

DISSERTATION

**LUMPED APPROACH FOR SORPTION OF ORGANIC
CONTAMINANT MIXTURES TO SIMULATED AQUIFER
SORBENTS**

Volume I

(Chapters 1-4)

Submitted by

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In partial fulfillment of the requirements

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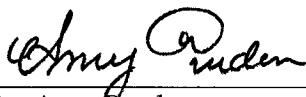
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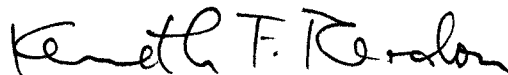
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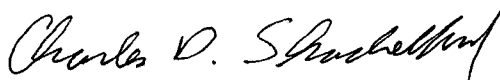
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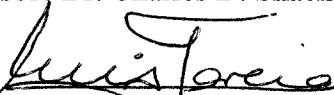
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ABSTRACT OF DISSERTATION

LUMPED APPROACH FOR SORPTION OF ORGANIC CONTAMINANT MIXTURES TO SIMULATED AQUIFER SORBENTS

In this study, the feasibility and accuracy of using a lumped approach to describe the sorption of 12 neutral organic compounds (NOCs), 6 polar NOCs (acetone, 2-butanone, 2-hexanone, phenol, *p*-cresol, and 2,4-dimethyl phenol) and 6 nonpolar NOCs (1,2,4-trichlorobenzene, 1,4-dichlorobenzene, chlorobenzene, *m*-xylene, toluene, benzene), in mixtures to simulated aquifer sorbents with fractions of organic carbon (f_{oc}) ranging from 0.005 to 0.221 % were evaluated. The lumped approach consists of grouping one or more components in mixtures of NOCs into a fewer number of pseudocompounds that exhibit similar behavior with respect to a process being considered (e.g., sorption). Batch equilibrium sorption tests (BESTs) were performed to measure the sorption behaviors of the 12 NOCs existing as both single NOCs and in mixtures of NOCs in aqueous solution with each sorbent. The results of the BESTs were analyzed using the Freundlich sorption equation, and the lumped approach was evaluated on the basis of experimentally derived lumping criteria (i.e., Freundlich sorption parameters). Also, the use of the ideal adsorbed solution theory (IAST) with the determined pseudocompounds for predicting the sorption of the 12 NOCs within complex mixtures to simulated aquifer sorbents was investigated.

The lumped approach for sorption of mixtures of NOCs to simulated aquifer sorbents was based on cluster analysis from statistics. Each pseudocompound contained components of relatively similar sorption capacities and nonlinearity, and approximated the sorption behavior of the NOC mixtures to within a 95 % confidence level of the Freundlich sorption isotherms for the pseudocompounds. The sorption behavior of the 12 NOCs in mixtures to the hydrophilic mineral surfaces was found to be described adequately on the basis of only four pseudocompounds, with each pseudocompound composed of from 2 to 4 NOCs. However, the number and composition of the pseudocompounds required to describe the sorption of the 12 NOCs in mixtures to humic acid-mineral complexes varied as a function of the f_{oc} due to the greater effect of f_{oc} on sorption for NOCs with greater hydrophobicity. For a given sorbent, the lumping schemes for the nonpolar NOCs in mixtures were consistent, i.e., independent of the compositions of the NOC mixtures, whereas those for the polar NOCs in mixtures were inconsistent, due to the complex mutual competition for hydrophilic specific sorption sites among the polar NOCs.

In addition to the experimentally derived lumping criteria (i.e., Freundlich sorption parameters), the potential for *a priori* theoretical lumping (i.e., prior to experimental evaluation) based on the quantitative structure-activity relationships of the NOCs was evaluated. The evaluation indicated that the lumping of the NOCs into pseudocompounds for sorption can be described according to the hydrophobicity (γ_w^{sat}) and the organic carbon partitioning coefficient (K_{oc}) of the NOCs in mixtures. Thus, the pseudocompounds could be determined directly *a priori* (i.e., without the need for experimentation) simply from the properties of the individual NOCs in mixtures.

Finally, based on comparisons of predicted sorption behavior using IAST with pseudocompounds to the measured sorption behavior, incorporating pseudocompounds into IAST to predict sorption of NOCs in complex mixtures was found to be feasible except in the case where the underlying assumptions of IAST (i.e., same access to sorption sites and ideal sorbed phase) became invalid. Nonetheless, further study is required to improve IAST predictions using pseudocompounds by incorporating terms to account for the differential availability of sorption sites and nonideal competition.

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CHAPTER 1

INTRODUCTION

1.1 Subsurface Contamination Resulting from Mixtures of Organic Compounds

Environmental contamination often results from the presence of mixtures of compounds in the subsurface. Such mixtures include gasoline, fuel hydrocarbon/chlorinated solvents, pesticides, and landfill leachates associated with a wide variety of sources, including underground and aboveground storage tanks, materials transport and transfer, oil production wells, subsurface percolation, injection wells, land application of wastewater and hazardous waste, landfills, and subsurface impoundments.

For example, gasoline can be comprised of as many as 500 distinct hydrocarbons with a substantial range of formula weights resulting in a large range of water solubilities, S_w , and hydrophobicities, K_{ow} (Rittman and McCarty 2001). Among the many possible additives for gasoline, the alcohols and methyl-*tert*-butyl ether (MTBE) can be major groundwater contaminants, along with gasoline hydrocarbons that are characterized by single-ring aromatics, such as benzene, toluene, ethylbenzene, and xylenes, which more commonly known as the BTEX compounds (Borden et al. 1997, Deeb et al. 2001).

In some instances, a mixture of related components that co-exist in a commercial product has contributed to subsurface contamination. An example of such a mixture is the polychlorinated biphenyls (PCBs) that can contain up to 209 individual chlorinated compounds due to substitution of chlorine (Cl) atoms on any of the 10 unlinked carbon atoms of the biphenyl group (Hutzinger et al. 1974).

Mixtures containing a wide range of disparate compounds also can occur in the subsurface when the compounds are co-disposed at a single site. For example, leachates generated at waste disposal sites often contain many organic and inorganic compounds that have contributed to subsurface contamination (Mcbean et al. 1995). Even when a single compound is released into the natural environment, intermediate compounds can be generated during the migration and degradation of the released compound in the subsurface. Additionally, these released and intermediate compounds also can react with soil organic matter (SOM) whose reaction and transport behavior may vary from one subcomponent to another due to the complexity in a range of polyfunctional groups and molecular sizes (McKnight et al. 1992, Gu et al. 1995, Sutton and Sposito 2005).

1.2 Sorption of Neutral Organic Compounds by Natural Geosorbents

Structurally and physicochemically different components of geosorbents, such as amorphous versus condensed SOM and high-surface-area carbonaceous material, macroporous versus meso- and micro-porous mineral matrices, and interlayer surfaces of swelling clays, have been found to interact differently with neutral organic compounds (NOCs) in terms of binding energies and rates of associated sorption and desorption (Chiou et al. 1979, McCarty et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Ball and Roberts 1991, Weber et al. 1992, Huang et al. 1996, Xing et al. 1996, Luthy et al. 1997, Mader et al. 1997, Chiou and Kile 1998, Xia and Ball 1999, Li and Werth 2001, Allen-King et al. 2002, Weber et al. 2002, Cornelissen et al. 2005, Nguyen and Ball 2006, Pignatello et al. 2006, Su et al. 2006). In addition, the fractionation and variations in structural and chemical properties of SOM, and the mineral surface

blockage by SOM in SOM-mineral complexes contribute to the distinct sorption reactivities for NOCs (Karickhoff 1984, Murphy et al. 1994, Liljestrand and Shimizu 1991, Rebhun et al. 1992, Onken and Traina 1997, Laor et al. 1998, Jones and Tiller 1999, Shen and Jaffé 2000, Hur and Schlautman 2004, Wang and Xing 2005, Feng et al. 2006). As a result, the overall sorption of NOCs by natural geosorbents has been found to be represented by the sum of the contributions of several active components in heterogeneously combined geosorbents.

Despite the prevalence of subsurface contamination in the form of mixtures of organic compounds, most studies evaluating the interactions of NOCs with various geosorbents comprised of different inorganic and organic components have involved single-sorbate systems to reveal sorption mechanisms for each component and to reconcile models for heterogeneous natural geosorbents. Although model development can be approached mechanistically from the study of simpler systems (i.e., single-sorbate systems), single-sorbate interactions with specific components of geosorbents may be significantly altered by the presence and the quantity of other sorbates due to complex interactions (e.g., competitive or synergistic effect) among sorbates within mixtures. The existence of such complex interactions may contribute to significant errors in predicting the fate and transport of individual NOCs within mixtures based on models developed from single-sorbate systems. Therefore, both systematic characterization and quantification of potential interactions among sorbates within mixtures may be required for such predictions.

1.3 Fate and Transport of Neutral Organic Compounds in Mixtures

The fate and transport of NOCs in the subsurface can be influenced by various physical, chemical, and biological processes, including advective and diffusive transport, hydrodynamic dispersion, sorption, and biological transformation (Mackay et al. 1985, Borden and Bedient 1986, Brusseau 1994, Clement et al. 1998). Whereas the fate and transport of individual NOCs in the subsurface have been studied extensively in both saturated and unsaturated porous media (Zheng 1990), much less is known about the fate and transport of mixtures of NOCs. Additionally, models describing the simultaneous fate and transport of NOCs in complex mixtures routinely ignore mixture effects, such as competitive or synergistic interactions (Clement 1997, Clement et al. 1998).

However, when such mixture effects are significant, the determination of pairwise interaction parameters among NOCs is required to accurately predict the fate and transport of mixtures of neutral organic compounds. Although the entire system of differential equations with interaction parameters that describe the fate and transport of NOCs within mixtures can be solved simultaneously in space and time, this detailed approach can become increasingly more complicated and less computationally efficient as the number of NOCs within mixtures increases, limiting the practical utility of the overall approach. Consequently, a new paradigm that balances practicality with accuracy in terms of modeling the subsurface fate and transport of NOCs within mixtures is needed.

1.4 Lumped Approach

An alternative to the detailed and comprehensive approach (i.e., one equation per NOC with interaction parameters) is the so-called "lumped approach", which describes the fate and transport of NOCs in complex mixtures in terms of the fate and transport of a

fewer number of groups of NOCs with similar behaviors, commonly referred to as pseudocompounds as shown in Fig. 1.1. Such a lumped approach has been widely applied in the oil-refining industry to provide tractable approximations to the stoichiometry, thermodynamics, and kinetics of complex hydrocarbon mixtures (Coxson and Bischoff 1987, Quann and Jaffe 1992, Jaffe et al. 2005). Also, a lumped approach has been applied in describing multicomponent adsorption of organic compounds to granular activated carbon (Calligaris and Tien 1982, Mehrotra and Tien 1984, Ramaswami and Tien 1986, Moon et al. 1991), sorption of heavy metals to humic substances (Yu et al. 1996), wastewater treatment (Li et al. 1996), biodegradation rates of compound mixtures (Brown 1998), partitioning of secondary organic aerosol mixtures (Bian and Bowman 2002, 2005), toxicology of compound mixtures (Dennison et al. 2004), and reactive transport of compound mixtures in the unsaturated zone (Karapanagioti et al. 2004).

Based on the successful application of the lumped approach to various complex systems, the use of a lumped approach to describe the sorption of NOCs within mixtures in terms of the sorption of a fewer number of pseudocompounds with similar sorption affinities may be a more practical and efficient approach, as shown in Fig. 1.2. In terms of grouping NOCs into pseudocompounds, all NOCs in mixtures can be grouped into a single pseudocompound in terms of parameters such as the total organic carbon (TOC), biological oxygen demand (BOD), or total Kjeldahl nitrogen (TKN). However, such a single pseudocompound approach, although convenient, is likely to be too simplistic and prone to inaccuracy, especially when the grouping parameter is not relevant in terms of distinguishing dissimilar behaviors among the NOCs within mixtures. Additionally, if knowledge of individual priority NOCs within mixtures is required, then this simple

approach may not be appropriate. Consequently, a more viable approach is to consider grouping the various NOCs into several pseudocompounds. This lumped approach must be sufficiently practical for use with larger mixtures, without the loss of accuracy through oversimplification. Also, the lumped approach must be flexible enough to track the individual priority NOCs within mixtures when necessary.

1.5 Goal and Objectives of Research

As a result of the aforementioned considerations, the primary goal of this research was to evaluate both the feasibility and accuracy of using the lumped approach to describe the sorption of mixture of 12 NOCs with a wide range of hydrophobicities (i.e., $-0.24 \leq \log K_{ow} \leq 4.23$) to several types of low-surface-area simulated aquifer sorbents, including hydrophilic mineral surfaces (i.e., uncoated, FeOOH-coated, and Al₂O₃-coated sands) and humic acid-mineral complexes with different f_{oc} values. This goal will be achieved by accomplishing the following objectives:

- (1) evaluate the contributions of SOM and mineral surface to the overall sorption of nonpolar NOCs by humic acid-coated sands with different fractions of organic carbon (f_{oc}) ranging from 0.024 to 0.154 %;
- (2) investigate the effect of various mineral surfaces on the adsorption-desorption of dissolved bulk, terrestrial humic acid to three simulated aquifer sorbents [uncoated, FeO(OH)-coated, and Al₂O₃-coated sands] at two equilibrium pH values;

- (3) investigate the roles of mineral surface and mineral-bound humic acid in the sorption of nonpolar NOCs to humic acid-mineral complexes with low fractions of organic carbon ($0.006 \% \leq f_{oc} \leq 0.044 \%$);
- (4) characterize both complex interactions and collective effects among NOCs at relatively low concentrations from either the same or the different neutral organic compound classes during the sorption to both mineral surfaces and humic acid-coated sands with different f_{oc} values;
- (5) assess the effectiveness of the lumped approach using both base case and random mixtures of NOCs in terms of sorption to different type of mineral surfaces and humic acid-coated sands with different f_{oc} values; and,
- (6) investigate both the feasibility and accuracy of the ideal adsorbed solution theory with Pseudocompounds to reduce difficulty and effort in computation in predictions of sorption of 12 NOCs in complex mixtures to simulated aquifer sorbents.

The approaches and results of each of these six objectives are described in Chapters 2 through 7, respectively of this dissertation.

1.6 Potential Impact of Research

The results of this research may have significant implications with respect to not only the feasibility and accuracy of the lumped approach, but also the complex interactions and collective effects among NOCs in mixtures during the sorption to both hydrophilic mineral surfaces (i.e., uncoated, FeOOH-coated, and Al₂O₃-coated sands) and humic acid-mineral complexes with different f_{oc} values. Furthermore, the results of this

research should advance our knowledge related to predictive tools describing sorption of NOCs within mixtures to various types of low-surface-area aquifer sorbents. Finally, the results of this research may impact our current approaches to risk assessment and risk management depending on the feasibility and accuracy of the lumped approach in terms of simplifying the description of the fate and transport of NOCs within mixtures, reducing experimental efforts by the use of theoretical lumping criteria, and providing results that are sufficiently accurate for practical purposes.

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Chemical Lumping (Species Grouping)

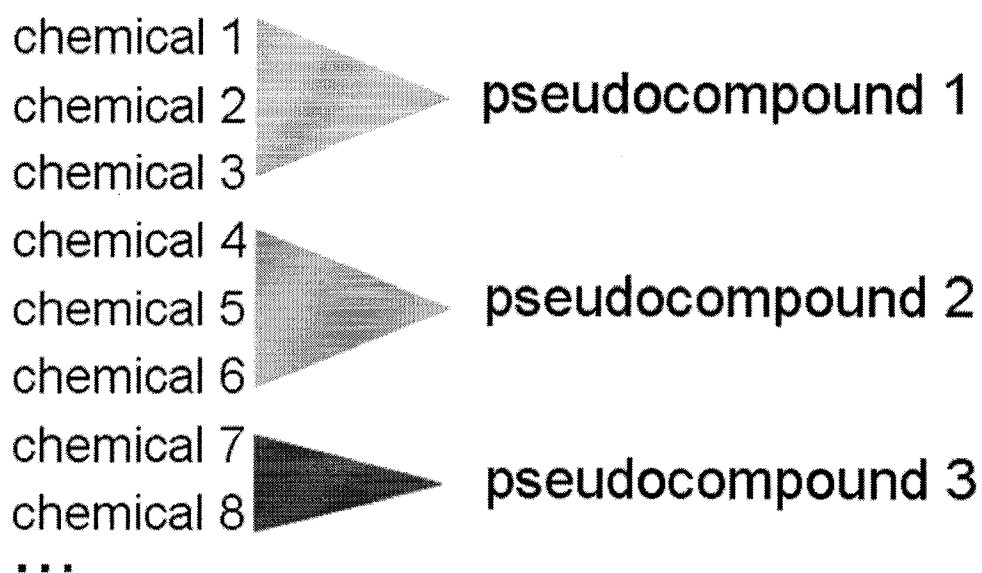


Fig. 1.1 A schematic diagram illustrating chemical lumping.

Detail Strategy vs. Lumping Strategy

Detail strategy

$$\begin{aligned}\frac{\partial C_1}{\partial t} &= D_{z,1} \frac{\partial^2 C_1}{\partial z^2} - v_z \frac{\partial C_1}{\partial z} - \frac{\rho_b}{n} \frac{\partial (K_{f,1} C_1^{a,1})}{\partial t} \\ \frac{\partial C_2}{\partial t} &= D_{z,2} \frac{\partial^2 C_2}{\partial z^2} - v_z \frac{\partial C_2}{\partial z} - \frac{\rho_b}{n} \frac{\partial (K_{f,2} C_2^{a,2})}{\partial t} \\ \frac{\partial C_3}{\partial t} &= D_{z,3} \frac{\partial^2 C_3}{\partial z^2} - v_z \frac{\partial C_3}{\partial z} - \frac{\rho_b}{n} \frac{\partial (K_{f,3} C_3^{a,3})}{\partial t} \\ \frac{\partial C_4}{\partial t} &= D_{z,4} \frac{\partial^2 C_4}{\partial z^2} - v_z \frac{\partial C_4}{\partial z} - \frac{\rho_b}{n} \frac{\partial (K_{f,4} C_4^{a,4})}{\partial t} \\ &\vdots \\ \frac{\partial C_n}{\partial t} &= D_{z,n} \frac{\partial^2 C_n}{\partial z^2} - v_z \frac{\partial C_n}{\partial z} - \frac{\rho_b}{\phi} \frac{\partial (K_{f,n} C_n^{a,n})}{\partial t}\end{aligned}$$

- No interaction/mixture effects
- Only sorption/no degradation
- No. of parameters = 3n
- No interaction → inaccuracies

Lumping strategy

$$\begin{aligned}\frac{\partial C_{PS1}}{\partial t} &= D_{z,PS1} \frac{\partial^2 C_{PS1}}{\partial z^2} - v_z \frac{\partial C_{PS1}}{\partial z} - \frac{\rho_b}{n} \frac{\partial (K_{f,PS1} C_{PS1}^{a,PS1})}{\partial t} \\ \frac{\partial C_{PS2}}{\partial t} &= D_{z,PS2} \frac{\partial^2 C_{PS2}}{\partial z^2} - v_z \frac{\partial C_{PS2}}{\partial z} - \frac{\rho_b}{n} \frac{\partial (K_{f,PS2} C_{PS2}^{a,PS2})}{\partial t} \\ &\vdots \\ \frac{\partial C_{PS3}}{\partial t} &= D_{z,PS3} \frac{\partial^2 C_{PS3}}{\partial z^2} - v_z \frac{\partial C_{PS3}}{\partial z} - \frac{\rho_b}{n} \frac{\partial (K_{f,PS3} C_{PS3}^{a,PS3})}{\partial t}\end{aligned}$$

- With interaction/mixture effects
- Only sorption/no degradation
- No. of parameters = 9+interaction
- More practical and not lose accuracy

Fig. 1.2 A schematic diagram illustrating the comparison between detail strategy and lumped strategy in terms of modeling the subsurface fate and transport of neutral organic compounds within mixtures.

CHAPTER 2

SORPTION OF NONPOLAR NEUTRAL ORGANIC COMPOUNDS TO HUMIC ACID-COATED SORBENTS SIMULATING LOW-CARBON AQUIFER SANDS

Abstract: The contributions of organic matter and mineral surface to the overall sorption of six nonpolar neutral organic compounds (1,2,4-trichlorobenzene, 1,4-dichlorobenzene, chlorobenzene, *m*-xylene, toluene, benzene) by five humic acid (HA)-coated sands with different fractions of organic carbon (f_{oc}) ranging from 0.024 to 0.154 % were evaluated on the basis of measured data and four different sorption models. Sorption of all six sorbates to both uncoated and heated sands was nearly linear due to the coverage of hydrophilic mineral surface with the ordered vicinal water region. Sorption of all six sorbates to the HA-coated sands was also essentially linear, and resulted from a combination of sorption to both organic matter and the mineral surface, with the dominance of either contribution depending on the properties of the sorbents (e.g., f_{oc}) and the sorbates (e.g., K_{ow}). A proposed two-component model for sorption including blocking effect was appropriate for quantifying the contributions of organic matter and the mineral surface to the overall sorption. However, conventional sorption models considering the contributions of both organic matter and mineral surface provided essentially as good agreement between predicted and measured distribution coefficients as the more complicated, two-component model for sorption that takes into account mineral surface blocking by HA.

Key Words: blocking effect, distribution coefficient, humic acid, hydrophobic partitioning, mineral surfaces, nonpolar neutral organic compounds, sorption

2.1 INTRODUCTION

The results of extensive research indicate that the sorption of organic compounds to surface soils, sediments, and aquifer materials is affected by the properties of the soil organic matter (SOM) and mineral compositions of these materials (Chiou et al. 1979, 1983, McCarty et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Garbarini and Lion 1986, Stauffer and MacIntyre 1986, Grathwohl 1990, Murphy et al. 1990, 1992, 1994, Ball and Roberts 1991, Rutherford et al. 1992, Weber et al. 1992, Schwarzenbach et al. 1993, Kile et al. 1995, Weber and Huang 1996, Huang et al. 1996, Xing et al. 1996, Luthy et al. 1997, Mader et al. 1997, Chiou and Kile 1998, Xia and Ball 1999, Shen and Jaffé 2000, Allen-King et al. 2002, Xiao et al. 2004, Nguyen and Ball 2006). In general, the sorption of polar neutral organic compounds (NOCs) to water saturated surface soils, sediments, and aquifer materials has been shown to be competitive and nonlinear at concentrations (C_e) that are low relative to the solubility of the compounds (S_w) (i.e., $C_e/S_w < 0.1$) (Xing et al. 1996, Chiou and Khile 1998). In contrast, the sorption of nonpolar and low-polarity NOCs to water saturated surface soils, sediments, and aquifer materials has been shown to be noncompetitive and relatively linear over limited concentration ranges (i.e., $C_e/S_w < 0.5$) (Chiou et al. 1979, 1983, McCarty et al. 1981, Schwarzenbach and Westall 1981, Karickhoff et al. 1984, Stauffer and MacIntyre 1986, Schwarzenbach et al. 1993, Huang et al. 1996, Mader et al. 1997, Shen and Jaffé 2000).

The difference in these results has been attributed to the difference in sorption mechanisms between polar versus nonpolar NOCs.

For example, nonlinear sorption of polar NOCs has been attributed to such complex mechanisms as hydrophobic partitioning, hydrogen bonding, and specific bonding of reactive moieties and sorbent surface atoms or groups (Isaacson and Frink 1984, Senesi 1992, Senesi et al. 1994, Schwarzenbach et al. 1993). In contrast, linear sorption of nonpolar NOCs has been attributed to hydrophobic partitioning into a highly amorphous and lipophilic humic matrix, together with suppressed adsorption onto mineral surfaces by water molecules coating the surfaces of sediments and aquifer materials (Chiou et al. 1979, Schwarzenbach and Westall 1981, Karickhoff et al. 1984, Schwarzenbach et al. 1993, Huang et al. 1996, Onken and Traina 1997, Mader et al. 1997, Shen and Jaffé 2000).

The results of several studies also indicate that linear hydrophobic partitioning of nonpolar NOCs to SOM, whereby the distribution coefficient (K_d) is equal simply to the product of the fraction of organic carbon (f_{oc}) and the organic carbon partitioning coefficient (K_{oc}) (i.e., $K_d = f_{oc}K_{oc}$), is unlikely for sorbents with $f_{oc} \leq 0.1$ % (Hassett et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Curtis et al. 1986, Kishi et al. 1990, Ball and Roberts 1991, Paya-Perez et al. 1991, Rebhun et al. 1992, Shen and Jaffé 2000). Therefore, since f_{oc} is less than 0.1 % for most aquifer sands (Stauffer et al. 1989, Burris et al. 1991, Larsen et al. 1992), sorption of nonpolar NOCs to aquifer sands likely results from both adsorption onto mineral surfaces and partitioning into organic carbon (e.g., McCarty et al. 1981, Karickhoff 1984, Curtis et al. 1986, Kishi et al. 1990, Paya-Perez et al. 1991, Rebhun et al. 1992, Weber et al. 1992). In contrast, Lion et al. (1990)

indicated that organic carbon still continues to play a dominant role even below the commonly cited threshold level for f_{oc} of 0.1 %. However, this threshold f_{oc} appears to vary as a function of the hydrophobicity of NOCs (Karickhoff 1984, Banerjee et al. 1985). Thus, the threshold values for f_{oc} also likely depend on the properties of the NOCs and sorbent of interest. As a result of these considerations, some modifications to the linear hydrophobic partitioning concept have been proposed (McCarty et al. 1981, Karickhoff 1984, Curtis et al. 1986, Kishi et al. 1990, Paya-Perez et al. 1991, Rebhun et al. 1992, Weber et al. 1992).

For example, McCarty et al. (1981) proposed the concept of a critical level of the f_{oc} in inorganic matrices, or f_{oc}^* , that represents the f_{oc} at which sorption to the organic and inorganic components is equal. Based on this concept, the organic component dominates sorption for sorbents with $f_{oc} > f_{oc}^*$, whereas the mineral component dominates sorption for sorbents with $f_{oc} < f_{oc}^*$. Karickhoff (1984) also postulated that the mineral contribution to the sorption of nonpolar NOCs becomes important for compounds with less than 10 carbons when the mass ratio of the mineral to the organic carbon in the sorbents is greater than 60, while the mineral contribution to the sorption of polar NOCs becomes important when the mass ratio is greater than 25 to 60. Therefore, the linear hydrophobic partitioning model may underestimate sorption when the mass ratio of the mineral to the organic carbon in sorbents is greater than the threshold value (i.e., 60 for nonpolar NOCs and 25 to 60 for polar NOCs).

Adsorption to mineral surfaces also may occur either independently or in concert with partitioning to organic carbon (Curtis et al. 1986). For example, the two-component model proposed by McCarty et al. (1981) assumes that adsorption onto mineral surfaces

occurs independent of partitioning into organic carbon, whereas the model proposed by Karickhoff (1984) assumes that adsorption onto mineral surfaces occurs in concert with partitioning into organic carbon. In addition, the contribution of adsorption onto mineral surfaces has been found to be negligible for some sorbents with relatively high f_{oc} (≥ 0.1 -1 %) (Chiou et al. 1979, 1983, Schwarzenbach and Westall 1981, Lion et al. 1990), but significant for other sorbents with relatively low f_{oc} (≤ 0.1 %), depending on the properties and amount of SOM as well as the surface properties of the sorbents (Banerjee et al. 1985, Curtis et al. 1986, Kishi et al. 1990, Liljestrand and Shimizu 1991, Paya-Perez et al. 1991, Larsen et al. 1992, Rebhun et al. 1992, Shen and Jaffé 2000). The differences in these results emphasize the need to determine (1) whether or not bound organic matter masks mineral sorption, and (2) if the dominance between partitioning into organic carbon versus adsorption onto mineral surfaces is a function of the properties of both the sorbates and the sorbent, such as the f_{oc} and surface area of the sorbent and the hydrophobicity of the sorbate.

Since linear adsorption of nonpolar NOCs onto mineral surfaces has been reported to occur simultaneously with linear partitioning into organic carbon, composite linear sorption models have been proposed to evaluate the relative contribution of adsorption onto mineral surfaces to the overall sorption (McCarty et al. 1981, Karickhoff 1984, Curtis et al. 1986, Liljestrand and Shimizu 1991, Rebhun et al. 1992, Shen and Jaffé 2000). However, such composite linear sorption models may not be appropriate if sorption to one or more sorbent components is nonlinear. For example, Weber et al. (1992) proposed a distributed reactivity model whereby the composite sorption behavior of NOCs is represented as the resultant of a series of near-linear partitioning or

absorption reactions and nonlinear adsorption reactions. In this model, the reactivities of NOCs are distributed to different soil fractions such that particle-scale heterogeneity significantly affects the sorption behavior of NOCs.

Based on the aforementioned considerations, two particle-scale domains (i.e., quartz and amorphous SOM) are hypothesized in this study as playing a dominant role in the sorption rate and equilibrium of six nonpolar NOCs to several sorbents with different f_{oc} simulating low-carbon aquifer sands. The specific objectives of this study are to (1) evaluate the effect of the content of SOM on the sorption of the six individual nonpolar NOCs, (2) elucidate the contributions of SOM and mineral surfaces to the overall sorption of six nonpolar NOCs, and (3) evaluate the use of a calibrated two-component model with single blocking parameter for adsorption of nonpolar NOCs onto minerals surfaces and hydrophobic partitioning of nonpolar NOCs into SOM. To achieve these objectives, organic-free sand was coated with a known amount of humic acid (HA) extracted from a commercial peat soil to produce aquifer sands with SOM simulating a mineral-bound monolayer of amorphous HA. This process provided sorbents that were more homogeneous than complex natural aquifer sands such that the roles of SOM and mineral surfaces in the sorption of nonpolar NOCs by low-carbon aquifer sands could be discerned. Also, to the best of the authors' knowledge, the investigation described in this study represents the first attempt to discern the effect of mineral phase blocking of low-surface-area coarse-grained aquifer materials (i.e., sands) by humic substances.

2.2 MATERIALS AND METHODS

2.2.1 Humic Acid

As noted in several studies (Piccolo 2001, Sutton and Sposito 2005), soil organic matter (SOM) is a complex mixture of diverse polyfunctional organic molecules from heterogeneous materials (e.g., plant parts, microorganisms, and any specifically identifiable biochemicals such as polysaccharides, proteins, and lignins) linked by hydrogen bonds and hydrophobic interactions. In ground water, the three primary natural sources of SOM derived from heterogeneous materials include: (i) deposits of organic matter such as buried peat, kerogen, and coal; (ii) humic substances in soils and sediments; and (iii) dissolved organic matter emanating from the overlying soil and vadose zone (Aiken 2002). Although the relative contributions of these sources of SOM vary between different water bodies, quantification of this variation based on chemical characterization of SOM is currently not possible (Aiken 2002). Thus, in this study, humic acid (HA) was extracted from a commercial peat soil (Voluntary Purchasing Groups, Inc., Bonham, TX) using the method recommended by International Humic Substances Society (Swift 1996) to represent the terrestrial HA that would be derived from overlying soils in the field. Although the extracted HA from a commercial peat soil may not be a representative of naturally occurring terrestrial HA, the extracted HA was used as a model surrogate for SOM in this study.

A 0.5-kg sample of peat soil was stirred in 5 L of 0.1 M NaOH under nitrogen gas ($N_{2(g)}$) for 12 h. The solution was centrifuged (MARATHON 21000R, Fisher Scientific Co., Pittsburgh, PA), and the supernatant was acidified to pH 1 with 6 M HCl. The precipitated HA from the supernatant was separated by centrifugation at 7,250 g for 20 min. The HA precipitate was treated subsequently with 0.3 M HF to remove ash, rinsed with nanopure water (Barnstead/Thermolyne, Dubuque, IA) in a dialysis tube with a

nominal molecular weight cutoff of 12,000-14,000 Daltons (Fisherbrand[®] dialysis tubing, Fisher Scientific Co., Pittsburgh, PA) until a silver nitrate test for chloride was negative, and then the dialyzed HA was heated at 40 °C until dry.

As recommended by Chen et al. (1977), the absorbance of each HA sample at 465 and 665 nm was measured with a spectrophotometer (DU[®] 640, Beckman Instruments, Inc., Fullerton, CA) by dissolving 20 mg of HA in 100 mL of 0.05 N NaHCO₃ (pH = 8.0) and filtering the resulting HA solution through glass fiber filter (Millipore AP40, Millipore Co., Bedford, MA). Similar to Schnitzer (1971), the measured ratios of absorbance at 465 nm to that at 665 nm, or E_4/E_6 , for the HA ranged from 5.12 to 5.40, as shown in Table 2.1. The elemental compositions of HA extracted from the commercial peat potting soil also are given in Table 2.1. As a first approximation to describe the affinity of HA used in this study for sorption of nonpolar NOCs, the elemental compositions of extracted HA indicate that HA used in this study is geologically immature and less condensed (Luthy et al. 1997, Allen-King et al. 2002).

