conclusions

The following conclusions are supported by this research:

1. The increased rate of sorption observed with the pulverized material when compared to the rate observed with the native material, followed by the approach to convergence of the sorption on the pulverized and native solid material suggests a rate-limited diffusion process.
2. The additional sorption occurring over long periods of time was significant. Increases in sorbed concentrations of approximately an order of magnitude were observed between 1 day and 3 months.
3. Sorption isotherms for naphthalene and phenanthrene on the Wagner material were best described by a nonlinear Freundlich model.
4. A reduction in the sorption of naphthalene in the presence of phenanthrene was observed in the bisolute system.

## 5.2 Recommendations

1. Effort should be made in future long-term studies to avoid the problems of volatilization and biodegradation encountered in this study by utilizing improved reactors, such as flame-sealed ampules, and improved methods of biological inhibition, such as mercuric chloride.
2. Further efforts should be made to isolate the diffusion mechanism responsible for rate limitations. It has been suggested that diffusion through pores, micropores and organic matter is responsible for rate limitations. Further studies isolating these characteristics may provide additional insight to the influence of these properties on rate limitations. Possible variations are conducting sorption experiments on nonporous material coated with organic matter, and pulverizing a solid to different degrees to provide a variation of path lengths on the same material.
3. The competitive effects observed in this system should be studied further. The effects in batch systems such as these should be compared to results from a flow-through reactor such as a column. The solutes could be added simultaneously, or one compound could be sorbed for a period of time before the other is introduced so that possible displacement of the first solute can be examined.
4. Comparisons of very early rate data from native and pulverized versions of a solid may provide additional insight to the controlling rate mechanism. In this study, a large portion of the sorption to the pulverized solid occurred prior to the initial sampling at 8 hours. Sampling a batch system by a headspace technique similar to that of Perlinger et al. (1993) might provide details of differences in sorption behavior at early times and short sampling intervals.

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## 6 References

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- Abdul, A. S. "Equilibrium Batch Experiments with Six Polycyclic Aromatic Hydrocarbons and Two Aquifer Materials." Hazardous Waste & Hazardous Materials 3, no. 2: 125--137 (1986).
- Abdul, A. S., T. L. Gibson, and D. N. Rai. "Statistical Correlations for Predicting the Partition Coefficient for Nonpolar Organic Contaminants between Aquifer Organic Carbon and Water." Hazardous Waste & Hazardous Materials 4, no. 3: 211--222 (1987).
- Physical Chemistry of Surfaces. Adamson, A. U. Wiley. (1990)
- Bahr, J. M. "Analysis of Nonequilibrium Desorption of Volatile Organics During Field Test of Aquifer Decontamination." Journal of Contaminant Hydrology 4 : 205--222 (1989).
- Ball, W. P. "Equilibrium Sorption and Diffusion Rate Studies with Halogenated Organic Chemicals and Sandy Aquifer Material." Ph.D. diss., Stanford, (1989).
- Ball, W. P., Ch. Buehler, T. C. Harmon, D. M. Mackay, and P. V. Roberts. "Characterization of a Sandy Aquifer Material at the Grain Scale." Journal of Contaminant Hydrology 5, no. 3: 253--295 (1990).
- Ball, W. P., and P. V. Roberts. "Long-Term Sorption of Halogenated Organic Chemicals by Aquifer Material. 1. Equilibrium." Environmental Science & Technology 25, no. 7: 1223--1236 (1991).
- Ball, W. P., and P. V. Roberts. "Long-Term Sorption of Halogenated Organic Chemicals by Aquifer Material. 2. Intraparticle Diffusion." Environmental Science & Technology 25, no. 7: 1237--1248 (1991).
- Bowman, R. S., N. S. Urquhart, and G. A. O'Connor. "Statistical Evaluation of Sorption Isotherm Data." Soil Science 137, no. 5: 360--369 (1984).
- Brusseau, M. L., "Nonequilibrium Transport of Organic Chemicals: The Impact of Pore Water Velocity." Journal of Contaminant Hydrology 9: 353--368 (1992).
- Brusseau, M. L., and P. S. C. Rao. "Sorption Nonideality during Organic Contaminant Transport in Porous Media." Critical Reviews in Environmental Control 19, no. 1: 33--99 (1989a).

- Brusseau, M. L., and P. S. C. Rao. "The Influence of Sorbate- Organic Matter Interactions on Sorption Nonequilibrium." Chemosphere 18, no. 9-10: 1691--1706 (1989b).
- Brusseau, M. L., P. S. C. Rao, R. E. Jessup, and J. M. Davidson. "Flow Interruption: A Method for Investigating Sorption Nonequilibrium." Journal of Contaminant Hydrology 4: 223-- 240 (1989c).
- Cameron, D. R., and A. Klute. "Convective-Dispersive Solute Transport with a Combined Equilibrium and Kinetic Adsorption Model." Water Resources Research 13, no. 1: 183--188 (1977).
- Cary, J. W., and C. W. Hayden. "An index for pore size distribution." Geoderma 9 : 249--256 (1973).
- Casida, L. E. "Microorganisms in unamended soil as observed by various forms of microscopy and staining." Applied Environmental Microbiology 21: 1040-- 1045 (1971).
- Chiou, C. T. "Partition Coefficients of Organic Compounds in Lipid Water Systems and Correlations with Fish Bioconcentration Factors." Environmental Science & Technology 19, no. 1: 57--62 (1985).
- Chiou, C. T. "Theoretical Considerations of the Partition Uptake of Nonionic Organic Compounds by Soil Organic Matter." Reactions and Movement of Organic Chemicals in Soils, 1--29. B. L. Sawhney, and K. Brown. Special Publication Number 22. , Special Publication Number 22. Madison, Wisconsin: Soil Science Society of America, Inc., (1989).
- Chiou, C. T., L. J. Peters, and V. J. Freed. "A Physical Concept of Soil-Water Equilibria for Non-Ionic Organic Compounds." Science 206, no. 16: 831--832 (1979).
- Chiou, C. T., P. E. Porter, and D. W. Schmedding. "Partition Equilibria of Nonionic Organic Compounds between Soil Organic Matter and Water." Environmental Science & Technology 17, no. 4: 227--231 (1983).
- Coates, J. T., and A. W. Elzerman. "Desorption Kinetics for Selected PCB Congeners from River Sediments." Journal of Contaminant Hydrology 1: 191--210 (1986).
- Crittenden, J. C., N. J. Hutzler, D. G. Geyer, J. L. Oravitz, and G. Friedman. "Transport of Organic Compounds with Saturated Groundwater Flow: Model Development and Parameter Sensitivity." Water Resources Research 22, no. 3: 271--284 (1986).
- Crittenden, J. C., P. Luft, D. W. Hand, J. L. Oravitz, S. W. Loper, and M. Ari. "Prediction of Multicomponent Adsorption Equilibria Using Ideal Adsorbed Solution Theory." Environmental Science & Technology 19: 1037--1043 (1985).
- Curtis, G. P., Paul V. Roberts, and M. Reinhard. "A Natural Gradient Experiment on Solute Transport in a Sand Aquifer, 4. Sorption of Organic Solutes and Its Influence on Mobility." Water Resources Research 22, no. 13: 2059--2067 (1986).