2.2.2 Sorbents

Organic coating of aquifer materials has been found to occur to different degrees, depending on aquifer mineralogy, water chemistry, and the composition and nature of SOM (Murphy et al. 1990, 1992, 1994, Wang and Xing 2005, Feng et al. 2006). Additionally, SOM can be modified by a wide variety of physical, chemical, and biological processes, including thermal alterations associated with either combustion and pyrolysis or deep burial (Luthy et al. 1997, Allen-King et al. 2002, Nguyen and Ball 2006). Although aquifer materials are heterogeneous and complex in terms of the

composition and structure of the inorganic and organic components, the specific sorption mechanisms and contributions of each component to overall sorption may be discerned through manipulating the type and composition of model sorbents (Murphy et al. 1990, 1992, 1994, Burris et al. 1991, Rebhun et al. 1992, Celis et al. 1997, Onken and Traina 1997, Shen and Jaffé 2000).

Based on consideration of the results of these studies (Murphy et al. 1990, 1992, 1994, Burris et al. 1991, Rebhun et al. 1992, Celis et al. 1997, Onken and Traina 1997, Shen and Jaffé 2000), three different types of model sorbents were used in this study, viz., (1) uncoated Ottawa sand, (2) acid washed Ottawa sand heated at 700 °C to remove total carbon, and (3) acid washed and heated Ottawa sand coated with HA to provide sorbents with varying f_{oc} . Ottawa sand (F-95, U.S. Silica, Berkeley Springs, WV) was used as the reference aquifer sand prior to any surface modification or treatment, because Ottawa sand is essentially absent of any impurities, such as metal oxides and SOM (see Table 2.2).

The sand was sieved (-60/+80 mesh sizes) by using the standard dry sieve technique (ASTM D 421), washed with nanopure water, air-dried, and sterilized by gamma irradiation (2.5 M rad) from a ^{137}Cs source (Cesium Irradiation Lab, Colorado State University, Fort Collins, CO). The resulting particle-size distribution for Ottawa sand based on dry mechanical sieve analysis is shown in Fig. 2.1. Gamma irradiation was used for sterilization because gamma irradiation has been found to have minimal impact on the sorption of contaminants by soil (Sheremata et al. 1997). The sterilized samples were stored before use in 50-mL screw-cap plastic tubes at room temperature (22 ± 2 °C). A model sorbent free of organic carbon ($f_{oc} = 0$ %) also was prepared by washing Ottawa

sand with 1 N HCl and heating the acid washed sand at 700 °C overnight. The heated sand also was sterilized by gamma irradiation prior to use and stored in 50-mL screw-cap plastic tubes.

Burris et al. (1991) suggested the use of silica sand coated with HA as a simplified sorbent to simulate aquifer sands that are heterogeneous with low f_{oc} . Based on this approach, aquifer sands with highly amorphous or soft SOM were simulated in this study by heating a mixture of the Ottawa sand and a known amount of extracted HA at 100 °C. Since the HA is the fraction of SOM that is soluble only under alkaline conditions (Swift 1996), solutions with initial HA concentrations of 0.5, 1, 2, 3, 4 g/L were prepared by dissolving dried, extracted HA in a 0.1-M NaOH solution (pH = 10.9) for 3 days and subsequently filtering the solutions through a glass-fiber filter (Millipore AP40, Millipore Co., Bedford, MA). The sand was acid washed with 1 N HCl (pH = 1.03) and heated at 700 °C overnight to remove all organic carbon ($f_{oc} = 0$ %) before being placed in a 6-L stainless-steel sample container filled with a 0.1-M NaOH solution containing HA. The mixture was acidified by titrating 1 N HCl drop-wise while stirring until the pH decreased to 1.5, after which the suspended HA was allowed to settle overnight before the supernatant was decanted. Finally, the HA precipitates and sand were mixed by hand using a stainless-steel scoop to achieve a homogeneous coating, and the mixture was heated at 100 °C to enhance attachment of the HA to the sand. Occasional hand mixing with the scoop was needed to break clumps and to enhance a more homogeneous coating of the HA onto the sand. The HA-coated sand was sieved and rinsed vigorously with 0.1-M phosphate buffer (pH = 7.40) using a reciprocating shaker (Rotomix, Thermolyne, Dubuque, IW) until the supernatant was clear. Finally, the HA-

coated sand was sterilized by gamma irradiation prior to use and stored in a 0.1-mm-thick low density polyethylene bags (Dyer Packing, Inc., Willowbrook, IL).

2.2.3 Characterization of Sorbents

The physical and chemical characterization of the model sorbents is summarized in Table 2.3. The total organic carbon (TOC) of each sorbent was determined by Huffman Laboratories (Golden, CO) as the difference between total carbon (TC) and total inorganic carbon (TIC). A high combustion method was used with a coulometrics detector (Coulometrics Model 5011 Coulometrics, Inc., Golden, CO) to measure TC. This combustion system is similar to the one described in ASTM D5373 whereby samples are combusted at 1000 °C in oxygen. Oxygen carrier gas sweeps the combustion products through catalysts to insure complete oxidation of all carbon (C) to carbon dioxide (CO₂) and hydrogen (H) to water (H₂O). Potentially interfering substances, such as halogens and sulfur, are removed or oxidized, H₂O is trapped, and the CO₂ is measured with a CO₂ coulometer. When the measurement is complete, water is released from the water trap. Finally, carbonyldiimidazole [(C₃H₃N₂)₂CO] hydrolyzes to CO₂, and CO₂ is measured by a second coulometer.

The TIC is determined using a UIC/Coulometrics system 140 carbonate carbon analyzer (Coulometrics, Inc., Golden, CO). A typical analysis consists of acidifying a sample with 0.1-N perchloric acid (HClO₄ in glacial acetic acid) to convert carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) to CO₂. The CO₂ then is swept to the CO₂ coulometer for quantification (ASTM D513-92B and EPA/600/8-87/020). The detection limits for TC,

TIC, and TOC were 0.05 %, 0.02 %, and 0.05 %, respectively. For trace analysis, the detection limits for TC, TIC, and TOC were all 0.005 %.

The surface area and intraparticle porosity of the sorbents were determined by Porous Materials, Inc. (Ithaca, NY) via a nitrogen adsorption analysis with a volumetric apparatus (BET Sorptometer, Porous Materials, Inc., Ithaca, NY). The equilibrium volume of nitrogen adsorbed on a sample was determined by measuring the decrease in pressure of a known volume of nitrogen at a controlled pressure and temperature. The decrease in pressure resulted from the expansion of nitrogen as nitrogen was released from the manifold to the sample cell and from nitrogen adsorbing onto the sample. The multi-point surface area was determined after low-temperature adsorption data were fitted by the BET method (Brunauer et al. 1938), and the total pore volume was determined.

The surface topography and HA-coating status were measured using a field emission scanning electron microscopy (SEM) [JEOL JSM-6500F, JEOL USA Inc. Peabody, MA]. The samples were coated with 10-nm-thick layer of gold by a sputter coater and were placed inside the vacuum column of the microscope. The appropriate observation mode, accelerating voltage, probe current, and working distance were adjusted for best results, and two different magnifications (i.e., x400 and x7000) of SEM images for each sorbent were obtained.

2.2.4 Aquifer Sands with Low Organic Carbon Content

The sand was coated with HA at two solid-to-liquid (S:L) ratios based on the procedures from Burris et al. (1991), and the resulting correlation between initial aqueous concentrations of HA and f_{oc} is shown in Fig. 2.2. As shown in Fig. 2.2, the amount of

HA coated onto the sand increases with increase in the initial aqueous concentration of HA, and increases with increase in the S:L ratio, indicating that the HA can be attached physically onto the surface of heated sand at different coverages. In addition, for a given S:L ratio, the correlation between the amount of HA coated onto the sand and the initial aqueous concentration of HA is linear. Thus, the value of f_{oc} for a given sorbent was controlled based on the correlation between the initial aqueous concentration of HA and f_{oc} . Most synthetic HA-mineral complexes have been prepared by chemisorption due to a variety of mechanisms including anion exchange, ligand exchange-surface complexation, hydrophobic interaction, entropic effects, hydrogen bonding, and cation bridging (Murphy et al. 1990, 1992, 1994, Rebhun et al. 1992, Celis et al. 1997, Onken and Traina 1997, Shen and Jaffé 2000, Wang and Xing 2005, Feng et al. 2006). Since coating the quartz sand with HA was achieved by physical attachment in this study, fractionation by preferential adsorption and variations in structural and chemical properties of mineral-bound HA were not considered.

The SEM images of four model sorbents at two different magnifications (i.e., x400 and x7000) are shown in Fig. 2.3. While the surfaces of the uncoated and heated sand (see Figs. 2.3a-2.3d) are shown to be nonporous and of purely quartz minerals without any coating and impurities based on SEM/EDS spectra, the surfaces of the HA-coated sand (see Figs. 2.3e-2.3h) are shown to be covered with relatively thin and amorphous SOM, typically about 0.05-0.11 μm in thickness. This narrow range of thickness of SOM is close to other studies that indicate the SOM thickness in natural solids is about tens of nanometers (Carroll et al. 1994, Mayer 1994). Although distinct shallow crevasses are apparent for the HA-coated sand with high f_{oc} (i.e., 0.119 and

0.152 %), the HA coating appears to be well distributed without significant isolated accumulations on the surface.

As shown in Table 2.3, both the specific surface area using $N_{2(g)}$ and intraparticle porosity of HA-coated sand are close to those of uncoated sand and heated sand, but increase slightly with increasing f_{oc} . As f_{oc} increases, exposed mineral surface area decreases, but new adsorption surfaces for $N_{2(g)}$ become available within the matrix of the HA. Thus, the overall total surface area is a combination of these two opposing trends. In addition, the HA used for coating does not contain carbonaceous materials with high surface areas, such as charcoal and soot, and the surface of HA-coated sand is coated with relatively thin and amorphous SOM matrices. Although the use of these model sorbents allows the roles of the SOM and mineral surfaces in the sorption of NNOCs by low-carbon aquifer sands to be discernable, the results reported in this study may not be directly applicable to field situations in cases where more complex aquifer materials are present.

2.2.5 Sorbates

A total of six nonpolar neutral organic compounds (NNOCs) were used as sorbates in this study, viz., 1,2,4-trichlorobenzene (1,2,4-TCB), 1,4-dichlorobenzene (1,4-DCB), chlorobenzene (CB), *m*-xylene (*m*-XYL), toluene (TOL), benzene (BZ). All of these sorbates are listed as priority hazardous compounds by the Agency for Toxic Substances and Disease Registry (ATSDR). All sorbates were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO) and Fisher Scientific Co. (Pittsburgh, PA), and were of the highest available purity. These included: 1,2,4-TCB (Aldrich, 99+ %), 1,4-

DCB (Aldrich, 99+ %), CB (Aldrich, 99.9 %), *m*-XYL (Aldrich, 99+ %), TOL (Fisher, ACS Grade), and BZ (Aldrich, 99+ %). Selected properties of all six sorbates are summarized in Table 2.4.

Solutions of each individual sorbate were prepared by adding the exact amount of neat compound to nanopure water in a 0.5-L flat-bottom glass flask with a short neck (Pyrex Brand, Fisher Scientific Co., Pittsburgh, PA) to reduce any volatile loss to the gas phase, and by mixing the contents with a magnetic stirrer (Fisher Scientific Co., Pittsburgh, PA) at 600 rpm for 24 h before use. A bacterial inhibitor in the form of 300 mg/L of sodium azide (NaN₃) (Fisher Scientific Co, Pittsburgh, PA) was added to all solutions. Due to the volatile losses of compounds to the head space in preparing the solutions, the total mass of neat compounds added, m_{TOT} (μmol), was compensated as follows (Reardon et al. 2000):

$$m_{TOT} = m_L + m_G = m_L \left[1 + \left(\frac{H}{RT} \right) \left(\frac{V_G}{V_L} \right) \right] = \lambda m_L \quad (2.1)$$

where m_L and m_G refer to the masses (μmol) of the volatile neat compounds in the liquid and gas phases, respectively, H is the dimensional Henry's law constant (atm·L/mol), R is the Universal gas constant (0.082 atm·L/mol/K), T is the absolute temperature (K), and V_L and V_G refer to the volumes (L) of the liquid and gas phases, respectively. Since the solutions of each individual sorbate were prepared in a constant-temperature room, and the volumes of liquid and gas essentially remain constant, the constant λ for each sorbate can be obtained.

2.2.6 Analytical Methods

The concentration of each sorbate was measured using gas chromatography (HP 5890 II, Hewlett-Packard Co., Inc) with a flame ionization detector (GC-FID) and an autosampler (Agilent Technologies, Inc., Santa Clara, CA) with a 10 μ L syringe (Hamilton Co., Reno, NV). Aqueous samples were placed in a 2-mL auto-sampler glass vial (National Scientific Co., Duluth, GA) and sealed with Teflon[®]-lined septa. The optimum injected volume was determined based on resolution and separation of the peaks by injecting increasing amounts of standard solutions of each sorbate. The best results were observed for an injection rate of 1.0 μ L/s for all sorbates. Sorbates are separated on a 30 m x 0.53 mm x 1.5 μ m EQUITY[™]-5 column (Supelco, Inc., Bellefonte, PA). The flow rates for the gases were 3 mL/min for high-purity helium, 27 mL/min for non-flammable nitrogen gas, 40 mL/min for hydrogen gas, and 400 mL/min for compressed air. The temperatures of the inlet and detector were 225 °C and 250 °C, respectively. The oven temperature was held at an initial value of 40 °C for 4 min, raised at 6 °C/min to 180 °C, then increased at 20 °C/min to 200 °C, and finally held at 200 °C for 1 min.

In order to facilitate the qualitative identifications and quantitative determination of each sorbate, the external standard curves were prepared for each sorbate. Also, in order to correct for the loss of sorbates during sample preparation or sample inlet process, the internal standard (i.e., *o*-XYL) was used for calibration by determining the ratio of the peak area of sorbate to the peak area of an internal standard.

2.2.7 Batch Sorption Methodology

The batch equilibrium sorption tests (BESTs) were performed by adding 17.25 g of sorbent to a 41-mL glass centrifuge tube (Kimble Glass Inc., Vineland, NJ) at a constant solid-to-liquid ratio, S:L, of 1:2 (w/w). The S:L of 1:2 (w/w) was selected based on achieving a minimum of 20 % sorption of the sorbates (Roy et al. 1991, Delle Site 2001). Diluted solutions of sorbates with 10 different initial concentrations (i.e., 6, 8, 10, 20, 40, 50, 80, 100, 120, and 150 $\mu\text{mol/L}$) were added and sealed immediately with a Teflon[®]-lined Mininert[®] valve (Valco Instruments Co. Inc., Houston, TX) without headspace. The tube then was initially vortex mixed using a vortexer (VWR, West Chester, PA) for 20 s, and subsequently mixed end-over-end at 10 rpm and 20 °C during the entire experimental period to minimize the abrasion of sorbents. After the equilibrium time was pre-determined for each sorbate-sorbent system, the tube was centrifuged at 450 g for 20 min, and 2-mL aliquots of the supernatant were transferred to 2-mL auto-sampler glass vial with gas-tight glass syringe (5 mL Purge and Trap Syringe, Hamilton Co., Reno, NV). The collected samples were stored at 4 °C in a refrigerator and analyzed within one week after sampling. The concentration of any HA in the supernatant resulting from shear forces that break HA apart from HA-coated sand during the BESTs was measured at 254 nm with the spectrophotometer after sampling, i.e., since partitioning of sorbates to dissolved HA decreases the observed sorption coefficient (Gschwend and Wu 1985). The pH of supernatant also was measured (Hach one laboratory pH meter, Hach Co., Loveland, CO).

The sorption of a sorbate to sorbent was calculated based on the concentration difference method, whereby the difference in aqueous sorbate concentration between the equilibrated sample without sorbent (blank) and the equilibrated sample with sorbent was

used to calculate the amount of sorbed sorbate at each equilibrium concentration (see Fig. 2.4). The resulting sorbate concentration in the solid-phase at equilibrium ($\mu\text{mol/kg}$ of solid), C_s , is given as follows:

$$C_s = \frac{(C_{e,B} - C_{e,S}) \cdot V_w}{M_s} \quad (2.2)$$

where $C_{e,B}$ and $C_{e,S}$ are the sorbate concentrations in the aqueous phase ($\mu\text{mol/L}$) in the blank and with the sorbent at equilibrium, respectively, V_w is the volume of the solution in the batch tube (34.50 mL), and M_s is the mass of sorbent added to the batch tube (17.25 g). The potential for partitioning to the negligible headspace and sorption to Teflon[®]-lined septa and glass surfaces of the tube were monitored carefully. The recoveries from the blank tests depended on the sorbate. Therefore, blank tests were performed simultaneously for all tests to determine $C_{e,B}$. In this study, relative errors in the measurement of distribution coefficients were sufficiently low (0.01-0.08), compared to magnitude of sorption to each model sorbents.

Kinniburgh (1986) suggested that unweighted, linearized regressions to measured data using the Freundlich and Langmuir sorption equations should not be performed because such regressions can lead to biased estimates of the sorption parameters. Thus, sorption parameters for sorbates to various sorbents were obtained by nonlinear Freundlich regression using TableCurve 2-D V. 5.01 (SYSTAT software Inc. Point Richmond, CA), since nonlinear regression enables these sorption equations to be fitted directly with constant variance and a normally distributed error (Kinniburgh 1986).

2.2.8 Theoretical Considerations

2.2.8.1 Modeling Sorption for Multi-Component Aquifer Materials

Mathematical models describing the distribution of sorbates among multi-component aquifer materials have been developed to assist in explaining contaminant sorption as a multiple reaction phenomenon (McCarty et al. 1981, Karickhoff 1984, Curtis et al. 1986, Liljestrand and Shimizu 1991, Weber et al. 1992). For example, McCarty et al. (1981) and Karickhoff (1984) suggested composite linear sorption to assess the relative importance of mineral surfaces for natural sorbents with heterogeneous compositions. Weber et al. (1992) proposed a composite sorption model with a linear partition contribution and a Freundlich nonlinear adsorption contribution on the basis that physicochemical and structural features of aquifer materials lead to energetic differences between or within individual particles such that different combinations of linear and nonlinear local sorption are likely. Based on the assumption of sorption additivity of these two contributions (i.e., linear partition and Freundlich nonlinear adsorption), total sorption of sorbates to aquifer materials can be estimated from the following equation:

$$C_s = \sum_{i=1}^p x_{l,i} K_{d,i} C_e + \sum_{j=1}^q x_{nl,j} K_{f,j} C_e^{n,j} \quad (2.3)$$

where C_s is the sorbate concentration in the solid-phase at equilibrium ($\mu\text{mol/kg}$ of solid), C_e is the sorbate concentrations in the aqueous phase ($\mu\text{mol/L}$) at equilibrium, $x_{l,i}$ is the mass fraction of the i^{th} linearly sorbing component (kg of linear fraction of soil solid/kg of soil solid), $K_{d,i}$ is the distribution coefficient for reaction i expressed on a per mass of component i (L/kg of linear fraction of soil solid), $x_{nl,j}$ is the mass fraction of the j^{th}

nonlinearly sorbing component (kg of nonlinear fraction of soil solid/kg of soil solid), $K_{f,j}$ and $n_{f,j}$ are Freundlich capacity coefficient (($\mu\text{mol/kg}$ of nonlinear fraction of soil solid)/($\mu\text{mol/L}$) ^{$n_{f,j}$}) and Freundlich exponent for reaction j expressed on a per mass of component j , respectively, and p and q are the number of distinguishable linear and nonlinear components, respectively.

Since each of the linearly sorbing components yields a linear sorption, Eq. 2.3 can be written more concisely as follows (McCarty et al. 1981, Karickhoff 1984, Weber et al. 1992):

$$C_s = x_l K_d C_e + \sum_{j=1}^q x_{nl,j} K_{f,j} C_e^{n_{f,j}} \quad (2.4)$$

where x_l is the summed mass fraction of solid phase exhibiting linear sorption (kg of linear fraction of soil solid/kg of soil solid), and K_d is the mass-averaged distribution coefficient for the summed linear components (L/kg of linear fraction of soil solid).

In this study, two particle-scale domains (i.e., quartz and amorphous SOM) were considered to play potentially dominant roles in the sorption rate and equilibrium of sorbates to HA-coated sand, viz., amorphous SOM as the domain for hydrophobic partitioning and quartz as the domain for mineral adsorption. Thus, based on the approach described by Weber et al. (1992), Eq. 2.4 can be further simplified in this case as follows:

$$C_s = f_{om} K_{om} C_e + f_{min} K_{f,min} C_e^{n_{f,min}} \quad (2.5)$$

where f_{om} and f_{min} are the fractional masses of SOM (kg of SOM/kg of solid) and mineral (kg of mineral/kg of solid) for the HA-coated sand, respectively, K_{om} is the organic-matter-normalized distribution coefficient (L/kg of SOM), and $K_{f,min}$ and n,min are Freundlich capacity coefficient ($(\mu\text{mol/kg of mineral})/(\mu\text{mol/L})^n$) and Freundlich exponent for the mineral component, respectively.

Evidence that the properties of water are anomalous near solid surfaces is extensive (Drost-Hansen 1969, 2001, Adamson 1990). For example, Drost-Hansen (1969) proposed a three-region model for the structures of water near solid surfaces. In this model, a region of ordered (structurally-oriented) water is expected to exist near the surfaces, and the ordering extends into the bulk water to several hundred angstroms and decreases with the distance from the surfaces. Between the structure of the bulk water (i.e., local disorder) and the ordered water near the surfaces, there may be a region of enhanced disorder due to the “lattice dissimilarity”. In addition, the nature and extent of ordering will depend on the nature of the surfaces.

Three-region models for the structures of water near polar and nonpolar surfaces as proposed by Drost-Hansen (1969) are illustrated schematically in Figs. 2.5a and 2.5b, respectively. As shown in Fig. 2.5a, a polar surface is covered by a layer of chemically adsorbed water molecules (i.e., a hydroxylation layer) overlain by additional layers of physically adsorbed water molecules that extend for several layers of water out toward the bulk water. The intermediate region is the disordered transition between the ordered water and differently structured bulk water.

In contrast, the water molecules near the nonpolar surface are structured by hydrophobic interactions (Fig. 2.5b). In this case, a nonpolar surface may stabilize structural water units already present in the bulk or induce stabilized structures near the nonpolar surface, with these induced, stabilized structures subsequently decreasing with distance from the surface. Whereas the structure of water in the intermediate region in the case of a polar surface is distinguishable by the significant lattice dissimilarity between the structures of the bulk water and the ordered water near the surface, the structure of water in the intermediate region in the case of a nonpolar surface is significantly less distinguishable. In view of this concept of ordered water (i.e., “vicinal water”), various thicknesses of the vicinal water regions are possible, depending on the type and nature of the surface.

In the case where the surface includes both polar and nonpolar regions, a disordered transition may also exist at locations where the polar and nonpolar surfaces meet, as illustrated schematically in Fig. 2.5c. This disordered transition likely would develop in the physically ordered water layer (i.e., from 2 to more than 10 water layers) rather than in the chemically ordered water layer (i.e., first water layer), since the first hydroxylation layer is the most strongly associated with the polar surfaces via H-bonding (Drost-Hansen 1969, 2001, Adamson 1990, Schwarzenbach et al. 1993, Huang et al. 1996). Under such circumstances, the disordered transition may influence the degree of ordering of the water molecules, and the volume and structure of the vicinal water near both surfaces.

As previously described, since polar mineral surfaces (e.g., mineral oxides and hydroxides) are covered with a layer of chemically adsorbed water molecules overlain by

layers of physically adsorbed water molecules (Drost-Hansen 1969, 2001, Adamson 1990, Schwarzenbach et al. 1993, Huang et al. 1996), nonpolar sorbates are adsorbed and enriched in the vicinal water, but the sorption is not localized at specific adsorption sites on the mineral surfaces. Thus, adsorption of nonpolar sorbates onto polar mineral surfaces should exhibit linear sorption data since surface coverage is low and energy differences among sites are small due to the vicinal water (Ball and Roberts 1991, Huang et al. 1996, Luthy et al. 1997). For example, linear sorption of nonpolar sorbates to non-porous minerals, including α -Al₂O₃, α -Fe₂O₃, quartz, kaolinite, and amorphous SiO₂, from aqueous solution was observed for concentrations ranging as high as 50 % of aqueous solubilities of several nonpolar sorbates (Huang et al. 1996, Mader et al. 1997). In the case where mineral adsorption yields near-linear sorption behavior (i.e., $n_{min} \approx 1$), Eq. 2.5 can be further simplified into the composite linear sorption model proposed by McCarty et al. (1981) and Karickhoff (1984), as follows:

$$\frac{C_s}{C_e} = K_d = f_{om} K_{om} + f_{min} K_{min} \quad (2.6)$$

where K_{min} is the distribution coefficient to the mineral component (L/kg of mineral). If only the organic and one mineral component are considered, the sum of f_{om} and f_{min} equals unity (i.e., $f_{om} + f_{min} = 1$). For a given mineral, K_{min} is the product of the specific surface area of the mineral component, S_A (m²/kg of mineral), and the surface-area-normalized distribution coefficient, K_S (L/m²) (Curtis et al. 1986, Huang et al. 1996). Therefore, since $f_{oc}K_{oc} = f_{om}K_{om}$ and $K_{min} = S_A K_S$, Eq. 2.6 can be rewritten as follows:

$$K_d = f_{oc} K_{oc} + f_{min} S_A K_S \quad (2.7)$$

where K_{oc} is the organic carbon partitioning coefficient (L/kg of organic carbon). However, if sorption by partitioning into organic carbon becomes dominant such that the effect of the mineral surface is apparently negligible, the overall sorption can be described by well-known linear model based on simple hydrophobic partitioning into organic carbon (Karickhoff 1979, Schwarzenbach and Westall 1981), as follows.

$$K_d = f_{om} K_{om} = f_{oc} K_{oc} \quad (2.8)$$

The contribution of the mineral fraction to total sorption of sorbates can be determined by plotting K_d values versus f_{oc} for the sorption of a sorbate to a series of model sorbents with different f_{oc} (Kishi et al. 1990, Paya-Perez et al. 1991, Rebhun et al. 1992, Shen and Jaffé 2000). In this case, K_d can be determined from the following expression:

$$K_d = f_{oc} K_{oc}^* + K_{min}^* \quad (2.9)$$

where K_{oc}^* (L/kg of organic carbon) is the slope of the linear regression of K_d plotted against f_{oc} , and K_{min}^* (L/kg of mineral) is the y-intercept at $f_{oc} = 0$. Whereas K_{oc} is the organic carbon partitioning coefficient including the mineral adsorption contribution, K_{oc}^* is the amended organic carbon partitioning coefficient without the mineral adsorption contribution. Also, whereas K_{min} is the distribution coefficient to the pure mineral surface,

K_{min}^* is the distribution coefficient to the exposed (uncoated) mineral surface, representing the component of adsorption attributed only to the mineral surface. Since K_{min}^* for aquifer materials with low f_{oc} has been found to be significantly greater than zero (Kishi et al. 1990, Rebhun et al. 1992, Shen and Jaffé 2000), K_{oc}^* for the sorbate without the mineral adsorption contribution should be determined by subtracting K_{min}^* from K_d .

2.2.8.2 Critical Organic Fraction

McCarty et al. (1981) proposed the concept of a critical level of f_{oc} in inorganic matrices, or f_{oc}^* , that represents the f_{oc} at which sorption to the organic and inorganic components is equal. As a result, the organic component dominates sorption for sorbents with $f_{oc} > f_{oc}^*$, whereas the mineral component dominates sorption for sorbents with $f_{oc} < f_{oc}^*$. They have shown that f_{oc}^* depends on the surface area of inorganic component, S_A , and the octanol-water partitioning coefficient for sorbate, K_{ow} , as follows:

$$f_{oc}^* = \frac{S_A}{200(K_{ow})^{0.84}} \quad (2.10)$$

Predicted values of f_{oc}^* for different sorbates based on Eq. 2.10 were reported by McCarty et al. (1981).

An alternative definition of f_{oc}^* can be proposed for the special case of the model sorbents consisting of quartz and amorphous SOM considered in the present study. In this case, Eq. 2.7 can be re-written in terms of f_{oc} as follows:

$$K_d = \underbrace{f_{oc} K_{oc}}_{\text{hydrophobic partitioning}} + \underbrace{(1 - R f_{oc}) S_A K_S}_{\text{mineral adsorption}} \quad (2.11)$$

where $R (> 1)$ is the ratio of the fraction of organic matter to the fraction of organic carbon (i.e., $R = f_{om}/f_{oc}$). By equating the two terms on the right-hand-side of Eq. 2.11 and solving the resulting expression for f_{oc} , an alternative definition for f_{oc}^* ($= f_{oc}$) results as follows:

$$f_{oc} = f_{oc}^* = \frac{S_A K_S}{K_{oc} + R S_A K_S} \quad (2.12)$$

However, the alternative expression for f_{oc}^* given by Eq. 2.12 is based on the assumption of simple hydrophobic partitioning of sorbates to organic carbon (i.e., Eq. 2.8), which, as previously discussed, is not likely to be valid for sorbents with low f_{oc} (≤ 0.1 %). Also, the binding of SOM to mineral surface results in a decrease in the availability of adsorption sites on the mineral surface such that $K_{min} \neq K_{min}^*$. Based on these considerations, the expression for f_{oc}^* obtained by equating the two terms on the right-hand-side of Eq. 2.9 is likely to be more accurate, or:

$$f_{oc}^* = \frac{K_{min}^*}{K_{oc}^*} \quad (2.13)$$

2.2.8.3 Available Fractions and the Concept of Blocking Parameters

The K_{oc} values for nonpolar sorbates on aquifer materials with low f_{oc} (≤ 0.1 %) have deviated significantly from predictions of K_{oc} based on empirical K_{oc} - K_{ow} relationships, and the K_{oc} values are widely divergent and tend to increase as f_{oc} decreases due to the mineral adsorption contribution (Hassett et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Curtis et al. 1986, Stauffer et al. 1989, Murphy et al. 1990, Onken and Traina 1997). Thus, the K_{oc}^* values, representing hydrophobic partitioning of sorbates to organic carbon without the mineral adsorption contribution, are likely to be more accurate than the K_{oc} values in predicting the hydrophobic partitioning of sorbates to organic carbon.

The fractions of the organic carbon and mineral components that are available for sorption of a sorbate can be taken into account by modifying Eq. 2.7 as follows (Karickhoff 1984, Liljestrand and Shimizu 1991):

$$K_d = \alpha_{oc} f_{oc} K_{oc}^* + \beta_{min} f_{min} S_A K_S \quad (2.14)$$

where α_{oc} and β_{min} are the available fractions of organic and mineral components for sorption, respectively. Both α_{oc} and β_{min} should be within the range $0 \leq \alpha_{oc}, \beta_{min} \leq 1$. If blocking of sorption to the organic carbon by the mineral component is assumed to be negligible, α_{oc} is equal to unity (Karickhoff 1984, Liljestrand and Shimizu 1991). In this case, the sum of Rf_{oc} and f_{min} equals unity such that Eq. 2.14 can be re-written as follows:

$$K_d = f_{oc} K_{oc}^* + \beta_{min} (1 - Rf_{oc}) S_A K_S \quad (2.15)$$

As previously shown in Figs. 2.2 and 2.3, coating of HA onto heated sand is linear and results in a coated monolayer of HA with an essentially uniform thickness, suggesting that the HA is physically distributed onto the surface of the heated sand in different coverages that are proportional to f_{om} . Thus, the available mineral surface area is expected to be inversely related to f_{om} ($S_{A,c} \neq S_A$). Additionally, the aforementioned ordered vicinal water immediately adjacent to HA-coating might be different from that of a pure mineral surface due to the disordered transition (see Fig. 2.5c), such that the mineral-component distribution coefficient for the HA-coated sand can be different from that for the heated sand ($K_{S,c} \neq K_S$). Thus, β_{min} is expected to be characterized not only by the ratio of available-to-total surface areas (i.e., $S_{A,c}/S_A$), but also by the ratio of the surface area-normalized distribution coefficient for the mineral component of the HA-coated sand ($K_{S,c}$) to that for the heated sand (K_S), as follows (e.g., see Appendix A):

$$\beta_{min} = \frac{S_{A,c}K_{S,c}}{S_AK_S} \quad (2.16)$$

where $S_{A,c}$ and $K_{S,c}$ are the available surface area of the mineral component (m^2/kg of mineral) and the surface-area-normalized distribution coefficient to the available surface area of the mineral component (L/m^2) in the combined solid components (i.e., HA-coated sand), respectively. As proposed by Karickhoff (1984) and Liljestrand and Shimizu (1991), if $K_{S,c} = K_S$, then β_{min} is a physical parameter that is independent of the sorbate.