- Farrell J., and M. Reinhard. "Desorption of Halogenated Organic from Model Solids, Sediments, and Soil under Unsaturated Conditions. 1. Isotherms." Environmental Science & Technology 28: 53--62 (1994).
- Fritz, W., and E. U. Schlunder. "Competitive Adsorption of Two Dissolved Organics onto Activated Carbon: 1. Adsorption Equilibria." Chemical Engineering Science 28: 1279--1282 (1981).
- Goring, C. A. I., and J. M. Thompson. Adsorption. In C. A. I. Goring and J. W. Hamaker (Eds.), Organic Chemicals in the Soil Environment. New York: Marcel Dekker. 51--145 (1972).
- Grathwohl P., and M. Reinhard. "Desorption of Trichloroethylene in Aquifer Material: Rate Limitation at the Grain Scale." Environmental Science & Technology 27: 2360--2366(1993).
- Mathematical Prediction of Cumulative Levels of Pesticides in Soil, Advances in Chemistry Series, 122--131. J. W. Hamaker. Washington, DC: American Chemical Society, (1966).
- Harrison, E. M., and James F. Barker. "Sorption and Enhanced Biodegradation of Trace Organics in a Groundwater Reclamation Scheme -- Gloucester Site, Ottawa, Canada." Journal of Contaminant Hydrology 1, no. 4: 349--373 (1987).
- Hassett, J. J., and W. L. Banwart. "The Sorption of Nonpolar Organics by Soils and Sediments." Reactions and Movement of Organic Chemicals in Soils, 31--44. B. L. Sawhney, and K. Brown. Special Publication Number 22. , Special Publication Number 22. Madison, Wisconsin: Soil Science Society of America, Inc., (1989).
- Hutzler, N. J., J. C. Crittenden, J. S. Gierke, and A. S. Johnson. "Transport of Organic Compounds with Saturated Groundwater Flow: Experimental Results." Water Resources Research 22, no. 3: 285--296 (1986).
- Jossens, L., J. M. Prausnitz, W. Fritz, E. U. Schlunder, and A. L. Myers. "Thermodynamics of multi-solute Adsorption from Dilute Aqueous Solutions." Chem. Eng. Sci. 33: 1097--1106 (1978).
- Karickhoff, S. W. "Semi-Empirical Estimation of Adsorption of Hydrophobic Pollutants on Natural Sediments and Soils." Chemosphere 10: 833--846 (1981).
- Karickhoff, S. W., D. S. Brown, and T. A. Scott. "Sorption of Hydrophobic Pollutants on Natural Sediments." Water Research 13: 241--248 (1979).
- Analytical Chemistry of Polycyclic Aromatic Hydrocarbons, Lee, M. L.; M. V. Novotry; K. D. Bartle, (Eds.), Academic Press, New York, (1981).
- Lion, L. W., T. B. Stauffer, and W. G. MacIntyre. "Sorption of Hydrophobic Compounds on Aquifer Materials: Analysis Methods and the Effect of Organic Carbon." Journal of Contaminant Hydrology 5, no. 3: 215--23 (1990).
- Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Mackay, C., W. Y. Shiu, and K. C. Ma. (Eds.). Ann Arbor, MI: Lewis Publishers.; 57--337 (1992).

- Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Mackay, C., W. Y. Shiu, and K. C. Ma. (Eds.). Ann Arbor, MI: Lewis Publishers.: 57--337 (1992).
- Mackay, D., and B. Powers. "Sorption of Hydrophobic Chemicals from Water: A Hypothesis for the Mechanism of the Particle Concentration Effect." Chemosphere 16: 745--757 (1987).
- Martin, R. J., and K. S. Al-Bahrani. "Adsorption Studies Using Gas-Liquid Chromatography: 2. Competitive Adsorption." Water Research. 11: 991--999 (1977).
- McCarty, Perry L., Martin Reinhard, and Bruce E. Rittman. "Trace Organics in Groundwater." Environmental Science & Technology 15, no. 1: 40--51 (1981).
- McGinley, P. M., L. E. Katz, and W. J. Weber Jr. "A Distributed Reactivity Model for Sorption by Soils and Sediments .2. Multicomponent Systems and Competitive Effects." Environmental Science & Technology 27, no. 8: 1524--1531 (August 1993).
- Means, Jay C., Susanne G. Wood, John J. Hassett, and Wayne L. Banwart. "Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils." Environmental Science & Technology 14, no. 12: 1524--1528 (1980).
- Miller, C. T., and J. A. Pedit. "Use of a Reactive Surface- Diffusion Model to Describe Apparent Sorption Desorption Hysteresis and Abiotic Degradation of Lindane in a Subsurface Material." Environmental Science & Technology 26, no. 7 :1417--1427(July1992).
- Miller, C. T., and Weber W. J. Jr. "Modeling the Sorption of Hydrophobic Contaminants by Aquifer Materials --- II: Column Reactor Systems." Water Research 22, no. 4: 465--474 (1988).
- Miller, C. T., and W. J. Weber. "Modeling the Sorption of Hydrophobic Compounds by Aquifer Materials---II. Column Reactor Studies." Water Resources Research 22, no. 4: 465--474 (1988).
- Miller, C. T., and W. J. Weber Jr. "Sorption of Hydrophobic Organic Pollutants in Saturated Soil Systems." Journal of Contaminant Hydrology 1: 243--261 (1986).
- Murali, V., and L. A. Aylmore. "Competitive Adsorption During Solute Transport in Soils: 1. Mathematical Models." Soil Science 135: 143--150 (1983a).
- Murali, V., and L. A. Aylmore. "Competitive Adsorption During Solute Transport in Soils: 2. Simulations of Competitive Adsorption." Soil Science 135): 203--213 (1983b).
- Murali, V., and L. A. Aylmore. "Competitive Adsorption During Solute Transport in Soils: 3. A Review of Experimental Evidence of Competitive Adsorption and an Evaluation of Simple Competition Models." Soil Science 136: 279--289 (1983c).