Although the total surface areas of HA-coated sands were measured, the fraction of mineral surface available for adsorption is difficult to estimate, since the total surface area is a combination of the surface area of the coated HA and the uncoated mineral

surface area. Therefore, β_{min} can be defined using a physical blocking parameter and the relative mass of organic carbon and mineral as follows (Karickhoff 1984, Liljestrand and Shimizu 1991):

$$\beta_{min} = \frac{f_{min}}{f_{min} + \omega_{oc-min} f_{oc}} = \frac{1}{1 + \omega_{oc-min} \frac{f_{oc}}{f_{min}}} \quad (2.17)$$

where ω_{oc-min} is a physical blocking parameter due to the blocking of the mineral surface by organic matter (see Appendix A). Substitution of Eq. 2.17 into Eq. 2.15 and rearrangement of the resulting expression give an equation for a line of the form:

$$\psi = \omega_{oc-min} \frac{f_{oc}}{f_{min}} + 1 \quad (2.18)$$

where ψ and f_{oc}/f_{min} are given by

$$\psi = \frac{(1 - Rf_{oc})S_A K_S}{K_d - f_{oc} K_{oc}^*}; \quad \frac{f_{oc}}{f_{min}} = \frac{f_{oc}}{(1 - Rf_{oc})} \quad (2.19)$$

and f_{oc}/f_{min} is the relative fractions of organic carbon to mineral. For the sorbents used in this study, R is equal to 1.89 ($= 1/0.528$; Table 2.1), such that ψ and f_{oc}/f_{min} are given by:

$$\psi = \frac{(1 - 1.89f_{oc})S_A K_S}{K_d - f_{oc} K_{oc}^*}; \quad \frac{f_{oc}}{f_{min}} = \frac{f_{oc}}{(1 - 1.89f_{oc})} \quad (2.20)$$

Based on Eq. 2.18, the y-intercept for a line regressed through data plotted as ψ versus f_{oc}/f_{min} for the HA-coated sand should yield an intercept not significantly different from unity and a slope representing the physical blocking parameter, ω_{oc-min} . Values for all parameters in Eq. 2.18 except ω_{oc-min} can be determined experimentally.

2.3 RESULTS AND DISCUSSION

2.3.1 Desorption of HA from HA-Coated Sand

Although HA-coated sand was vigorously prewashed using a reciprocating shaker prior to use, some HA was still released to solution during the mixing stage of the batch equilibrium sorption tests (BESTs) performed with the sorbates. As shown in Fig. 2.6, the concentration of dissolved organic carbon after the BESTs ranged from 0.55 to 9.85 mg/L, and increased with increase in the f_{oc} of the HA-coated sand. The solubilities of sorbates have been shown to increase in the presence of dissolved organic matter due to the binding of sorbates to dissolved macromolecules of organic matter (Hassett and Anderson 1979, Gschwend and Wu 1985, Curtis et al. 1986). As a result, the true distribution coefficient for sorbates partitioning to the solid-phase organic carbon (K_{oc}^T) is given as follows (Gschwend and Wu 1985):

$$K_{oc}^T = K_{oc}^{obs} (1 + K_{doc} C_{doc}) \quad (2.21)$$

where K_{oc}^{obs} is the observed organic carbon partitioning coefficient (L/kg of organic carbon), C_{doc} is the concentration of dissolved organic carbon after the BESTs (mg of

organic carbon/L), and K_{doc} is the distribution coefficient to dissolved organic carbon (L/kg of dissolved organic carbon). Although K_{doc} has been shown to vary with the type of humic substance, the solution pH, and the ionic strength (Carter and Suffet 1982), K_{doc} typically is assumed to be identical to K_{oc} (i.e., $K_{oc} = K_{doc}$) on the basis that the compositions of the dissolved organic carbon and parent organic carbon coated onto the sand are similar and sorption is truly a partitioning process (Gschwend and Wu 1985, Curtis et al. 1986). Thus, the effect of dissolved organic carbon on the K_{oc}^{obs} can be estimated using Eq. 2.21.

As shown in Fig. 2.7, for $0.55 \leq C_{doc} \leq 9.85$ mg/L, binding of sorbates to dissolved organic carbon is not significant even for 1,2,4-TCB (i.e., $1.000 \leq K_{oc}^T/K_{oc}^{obs} \leq 1.015$ for $C_{doc} \leq 9.85$ mg/L), which is the most hydrophobic sorbate used in this study. Thus, K_{oc}^{obs} is close to K_{oc}^T for all sorbates evaluated in this study. This finding is consistent with that of Curtis et al. (1986), who reported that the effect of dissolved organic carbon for representative natural systems (e.g., $C_{doc} < 50$ mg/L) on the total solubility of nonpolar sorbates was insignificant for sorbates with $\log K_{ow} < 4$. Therefore, based on this analysis, dissolved organic carbon concentrations less than 10 mg/L likely will have a relatively insignificant impact on the observed sorption coefficients measured in this study.

2.3.2 Sorption Rates

The results of studies evaluating the rate of sorption of nonpolar sorbates to natural solids indicate that the overall sorption behavior is initially fast but decreases to a slower, sustained rate. This decrease in sorption rate has been attributed to (i) diffusion of

the sorbate across the aqueous boundary layer onto the exterior of aquifer sand, (ii) pore or surface diffusion among the aggregated minerals, and (iii) diffusion of the sorbate within SOM matrices (Wu and Gschwend 1986, Ball and Roberts 1991, Huang et al. 1996, Weber and Huang 1996, Holmén and Gschwend 1997).

As a result, the kinetics for sorption of all six sorbates at an initial aqueous concentration of 150 $\mu\text{mol/L}$ to uncoated sand ($f_{oc} = 0.006\%$), heated sand ($f_{oc} < 0.005\%$), and HA-coated sand ($f_{oc} = 0.119\%$) was investigated. As shown in Fig. 2.8, the sorption for all six sorbates to both uncoated sand and heated sand approached equilibrium within 4 h, whereas sorption equilibrium was not achieved in the case of the HA-coated sand until about 24 h. The time required to attain apparent sorption equilibrium for the sorbates to the uncoated sand and heated sand is expected to be relatively short (i.e., ≤ 4 h) because: (1) diffusion of the sorbates across the aqueous boundary layer coating these sorbents is considered to be fast (Holmén and Gschwend 1997); (2) the pore volumes for the sorbents are low (i.e., $\leq 2.7\text{ mm}^3/\text{g}$); and (3) the SOM contents are very low (i.e., $f_{oc} \leq 0.006\%$). This result also is similar to that of previous studies indicating that the rates of sorption of nonpolar sorbates onto nonporous mineral surfaces are relatively fast (i.e., ≤ 4 h), and intraparticle diffusion in nonporous mineral surfaces does not affect overall sorption rates (Schwarzenbach et al. 1993, Huang et al. 1996).

However, in the case of the HA-coated sand ($f_{oc} = 0.119\%$), longer times were required to attain sorption equilibrium of all six sorbates, suggesting that diffusion of nonpolar sorbate within SOM matrix is the rate-limiting sorption process in the nonaggregated sorbents. Since the HA coating is relatively thin, not present as isolated

aggregates on the surface (see Fig. 2.3e-h), and highly hydrated and flexible, the domain represented by the amorphous HA coating likely is readily accessible to sorbates such that the associated sorption rates are relatively fast (i.e., ≤ 24 h) compared to those (i.e., days to months) for condensed SOM (Weber and Huang 1996, Luthy et al. 1997, Xia and Ball, 1999, Xiao et al. 2004). This finding is similar to that of Burris et al. (1991), who reported that sorption equilibrium of tetrachloroethylene to HA-coated silica ($f_{oc} = 0.073$ %) required as much as 24 h.

2.3.3 Sorption of Nonpolar Neutral Organic Compounds

2.3.3.1 Sorption to Uncoated and Heated Sands

The sorption isotherm parameters for six individual sorbates resulting from fitting the measured sorption data with both Freundlich and linear sorption models, as well as the surface-area-normalized distribution coefficients (K_d), and the pH of the aqueous solution at equilibrium, are summarized for uncoated sand and heated sand in Tables 2.5 and 2.6, respectively. The measured equilibrium sorption data and the fitted linear and nonlinear (Freundlich) sorption models for the six individual sorbates and uncoated sand are shown in Figs. 2.9 and 2.10, respectively. The fitted distribution coefficients for the six sorbates are relatively low (i.e., $K_d \leq 0.214$ L/kg of solid), although the sorption of 1,2,4-TCB and *m*-XYL was greater than that of 1,4-DCB, CB, TOL, and BZ. The sorption behavior of the sorbates to the uncoated sand is nearly linear, with values of the exponents (n) in the Freundlich sorption model ranging from 0.869 to 1.11 (Fig. 2.10). This result is similar to that of Huang et al. (1996), who reported low and linear sorption of phenanthrene to nonporous α -Al₂O₃, quartz, kaolinite, and amorphous SiO₂ from

aqueous solution, as well as that of Mader et al. (1997) who found the sorption isotherms for a series of polyaromatic hydrocarbons and chlorobenzenes from aqueous solution to α -Al₂O₃ and α -Fe₂O₃ to be linear to at least 50 % of sorbate aqueous solubility. These results can be attributed to the lack of interaction between the sorbates and surfaces of the uncoated sand due to the negligible f_{oc} of the sand and the coverage of mineral surfaces with ordered vicinal water as previously discussed (Drost-Hansen 1969, 2001, Adamson 1990, Schwarzenbach et al. 1993).

The measured equilibrium sorption data and the fitted linear and nonlinear (Freundlich) sorption models for the six individual sorbates and heated sand are shown in Figs. 2.11 and 2.12, respectively. Although heating the sand to 700 °C was expected to alter the sand surface, the sorption of the sorbates to the heated sand was not significantly different (i.e., within a 95 % confidence interval) relative to that for the uncoated sand. The distribution coefficients of six sorbates are still relatively low (i.e., $K_{min} \leq 0.217$ L/kg of solid), the sorption of 1,2,4-TCB, 1,4-DCB and *m*-XYL was still greater than that of CB, TOL, and BZ, and the sorption isotherms for the sorbates to the heated sand are also nearly linear, with n values ranging from 0.870 to 1.04 (Fig. 2.12). This similarity in results between the uncoated and heated sands suggests that the f_{oc} in both sorbents is sufficiently negligible ($f_{oc} \leq 0.006$ %), such that f_{oc} is not a significant factor affecting the sorption of the sorbates used in this study to these sorbents, and that water molecules are preferentially adsorbed to both surfaces of uncoated and heated sand (Drost-Hansen 1969, 2001, Adamson 1990, Schwarzenbach et al. 1993).

For sorption to the uncoated sand, the K_S values calculated using the specific surface area based on nitrogen adsorption are on the order of 10^{-5} L/m² and, with the

exception of 1,4-DCB, increase with increasing hydrophobicity (i.e., K_{ow}) of sorbates. The K_S values reported in Tables 2.5 and 2.6 are greater than K_S values for other sorbates and sorbents reported in the literature. For example, Schwarzenbach and Westall (1981) reported K_S values for CB, 1,4-DCB, and 1,2,4-TCB to porous silica of 0.84×10^{-5} , 1.2×10^{-5} , and 1.52×10^{-5} L/m², respectively. Mader et al. (1997) reported K_S values of 1,4-DCB and 1,2,4-TCB to α -Fe₂O₃ of 3.98×10^{-6} L/m² and 8.76×10^{-6} L/m². The differences in the K_S values for the sorbates reported in both Tables 2.5 and 2.6 and those reported by Schwarzenbach and Westall (1981) and Mader et al. (1997) can be attributed, in part, to differences in solution chemistry, the types of mineral surfaces, and the experimental systems that can result in differences in the structures and volumes of ordered vicinal water (Drost-Hansen 1969, Schlautman and Morgan 1994).

Backhus (1990), Schwarzenbach et al. (1993), and Mader et al. (1996) indicate that the free energy of sorption of neutral sorbates onto mineral surfaces as represented by K_S is inversely related to the free energy of aqueous dissolution of neutral sorbates, or $1/\gamma_w^{sat}$, where γ_w^{sat} is the aqueous activity coefficient at saturation. Accordingly, the log of the average K_S values based on the results for the uncoated sand are plotted versus $\log \gamma_w^{sat}$ for the sorbates (see Table 2.4) in Fig. 2.13a, with linear regression of the data resulting in a slope and y-intercept of 0.029 and -4.18, respectively. Schwarzenbach et al. (1993) found a similar trend in the log of K_S versus $\log \gamma_w^{sat}$ for a variety of sorbates ($4 \leq \log \gamma_w^{sat} \leq 6$) and silica sorbents, indicating that the free energies for the sorption of sorbates with $\log \gamma_w^{sat}$ ranging from 4 to 6 are not significantly different in spite of the different free energies for aqueous dissolution of sorbates.

Although the adsorption of sorbates to uncoated sand is affected by factors other than the hydrophobicity of the sorbate in aqueous solution, the use of linear free energy relationships to estimate K_S of sorbates still appears to be feasible. For example, as shown in Fig. 2.13b, the K_S values for the uncoated sand can still be estimated reasonably well based on either the octanol-water partitioning coefficient (K_{ow}) or the solubilities (S_w) of the sorbates.

For sorption to the heated sand, the K_S values calculated using the specific surface area based on nitrogen adsorption are on the order of 10^{-5} L/m², i.e., similar to those for uncoated sand. This similarity is expected since the low f_{oc} for the heated sand ($f_{oc} < 0.005$ %) is not significantly different from that of the uncoated sand ($f_{oc} = 0.006$ %) and, therefore, the organic carbon content ($f_{oc} = 0.006$ %) apparently does not play a significant role on the sorption of the sorbates. In addition, no significant changes in structures and volumes of ordered vicinal water between the heated sand and uncoated sand apparently were involved. Similar to uncoated sand, the log of the average K_S values based on the results for the heated sand increases with the log γ_w^{sat} for the sorbates, and linear regression of the data in Fig. 2.14a results in a slope and y-intercept of 0.038 and -4.22, respectively, indicating that the free energy of sorption of sorbates onto heated sands is inversely related to the free energy of aqueous dissolution of sorbates. As shown in Fig. 2.14b, the sorption of sorbates to heated sands also can be estimated reasonably well from the K_{ow} and S_w of the sorbates.

2.3.3.2 Sorption to Humic Acid-Coated Sand

The results of the BESTs for the six individual nonpolar NOCs and five humic acid (HA)-coated sands with different average f_{oc} values (i.e., 0.025, 0.051, 0.072, 0.119, and 0.152 %) are shown in Fig. 2.15 for linear model and Fig. 2.16 for Freundlich sorption model based on the use of all of the data from the different replicates in one plot. The average sorption isotherm parameters for all six sorbates resulting from fitting the measured sorption data with both linear and Freundlich sorption models, as well as the organic carbon partitioning coefficient (K_{oc}), the average f_{oc} of HA-coated sand, and the pH of aqueous solution at equilibrium are summarized in Table 2.7.

As shown in Figs. 2.15 and 2.16 and Table 2.7, the sorption isotherms are essentially linear ($0.876 \leq n \leq 1.126$) at low C_e/S_w (< 0.5). Similar sorption linearity for sorption of nonpolar sorbates to soils with low f_{oc} has been reported in a number of other studies. For example, Schwarzenbach and Westall (1981) reported linearity in the sorption of chloro- and methyl- benzenes to very fine sand with low f_{oc} (≤ 0.73 %). Larsen et al. (1992) showed linear behavior for benzene, 1,1,1-trichloroethane, and naphthalene sorbing to aquifer materials with low f_{oc} (0.006-0.21 %). In addition, Onken and Traina (1997) found that sorption isotherms of pyrene and anthracene to HA-mineral complexes were linear for f_{oc} systems (> 0.003 %). Finally, Shen and Jaffé (2000) reported that linear adsorption isotherms were obtained for total petroleum hydrocarbons and individual aromatic hydrocarbons on HA-coated mineral surfaces with $f_{oc} \leq 0.8$ %.

Linear sorption of nonpolar sorbates is thermodynamically expected for hydrophobic partitioning and also for adsorption at low surface coverage, where sorption sites are sufficiently homogeneous to give constant differential enthalpy of adsorption (Chiou et al. 1979, Ball and Roberts 1991). Also, as is evident by the high oxygen/carbon

ratio of HA (Table 2.1) and the low surface areas (Table 2.3), the HA used for coating likely does not have site-specific and capacity-limited condensed organic domains or contain carbonaceous material with high surface areas such as charcoal and soot (Chiou and Kile 1998, Xia and Ball 1999, Allen-King et al. 2002, Xiao et al. 2004, Nguyen and Ball 2006). As a result, strong sorbate adsorption is not likely over the low concentration ranges such that linear sorption behavior is expected.

The dependence of the measured K_d values on f_{oc} for each sorbate is shown in Fig. 2.17. In general, the greater the hydrophobicity of sorbates, the greater the dependency of K_d on f_{oc} , as expected. For example, the hydrophobicity of the six sorbates considered in this study based on K_{ow} increases in the order (see Table 2.4), BZ < TOL < CB < *m*-XYL < 1,4-DCB < 1,2,4-TCB, and the sensitivity of K_d to f_{oc} also increases in the same order.

The apparent organic carbon partitioning coefficients (K_{oc}) were calculated from the each K_d shown in Fig 2.17 according to the relation, $K_{oc} = K_d/f_{oc}$, and the dependence of the calculated apparent K_{oc} values on f_{oc} for each sorbate is shown in Fig. 2.18. As shown in Fig. 2.18, for f_{oc} greater than about 0.1 %, the apparent K_{oc} values are essentially independent of f_{oc} . However, for f_{oc} less than 0.1 %, the apparent K_{oc} values are widely divergent and tend to increase with decreasing f_{oc} . These results indicate that when f_{oc} is less than some threshold value (i.e., 0.1 % in this case), sorption of nonpolar sorbates to aquifer sands likely results from both adsorption onto mineral surfaces and partitioning into organic carbon. In contrast, when f_{oc} is greater than the threshold value, sorption by partitioning into organic carbon becomes dominant such that the effect of the mineral surface is negligible. Also, the value for the threshold f_{oc} of 0.1 % in this study

appears to be similar among all sorbates (Fig. 2.18), even though the individual values for limiting apparent K_{oc} values are sorbate dependent.

Linear regressions of plots of K_d versus f_{oc} are shown in Fig. 2.19. In Figs. 2.19a and 2.19b, arithmetic plots of K_d for the six sorbates versus f_{oc} for the HA-coated sands are regressed based on Eq. 2.8 ($K_d = f_{oc}K_{oc}$) and Eq. 2.9 ($K_d = f_{oc}K_{oc}^* + K_{min}^*$), respectively. A comparison of the coefficients of determination (r^2) for each sorbate in Fig. 2.19a with that for the same sorbate in Fig. 2.19b indicates that the regressions based on Eq. 2.9 shown in Fig. 2.19b all fit the data better than those based on Eq. 2.8 shown in Fig. 2.19a. Thus, in general, predictions of K_d that include a mineral-phase component of adsorption (i.e., Eq. 2.9) appear to be more accurate than those based on the simple hydrophobic partitioning concept with zero intercept (i.e., Eq. 2.8). This observation is more apparent when the results shown in Figs. 2.19a and 2.19b are plotted on log-log form as shown in Figs. 2.19c and 2.19d, respectively.

Since the sum of squared residuals ($SS_{residual}$) is greater than total sum of square (SS_{total}) for TOL and BZ in Fig. 2.19a, $r^2 [= (SS_{total} - SS_{residual})/SS_{total}]$ is negative, indicating that simple linear regression through the origin fits the data worse than a horizontal line at the mean K_d value (Kvalseth 1985). This finding suggests that simple hydrophobic partitioning concept with zero intercept (i.e., Eq. 2.8) is totally inappropriate as a least-squares regression model since the y-intercept is fixed to an inappropriate constant value, i.e., $y = 0$ (see Appendix B). Instead of using ambiguous and negative r^2 values, Montgomery and Peck (1982) proposed an alternative r^2 statistic that yields different positive r^2 values for linear regression with zero intercept by using SS_{total} about the origin (i.e., $\sum_{i=1}^n (y_i)^2$). However, r^2 for linear regression with intercepts is calculated

differently from r^2 for linear regression with zero intercept, such that two r^2 values should not be directly compared and may produce misleading results (Kvalseth 1985). Thus, in this study, only r^2 for linear regression with intercepts (i.e., SS_{total} about the mean $\bar{y}$, $\sum_{i=1}^n (y_i - \bar{y})^2$) is utilized for comparison.

Consequently, use of the simple hydrophobic partitioning concept (i.e., Eq. 2.8) appears to be relatively accurate when $f_{oc} > 0.001$, whereas K_d is significantly underestimated when $f_{oc} < 0.001$. Also, the dependency of K_d on f_{oc} is greater as the hydrophobicity of sorbates increases. This observation suggests that, for $f_{oc} < 0.001$, the sorbates with relatively low K_{ow} , such as TOL and BZ, are influenced primarily by adsorption onto mineral surfaces, whereas the sorbates with relatively high K_{ow} (e.g., 1,2,4-TCB, 1,4-DCB, CB, and *m*-XYL) are influenced by a combination of hydrophobic partitioning and mineral adsorption. Thus, as f_{oc} increases, hydrophobic partitioning becomes more dominant. However, as f_{oc} decreases, the contribution of mineral adsorption also must be considered.

In addition, the results of the regressions shown in Fig. 2.19b allow for the determination of the amended organic carbon partitioning coefficient (K_{oc}^*) and the mineral-phase adsorption coefficient (K_{min}^*) represented by the slopes and y-intercepts of the regressions, respectively (Kishi et al. 1990, Paya-Perez et al. 1991, Rebhun et al. 1992, Shen and Jaffé 2000). Whereas K_{oc} in Fig. 2.18 was calculated from each K_d in Fig 2.17, overall K_{oc} and K_{oc}^* values can be determined from the regressions such as those shown in Fig. 2.19a and in Fig. 2.19b, respectively. The resulting values of overall K_{oc} and K_{oc}^* , and K_{min}^* are summarized in Table 2.8 along with the K_{min} values based on the results using the heated sand.

As shown in Fig. 2.20a, the K_{oc}^* values for all six sorbates based on the regressions shown in Fig. 2.19b are lower by approximately 145 L/kg than the corresponding K_{oc} values based on the regressions shown in Fig. 2.19a, indicating that the contribution of adsorption onto the mineral surface can be significant. However, the significance of the contribution of adsorption onto the mineral surface appears to be a function of the hydrophobicity of the sorbates. For example, as shown in Fig. 2.20b, the ratio K_{oc}^*/K_{oc} approaches unity as the hydrophobicity of sorbates (i.e., K_{ow}) increases. Thus, as the hydrophobicity of the sorbate increases, hydrophobic partitioning into organic carbon becomes increasingly more dominant such that the significance of the contribution of adsorption onto the mineral surface consequently decreases. These observations suggest that, for sorbents with low f_{oc} ($< 0.1\%$) and/or for sorbates with relatively low hydrophobicity ($\log K_{ow} < 2.84$), the contribution of adsorption onto mineral surface is sufficiently significant such that accurate estimates of K_d can be obtained only by determining and using K_{oc}^* and K_{min}^* (i.e., Eq. 2.9) as opposed to using just the simple hydrophobic partitioning concept (i.e., Eq. 2.8).

As shown in Fig. 2.21a, the measured K_{min} values for each sorbate to the heated sand (see Table 2.6) are all greater than the values for mineral adsorption of the same sorbate to the HA-coated sand (K_{min}^*), suggesting that the binding of HA to the heated sand surface decreases the availability of adsorption sites on the mineral surface. Although the extent of blocking due to the HA coating onto mineral surface is a function of f_{om} , an overall availability of adsorption sites on the mineral surface is reflected by the ratio K_{min}^*/K_{min} (Rebhun et al. 1992, Shen and Jaffé 2000).

For example, as shown in Fig. 2.21b, K_{min}^*/K_{min} decreases slightly from 0.93 for BZ ($\log K_{ow} = 2.13$) to 0.84 to 1,2,4-TCB ($\log K_{ow} = 4.23$) as the hydrophobicity of the sorbates increases, indicating that from 7 to 16 % of the mineral surface is blocked by HA depending on the sorbate. However, even though the binding of HA to the heated sand surface decreases the availability of adsorption sites on the mineral surface, new partitioning sites become available within the HA matrix. Therefore, overall sorption is determined by both hydrophobic partitioning and mineral adsorption, and the dominance of either contribution depends on f_{oc} , and the properties of the sorbates (e.g., K_{ow} and S_w), as well as the surface properties of the sorbents (e.g., surface area, pore geometry, and intrinsic sorptive affinity of mineral surfaces).

Similar results have been reported by Karickhoff (1984), Rebhun et al. (1992), and Shen and Jaffé (2000). For example, Karickhoff (1984) postulated that the mineral fraction of most soils or sediments was unavailable for pollutant sorption due to blocking by organic carbon and an analogous reduction in organic carbon availability was observed when incorporated into aggregates of soil or sediment. Rebhun et al. (1992) postulated that the contribution of clay minerals to adsorption of several organic sorbates covering a wide range of hydrophobicity was significant for soils with $f_{oc} < 0.05$, in spite of the fact that half of the sorption sites on the mineral surface were blocked by humic materials. Finally, Shen and Jaffé (2000) reported that about 50 % of the surface of pure kaolinite mineral was blocked by HA for sorption of total petroleum hydrocarbons to HA-coated kaolinite ($f_{oc} \leq 0.003$). However, the available mineral surface area is a function of the coverage of mineral surface with the HA and, therefore, should be inversely related to the magnitude of f_{om} .

2.3.3.3 Critical Organic Carbon Content

Values for the critical organic carbon content, f_{oc}^* , of the six sorbates calculated using both Eqs. 2.12 and 2.13 are compared in Fig. 2.22 with calculated values of f_{oc}^* based on Eq. 2.10 from McCarty et al. (1981). The calculations were based on the S_A for the heated sand of 2.036 m²/g (see Table 2.3), the R of 1.89 (= 1/0.528; Table 2.1), and the values for K_{ow} , K_S , K_{oc} , K_{oc}^* , and K_{min}^* from Tables 2.4, 2.6, and Table 2.8. As shown in Fig. 2.22, the f_{oc}^* values based on Eq. 2.10 from McCarty et al. (1981) range from about one to two orders-of-magnitude lower than the f_{oc}^* values based on either K_{oc} (Fig. 2.22a) or K_{oc}^* (Fig. 2.22b). These differences in f_{oc}^* may result, in part, from the assumptions inherent in the derivation of Eq. 2.10.

For example, McCarty et al. (1981) used the empirical relationship between K_{oc} and K_{ow} proposed by Karickhoff et al. (1979) for a variety of sorbates (i.e., $K_{oc} = 0.63K_{ow}$). However, many experimental and K_{ow} -derived K_{oc} values for sorbates reported in the literature since then fail to explain variations in the structure and composition of SOM (Garbarini and Lion 1986, Grathwohl 1990, Rutherford et al. 1992, Kile et al. 1995). Furthermore, separate correlations between K_{oc} and K_{ow} for individual classes of sorbates based on molecular structure (e.g., apolar, monopolar, and bipolar sorbates) are required for more accurate estimation of K_{oc} (Schwarzenbach et al. 1993, Seth et al. 1999, Allen-King et al. 2002, Nguyen et al. 2005). As a result, estimates of f_{oc}^* based on the simple empirical relationship between K_{oc} and K_{ow} proposed by Karickhoff et al. (1979), instead of class- and SOM-specific linear free energy relationships, may not be accurate.

Finally, in developing Eq. 2.10, McCarty et al. (1981) used an expression derived from a free-energy relationship to approximate sorption by silica surfaces. However, since the surface area, pore geometry, and intrinsic sorptive affinity of mineral surfaces have since been shown to play a significant role in the sorption of nonpolar sorbates (Huang et al. 1996, Mader et al. 1997), the discrepancy between f_{oc}^* values based on Eq. 2.10 versus those based on the results of this study also may be due, in part, to differences in these factors.

2.3.3.4 Blocking Parameters

Based on Eqs. 2.18 through 2.20, linear regression of a plot of ψ versus f_{oc}/f_{min} for HA-coated sands should yield a y-intercept that is not significantly different from unity and a slope that represents the blocking parameter, ω_{oc-min} . Accordingly, plots of ψ versus f_{oc}/f_{min} for the results of this study are shown in Fig. 2.23. Linear regressions of the data shown in Fig. 2.23 result in values of r^2 ranging from 0.740 to 0.932, with y-intercepts that are all close to unity (i.e., 1.00-1.06), and ω_{oc-min} values ranging from 88.6 for CB to 126 for 1,2,4-TCB, as shown in Table 2.9.

Karickhoff (1984) stated that blocking models should discriminate the effective mineral surface from combined sorbents, independent of the sorbates. Also, from their results using HA-coated sorbents, Liljestrand and Shimizu (1991) postulated that blocking is a physical parameter that is independent of the sorbate. However, these assertions by Karickhoff (1984) and Liljestrand and Shimizu (1991) were based on the results of limited ranges of sorbates and sorbents (one or two).

Therefore, two statistical analyses for a single or multiple factors were performed using the statistical software (SAS® 9.1, Cary, NC) to determine if the effect of blocking the mineral surface by HA was independent of the sorbates used in this study. First, the analysis of variance (ANOVA) F -test was applied to test the null hypotheses H_0 that the mean ψ values for all six sorbates are equivalent (Ott and Longnecker 2001). Second, multiple comparison procedures (MCPs) were applied to distinguish any differences among mean ψ values for the six sorbates evaluated in this study (Westfall et al. 1999).

The results of the ANOVA F -test from the SAS output are summarized in Table 2.10 (also see Appendix C for SAS Code). If the value for F_0 , which represents the ratio of the mean square in variability between the sorbates to the mean square in variability within the sorbates, exceeds the critical value of F ($F_{0.05, v_1, v_2}$) for a given associated probability, α , of 0.05 and two degrees of freedom, the null hypothesis H_0 of equality of the mean ψ among sorbates is rejected (Ott and Longnecker 2001). Therefore, since all the resulting F_0 values are greater than the corresponding $F_{0.05, v_1, v_2}$ values (Table 2.10), the null hypothesis H_0 of equality of the mean ψ among sorbates is rejected at the 0.05 ($=\alpha$) level of statistical significance, indicating that at least one of the mean ψ values for the sorbates differs from that of the rest of the sorbates.

The results of the MCPs using the procedure proposed by Tukey (1953) are summarized in Table 2.11 (also see Appendix C for SAS Code). Tukey's procedure for MCPs was designed specifically for pair-wise comparisons based on studentized range of ψ values to distinguish any differences among mean ψ values for the six sorbates evaluated in this study. The level of significance represented by the p -value is the probability of obtaining a value of the test statistic that is likely to reject H_0 (Ott and

Longnecker 2001). Thus, if the p -value is less than α , H_0 is rejected. In contrast, if the p -value is greater than α , then H_0 can not be rejected.

As shown in Table 2.11, the p -values among BZ, TOL, m -XYL, and CB (see the shaded area) are considerably greater than α ($= 0.05$), whereas the p -values between 1,4-DCB versus the other sorbates and between 1,2,4-TCB versus the other sorbates are lower than α ($= 0.05$). Therefore, the null hypothesis H_0 for the equality of the mean ψ values is rejected at the 0.05 ($= \alpha$) level of statistical significance for both 1,4-DCB and 1,2,4-TCB. As a result, linear regressions of a plot of ψ versus f_{oc}/f_{min} for 1,4-DCB and 1,2,4-TCB yield slopes (ω_{oc-min}) and y-intercepts that are statistically different from those for the other sorbates, as shown in Fig. 2.24.

The reasons for the apparent difference in blocking behavior of 1,4-DCB and 1,2,4-TCB relative to the other four sorbates are not entirely clear, particularly since Karickhoff (1984) and Liljestrand and Shimizu (1991) concluded that the blocking parameters should be independent of the sorbates. However, the results by Karickhoff (1984) and Liljestrand and Shimizu (1991) were based on the sorption of only one sorbate to natural solids and model solids, respectively, whereas the results of this study are based on six sorbates with several different model sorbents. Therefore, the limited number of sorbates and sorbents used by Karickhoff (1984) and Liljestrand and Shimizu (1991) may have precluded consideration of the potential dependence of the blocking parameters on the sorbate.

For example, β_{min} can be considered to be characterized not only by the ratio of available-to-total surface areas ($S_{A,c}/S_A$) of the sorbent, but also by the ratio of the surface area-normalized distribution coefficient for the mineral component of the HA-coated

sand to that for the heated sand ($K_{S,c}/K_S$). Also, based on Eq. 2.17, different ω_{oc-min} values for a given f_{oc}/f_{min} result in different β_{min} values. Therefore, since ω_{oc-min} values for 1,2,4-TCB and 1,4-DCB are statistically different from those for other sorbates, the β_{min} values for 1,2,4-TCB and 1,4-DCB also are expected to be different from those for other sorbates at a given f_{oc}/f_{min} , i.e., since f_{oc}/f_{min} is constant for a given sorbent. Since constant f_{oc}/f_{min} also means constant $S_{A,c}/S_A$, $K_{S,c}$ cannot be equivalent to K_S according to Eq. 2.16. As a result, if β_{min} is different for different sorbates, blocking must be dependent not only on the sorbent via $S_{A,c}/S_A$ but also on the sorbate via $K_{S,c}/K_S$. This result suggests that a physical blocking model (i.e., model based only on $S_{A,c}/S_A$) is not necessarily appropriate for quantifying the contribution of each solid component to the overall sorption in this study.

A second consideration is that the results from Karickhoff (1984) and Liljestrand and Shimizu (1991) were based on sorption to high-surface-area clays, compared to the low-surface-area, coarse-grained aquifer materials (i.e., sands) used in this study. Because the high-surface-area clays would be expected to possess a greater volume of vicinal water, the aforementioned disordered transition at locations where the polar and nonpolar surfaces meet would not be expected to influence the volume and structure of the vicinal water near both surfaces to the same extent as expected for the low-surface-area, coarse-grained aquifer materials used in this study. As a result, the structure and volume of the vicinal water coating the pure clay mineral surfaces would be expected to be the same as those for the HA-coated clay mineral surfaces, such that no significant difference in sorptive affinity would be expected (i.e., $K_S = K_{S,c}$). In this case, the ratio of

available-to-total surface areas ($S_{A,c}/S_A$) would be the dominant variable affecting the magnitude of the sorption coefficient to the HA-coated clay mineral surfaces.

In terms of thermodynamics, enthalpy changes accompanying sorption can be used to examine the molecular-scale interactions associated with the sorption process. Since sorption involves removing the sorbates from bulk water and displacing water molecules from sorption sites, the observed sorption enthalpy (ΔH_{obs}) includes contributions from sorbate-surface, water-surface, sorbates-water, and water-water interactions (Chiou et al. 1979, Farrell et al. 1999), as follows:

$$\Delta H_{obs} = \Delta H_{int}^{sorbate} - \Delta H_{int}^{water} - \Delta H_{diss}^{sorbate} \quad (2.22)$$

where $\Delta H_{int}^{sorbate}$ and ΔH_{int}^{water} are the enthalpy changes associated with formation of sorbate-surface and water-surface interactions, respectively, and $\Delta H_{diss}^{sorbate}$ is the enthalpy change associated with dissolution of the sorbates in water. As previously noted, nonpolar sorbates cannot displace strongly adsorbed water molecules from the mineral surfaces (Drost-Hansen 1969, 2001, Huang et al. 1996, Mader et al. 1997), such that ΔH_{int}^{water} can be neglected (Schwarzenbach et al. 1993, Mader et al. 1997). Additionally, both Schwarzenbach et al. (1993) and Mader et al. (1997) suggest that $\Delta H_{diss}^{sorbate}$ dominates ΔH_{obs} such that $\Delta H_{int}^{sorbate}$ is negligible. Instead, sorption of nonpolar sorbates to mineral surfaces is promoted by the hydrophobicity of the sorbates which can be attributed to the reduced entropy of the bulk water (i.e., $S_{BW} \rightarrow S_{BW}^*$ in Fig. 2.5) comprising the solvation envelope around the nonpolar sorbates, as illustrated schematically in Fig. 2.5 (Schwarzenbach et al. 1993). However, for the sorption of

nonpolar sorbates to a nonpolar surface (e.g., HA), weak sorbate-surface interactions lead to low values for $\Delta H_{int}^{sorbate}$.

The mineral component can affect the sorption of nonpolar sorbates only by the manner in which the mineral surface affects the structure and volume of the vicinal water, i.e., since nonpolar sorbates interact with the ordered vicinal water as opposed to the mineral surface (Drost-Hansen 1969, 2001, Huang et al. 1996, Mader et al. 1997). In this regard, the structure and volume of the vicinal water coating the heated sand (e.g., Fig. 2.5a) may not be the same as those for the HA-coated sand (e.g., Fig. 2.5c), since the disordered transition at locations where the polar and nonpolar surfaces meet may influence the volume and structure of the vicinal water near both surfaces. As a result, differences in the partitioning behavior of the more hydrophobic sorbates (e.g., 1,2,4-TCB and 1,4-DCB) between the relatively disorganized bulk water and the volume of vicinal water near the exposed mineral surface may be possible. In particular, since the disordered transition may also influence the degree of ordering of the water molecules, the entropy gained upon transfer of the sorbates from the bulk water into the ordered vicinal water of the HA-coated sands (ΔS_{MS}) is less than the entropy gained upon transfer of the sorbates that from the bulk water into the ordered vicinal water of heated sand (ΔS_{PS}), as illustrated in Fig. 2.5.

Finally, for the more hydrophobic sorbates, the enthalpy changes associated with sorbate-HA interactions ($\Delta H_{int}^{sorbate}$) contribute more to free energy of sorption than the entropy gained upon transfer of the sorbates (ΔS_{MS}). Therefore, the free energy associated with adsorption of the sorbates to the exposed mineral surface of HA-coated sands decreases for the more hydrophobic sorbates, such that $K_{S,c}$ can be expected to be lower

than K_S . As a result, sorption of the more hydrophobic sorbates to the ordered vicinal water of HA-coated mineral surfaces may be blocked to a greater extent than that of less hydrophobic sorbates.

Based on these considerations, the values for the blocking parameter (ω_{oc-min}) for the sorbates are shown in Fig. 2.25 as a function of K_{ow} and S_w . As the hydrophobicity of sorbates (i.e., K_{ow}) increases, ω_{oc-min} increases slightly. These results suggest that sorption of the more hydrophobic sorbates to the ordered vicinal water of HA-coated mineral surfaces may be blocked to a greater extent than that of less hydrophobic sorbates. Overall, adsorption of sorbates with higher hydrophobicity to the mineral component is more effectively blocked by low f_{oc} than adsorption of sorbates with lower hydrophobicity, even though the physical coverage of the mineral adsorption sites by HA is identical (i.e., $S_{A,c}/S_A = \text{constant}$). In this case, β_{min} cannot be estimated directly using only physical coverage of mineral surface area with f_{oc} . Thus, in contrast to the results of previous studies suggesting that surface area is the most important variable affecting the magnitude of the sorption coefficient to mineral surface (i.e., Karickhoff 1984, Liljestrand and Shimizu 1991), the results of this study suggest that the change in sorptive affinity (i.e., $K_S \neq K_{S,c}$) to modified mineral surfaces with a range of surface coverage may also be important. However, the β_{min} values depend primarily on the surface area of the mineral surfaces, and variations in the β_{min} values among sorbates are observed as the second-order effects.

2.3.3.5 Comparison of Models

Based on observation of a composite linear sorption behavior, with pure mineral-phase adsorption at $f_{oc} \approx 0$ represented by $S_A K_S$, and the linear sorption at increasing f_{oc} given by $f_{oc} K_{oc}^*$, the two-component model with the blocking effect (i.e., Eq. 2.15) was used to predict the sorption behavior over the entire range of f_{oc} ($0 \leq f_{oc} \leq 0.154\%$) evaluated in this study. The predicted sorption behavior using Eq. 2.15 (i.e., $K_d = f_{oc} K_{oc}^* + \beta_{min}(1 - R f_{oc}) S_A K_S$) is based on the previously determined value for S_A for the heated sand of $2.036 \text{ m}^2/\text{g}$ (see Table 2.3), an $R (= f_{om}/f_{oc})$ of 1.89, the values for K_S and K_{oc}^* from Tables 2.6 and 2.8, respectively, and the values of β_{min} at different f_{oc}/f_{min} . As shown in Fig. 2.26, the predicted distribution coefficients from the two-component model with the blocking effect simulate the measured distribution coefficients well with $r^2 \geq 0.911$ for all sorbates.

In order to compare the common sorption models based on f_{oc} , K_{oc} (or K_{oc}^*), and K_{min}^* , the measured sorption data for all six sorbates to all sorbents including heated, uncoated, and HA-coated sands with different f_{oc} are compared in Fig. 2.27 with the predicted sorption behavior using four sorption models. Although some of differences in r^2 values are virtually negligible, the agreement between predicted and measured distribution coefficients increases in the order of linear model with zero intercept (Eq. 2.8; Fig. 2.27a) < two-component model without blocking effect (Eq. 2.15 with $\beta_{min} = 1$; Fig. 2.27c) < modified linear model (Eq. 2.9; Fig. 2.27b) $\leq$ two-component model with blocking effect (Eq. 2.15 with $\beta_{min} \leq 1$; Fig. 2.27d).

However, since some r^2 values are negative, an alternative method of parameter estimation, known as the method of maximum likelihood, also was used to discriminate among the models. Maximum likelihood estimation is a preferred method for parameter

estimation for many statistical modeling techniques due to sufficiency, consistency, efficiency, and parameter invariance (Montgomery and Peck 1982, Myung 2003).

For each sorption model, the values for the log of the likelihood function (LLF) and the proportion of variance explained (PVE, equivalent to r^2) are summarized in Table 2.12 for each sorbate. Based on the values of LLF and PVE, the two-component model with blocking effect (Fig. 2.27d) provides better agreement between the predicted and measured distribution coefficients than the linear model with no intercept (Fig. 2.27a) and the two-component model without blocking effect (Fig. 2.27c). Although the modified linear model (Fig. 2.27b) and the two-component model with blocking effect (Fig. 2.27d) have similar PVE values for all sorbates, the two-component model with blocking effect is statistically better based on a comparison of the LLF values.

2.3.3.5.1 Two-Component Model with Blocking Effect vs. Linear Model

Relative to the well-known linear model based on simple hydrophobic partitioning into organic carbon (i.e., Eq. 2.8; see Fig. 2.27a), the two-component model with blocking effect (Eq. 2.15) provides better agreement between the predicted distribution coefficients and the measured distribution coefficients for $f_{oc} < 0.1$ % (Fig. 2.27d). Additionally, while the linear model does not estimate adsorption onto mineral surfaces (i.e., K_{min}), the two-component model with blocking effect provides for pure mineral adsorption for $f_{oc} < 0.005$ %. These results indicate that the two-component model that includes both adsorption onto mineral surfaces and partitioning into organic carbon should be considered when predicting the sorption behavior using sorbents with relatively low f_{oc} (≤ 0.1 %).

2.3.3.5.2 Two-Component Model with Blocking Effect vs. Modified Linear Model

Based on a comparison of the results shown in Figs. 2.27b and 2.27d, the two-component model with blocking effect (Eq. 2.15; Fig. 2.27d) explains the measured adsorption onto mineral surfaces for $f_{oc} < 0.005\%$ (i.e., K_{min}) as shown in Fig. 2.27d slightly better than the modified linear model given by Eq. 2.9 (i.e., $K_d = f_{oc}K_{oc}^* + K_{min}^*$), which underestimates pure mineral adsorption for $0.07 \leq K_{min}^*/K_{min} \leq 0.16$ (see Fig. 2.21b). However, both models provide good agreement between the predicted distribution coefficients and the measured distribution coefficients for $f_{oc} > 0.005\%$. These results also show that the two-component model with blocking effect describes the measured distribution coefficient over the whole range of f_{oc} better than the modified linear model. However, a modified linear model also provides good agreement between the predicted distribution coefficients and the measured distribution coefficients over the low range of f_{oc} ($\leq 0.154\%$).

2.3.3.5.3 Two-Component Model with and without Blocking Effect

A comparison of the results shown in Figs. 2.27c and 2.27d indicates that better agreement between the predicted distribution coefficients and the measured distribution coefficients is provided when the blocking effect is included in the two-component model (Eq. 2.15 with $\beta_{min} \leq 1$) as shown in Fig. 2.27d relative to when the blocking effect is not included (Eq. 2.15 with $\beta_{min} = 1$) as shown in Fig. 2.27c. However, both models provide good estimates of measured adsorption onto mineral surfaces for $f_{oc} < 0.005\%$ (i.e., K_{min}).

Also, a comparison of the results shown in Figs. 2.27b and 2.27c indicates that the blocking effect of mineral surface by HA should be included in the sorption model.

In order to elucidate the effect of blocking based on the two-component model, the predicted sorption behaviors both with and without blocking are compared to the measured sorption data for each of the six sorbates in Figs. 2.28 through 2.33. Based on the r^2 values shown in Figs. 2.28 through 2.33, the predicted sorption behavior that includes the effect of blocking of the mineral phase by HA (Eq. 2.15 with $\beta_{min} \leq 1$) fits the measured data better for all sorbates and sorbents than the predicted sorption behavior that ignores any blocking effects (Eq. 2.15 at $\beta_{min} = 1$). In the cases of 1,2,4-TCB and 1,4-DCB (Figs. 2.28 and 2.29, respectively), the improvement in predicted behavior resulting from incorporating the effect of blocking is almost imperceptible, whereas the improvement in prediction resulting from incorporating the effect of blocking is more significant in the cases of CB, *m*-XYL, TOL, and BZ (Figs. 2.30-2.33). Since sorption of sorbates with high K_{ow} (i.e., 1,2,4-TCB and 1,4-DCB) are dominated by hydrophobic partitioning to organic carbon, the contribution of mineral adsorption is negligible relative to that attributed to f_{oc} . However, in the case of the less hydrophobic sorbates (i.e., CB, *m*-XYL, TOL, and BZ), the concept of sorptive additivity without inclusion of the blocking effect can be improved by incorporating the effect of blocking using blocking parameters.

As a result, predictions of sorption behavior based on the model that includes the effect of blocking and the available fraction of each component over the entire range of f_{oc} were only slightly better than those based on the common sorption models based on f_{oc} , K_{oc} (or K_{oc}^*), and K_{min}^* for the sorbates and sorbents used in this study, regardless of the

dominance of the sorption mechanism. Over the entire range of f_{oc} (≤ 0.154 %) evaluated in this study, the simpler modified linear model provided essentially as good agreement between predicted and measured distribution coefficients as did the model that includes the blocking effect.

2.4 SUMMARY AND CONCLUSIONS

The use of a calibrated two-component model with blocking parameters for adsorption onto minerals surfaces and hydrophobic partitioning into soil organic matter (SOM) of six nonpolar neutral organic compounds (i.e., 1,2,4-trichlorobenzene, 1,4-dichlorobenzene, chlorobenzene, *m*-xylene, toluene and benzene) was evaluated in this study. In order to discern the role of SOM and mineral surfaces in the sorption of the sorbates by low-carbon aquifer sands, model sorbents were used. The model sorbents were created by coating sand with a known amount of humic acid (HA) to simulate aquifer sands with a uniform thickness of a mineral-bound monolayer of amorphous HA. The HA was physically attached to the sand particles using mixtures of sand and solutions of HA at different initial aqueous concentrations and solid-to-liquid (S:L) ratios to provide sorbents with different coverages of HA and, therefore, different fractions of organic carbon (f_{oc}).

For all nonpolar neutral organic compounds (NOCs), the sorption to both the uncoated sand and the sand heated to 700 °C approached equilibrium within 4 h, whereas sorption equilibrium was not achieved in the case of the HA-coated sand until about 24 h, indicating that diffusion of NOCs within the HA matrix was the rate-limiting sorption process in the non-aggregated sorbents. Due to the negligible f_{oc} of the uncoated sand (i.e.,

≤ 0.006 %), and the coverage of mineral surfaces with ordered vicinal water, the sorption behavior of all NOCs to the uncoated sand or the heated sand is nearly linear and can be estimated from the linear free energy relationships [e.g., activity coefficient in water at saturation (γ_w^{sat}), octanol-water partitioning coefficient (K_{ow}), and aqueous solubility (S_w)]. For HA-coated sands with $0.024\% \leq f_{oc} \leq 0.154\%$, the sorption behavior of all NOCs was essentially linear as expected based on thermodynamic considerations for hydrophobic partitioning into amorphous HA at low surface coverages.

The dependency of distribution coefficient (K_d) on f_{oc} was greater as the hydrophobicity of NOCs increased. For $f_{oc} < 0.11\%$, the NOCs with low K_{ow} , such as toluene and benzene, were found to be influenced primarily by adsorption onto mineral surfaces, whereas the NOCs with high K_{ow} (e.g., 1,2,4-trichlorobenzene, 1,4-dichlorobenzene, chlorobenzene, and *m*-xylene) were found to be influenced by a combination of hydrophobic partitioning and mineral adsorption. However, as f_{oc} increased, hydrophobic partitioning became more dominant for all NOCs. Thus, overall sorption in this study was determined by both hydrophobic partitioning and mineral adsorption, and the dominance of either contribution depended on f_{oc} , and the properties of the sorbates (e.g., K_{ow} and S_w).

Values for the critical organic carbon content (f_{oc}^*) of the six sorbates calculated using both the organic carbon partitioning coefficient (K_{oc}) and the amended organic carbon partitioning coefficient (K_{oc}^*) in this study were compared with calculated values of f_{oc}^* based on surface area (S_A) and K_{ow} from McCarty et al. (1981). The f_{oc}^* values from McCarty et al. (1981) ranged from about one to two orders-of-magnitude lower than the f_{oc}^* values based on either K_{oc} or K_{oc}^* . These differences in f_{oc}^* may result, in part,

from the assumptions inherent in the derivation of the f_{oc}^* values from McCarty et al. (1981) (i.e., $K_{oc} = 0.63K_{ow}$ and linear free-energy relationships).

The adsorption of NOCs with higher K_{ow} to the mineral component was more effectively blocked by low f_{oc} than that of NOCs with lower K_{ow} for sorbents with identical physical coverages of the mineral adsorption sites by HA. In contrast to the results of previous studies suggesting that surface area is the most important variable affecting the magnitude of the sorption coefficient to mineral surface, the results of this study suggest that the change in sorptive affinity (i.e., $K_S \neq K_{S,c}$) to modified mineral surfaces with a range of surface coverage is also important.

Finally, predictions of sorption behavior based on the model that includes the effect of blocking and the available fraction of each component over the entire range of f_{oc} were only slightly better than those based on the common sorption models based on f_{oc} , K_{oc} (or K_{oc}^*), and K_{min}^* for the sorbates and sorbents used in this study, regardless of the dominance of the sorption mechanism. Over the entire range of f_{oc} ($\leq 0.154\%$) evaluated in this study, the simpler modified linear model provided essentially as good agreement between predicted and measured distribution coefficients as did the model that includes the blocking effect.

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2.5 REFERENCES

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Table 2.1 The E₄/E₆ ratios and elemental compositions of humic acid (HA) extracted from a commercial peat soil.

HA Sample	E ₄ /E ₆ value			Elemental composition (mass %) ^c					Ash content ^c (%)
	E ₄ ^a	E ₆ ^b	E ₄ /E ₆	C	H	N	O	O/C	
HA 1	0.779	0.152	5.12	52.8 ^d	5.25	1.76	34.7	0.658	0.38
HA 2	0.815	0.151	5.40	52.8	5.23	1.81	33.8	0.641	0.44
Aldrich HA ^e	0.930	0.224	4.15	38.3	4.71	0.63	49.2	1.45	NA ^f

^a Absorbance at 465 nm

^b Absorbance at 665 nm

^c Based on analyses performed by Huffman Laboratories, Golden, CO

^d $R = f_{om}/f_{oc} = 1/0.528 = 1.89$

^e Commercially-available humic acid

^f Not available

Table 2.2 Physical and chemical properties of Ottawa sand (F-95 Unground Silica) used in this study.

Property	Standard	Value
Specific Gravity	ASTM D854	2.65
Soil Classification	ASTM D2487	SP
Moisture Content (%)	*	<0.05
Melting Point (°F)	*	3100
Grain Shape	*	Round
Color	*	White
Soil pH	*	7.0
Principal Compositions (%)		
Silicon Dioxide (SiO ₂)		99.8
Iron Oxide (Fe ₂ O ₃)		0.03
Aluminum Oxide (Al ₂ O ₃)		0.08
Titanium Oxide (TiO ₂)	*	0.02
Calcium Oxide (CaO)		<0.01
Magnesium Oxide (MgO)		<0.01
Sodium Oxide (Na ₂ O)		<0.01
Potassium Oxide (K ₂ O)		<0.01
Loss on Ignition (LOI)		0.1

* Product literature supplied by vendor, U.S. Silica Company, Berkeley Springs, WV

Table 2.3 Physical and chemical properties of model sorbents.

Model Sorbent		Carbon Content (%) ^a			BET Surface Area, S_A^b (m ² /g)	Intra-particle Porosity ^b (mm ³ /g)
Type	No.	Replicate	Organic	Inorganic		
Uncoated sand	1	1	0.005	<0.005	2.045	2.7
		2	0.005	<0.005		
		3	0.006	<0.005		
		4	0.006	<0.005		
		Average	0.006	<0.005		
Acid washed sand heated @ 700 °C	2	1	<0.005	<0.005	2.036	2.6
		2	<0.005	<0.005		
		3	<0.005	<0.005		
		4	<0.005	<0.005		
		Average	<0.005	<0.005		
Humic acid-coated sand	3	1	0.024	<0.005	2.067	2.9
		2	0.026	<0.005		
		3	0.024	<0.005		
		4	0.024	<0.005		
		Average	0.025	<0.005		
	4	1	0.048	<0.005	2.058	2.8
		2	0.051	<0.005		
		3	0.053	<0.005		
		4	0.051	<0.005		
		Average	0.051	<0.005		
	5	1	0.071	<0.005	2.090	2.8
		2	0.071	<0.005		
		3	0.072	<0.005		
		4	0.072	<0.005		
		Average	0.072	<0.005		
	6	1	0.118	<0.005	2.089	2.9
		2	0.116	<0.005		
		3	0.119	<0.005		
		4	0.122	<0.005		
		Average	0.119	<0.005		
	7	1	0.148	<0.005	2.137	3.6
		2	0.154	<0.005		
		3	0.153	<0.005		
		4	0.152	<0.005		
		Average	0.152	<0.005		

^aDetermined by Huffman Laboratories, Golden, CO^bMeasured by Porous Materials Inc., Ithaca, NY

Table 2.4 Physical and chemical properties of six nonpolar sorbates.

Compound			Aqueous ^a Solubility (mg/L)	Log ^b γ_w^{sat}	Log ^c K_{oc}	Log ^d K_{ow}	ATSDR ^e
Name	Formula	Molecular Weight					
1,2,4-trichlorobenzene	C ₆ H ₃ Cl ₃	181.45	31.3 at 25 °C	5.51	3.16	4.23	203
1,4-dichlorobenzene	C ₆ H ₄ Cl ₂	147.00	49 at 22 °C	5.22	2.89	3.39	159
chlorobenzene	C ₆ H ₅ Cl	112.56	500 at 20 °C	4.09	2.52	2.84	105
<i>m</i> -xylene	C ₈ H ₁₀	106.17	161.91 at 20 °C	4.56	2.54	3.20	59
toluene	C ₇ H ₈	92.14	515 at 20 °C	3.99	2.18	2.65	71
benzene	C ₆ H ₆	78.11	1780 at 20 °C	3.38	1.96	2.13	6

^aAqueous solubility from Montgomery (1996)

^bCalculated activity coefficient in water at saturation by using aqueous solubility from Montgomery (1996)

^cOrganic carbon partitioning coefficient from Montgomery (1996) and Delle Site (2001)

^dOctanol-water partitioning coefficient from Montgomery (1996)

^eAgency for Toxic Substances and Disease Registry (2005 Ranking in Priority List of Hazardous Substances)

Table 2.5 Parameter values (average $\pm$ standard deviation) from fitting Freundlich and liner sorption models to measured sorption data for six individual nonpolar sorbates and uncoated sand.

Compound	Freundlich Model ^a		Linear Model ^a		pH	
	Freundlich Capacity Coefficient, $K_f (\mu\text{mol/kg})/(\mu\text{mol/L})^n$	Freundlich Exponent, n	Distribution Coefficient, $K_d (\text{L/kg})$	Surface-Area-Normalized Distribution Coefficient, K_s^b ($\times 10^{-5} \text{ L/m}^2$)	Range	Average
1,2,4-trichlorobenzene	0.305 ± 0.046	0.918 ± 0.039	0.205 ± 0.009	10.1 ± 0.444	6.9 – 7.6	7.3
1,4- dichlorobenzene	0.218 ± 0.034	0.954 ± 0.019	0.175 ± 0.012	8.56 ± 0.587	7.2 – 7.6	7.4
chlorobenzene	0.171 ± 0.050	1.015 ± 0.067	0.176 ± 0.008	8.62 ± 0.425	7.3 – 7.5	7.4
<i>m</i> -xylene	0.290 ± 0.016	0.908 ± 0.017	0.189 ± 0.009	9.28 ± 0.464	7.1 – 7.6	7.5
toluene	0.268 ± 0.035	0.906 ± 0.028	0.171 ± 0.007	8.36 ± 0.344	7.0 – 7.6	7.5
benzene	0.169 ± 0.045	1.010 ± 0.069	0.172 ± 0.012	8.39 ± 0.568	7.1 – 7.4	7.3

^a Number of observations = 4

^b $K_s = K_d/S_A$ and $S_A = 2.045 \text{ m}^2/\text{g}$ from Table 2.3

Table 2.6 Parameter values (average $\pm$ standard deviation) from fitting Freundlich and liner sorption models to measured sorption data for six individual nonpolar sorbates and heated sand.

Compound	Freundlich Model ^a		Linear Model ^a		pH	
	Freundlich Capacity Coefficient, $K_f (\mu\text{mol/kg})/(\mu\text{mol/L})^n$	Freundlich Exponent, n	Distribution Coefficient, $K_{min} (\text{L/kg})$	Surface-Area-Normalized Distribution Coefficient, K_s^b ($\times 10^{-5} \text{ L/m}^2$)	Range	Average
1,2,4-trichlorobenzene	0.223 ± 0.037	0.984 ± 0.018	0.206 ± 0.016	10.1 ± 0.799	7.2 – 7.4	7.3
1,4- dichlorobenzene	0.194 ± 0.044	0.996 ± 0.065	0.188 ± 0.016	9.23 ± 0.739	7.2 – 7.5	7.4
chlorobenzene	0.169 ± 0.028	1.001 ± 0.029	0.168 ± 0.006	8.24 ± 0.302	7.4 – 7.5	7.5
<i>m</i> -xylene	0.327 ± 0.033	0.881 ± 0.016	0.188 ± 0.005	9.21 ± 0.243	7.3 – 7.5	7.4
toluene	0.255 ± 0.075	0.923 ± 0.042	0.174 ± 0.017	8.55 ± 0.836	7.2 – 7.4	7.4
benzene	0.258 ± 0.058	0.916 ± 0.046	0.171 ± 0.003	8.36 ± 0.144	7.2 – 7.3	7.2

^a Number of observations = 2

^b $K_s = K_{min}/S_A$ and $S_A = 2.036 \text{ m}^2/\text{g}$ from Table 2.3

Table 2.7 Parameter values (average $\pm$ standard deviation) from fitting Freundlich and liner sorption models to measured sorption data for six individual nonpolar sorbates and humic acid-coated sand with different f_{oc} .

Compound	Average Organic Carbon Content, f_{oc}	Linear Model ^a		Freundlich Model ^a		pH	
		Distribution Coefficient, K_d (L/kg)	Organic Carbon Partitioning Coefficient, K_{oc} (L/kg) ^b	Freundlich Capacity Coefficient, K_f ($\mu\text{mol/kg}$)/($\mu\text{mol/L}$) ⁿ	Freundlich Exponent, n	Range	Average
1,2,4-trichlorobenzene	0.00025	0.541 $\pm$ 0.016	2259 $\pm$ 70.1	0.452 $\pm$ 0.096	1.042 $\pm$ 0.045	5.6 – 6.0	5.8
	0.00051	0.933 $\pm$ 0.027	1838 $\pm$ 23.9	1.097 $\pm$ 0.234	0.968 $\pm$ 0.042	5.8 – 6.2	6.1
	0.00072	1.236 $\pm$ 0.006	1729 $\pm$ 5.43	1.335 $\pm$ 0.414	0.991 $\pm$ 0.073	5.8 – 6.1	6.0
	0.00119	1.923 $\pm$ 0.029	1620 $\pm$ 10.0	2.166 $\pm$ 0.087	0.970 $\pm$ 0.012	5.6 – 6.0	5.9
	0.00152	2.403 $\pm$ 0.040	1539 $\pm$ 2.10	2.953 $\pm$ 0.284	0.951 $\pm$ 0.019	5.8 – 6.2	6.1
1,4-dichlorobenzene	0.00025	0.315 $\pm$ 0.007	1315 $\pm$ 50.9	0.358 $\pm$ 0.071	0.975 $\pm$ 0.041	6.0 – 6.3	6.2
	0.00051	0.463 $\pm$ 0.015	913.2 $\pm$ 9.18	0.561 $\pm$ 0.088	0.960 $\pm$ 0.037	6.1 – 6.4	6.2
	0.00072	0.584 $\pm$ 0.006	816.6 $\pm$ 6.52	0.584 $\pm$ 0.044	1.000 $\pm$ 0.018	6.2 – 6.5	6.3
	0.00119	0.843 $\pm$ 0.015	710.4 $\pm$ 4.57	1.029 $\pm$ 0.206	0.959 $\pm$ 0.046	6.0 – 6.4	6.1
	0.00152	1.029 $\pm$ 0.011	678.0 $\pm$ 4.83	1.271 $\pm$ 0.207	0.953 $\pm$ 0.036	6.1 – 6.5	6.2
chlorobenzene	0.00025	0.179 $\pm$ 0.005	746.4 $\pm$ 32.7	0.148 $\pm$ 0.025	1.043 $\pm$ 0.040	6.2 – 6.7	6.5
	0.00051	0.251 $\pm$ 0.004	495.0 $\pm$ 13.2	0.268 $\pm$ 0.023	0.986 $\pm$ 0.020	6.3 – 6.5	6.3
	0.00072	0.289 $\pm$ 0.004	404.7 $\pm$ 3.12	0.372 $\pm$ 0.070	0.948 $\pm$ 0.037	6.3 – 6.6	6.4
	0.00119	0.371 $\pm$ 0.010	312.6 $\pm$ 3.02	0.619 $\pm$ 0.168	0.897 $\pm$ 0.059	6.1 – 6.4	6.2
	0.00152	0.428 $\pm$ 0.003	282.4 $\pm$ 3.36	0.517 $\pm$ 0.029	0.959 $\pm$ 0.011	6.2 – 6.7	6.4
<i>m</i> -xylene	0.00025	0.228 $\pm$ 0.008	951.0 $\pm$ 39.8	0.256 $\pm$ 0.053	0.978 $\pm$ 0.048	6.3 – 6.7	6.5
	0.00051	0.331 $\pm$ 0.009	648.2 $\pm$ 15.9	0.330 $\pm$ 0.079	1.006 $\pm$ 0.059	6.1 – 6.4	6.2
	0.00072	0.389 $\pm$ 0.005	544.9 $\pm$ 4.99	0.322 $\pm$ 0.063	1.045 $\pm$ 0.044	6.2 – 6.7	6.4
	0.00119	0.525 $\pm$ 0.008	442.2 $\pm$ 5.06	0.676 $\pm$ 0.130	0.948 $\pm$ 0.044	6.1 – 6.5	6.4
	0.00152	0.623 $\pm$ 0.005	410.4 $\pm$ 4.51	0.785 $\pm$ 0.151	0.950 $\pm$ 0.042	6.3 – 6.6	6.5
toluene	0.00025	0.179 $\pm$ 0.002	747.1 $\pm$ 35.7	0.186 $\pm$ 0.032	0.994 $\pm$ 0.035	6.2 – 6.5	6.2
	0.00051	0.231 $\pm$ 0.009	454.6 $\pm$ 6.17	0.257 $\pm$ 0.040	0.978 $\pm$ 0.039	6.2 – 6.4	6.4
	0.00072	0.261 $\pm$ 0.002	364.5 $\pm$ 1.00	0.318 $\pm$ 0.041	0.958 $\pm$ 0.029	6.1 – 6.7	6.2
	0.00119	0.324 $\pm$ 0.009	272.7 $\pm$ 4.18	0.569 $\pm$ 0.060	0.878 $\pm$ 0.022	6.3 – 6.4	6.4
	0.00152	0.364 $\pm$ 0.012	239.8 $\pm$ 4.71	0.463 $\pm$ 0.087	0.950 $\pm$ 0.051	6.3 – 6.8	6.6
benzene	0.00025	0.171 $\pm$ 0.004	713.0 $\pm$ 29.5	0.236 $\pm$ 0.086	0.942 $\pm$ 0.086	6.0 – 6.3	6.3
	0.00051	0.182 $\pm$ 0.004	358.8 $\pm$ 8.47	0.142 $\pm$ 0.086	1.078 $\pm$ 0.112	6.4 – 6.8	6.5
	0.00072	0.197 $\pm$ 0.010	274.8 $\pm$ 12.1	0.298 $\pm$ 0.091	0.915 $\pm$ 0.067	6.4 – 6.7	6.5
	0.00119	0.235 $\pm$ 0.011	197.9 $\pm$ 6.41	0.277 $\pm$ 0.058	0.968 $\pm$ 0.039	6.4 – 6.8	6.7
	0.00152	0.242 $\pm$ 0.007	159.6 $\pm$ 2.55	0.276 $\pm$ 0.085	0.979 $\pm$ 0.065	6.4 – 6.6	6.4

^a Number of observations = 4, ^b $K_{oc} = K_d/f_{oc}$

Table 2.8 Organic-carbon and mineral-component distribution coefficients for sorption of six individual nonpolar sorbates to humic-acid coated sand.

Compound	Linear Regression with zero Intercept		Linear Regression with Intercept			Heated Sand
	K_{oc}^a (L/kg)	r^2	K_{oc}^{*b} (L/kg)	K_{min}^{*c} (L/kg)	r^2	K_{min}^d (L/kg)
1,2,4-trichlorobenzene	1636	0.982	1476	0.172	0.999	0.206
1,4-dichlorobenzene	726.5	0.893	575.8	0.162	0.998	0.188
chlorobenzene	325.3	0.084	183.4	0.153	0.989	0.168
<i>m</i> -xylene	457.7	0.567	298.9	0.171	0.997	0.188
toluene	284.6	-0.707	138.2	0.158	0.988	0.174
benzene	204.8	-8.30	57.43	0.159	0.916	0.171

^a Overall organic carbon partitioning coefficient from Fig. 2.19a and 2.19c

^b Overall amended organic carbon partitioning coefficient from Fig. 2.19b and 2.19d

^c Y-intercept at $f_{oc}=0$ from Fig. 2.19b and 2.19d

^d Average distribution coefficient to heated sand summarized in Table 2.6

Table 2.9 Results of the least-square linear regression of ψ versus (f_{oc}/f_{min}) for HA-coated sand and six nonpolar sorbates.