- Identifying and Estimating the Genetic Impact of Chemical Mutagens, National Research Council, National Academy Press, Washington, D.C., (1983).
- Nkedi-Kizza, P., P. S. C. Rao, and A. G. Hornsby. "Influence of Organic Cosolvents on Sorption of Hydrophobic Organic Chemicals by Soils." Environmental Science & Technology 19, no. 10: 975--979 (1985).
- Nkedi-Kizza, P., M. L. Brusseau, P. S. C. Rao, and A. G. Hornsby. "Nonequilibrium Sorption During Displacement of Hydrophobic Organic Chemicals through Soil Columns with Aqueous and Mixed Solvents." Environmental Science & Technology 23, no. 7: 814--820 (1989).
- Ogram, A. V., R. E. Jessup, L. T. Ou, and P. S. C. Rao. "Effects of Sorption on Biological Degradation Rates of (2,4- Dichlorophenoxy)acetic Acid in Soils." Applied and Environmental Microbiology 49, no. 3 (1985): 582--587.
- Pedit, J. A., and C. T. Miller. "Heterogeneous Sorption Processes in Subsurface Systems: 1. Model Formulations." Environmental Science and Technology : in review (1994a).
- Pedit, J. A., and C. T. Miller. "Heterogeneous Sorption Processes in Subsurface Systems: 2. Model Applications." Environmental Science and Technology : in review (1994b).
- Pedit, J. A., and C. T. Miller. "Heterogeneous Sorption Processes in Subsurface Systems: 3. Diffusion Modeling Approaches." Environmental Science and Technology : in review (1994c).
- Perlanger, J. A., S. J. Eisenreich, and P. D. Capel. "Application of Headspace Analysis to the Study of Sorption of Hydrophobic Organic Chemicals to  $\alpha$ - $\text{Al}_2\text{O}_3$ ." Environmental Science & Technology 27, no. 5: 928--937 (May 1993).
- Pignatello, J. J. "Bisolute Effects in Sorption of Nonpolar Organic Compounds by Aqueous Soil Suspensions." Manuscript submitted for publication (1990).
- Powell, R. M., B. E. Bledsoe, G. P. Curtis, and R. L. Johnson. "Interlaboratory Methods Comparison for the Total Organic Carbon Analysis of Aquifer Materials." Environmental Science & Technology 23, no. 10: 1246--1249 (1989).
- Rabideau, A. J., and C. T. Miller. "Two-Dimensional Modeling of Aquifer Remediation Influenced by Sorption Nonequilibrium and Hydraulic Conductivity Heterogeneity." Water Resources Research 30, no. 5: 1457--1470 (1994).
- Rao, P. S. C., A. G. Hornsby, D. P. Kilcrease, and P. Nkedi-Kizza. "Sorption and Transport of Toxic Organic Substances in Aqueous and Mixed Solvent Systems." Journal of Environmental Quality 14, no. 3: 376--383 (1985).
- Rao, P. S. C., and R. E. Jessup. "Development and Verification of Simulation Models for Describing Pesticide Dynamics in Soils." Ecological Modeling 16: 67--75 (1982).
- Rao, P. S., L. S. Lee, and R. Pinal. "Cosolvency and Sorption of Hydrophobic Organic Chemicals." Environmental Science & Technology 24, no. 5: 647-- 654 (1990).