Compound	Linear Regression with Intercept		
	Blocking Parameter, ω_{oc-min}	Intercept	r^2
1,2,4-trichlorobenzene	126	1.06	0.740
1,4-dichlorobenzene	116	1.03	0.842
chlorobenzene	88.6	1.00	0.873
<i>m</i> -xylene	99.1	1.00	0.925
toluene	92.5	1.01	0.932
benzene	92.7	1.01	0.833

Table 2.10 Results of the analysis of variance (ANOVA) for a single or multiple factors using statistical software (SAS® 9.1, Cary, NC).

Model	Source of Variation	Degree of Freedom	Sum of Squares	Mean Square	F_0 value ^a	$F_{0.05,v1,v2}$ ^b	p -value ^c	Conclusion
$\psi = f(f_{oc}/f_{min})$	Between sorbates	1	0.308	0.308	191	3.92	< 0.0001	Reject H_0 ^d
	Within sorbates	118	0.190	0.002				
	Total	119	0.498					
$\psi = f(f_{oc}/f_{min}, \text{sorbates})$	Between sorbates	6	0.437	0.073	134	2.18	< 0.0001	Reject H_0
	Within sorbates	113	0.061	0.00054				
	Total	119	0.498					
$\psi = f(f_{oc}/f_{min}, \text{sorbates}, f_{oc}/f_{min} \times \text{sorbates})$	Between sorbates	11	0.443	0.040	77.5	1.86	< 0.0001	Reject H_0
	Within sorbates	108	0.056	0.00052				
	Total	119	0.499					

^a F_0 value = mean square between sorbates/mean square within sorbates.

^b $F_{0.05,v1,v2}$ value = the critical value of F from Ott and Longnecker (2001) for $\alpha = 0.05$ and two different degree of freedom.

If $F_{0.05,v1,v2}$ value < F_0 value, then reject H_0 .

^cLevel of significance. If the p -value $\leq \alpha$ ($=0.05$), then reject H_0 .

^dNull hypothesis H_0 = mean ψ values for all six sorbates are equivalent

Table 2.11 The multiple-comparison output using Tukey's procedure in statistical software (SAS® 9.1, Cary, NC)

<i>p</i> -value ^a for $H_0 : \text{LSM}^b \psi (i) = \text{LSM} \psi (j)$						
i/j (<i>p</i>-value)	1,2,4-trichlorobenzene	1,4-dichlorobenzene	chlorobenzene	<i>m</i> -xylene	toluene	benzene
1,2,4-trichlorobenzene		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
1,4-dichlorobenzene	<0.0001		<0.0001	<0.0001	<0.0001	<0.0001
chlorobenzene	<0.0001	<0.0001		0.9159	0.8026	0.4352
<i>m</i> -xylene	<0.0001	<0.0001	0.9159		0.9998	0.9569
toluene	<0.0001	<0.0001	0.8026	0.9998		0.9916
benzene	<0.0001	<0.0001	0.4352	0.9569	0.9916	

^aLevel of significance. If the *p*-value $\leq \alpha$ ($= 0.05$), then reject the null hypothesis, H_0 .

^bLeast squares means

Table 2.12 Comparison of model representations of experimental data using the log of the likelihood function (LLF) and proportion of variance explained (PVE).

Model	1,2,4-TCB		1,4-DCB		CB		<i>m</i> -XYL		TOL		BZ	
	LLF ^a	PVE ^b	LLF	PVE	LLF	PVE	LLF	PVE	LLF	PVE	LLF	PVE
Linear model with no intercept (Eq. 2.8)	19.8	0.979	21.4	0.876	23.4	0	20.5	0.505	22.6	0	22.5	0
Linear model with intercept (Eq. 2.9)	58.3	0.999	64.9	0.996	76.4	0.984	80.8	0.995	78.5	0.983	79.9	0.909
Two-component model without blocking effect ($\beta_{min} = 1$) (Eq. 2.15)	49.4	0.997	56.2	0.991	68.4	0.967	67.2	0.986	68.5	0.942	73.0	0.772
Two-component model with blocking effect ($\beta_{min} \leq 1$) (Eq. 2.15)	67.1	0.999	71.4	0.996	80.0	0.985	84.6	0.995	83.6	0.985	85.1	0.911

^a Estimate the log of the likelihood function using SAS® 9.1 (Cary, NC) (GENMOD Procedure)

^b Equivalent to the r^2 and negative r^2 is treated as $r^2 = 0$

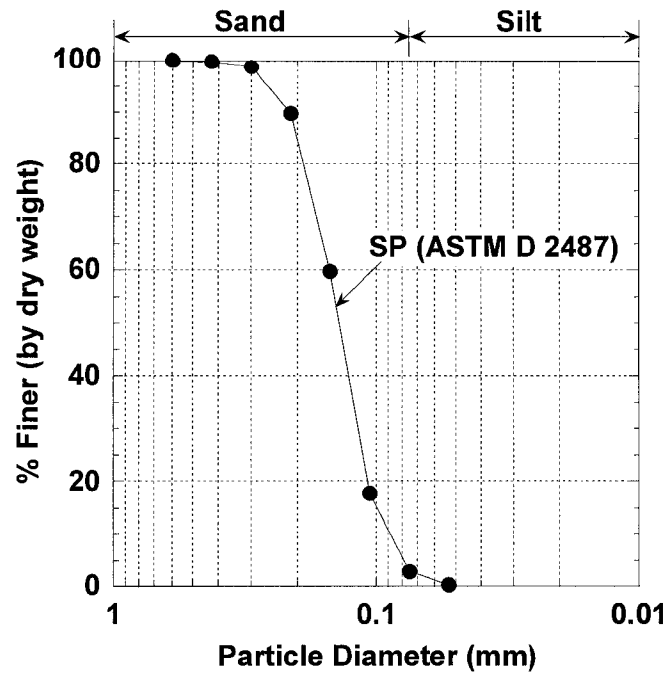


Fig. 2.1 Particle-size distribution for Ottawa sand based on mechanical sieve (dry) analysis (ASTM D 421)

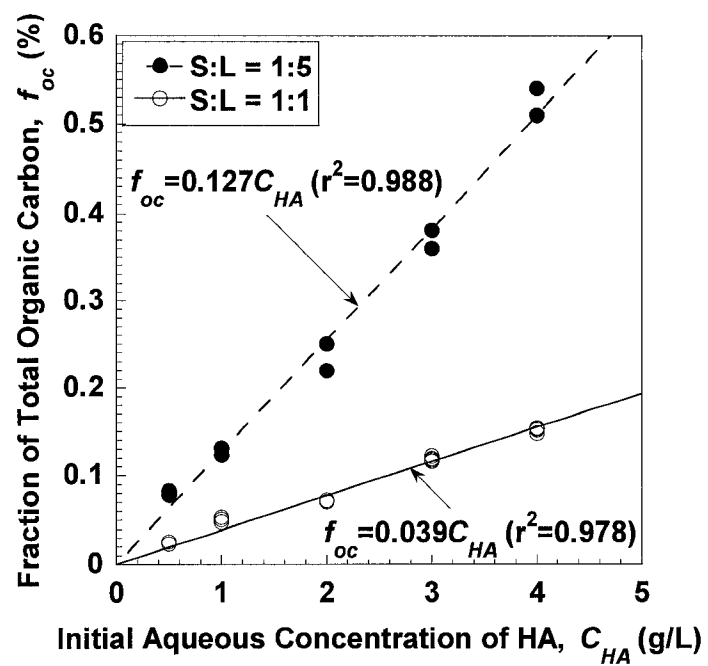


Fig. 2.2 Relationship between initial aqueous concentration of humic acid (HA) and the fraction of total organic carbon (f_{oc}) for different solid-to-liquid (S:L) ratios.

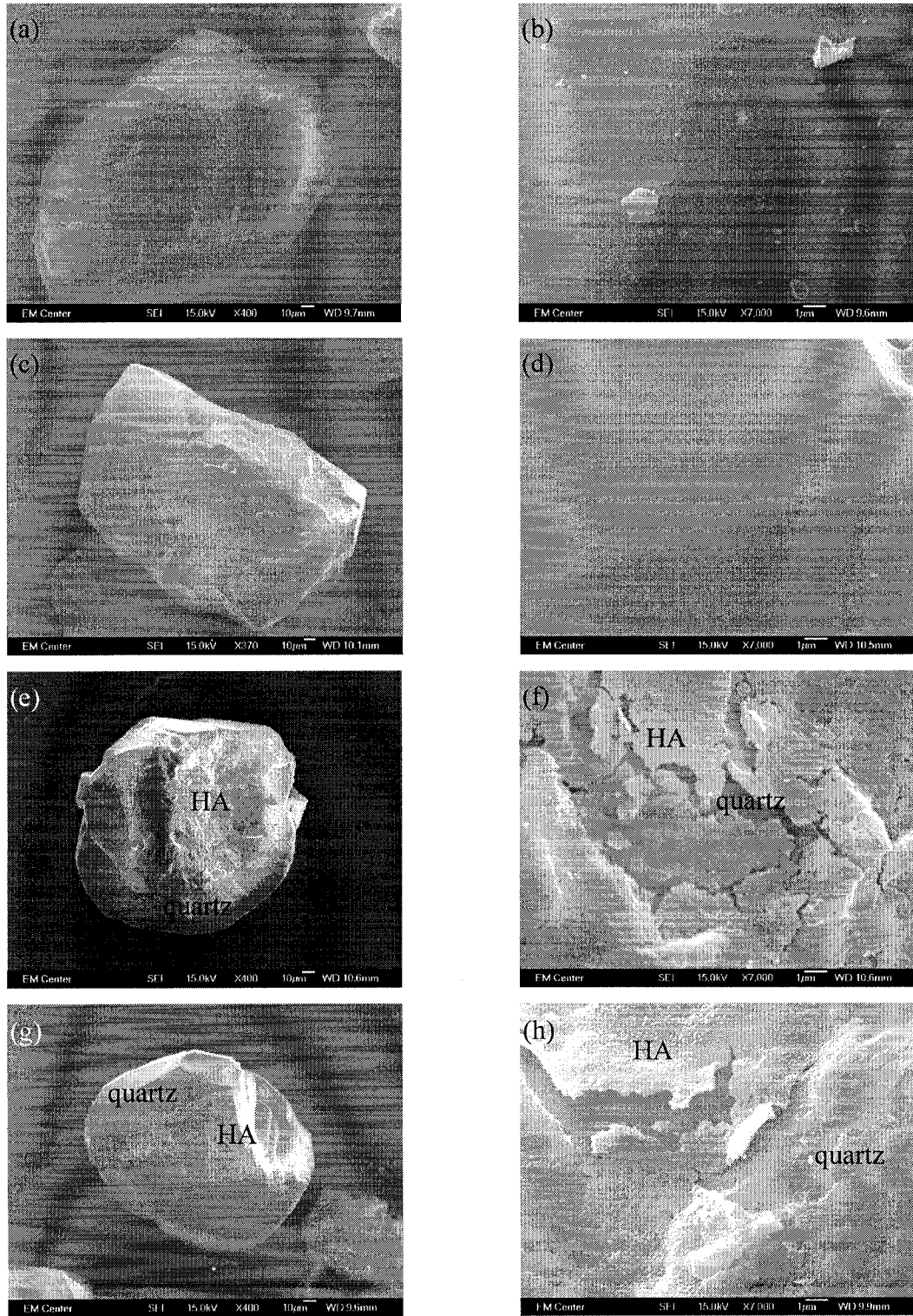


Fig. 2.3 Scanning electron microscopic images at different resolutions: (a) & (b), uncoated sand; (c) & (d), heated sand; (e) & (f), humic acid-coated sand ($f_{oc} = 0.119\%$); and (g) & (h), humic acid-coated sand ($f_{oc} = 0.152\%$).

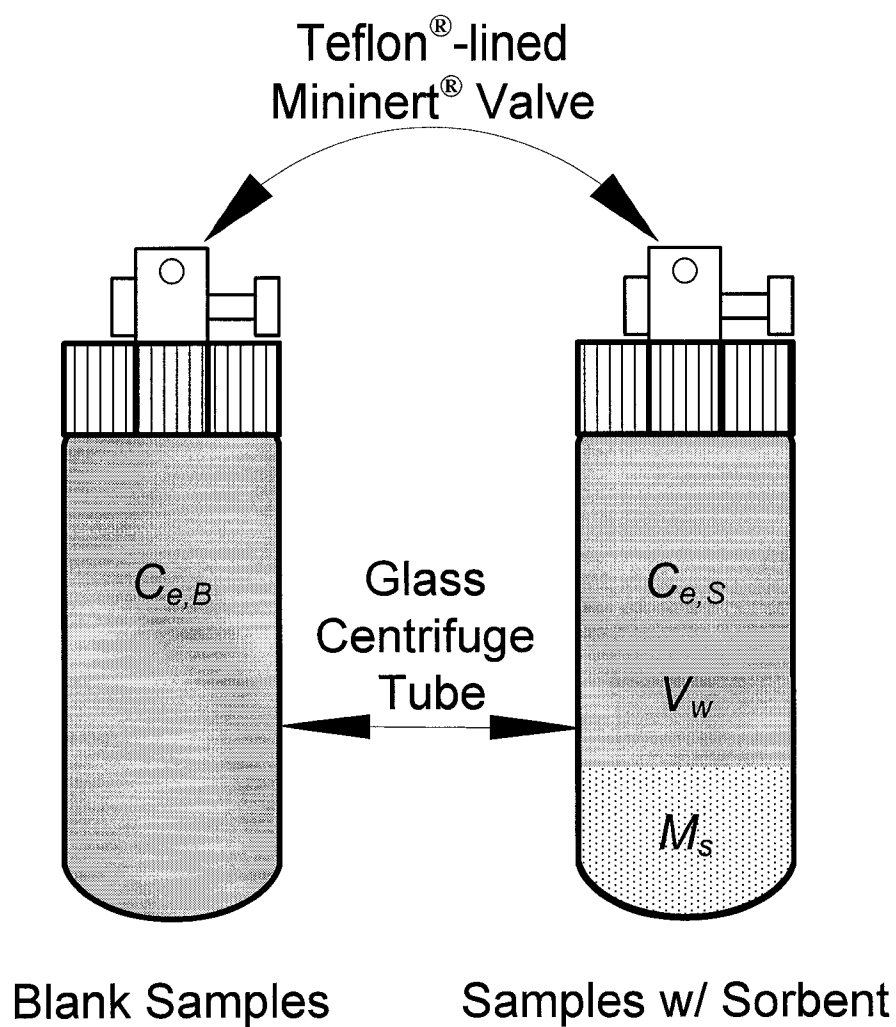
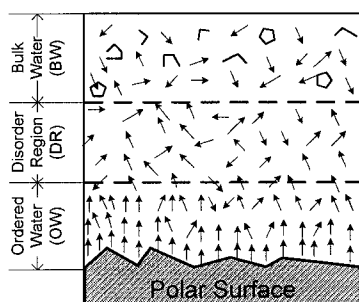


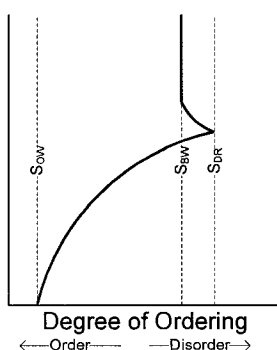
Fig. 2.4 Schematic illustration of sample tubes for batch equilibrium sorption tests

Three-Region Model

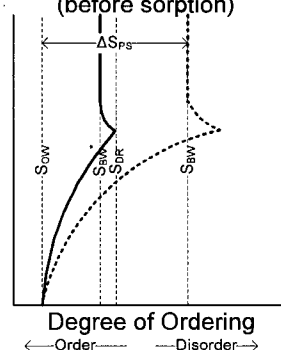


Possible States of Order of Vicinal Water

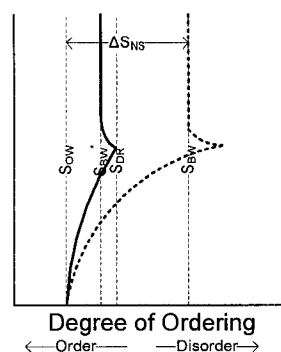
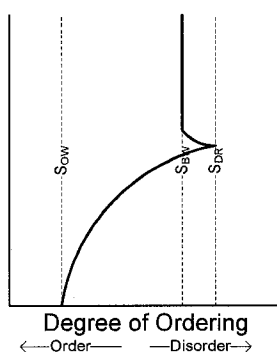
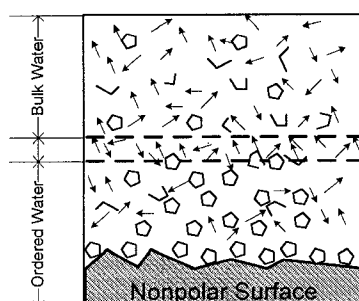
1. Water Only



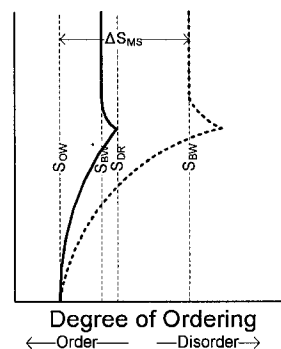
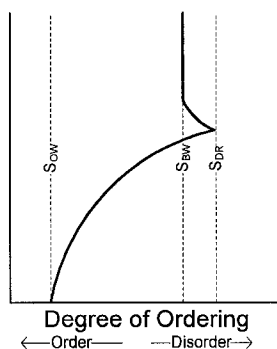
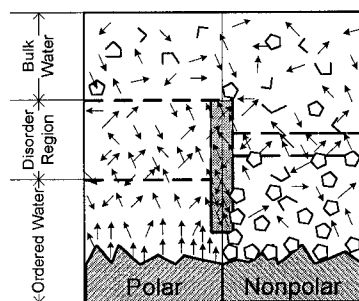
2. Water + Nonpolar Sorbate (before sorption)



(a) Polar Surface (PS)



(b) Nonpolar Surface (NS)



(c) Mixed Surface (MS)

Notes:

- (1) : clathrate cage-like of water molecules
- (2) : high-pressure ice polymorphs of water molecules
- (3) : monomeric water molecules
- (4) : disordered transition between polar and nonpolar surface
- (5) : interface between zones
- (6) S : entropy of each region, S^* : entropy before sorption

Fig. 2.5 Three-region models for the structures of water near solid surfaces: (a) and (b) after Drost-Hansen (1969); (c) three-region model for mixed polar and nonpolar surfaces proposed herein.

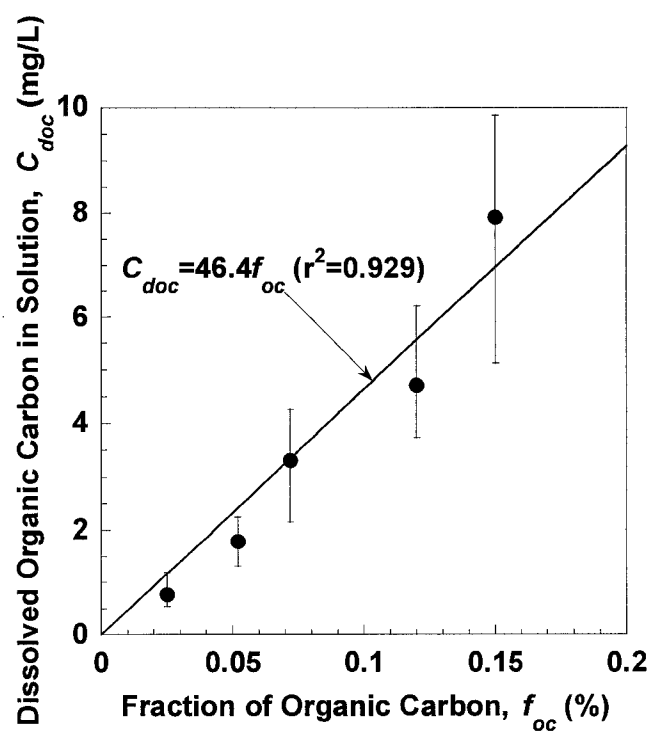


Fig. 2.6 The concentration of dissolved organic carbon resulting after the batch equilibrium sorption tests for HA-coated sand with different f_{oc} .

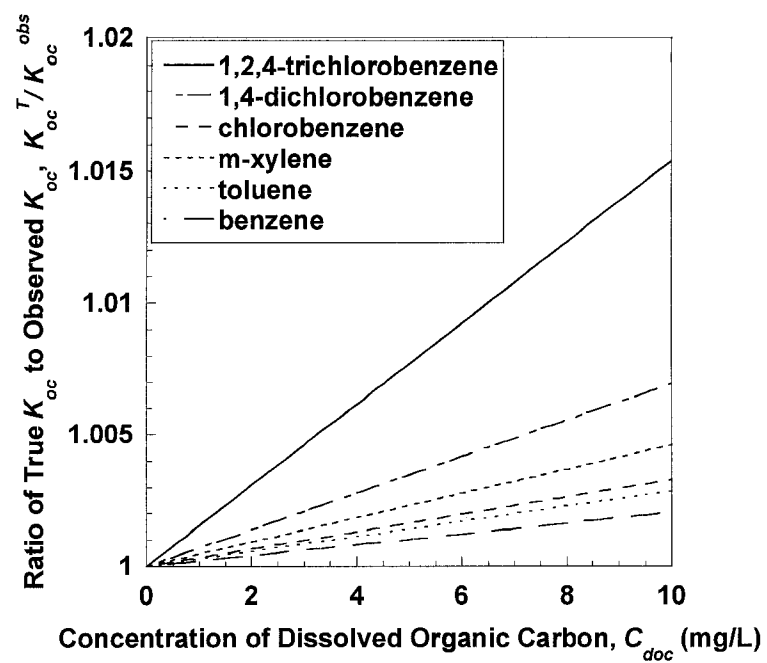


Fig. 2.7 The effect of dissolved organic carbon on the observed organic carbon partitioning coefficient for the six nonpolar sorbates used in this study.

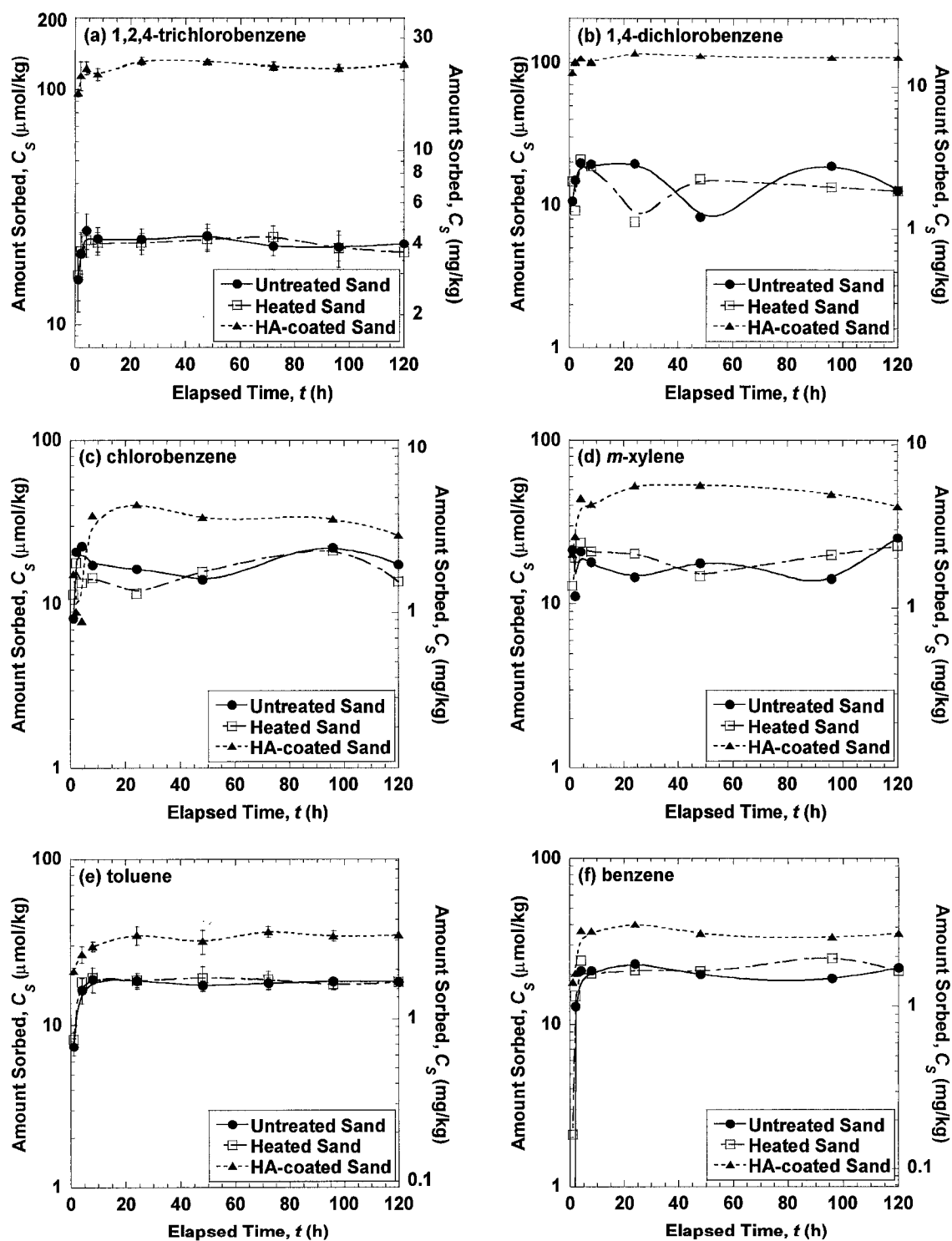


Fig. 2.8 Sorption kinetics for six individual sorbates to uncoated ($f_{oc} = 0.006\%$), heated ($f_{oc} < 0.005\%$), and humic acid (HA)-coated sand ($f_{oc} = 0.119\%$) at an initial aqueous concentration of $150\ \mu\text{mol/L}$.

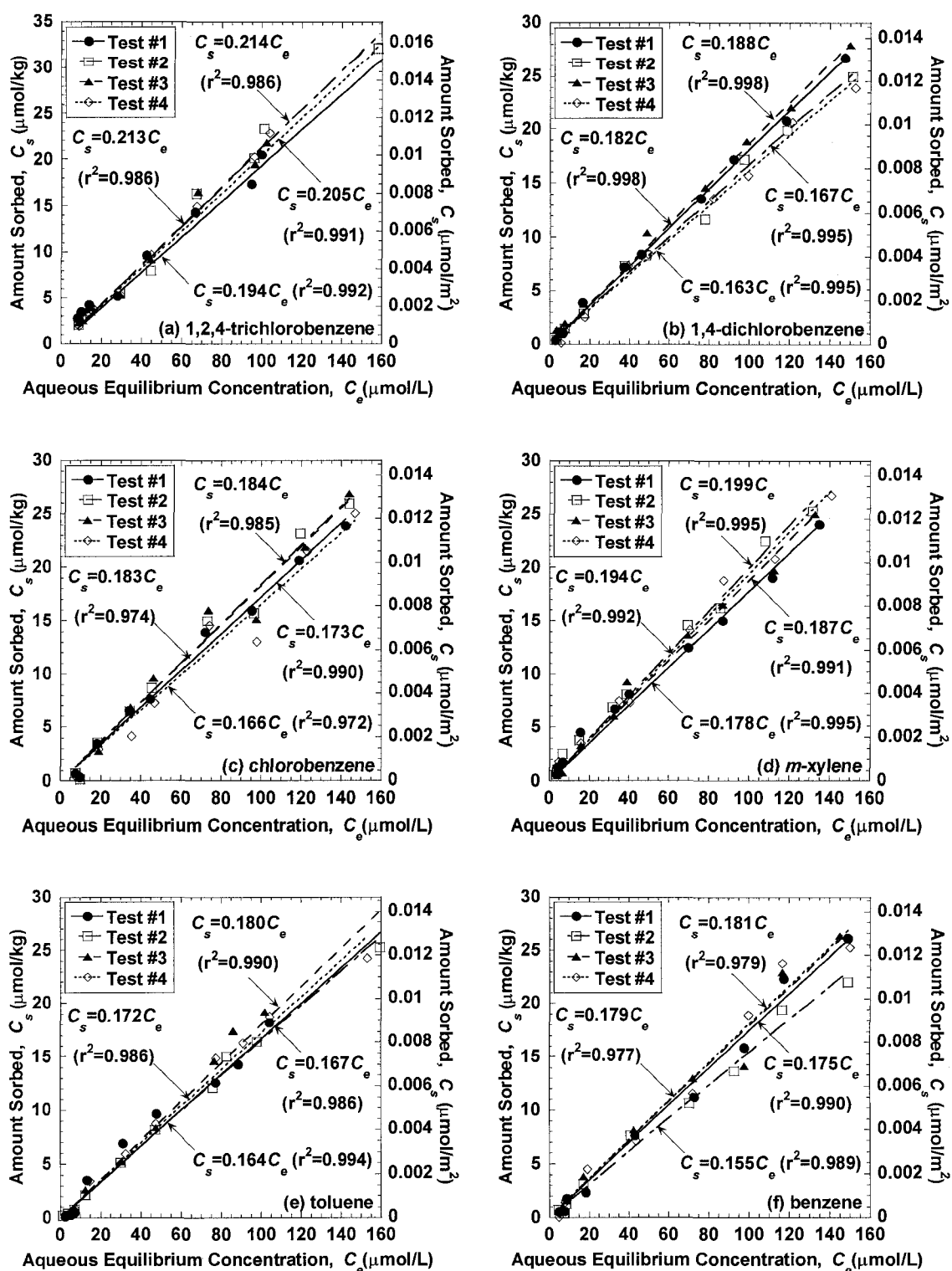


Fig. 2.9 Measured and linearly fitted sorption data for six individual sorbates and uncoated sand ($f_{oc} = 0.006\%$).

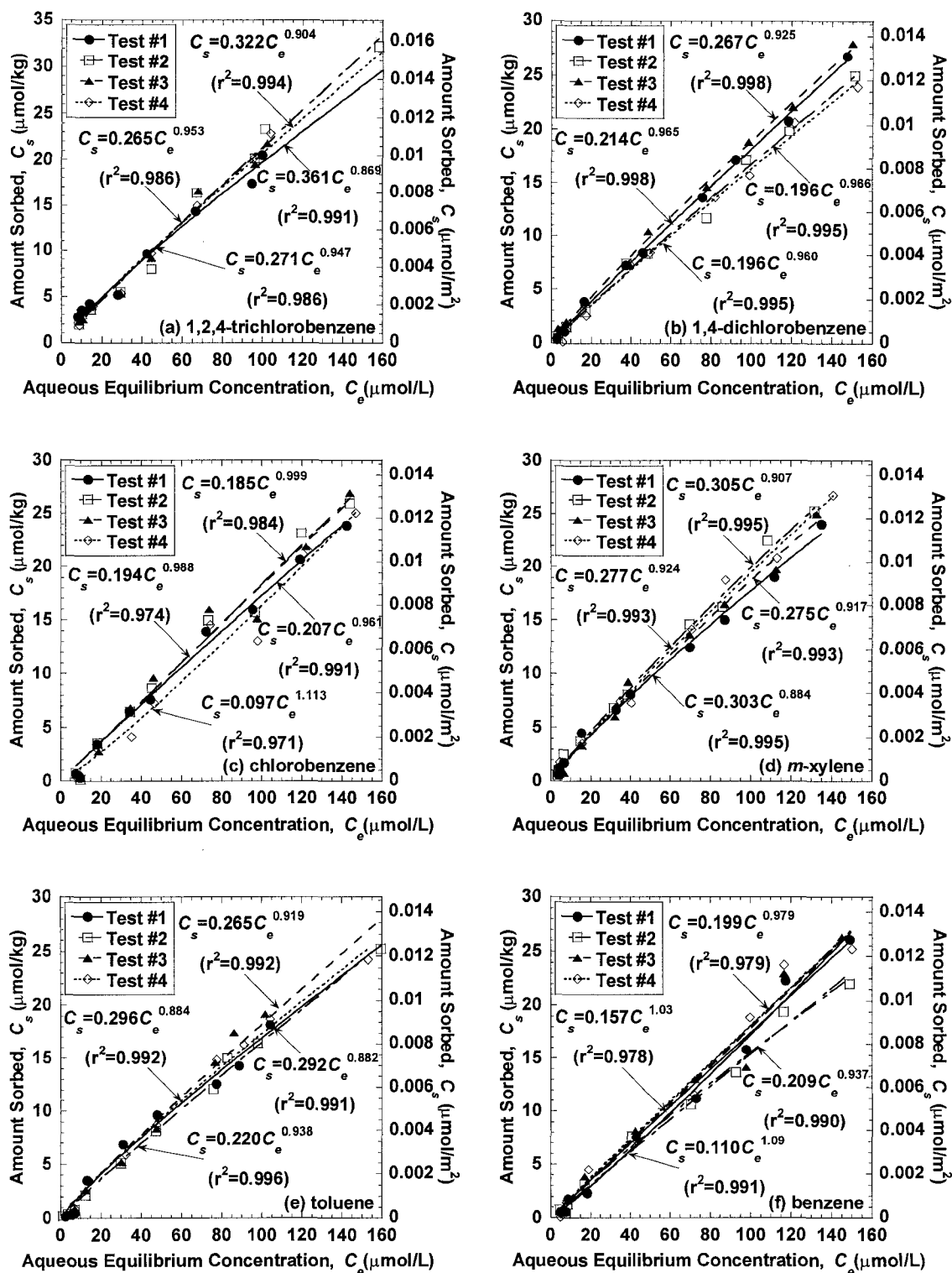


Fig. 2.10 Measured and nonlinearly fitted Freundlich sorption data for six individual sorbates and uncoated sand ($f_{oc} = 0.006\%$).

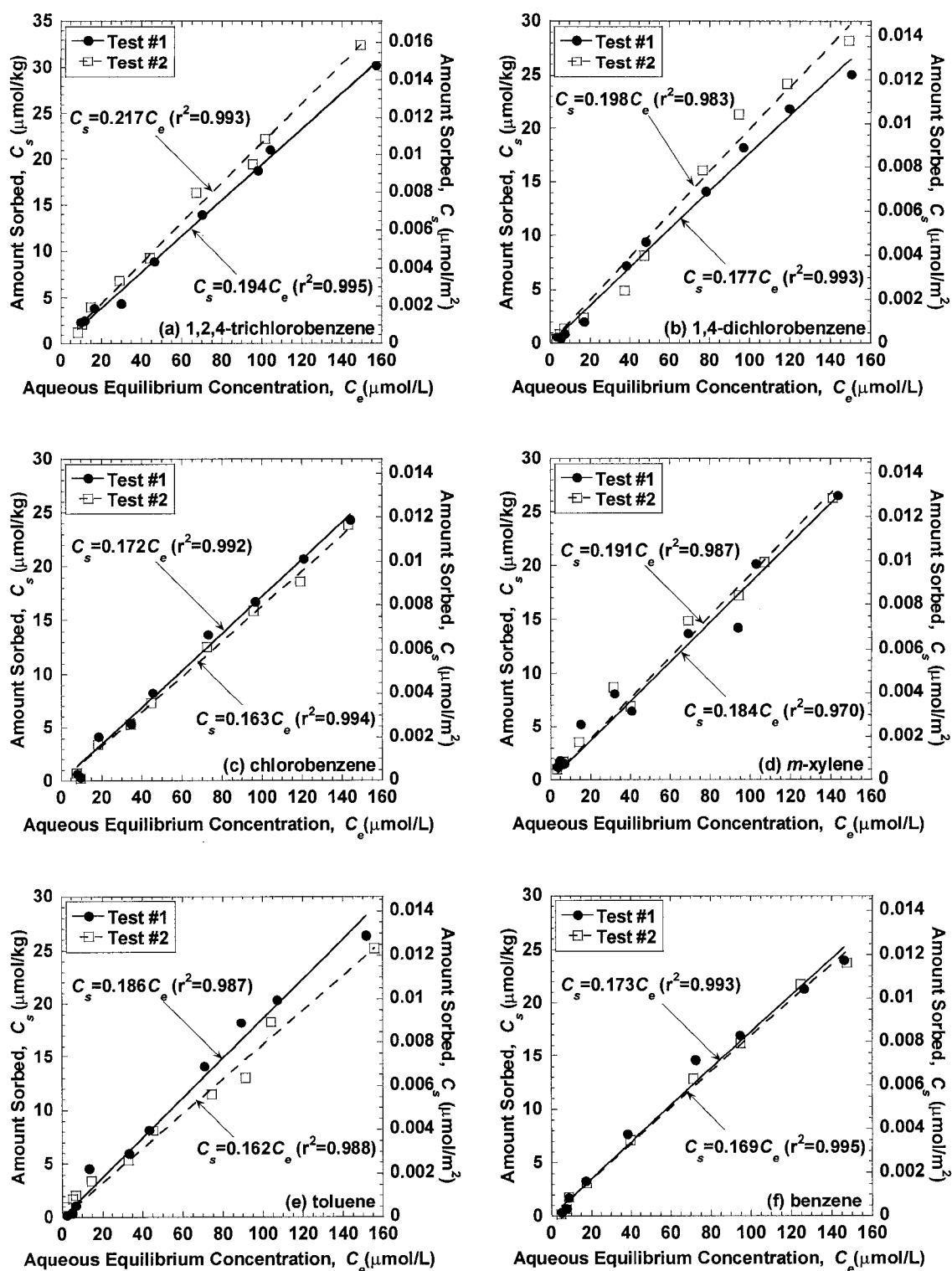


Fig. 2.11 Measured and linearly fitted sorption data for six individual sorbates and heated sand ($f_{oc} < 0.005\%$).

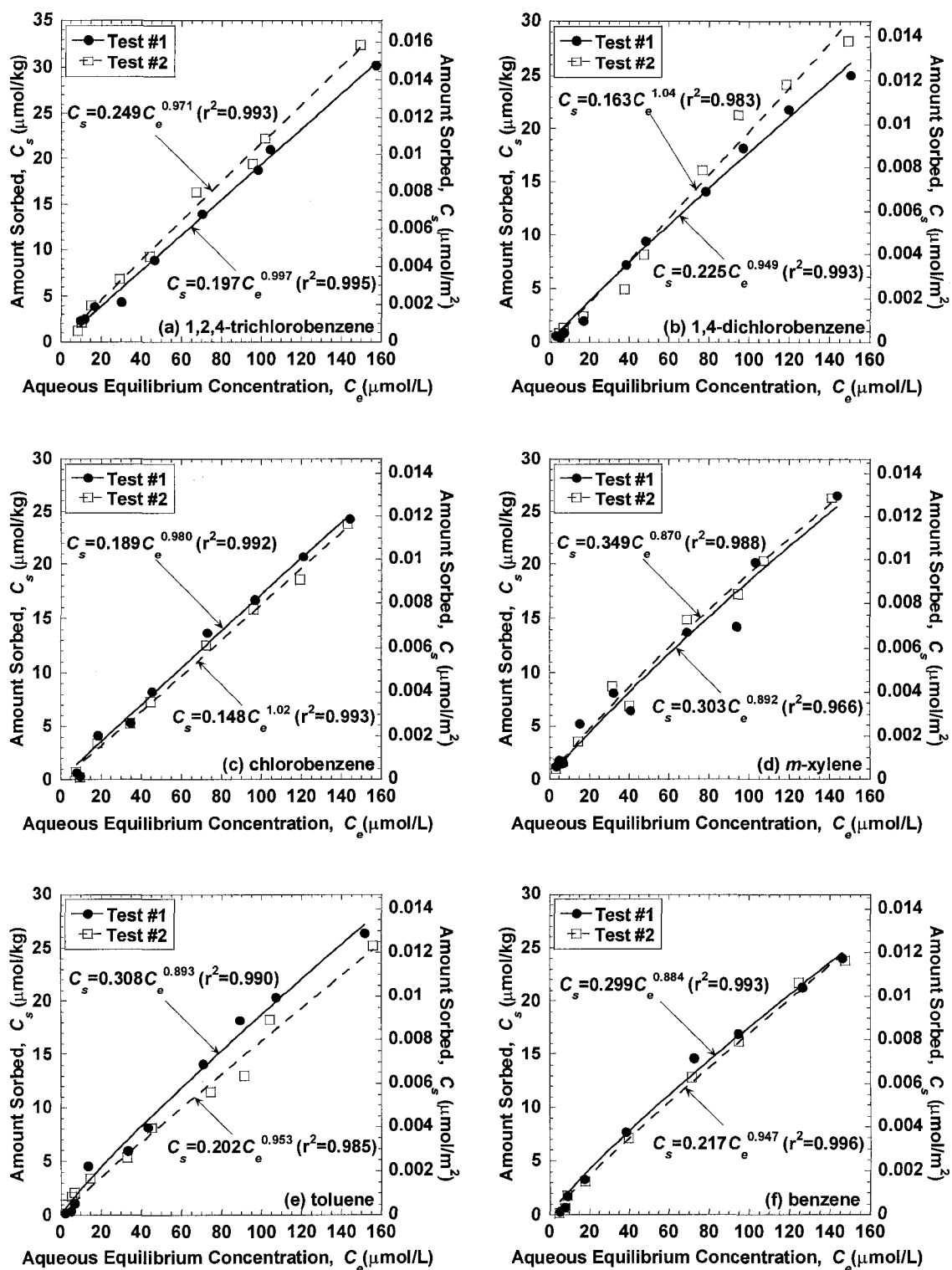


Fig. 2.12 Measured and nonlinearly fitted Freundlich sorption data for six individual sorbates and heated sand ($f_{oc} < 0.005\%$).

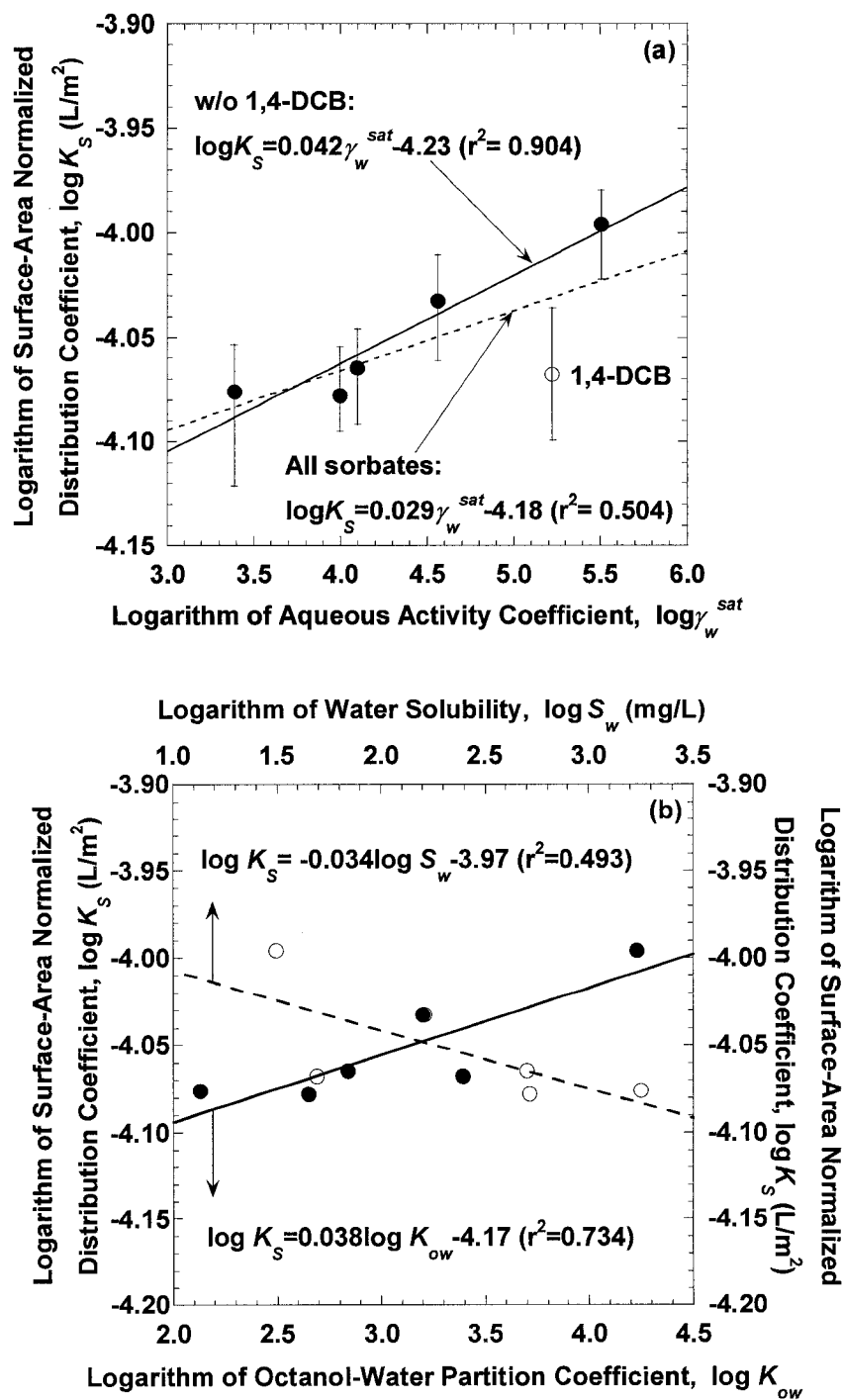


Fig. 2.13 Relationship of $\log K_S$ to uncoated sand and properties of the six sorbates used in this study: (a) $\log \gamma_w^{sat}$ and (b) $\log K_{ow}$ and $\log S_w$ ($7.2 \leq \text{pH} \leq 7.5$ and $T = 20^\circ \text{C}$).

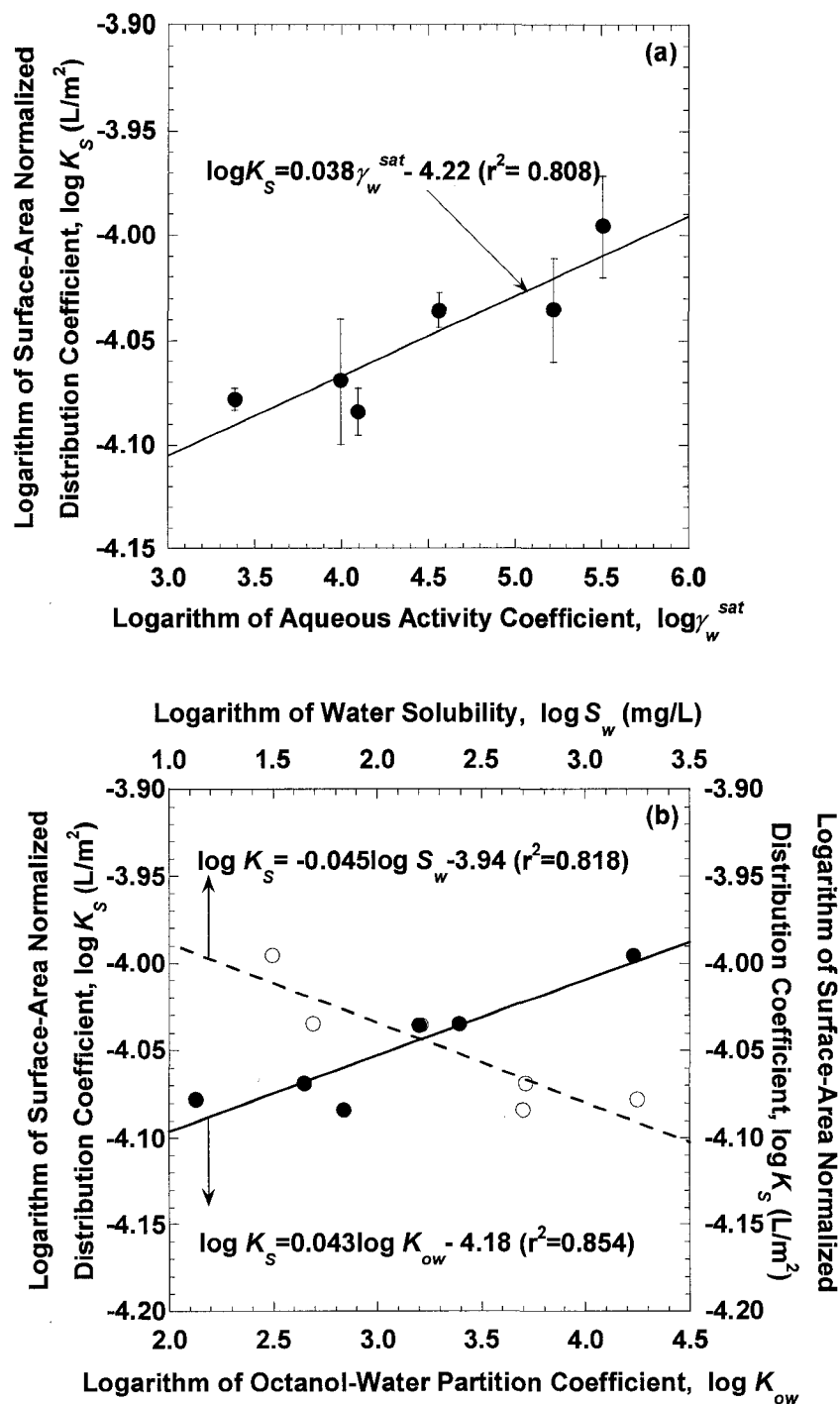


Fig. 2.14 Relationship of $\log K_S$ to heated sand and properties of the six sorbates used in this study: (a) $\log \gamma_w^{sat}$ and (b) $\log K_{ow}$ and $\log S_w$. ($7.2 \leq \text{pH} \leq 7.5$ and $T = 20^\circ \text{C}$).

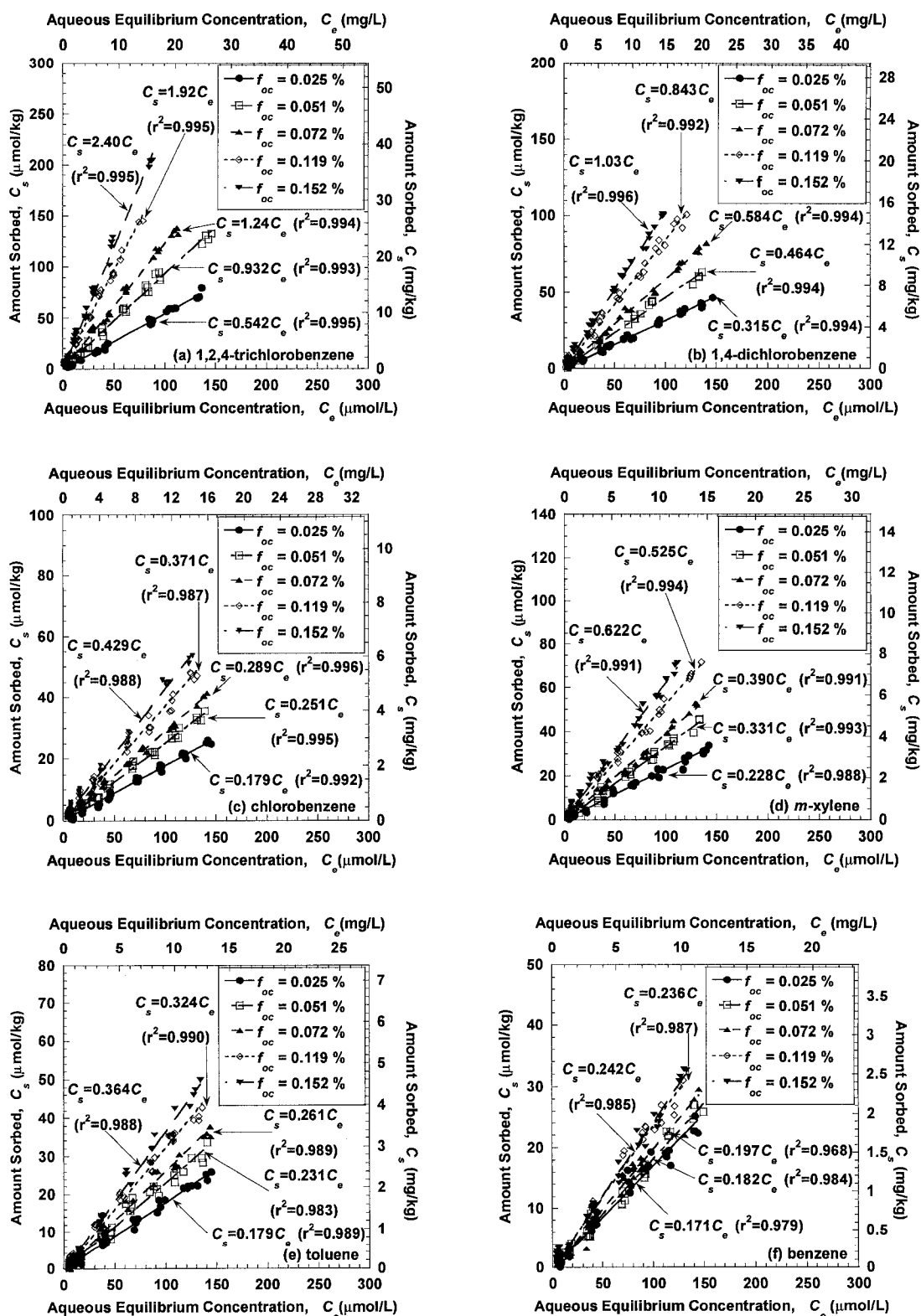


Fig. 2.15 Measured and linearly fitted sorption data for six sorbates and humic acid (HA)-coated sand with different f_{oc} .

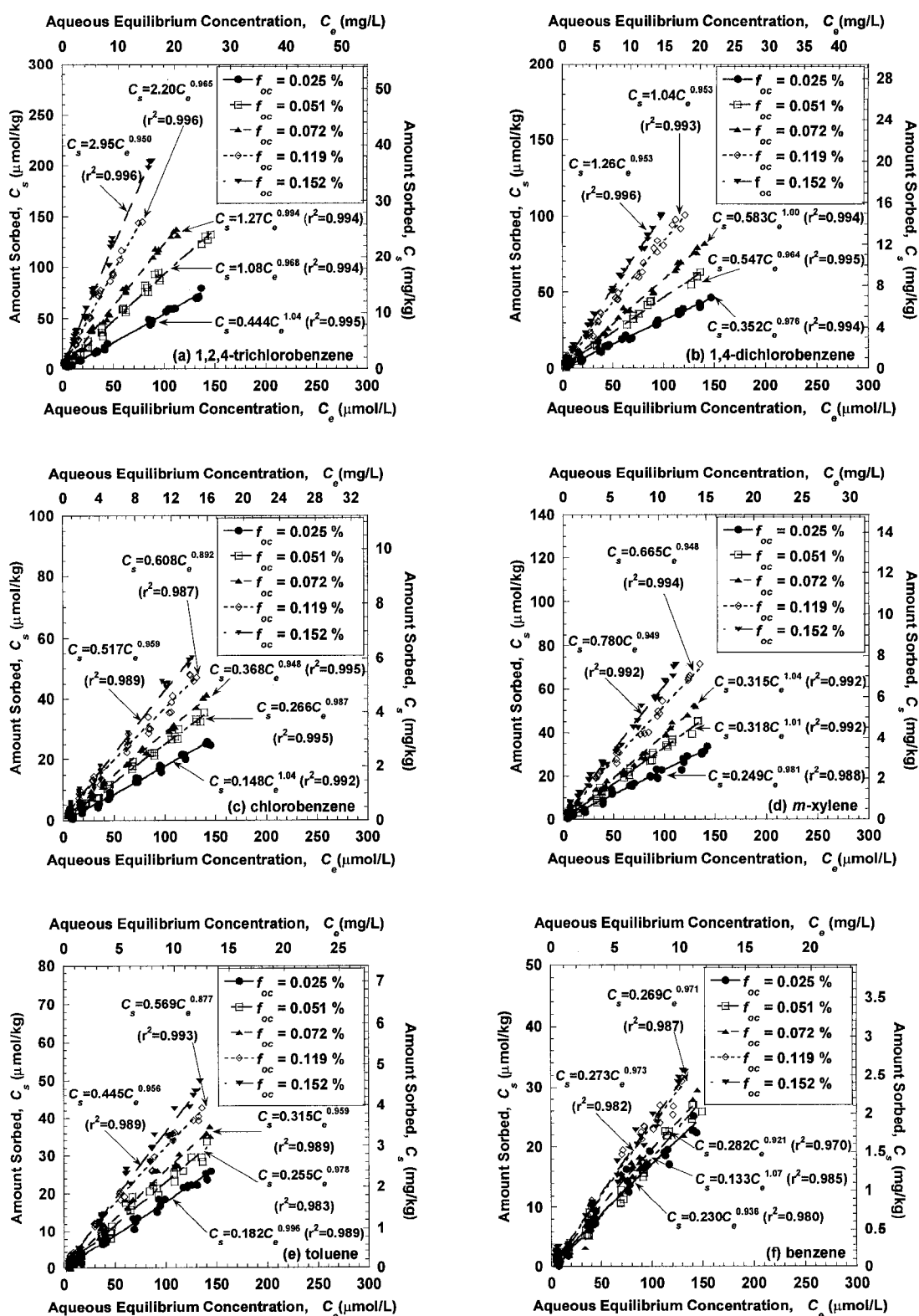


Fig. 2.16 Measured and nonlinearly fitted Freundlich sorption data using Freundlich model for six sorbates and humic acid (HA)-coated sand with different f_{oc} .

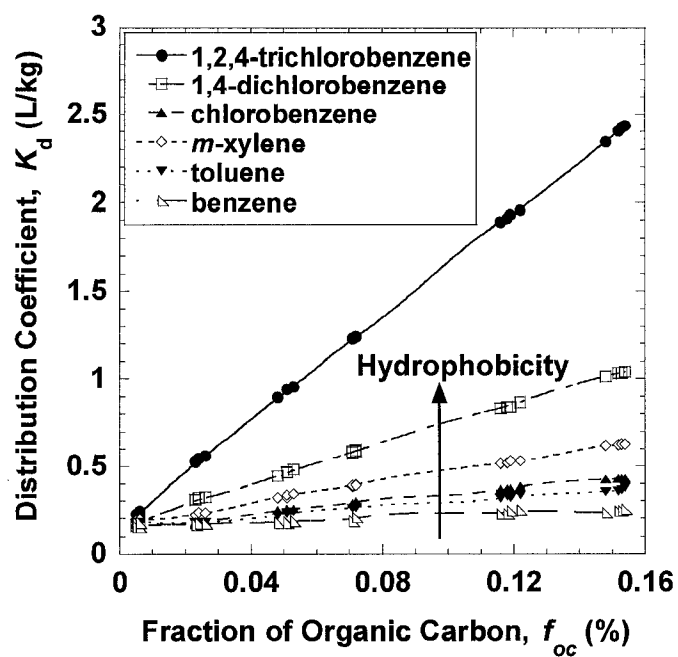


Fig. 2.17 Dependence of K_d on f_{oc} for six sorbates and humic acid (HA)-coated sands.

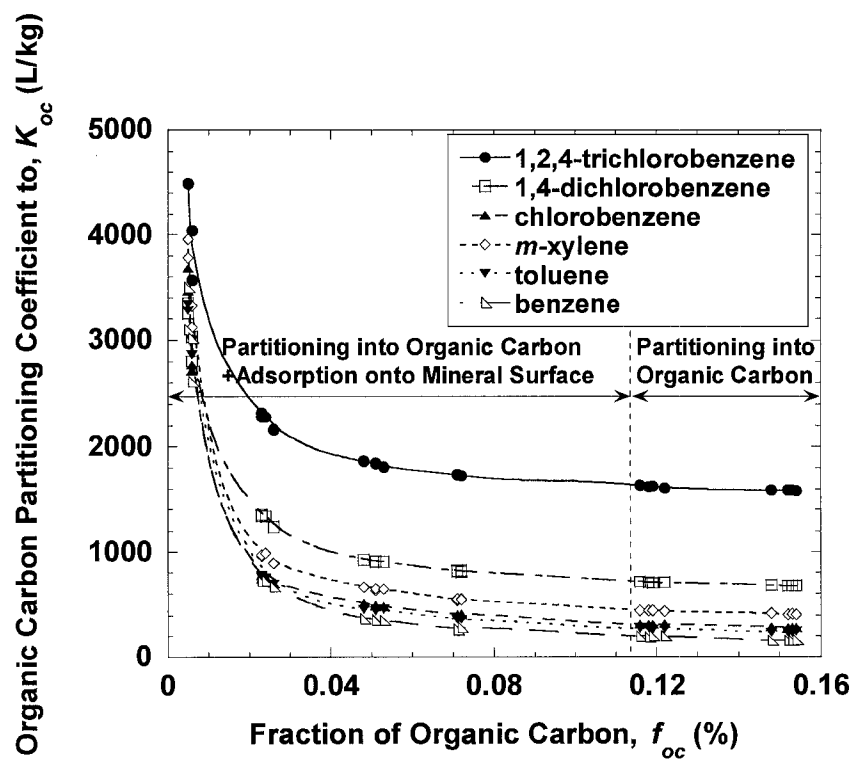


Fig. 2.18 Dependence of K_{oc} ($=K_d/f_{oc}$) on f_{oc} for six sorbates and humic acid (HA)-coated sands.

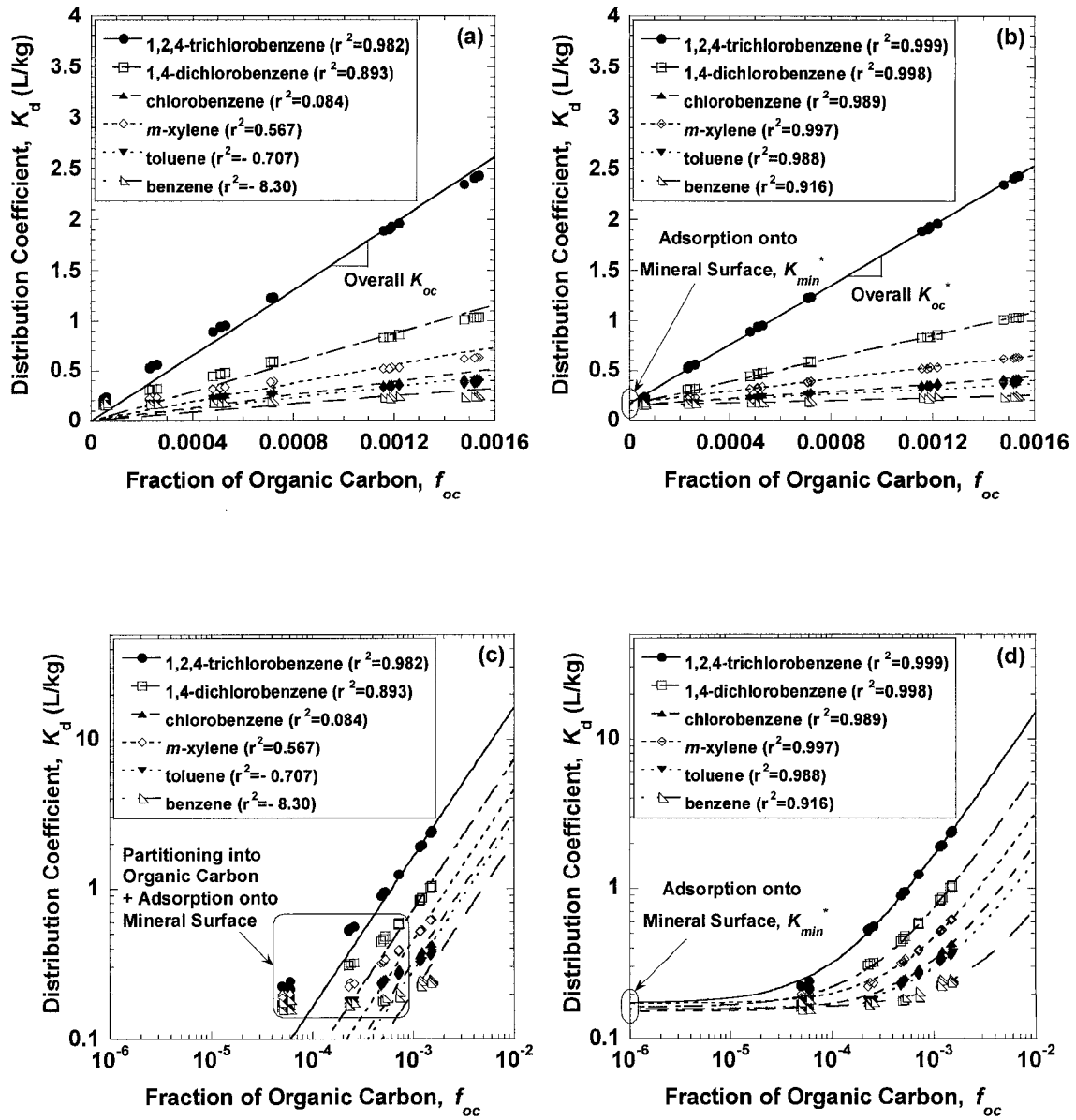


Fig. 2.19 Linear regressions of K_d for six sorbates versus f_{oc} for humic acid-coated sands: (a) and (b), arithmetic plots with regressions of the forms $K_d = f_{oc}K_{oc}$ and $K_d = f_{oc}K_{oc}^* + K_{min}^*$, respectively; (c) and (d), log-log plots with regressions of the forms $K_d = f_{oc}K_{oc}$ and $K_d = f_{oc}K_{oc}^* + K_{min}^*$, respectively.