- Roberts, Paul V., M. N. Goltz, R. Scott Summers, J. C. Crittenden, and P. Nkedi-Kizza. "The Influence of Mass Transfer on Solute Transport in Column Experiments with an Aggregated Soil." Journal of Contaminant Hydrology 1, no. 4: 375--393 (1987).
- Roberts, Paul V., M. N. Goltz, and D. M. Mackay. "A Natural Gradient Experiment on Solute Transport in a Sand Aquifer, 3. Retardation Estimates and Mass Balances for Organic Solutes." Water Resources Research 22, no. 13: 2047--2058 (1986).
- Schwarzenbach, R. P., and John Westall. "Transport of Nonpolar Organic Compounds from Surface Water to Groundwater. Laboratory Sorption Studies." Environmental Science & Technology 15, no. 11: 1360--1367 (1981).
- Schwarzenbach, R. P., and John Westall. Sorption of Hydrophobic Trace Organics in Groundwater Systems. In E. Arvin (Ed.), Proc. Symp. Degradation, Retention Dispersion Pollutants Groundwater.: 39--55 (1984).
- Sheindorf, C. H., M. Rebhun, and M. Sheintuch. "Organic Pollutants Adsorption from Multicomponent Systems Modeled by the Freundlich Type Isotherm." Water Research 16: 357--362 (1982).
- Spurlock, F. C., and J. W. Biggar. "Thermodynamics of Organic Chemical Partition in Soils. 1. Development of a General Partition Model and Application to Linear Isotherms." Environmental Science & Technology 28: 989--995 (1994).
- Steen, W. C., D. F. Paris, and G. L. Baughman. "Chapter 23: Effects of Sediment Sorption on Microbial Degradation of Toxic Substances." Contaminants and Sediments, 477--482. ed. R. A. Baker. I. Ann Arbor, MI: Ann Arbor Science Publishers, Inc. (1980).
- Steinberg, Spencer M., J. J. Pignatello, and B. L. Sawhney. "Persistence of 1,2-Dibromoethane in Soils: Entrapment in Intraparticle Micropores." Environmental Science & Technology 21, no. 12: 1201--1208 (1987).
- Stumm, W., and J. J. Morgan. Aquatic Chemistry. New York: John Wiley and Sons, (1981).
- Szecsody, J. E., and R. C. Bales. "Sorption Kinetics of Low-Molecular-Weight Hydrophobic Organic Compounds on Surface-Modified Silica." Journal of Contaminant Hydrology 4: 181--203 (1989).
- Voice, T. C., C. P. Rice, and W. J. Weber. "Effect of Solids Concentration of the Sorptive Partitioning of Hydrophobic Pollutants on Aquatic Systems." Environmental Science and Technology 17, no. 9: 513--518 (1983).
- Voice, T. C., and W. J. Weber Jr. "Sorbent Concentration Effects in Liquid/Solid Partitioning." Environmental Science & Technology 19: 789--796 (1985).
- Weber, W. J. Jr., Y. P. Chin, and C. P. Rice. "Determination of Partition Coefficients and Aqueous Solubilities by Reverse Phase Chromatography --- I. Theory and Background." Water Research 20, no. 11: 1433--1442 (1986).

- Weber, W. J. Jr., P. M. McGinley, and L. E. Katz. "A Distributed Reactivity Model for Sorption By Soils and Sediments: 1. Conceptual Basis and Equilibrium Assessments." Environmental Science and Technology: 1--20 (1992).
- Weber, W. J. Jr., P. M. McGinley, and L. E. Katz. "Sorption Phenomena in Subsurface Systems: Concepts, Models and Effects on Contaminant Fate and Transport." Water Research 25, no. 5: 499--528 (1991).
- Weber, W. J. Jr., and C. T. Miller. "Modeling the Sorption of Hydrophobic Contaminants by Aquifer Materials--- I: Rates and Equilibria." Water Research 22, no. 4: 457--464 (1988).
- Wu, S. C., and P. M. Gschwend. "Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments and Soils." Environmental Science & Technology 20, no. 7: 717--724 (1986).
- Wu, Shian-C, and P. M. Gschwend. "Numerical Modeling of Sorption Kinetics of Organic Compounds to Soil and Sediment Particles." Water Resources Research 24, no. 8: 1373--1383 (1988).