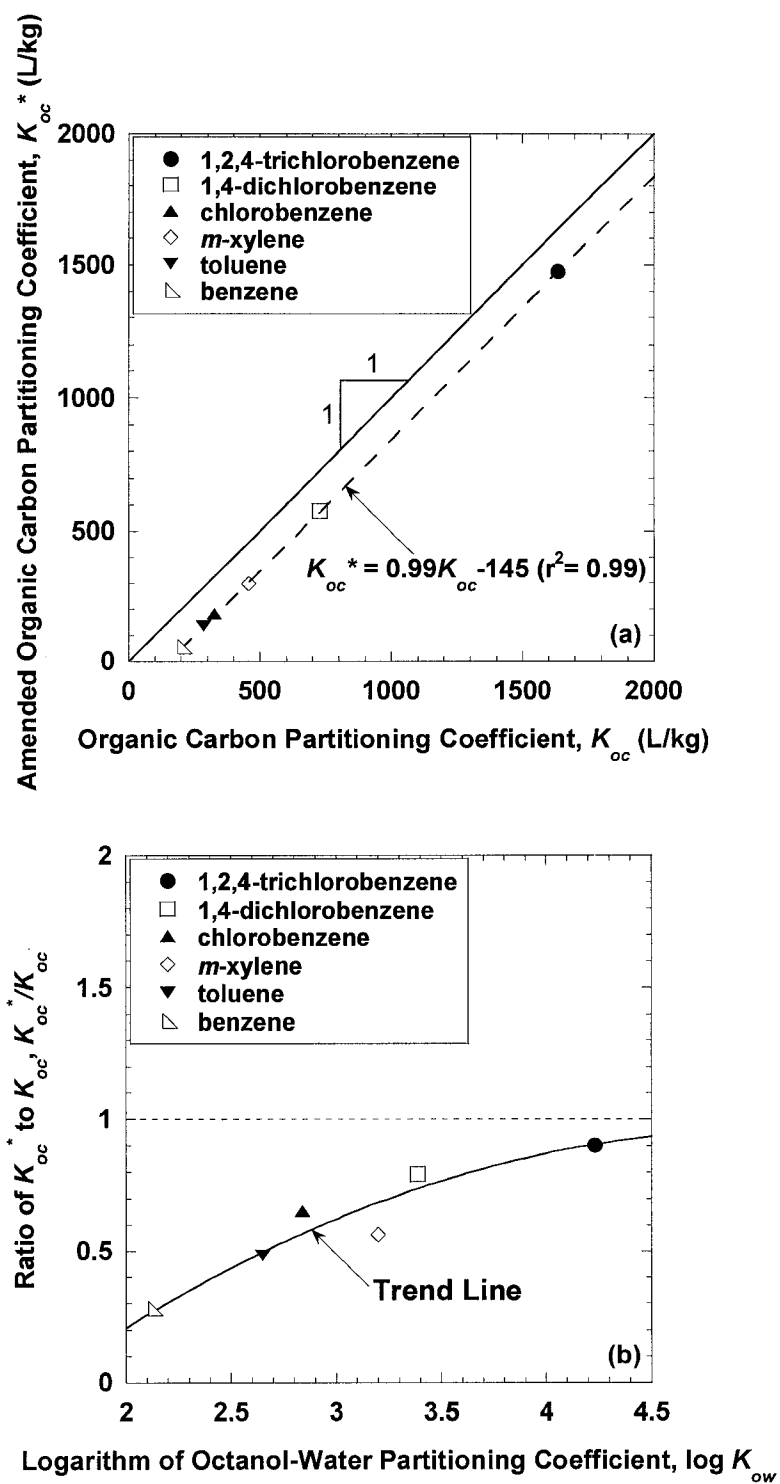


Fig. 2.20 (a) Organic carbon partitioning coefficient (K_{oc}) versus amended organic carbon partitioning coefficient (K_{oc}^*) for six sorbates, and (b) relationship between the ratio of K_{oc}^* to K_{oc} and the hydrophobicity (K_{ow}) of the sorbates.

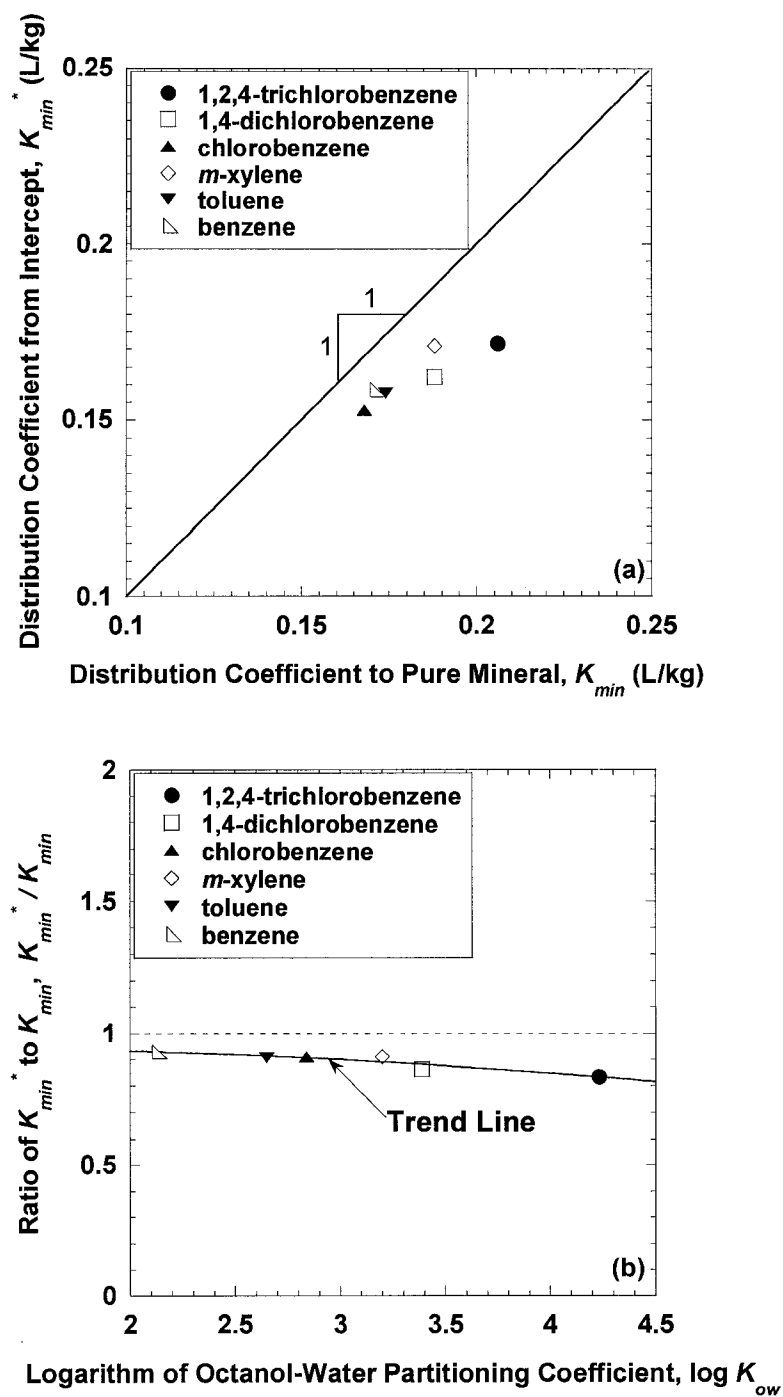


Fig. 2.21 (a) Distribution coefficient to mineral surface based on results for heated sand (K_{min}) versus distribution coefficient to mineral surface based on intercept at $f_{oc} = 0$ (K_{min}^*) for six sorbates, and (b) relationship between the ratio of K_{min}^* to K_{min} and the hydrophobicity (K_{ow}) of the sorbates.

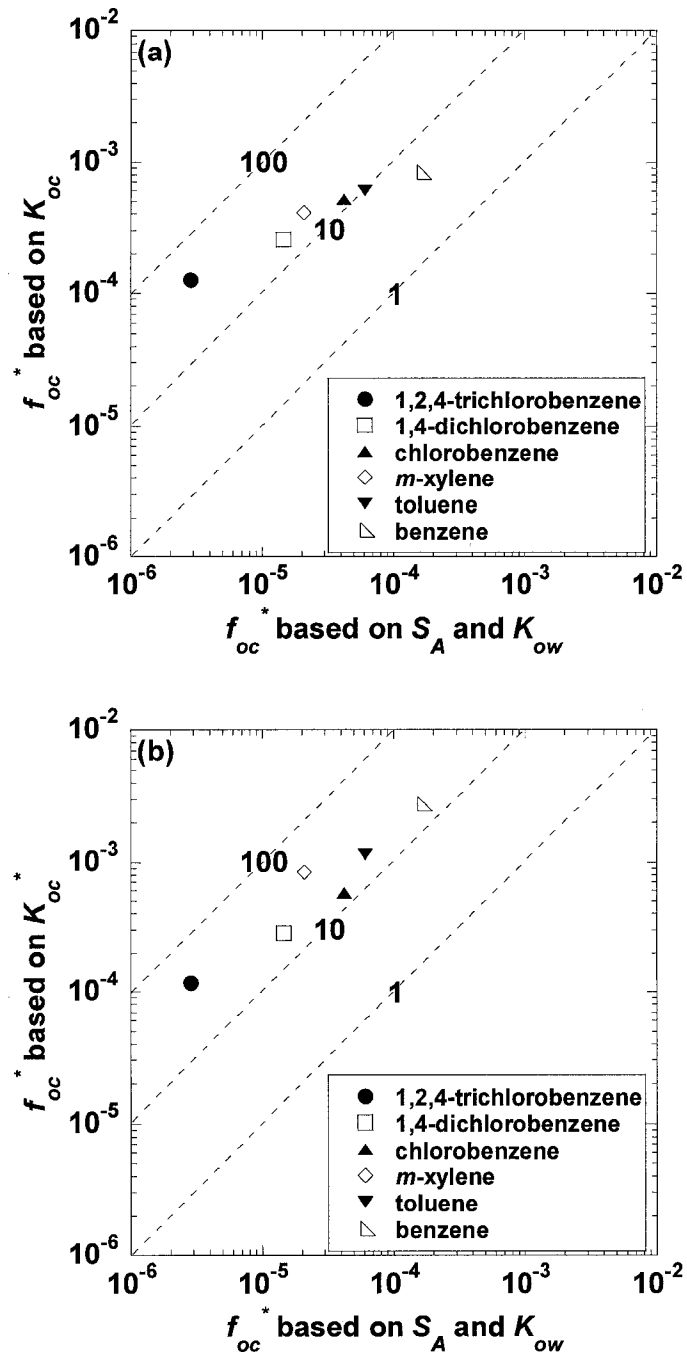


Fig. 2.22 Critical organic carbon content (f_{oc}^*) from McCarty et al. (1981) versus f_{oc}^* from (a) the organic carbon partitioning coefficient (K_{oc}), and (b) the amended organic carbon partitioning coefficient (K_{oc}^*).

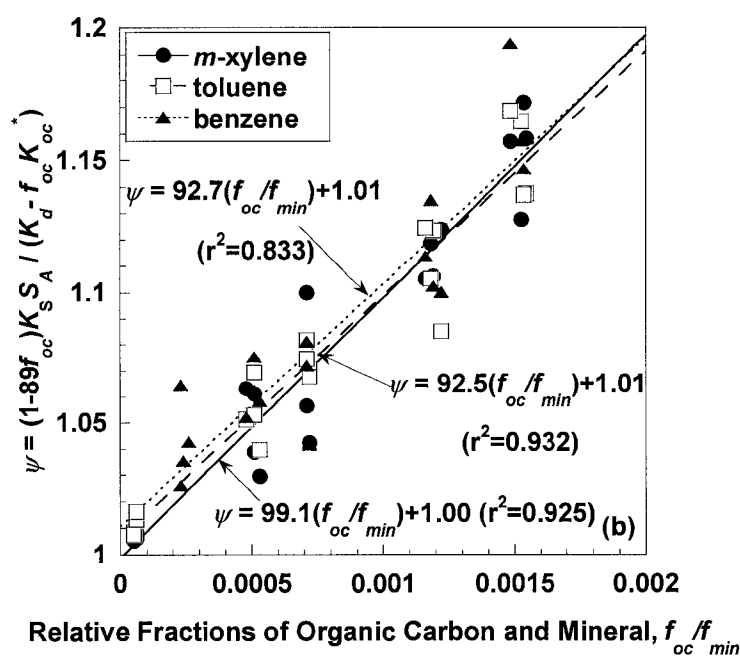
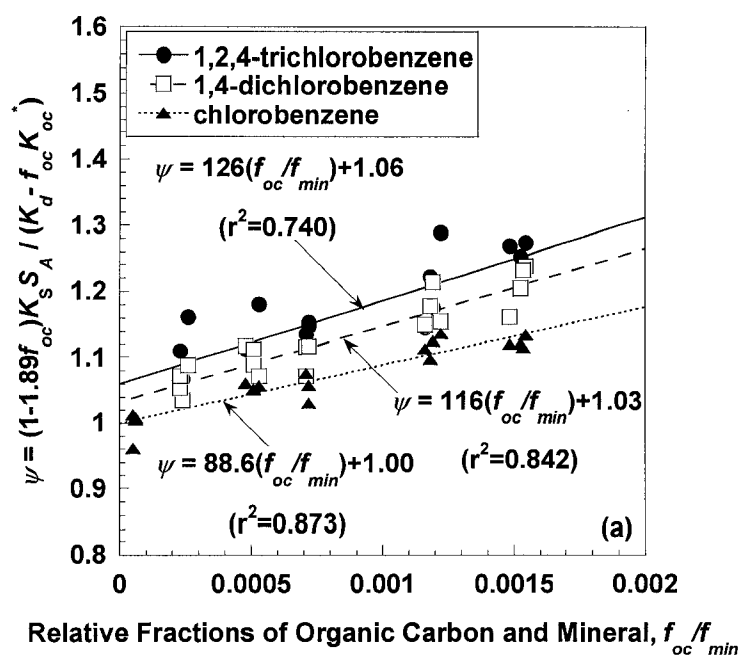


Fig. 2.23 The least-square linear regression of ψ versus (f_{oc}/f_{min}) for humic acid (HA)-coated sand and for six individual nonpolar sorbates.

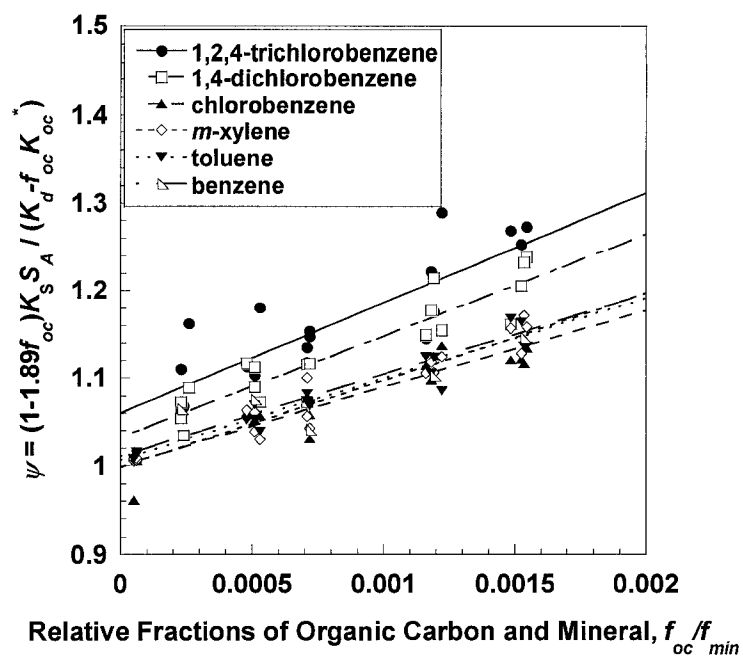


Fig. 2.24 The least-square linear regression of ψ versus (f_{oc}/f_{min}) for all six nonpolar sorbates.

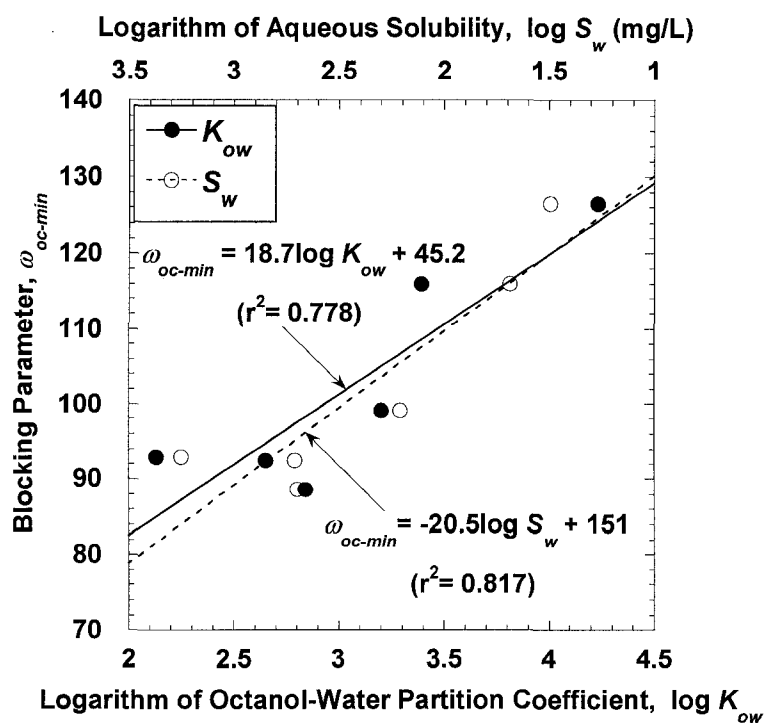


Fig. 2.25 Relationship of blocking parameter (ω_{oc-min}) values from linear regression and the properties of nonpolar sorbates used in this study.

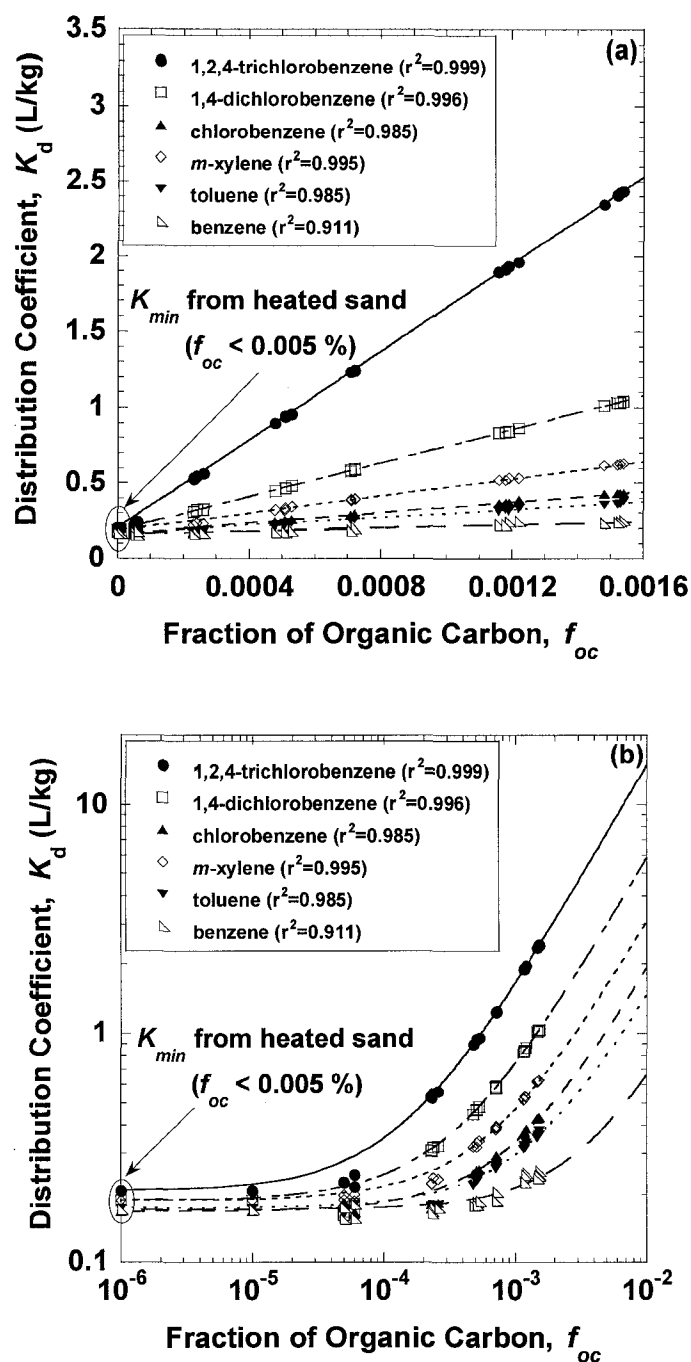


Fig. 2.26 Comparison of measured versus predicted distribution coefficients based on the two-component sorption model with blocking effect (Eq. 2.15): (a) arithmetic plot; and (b) logarithmic plot.

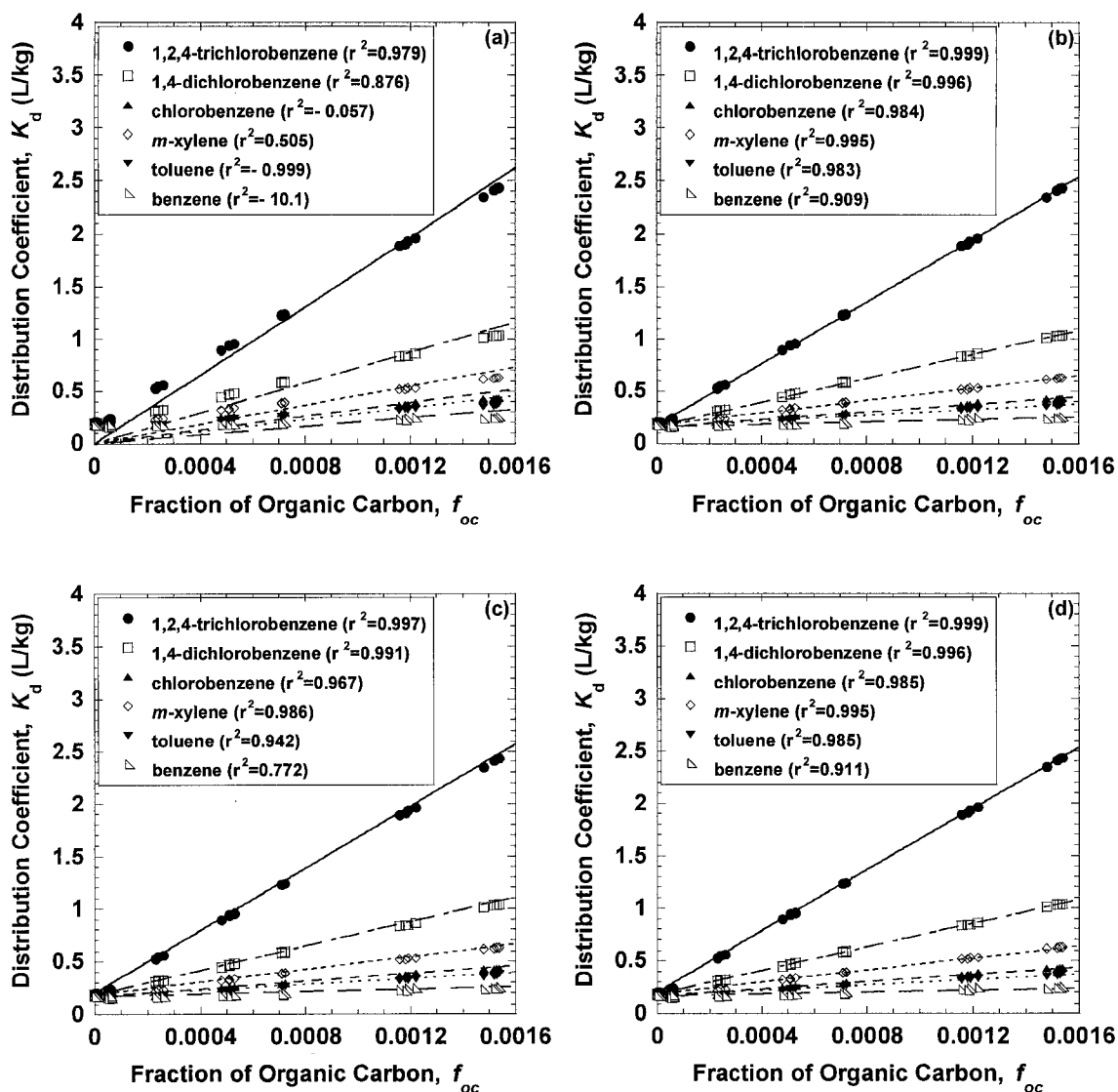


Fig. 2.27 Comparison of measured versus predicted distribution coefficients based on four sorption models: (a) $K_d = f_{oc}K_{oc}$ (Eq. 2.8); (b) $K_d = f_{oc}K_{oc}^* + K_{min}^*$ (Eq. 2.9); (c) two-component model without blocking effect (Eq. 2.15 with $\beta_{min} = 1$); and (d) two-component model with blocking effect (Eq. 2.15 with $\beta_{min} \leq 1$).

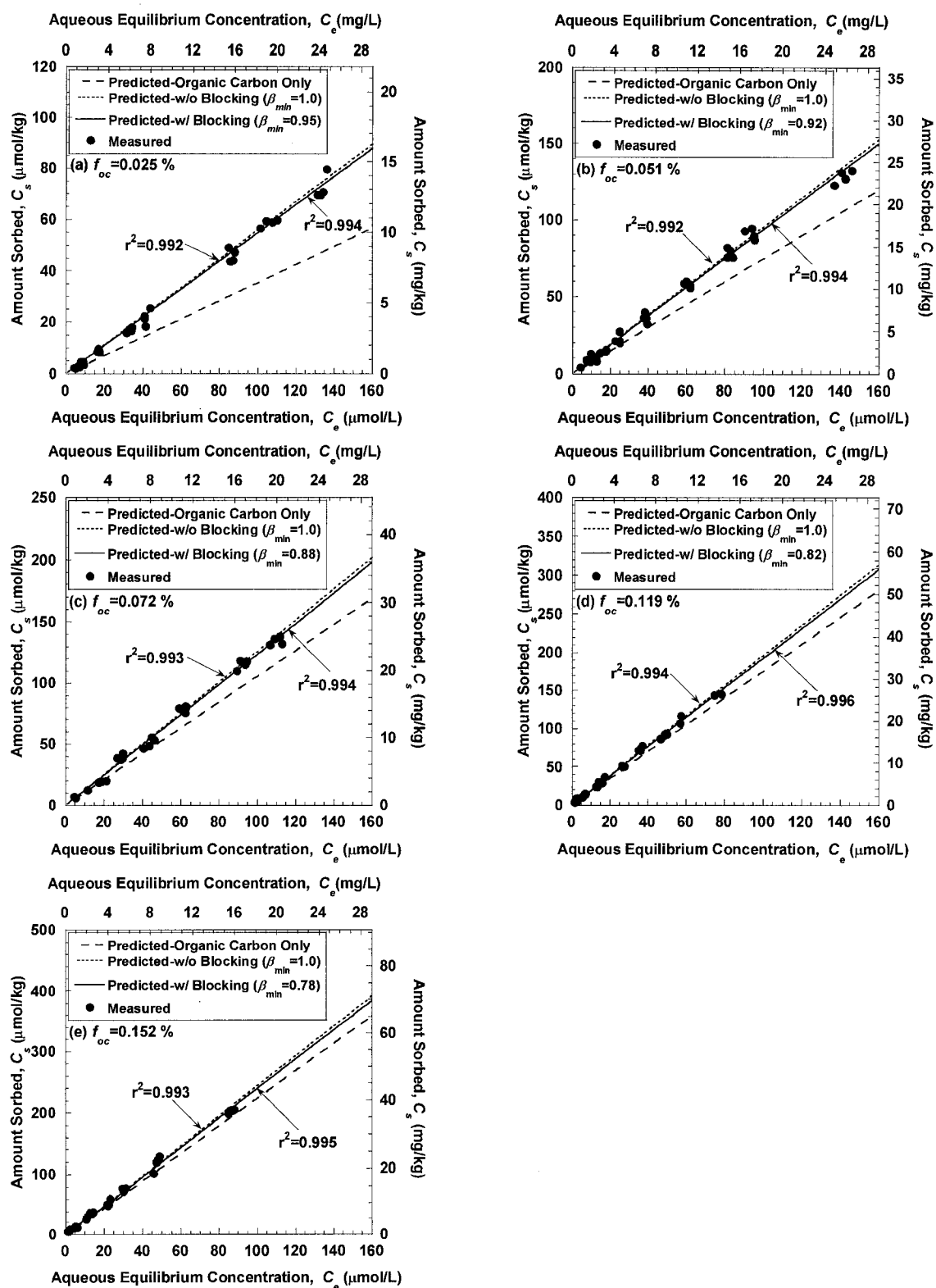


Fig. 2.28 The prediction of 1,2,4-trichlorobenzene sorption to HA-coated sand by incorporating the available fraction of the mineral component using blocking parameters.

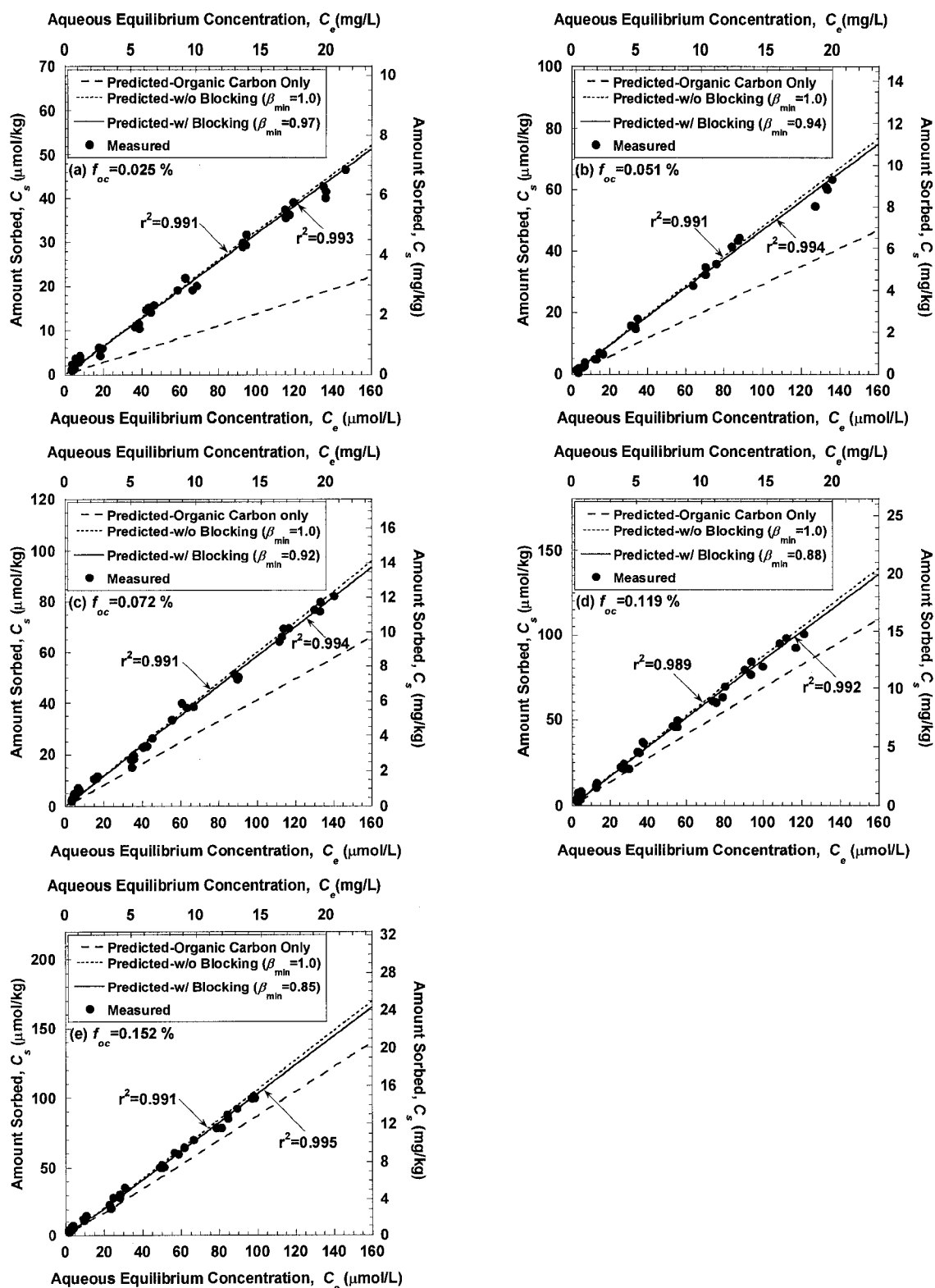


Fig. 2.29 The prediction of 1,4-dichlorobenzene sorption to HA-coated sand by incorporating the available fraction of the mineral component using blocking parameters.

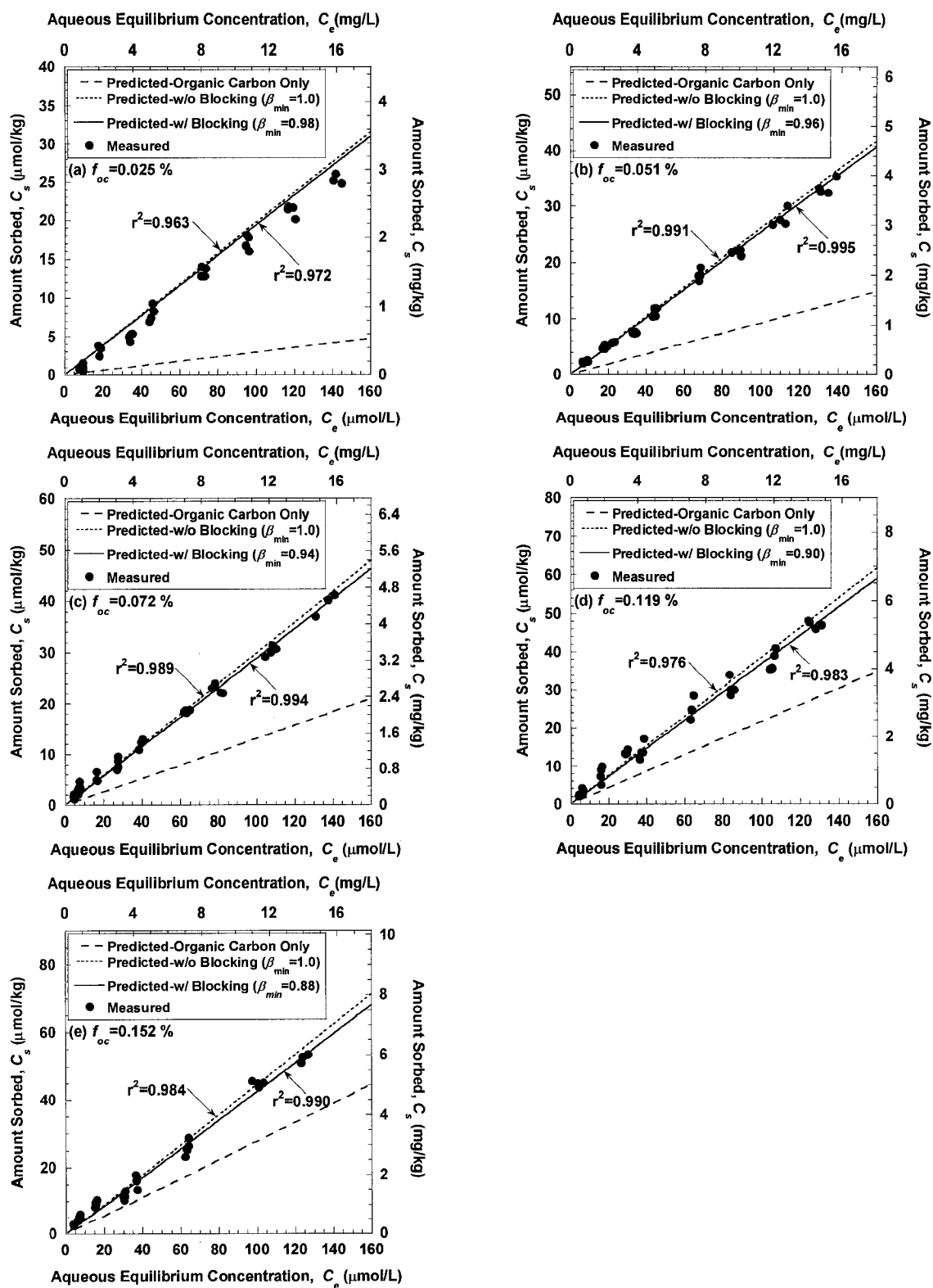


Fig. 2.30 The prediction of chlorobenzene sorption to HA-coated sand by incorporating the available fraction of the mineral component using blocking parameters.

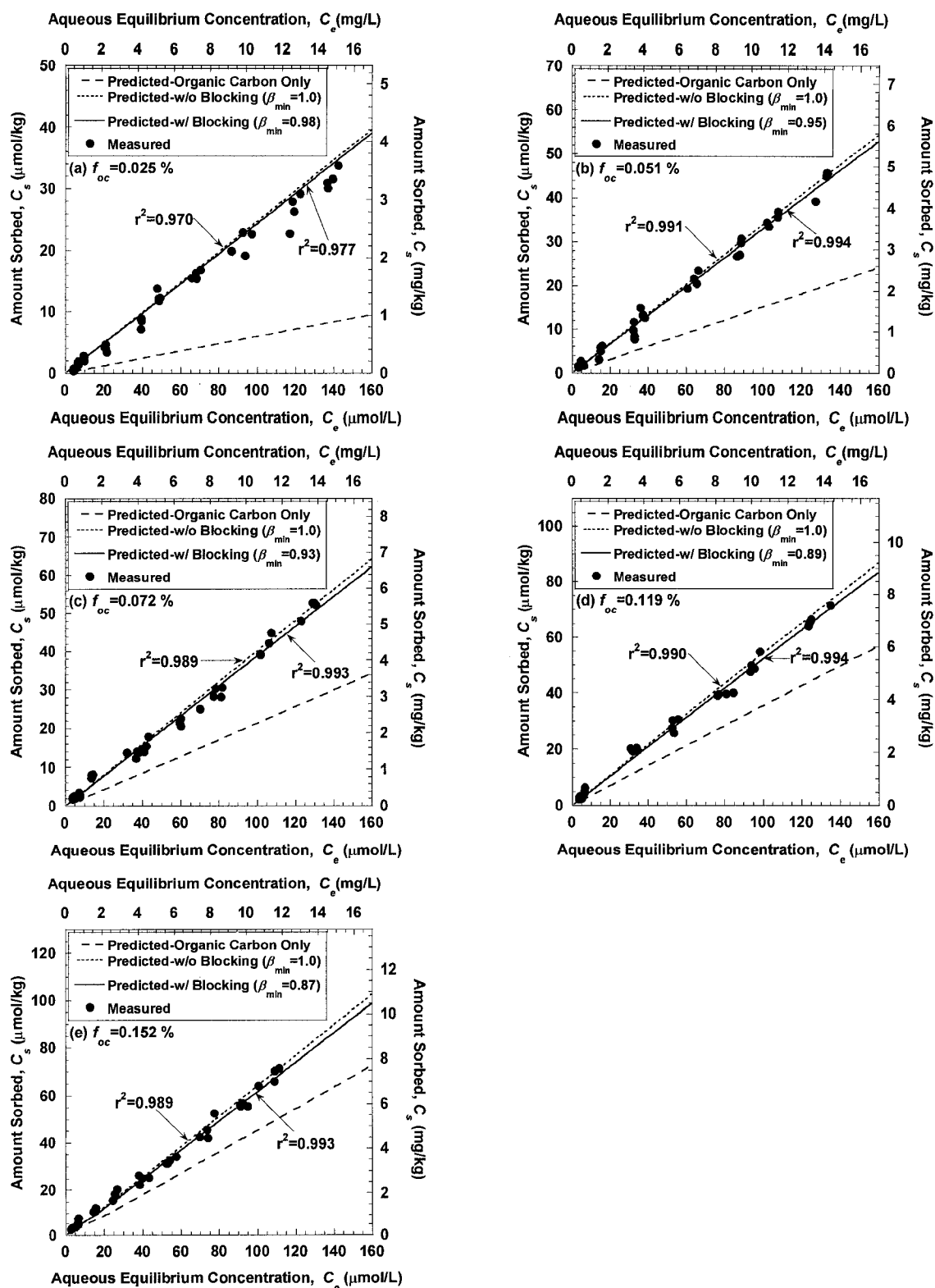


Fig. 2.31 The prediction of *m*-xylene sorption to HA-coated sand by incorporating the available fraction of the mineral component using blocking parameters.

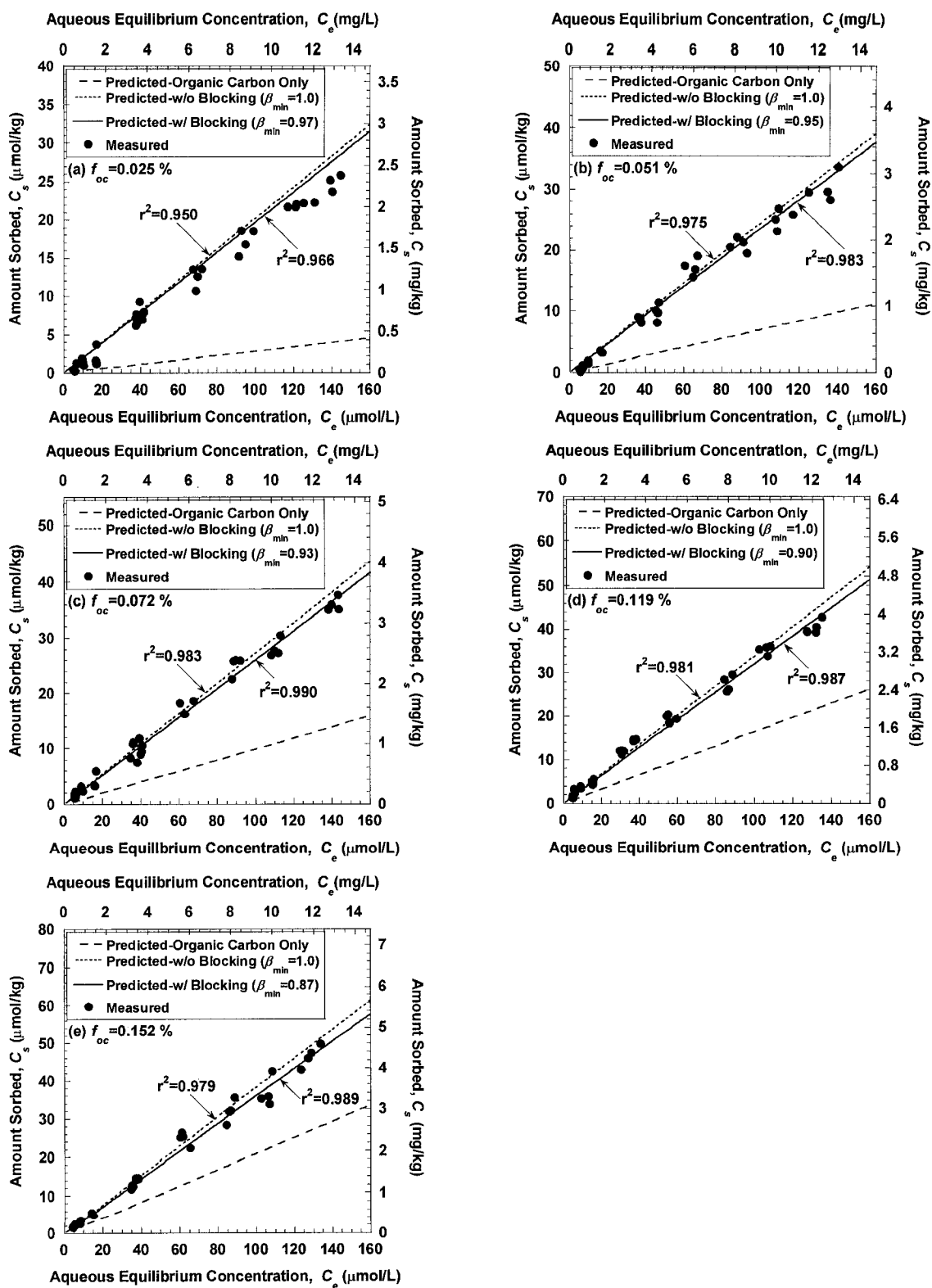


Fig. 2.32 The prediction of toluene sorption to HA-coated sand by incorporating the available fraction of the mineral component using blocking parameters.

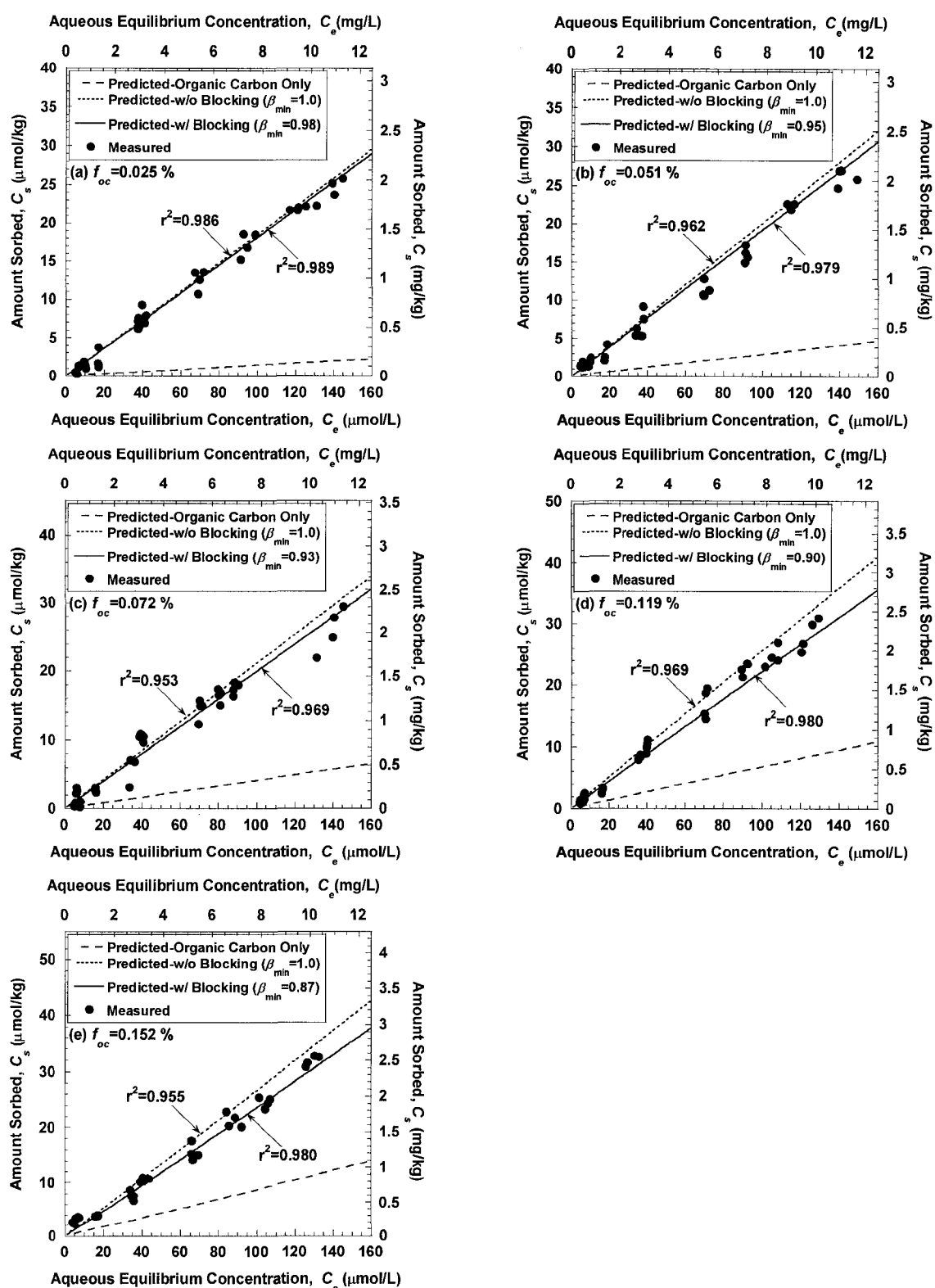


Fig. 2.33 The prediction of benzene sorption to HA-coated sand by incorporating the available fraction of the mineral component using blocking parameters.

CHAPTER 3

ASSOCIATION OF HUMIC ACID WITH METAL (HYDR)OXIDE-COATED SANDS AT SOLID-WATER INTERFACES

Abstract: Mineral-bound humic acid (HA) can significantly modify the physicochemical properties of the mineral surfaces and vice versa, thereby influencing the fate and transport of organic compounds in the subsurface. The effect of various mineral surfaces on the adsorption-desorption of dissolved bulk, terrestrial HA was evaluated using three model sorbents [uncoated, FeO(OH)-coated, and Al₂O₃-coated sands] at two equilibrium pH values. The results of SEM/EDS and XPS analyses revealed relatively uniform and stable metal (hydr)oxide coatings on quartz surface and the presence of the HA coating. Strong hysteresis effects were observed for both metal (hydr)oxide-coated sands whereas a weaker hysteresis effect was observed for uncoated sand, suggesting that the adsorption-desorption of HA to model sorbents is dependent on the affinity of chemical interactions between the HA and surface composition of model sorbents. Adsorption of HA molecules onto metal (hydr)oxide-coated sands can be attributed to ligand exchange for lower molecular weight (MW) HA fractions and hydrophobic interaction for higher MW HA fractions, illustrating that both kinetic and fractional adsorption-desorption of HA subcomponents are important considerations.

Key Words: adsorption, desorption, hysteresis, metal (hydr)oxide-coated sands, molecular weight fraction, terrestrial humic acid

3.1 INTRODUCTION

The sorption of organic compounds to surface soils, sediments, and aquifer solids is characterized to a great extent by the properties of the soil organic matter (SOM) and mineral compositions of these solids (Chiou et al. 1979, Hassett et al. 1981, McCarty et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Curtis et al. 1986, Murphy et al. 1990, 1992, 1994, Ball and Roberts 1991, Paya-Perez et al. 1991, Barber et al. 1992, Rebhun et al. 1992, Weber et al. 1992, Huang et al. 1996, Weber and Huang 1996, Xing et al. 1996, Luthy et al. 1997, Mader et al. 1997, Onken and Traina 1997, Chiou and Kile 1998, Laor et al. 1998, Xia and Ball 1999, Shen and Jaffé 2000, Allen-King et al. 2002, Hur and Schlautman 2004, Xiao et al. 2004, Nguyen et al. 2005, Wang and Xing 2005, Feng et al. 2006, Pignatello et al. 2006). Although the SOM fraction has been regarded as the dominant sorbent for sorption of nonpolar neutral organic compounds (NNOCs), mineral surfaces also contribute significantly to, and may even control, the overall sorption of NNOCs by sorbents having low fractions of organic carbon, or f_{oc} (McCarty et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Curtis et al. 1986, Murphy et al. 1990, Ball and Roberts 1991, Paya-Perez et al. 1991, Onken and Traina 1997, Shen and Jaffé 2000), low moisture content (Goss and Eisenreich 1996, Goss and Schwarzenbach 2002), or relatively high clay contents (Hassett et al. 1981, Karickhoff 1984, Rebhun et al. 1992, Shen and Jaffé 2000).

In general, soil organic matter (SOM) is a complex mixture of diverse polyfunctional organic molecules from heterogeneous materials (e.g., plant parts, microorganisms, and any specifically identifiable biochemicals such as polysaccharides, proteins, and lignins) linked by hydrogen bonds and hydrophobic interactions (Stevenson

1994, Piccolo 2001, Simpson et al. 2002, Sutton and Sposito 2005, Kelleher and Simpson 2006). Additionally, SOM can undergo a variety of physical and chemical changes when SOM is associated with mobile or immobile particles (Murphy et al. 1990, 1992, 1994, Jones and Tiller 1999, Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2003, 2004, Wang and Xing 2005, Feng et al. 2006). Thus, the extent of surface coating of aquifer solids with SOM in ground water varies extensively, depending on the mineralogy of the solid particles, the chemistry of the pore water, and the nature and fractionation of the SOM (Tipping 1981, Davis 1982, Murphy et al. 1990, 1992, 1994, Schlautman and Morgan 1993, Gu et al. 1994, 1995, 1996, Spark et al. 1997, Laor et al. 1998, Jones and Tiller 1999, Shen 1999, Namjesnik-Dejanovic et al. 2000, Shen and Jaffé 2000, Hur and Schlautman 2003, 2004, Wang and Xing 2005, Feng et al. 2006). This complex nature in organic coating over aquifer solids subsequently complicates the fate and transport of NNOCs in the subsurface (Murphy et al. 1990, 1992, 1994, Weber and Huang 1996, Luthy et al. 1997, Onken and Traina 1997, Laor et al. 1998, Jones and Tiller 1999, Shen and Jaffé 2000, Hur and Schlautman 2004, Wang and Xing 2005, Feng et al. 2006).

The subsurface mobility of dissolved organic matter (DOM), such as dissolved humic acid (HA) and fulvic acid (FA), can be influenced strongly by adsorption onto mineral surfaces due to a variety of mechanisms, including anion exchange, ligand exchange-surface complexation, hydrophobic interaction, entropic effects, hydrogen bonding, and cation bridging (Sposito 1989, Murphy et al. 1990, 1992, 1994, Schlautman and Morgan 1993, Gu et al. 1994, 1995, 1996, Spark et al. 1997, Laor et al. 1998, Jones and Tiller 1999, Shen 1999, Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2003, 2004, Wang and Xing 2005, Feng et al. 2006). The reactive properties of DOM can

significantly modify the physicochemical properties of the mineral surfaces by binding to mineral surfaces and vice versa. Thus, adsorption of DOM onto a variety of mineral surfaces has been studied as a function of pH, ionic strength, electrolyte concentration, types of humic substances, and types of mineral surfaces (Tipping 1981, Davis 1982, Murphy et al. 1990, 1992, 1994, Schlautman and Morgan 1993, Gu et al. 1994, 1995, 1996, Spark et al. 1997, Laor et al. 1998, Jones and Tiller 1999, Shen 1999, Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2003, 2004, Wang and Xing 2005, Feng et al. 2006).

For example, Tipping (1981) and Davis (1982) reported that positively-charged mineral surfaces (e.g., goethite, alumina) have strong adsorption affinities for naturally occurring DOM due to surface complexation with phenolic and carboxylic functional groups of the DOM. Murphy et al. (1990, 1992, 1994) suggested that the configuration of HA in solution influenced the structure of HA on the mineral surface since the adsorption of peat HA onto hematite and kaolinite varied with ionic strength and electrolyte cation. Schlautman and Morgan (1993) postulated that the effect of solution chemistry is to alter the mechanisms by which the humic substances adsorb to (hydr)oxide surfaces, and the different adsorption mechanisms, in turn, affect how tightly bound the humic substance is held at the surface. Gu et al. (1994, 1994, 1996) reported that ligand exchange between carboxyl/hydroxyl functional groups of DOM and iron oxide was the dominant interaction mechanism, especially under acidic or slightly acidic pH conditions. Spark et al. (1997) reported that positively charged mineral surfaces such as aluminum and iron oxides strongly adsorb DOM, whereas negatively charged mineral surfaces such as silica and kaolinite weakly adsorb DOM. Laor et al. (1998) postulated that adsorption of HA

onto iron oxide is dominated by the ligand exchange mechanism whereas adsorption of HA onto montmorillonite is dominated by the cation-bridge mechanism. Jones and Tiller (1999) suggested that the configuration of the adsorbed humic substance on mineral surface depends on the surface density and distribution of the reactive sites, and the degree of ionization of carboxylic and phenolic groups of the humic substance. Shen (1999) reported that the existence of a correlation between the elemental ratio of (Al+Fe):Si of soil colloid and the HA adsorption capacity, where the soil colloids with larger values of the (Al+Fe):Si ratio can adsorb HA more efficiently. Namjesnik-Dejanovic et al. (2000) postulated that the molecular weight (MW) of humic substance is a key factor controlling organic pollutant partitioning, and suggested smaller molecules were adsorbed first and were replaced by larger molecules whose adsorption was thermodynamically favored based on kinetic experiments. Hur and Schlautman (2003, 2004) suggested that preferential adsorption of smaller size fractions of HA may be associated more with ligand exchange and electrostatic attraction, whereas preferential adsorption of larger size fractions may be more dependent on hydrophobic interactions. Wang and Xing (2005) observed that the aliphatic fractions were preferentially adsorbed by clay minerals, and provided the direct evidence for HA fractionation during adsorption onto clay minerals by using solid- and liquid-state ^{13}C nuclear magnetic resonance (NMR). Finally, Feng et al. (2006) reported that preferential adsorption of polymethylene groups on kaolinite and aromatic moieties on montmorillonite was observed by using ^1H high resolution magic angle spinning NMR.

In view of the inherent complexity of DOM-mineral systems, a fundamental evaluation of the relative contributions of the organic and mineral fractions to the overall

sorption of NNOCs cannot be obtained using natural aquifer solids. However, an evaluation of the relative contributions of the organic and mineral fractions to the overall sorption of NNOCs may be discerned through manipulating the type and composition of the sorbents and the chemistry of the solution.

In this chapter, the preparation procedure and characterization of model sorbents are presented by employing a scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectrometer (EDS) and a X-ray photoelectron spectroscopy (XPS) to quantify the microchemical surface compositions of model sorbents. In addition, the preferential binding of certain fractions from a mixture of HA molecules during adsorption onto the mineral surfaces is evaluated by employing a Ultraviolet (UV)-Visible spectroscopy. An assessment of the contributions of mineral-bound HA and mineral surfaces to the overall sorption of individual NNOCs, and an evaluation of the predictive capabilities of four different sorption models are contained in the subsequent chapter. The specific objectives of this study are to (1) investigate the kinetics of HA adsorption at solid-water interfaces, (2) investigate the adsorption and desorption of HA to different model sorbents, (3) evaluate the molecular weight fractionation of HA during adsorption onto the mineral surfaces, and (4) characterize the model sorbents by using SEM-EDS and XPS.

3.2 MATERIALS AND METHODS

3.2.1 Humic Acid (HA)

In ground water, the three primary natural sources of SOM derived from heterogeneous materials include: (i) deposits of organic matter such as buried peat,

kerogen, and coal; (ii) humic substances in soils and sediments; and (iii) DOM emanating from the overlying soil and vadose zone (Aiken 2002). Although the relative contributions of these sources of SOM vary between different water bodies, quantification of this variation based on chemical characterization of SOM is currently not possible (Aiken 2002). Thus, in this study, DOM emanating from the overlying soil and vadose zone is proposed as the source of SOM in ground water. Additionally, HA generally has higher molecular weight (MW), greater phenolic and aromatic carbon contents, and lower oxygen/carbon (O/C) ratios than FA (Stevenson 1994, Swift 1996, Allen-King et al. 2002). As a result, HA is more likely to bind to hydroxylated sites on mineral surfaces, and strongly adsorbed onto aquifer solids than FA, which is enriched within the DOM of ground water (Thurman et al. 1985).

As a result, the terrestrial HA used in this study was extracted from a commercial peat soil (Ultimate potting mix in ferti-loam[®], Voluntary Purchasing Groups, Inc., Bonham, TX) using the method recommended by International Humic Substances Society (Swift 1996), and the detailed extraction procedures were previously described in Chapter 2 (Section 2.2.1). In order to investigate the MW fractionation from a mixture of HA molecules during the adsorption onto the mineral surfaces, the HA precipitate was rinsed with nanopure water (Barnstead/Thermolyne, Dubuque, IA) in a dialysis tube with a nominal MW cutoff of 3,500 Daltons (Fisherbrand[®] dialysis tubing, Fisher Scientific Co., Pittsburgh, PA). The ratio of absorbance at 465 and 665 nm (E_4/E_6) and the elemental compositions of HA extracted from the commercial peat soil are given in Table 3.1.

3.2.2 Model Sorbents

In this study, a quartz sand coated with iron or aluminum (hydr)oxide and HA (e.g., see Fig. 3.1) was used as the principle media representing aquifer solids, since quartz sands coated with iron or aluminum (hydr)oxides are known to be prominent sources of aquifer solids (Ball et al. 1990, MacIntyre et al. 1991). Additionally, iron or aluminum (hydr)oxides appear to cement various other fines such as the aluminosilicate clays and SOM together as coatings on larger sand grains (Ryan and Gschwend 1992).

For the purpose of developing relatively uniform metal (hydr)oxide-coated quartz sands, Ottawa sand (F-95, U.S. Silica, Berkeley Springs, WV) was used as the reference quartz sand prior to any surface modification or treatment, because Ottawa sand is essentially absent of any impurities, such as metal (hydr)oxides and SOM (see Table 2.2). As shown in Fig. 3.1, Ottawa sand was modified first by precipitating metal (hydr)oxides over the surfaces of sand using *in situ* precipitation of metal (hydr)oxides (Ahammed and Chaudhuri 1996, Lukasik et al. 1996, 1999, Scott et al. 2002), since this approach has been shown to provide a relatively uniform and stable metal (hydr)oxide coating (Ahammed and Chaudhuri 1996, Lukasik et al. 1999). After *in situ* metal (hydr)oxide precipitation, the extracted HA was adsorbed onto the metal (hydr)oxide-coated sand at desired ionic compositions and pHs to provide relatively uniform metal (hydr)oxide- and HA-coated aquifer sands.

Overall, four different types of model sorbents were used in this study, viz., (1) FeO(OH)-coated sand (FES), (2) FeO(OH)- and HA-coated sand with different f_{oc} (FEHAS), (3) Al₂O₃-coated sand (ALS), and (4) Al₂O₃- and HA-coated sand with different f_{oc} (ALHAS). Ottawa sand was sieved (-60/+80 mesh sizes) by using the

standard dry sieve technique (ASTM D 421), washed with nanopure water (Barnstead/Thermolyne, Dubuque, IA), and air-dried. The sand then was coated with metal (hydr)oxide using the procedure developed by Lukasik et al. (1996, 1999) and Scott et al. (2002). In this procedure, 4 kg of sand were soaked in 2 L of 1.0 M ferric chloride, FeCl_3 (Acros, Morris Plains, NJ) at pH = 0.62, or aluminum chloride, AlCl_3 (Acros, Morris Plains, NJ) at pH = 2.0, to cover the sand completely. After 2 h, the solution was poured off and the sand was heated at 60 °C until dry. The sand was hand mixed occasionally using a stainless-steel scoop to break up any clumps and to facilitate drying. Then, the dried sand was soaked again in 2 L of 3.0 M ammonium hydroxide, NH_4OH (Mallinckrodt Laboratory Chemicals, Phillipsburg, NJ) at pH = 12.2. After 1 h, the solution was poured off and the sand was heated at 60 °C with occasional hand mixing until dry. Finally, the metal (hydr)oxide-coated sand was sieved (-60/+80 mesh sizes), rinsed vigorously with nanopure water by a reciprocating shaker (Rotomix, Thermolyne, Dubuque, IA) until the supernatant was clear, centrifuged at 760 g for 20 min (MARATHON 21000R, Fisher Scientific Co., Pittsburgh, PA), and dried again with occasional hand mixing.

The adsorption of soluble ferric or aluminum chloride onto sands, followed by drying of the sands and precipitation of the metals as (hydr)oxides, results in the formation of uniform and stable coatings of metal (hydr)oxide over the surfaces of quartz sands (Lukasik et al. 1996, 1999, Scott et al. 2002). Additionally, no iron or aluminum was detected in the residual solution resulting after rinsing the metal (hydr)oxide-coated sand several times with nanopure water vigorously.

3.2.3 Adsorption and Desorption of HA onto Model Sorbents

A preliminary phase was undertaken to understand the adsorption and desorption of HA to FES or ALS resulting from batch equilibrium sorption tests (BESTs). Selected glassware was cleaned with concentrated H_2SO_4 and HNO_3 , rinsed with nanopure water several times, and dried at 200 °C to remove any background DOM. Stock solutions of HA were prepared by dissolving 200 mg of extracted HA into 1.0 L of 0.01 M NaOH (pH = 11.0) containing 0.01 M NaCl at 20 °C until HA was completely dissolved. The HA stock solutions then were diluted using 0.01 M NaCl (pH = 6.78) resulting in HA concentrations of 10, 20, 30, 40, 50, 60, 80, 100, 120, and 150 mg/L. The resulting absorbance of these solutions was measured at 254 and 400 nm using a spectrophotometer (DU[®] 640, Beckman Instruments, Inc., Fullerton, CA) and plotted versus the HA concentration or dissolved organic carbon (DOC) concentration to provide external calibration curves for each sorbent. However, a poor linear relationship ($r^2 = 0.866$) between UV-Visible absorbance at 254 nm and DOC concentration after adsorption were obtained due to the preferential adsorption of UV-absorbing organic molecules by mineral surfaces. Thus, the DOC concentrations were determined based on a linear relationship ($r^2 = 0.987$) between UV-Visible absorbance at 400 nm and DOC concentration after adsorption. The pH of each sample was adjusted by adding 1.0 M HCl (pH = 1.03) or 0.1 M NaOH (pH = 11.0) containing 0.01 M NaCl to achieve the desired pHs (i.e., 4.0 ± 0.2 or 6.5 ± 0.2) and ionic strength ($I = 0.01$ M NaCl) at equilibrium.

The adsorption kinetics of HA at an initial concentration of 40 mg/L onto different model sorbents was conducted at a constant solid-to-liquid ratio (S:L) of 1:4 (w/w) for 72 h at 20 °C. Based on the preliminary kinetic results shown in Fig. 3.2, HA

adsorption onto sorbents evaluated in this study was fast and equilibrated within 4 h. Thus, the sorbents and HA solutions were placed in 41-mL glass centrifuge tubes (Kimble Glass Inc., Vineland, NJ) at the same S:L of 1:4 (w/w), and the centrifuge tubes were tumbled at 10 rpm for 48 h at 20 °C. After tumbling, aliquots of the solutions from the blank test (i.e., without sorbent) and the tests with sorbents [i.e., uncoated sand, FeO(OH)-coated sand (FES), or Al₂O₃-coated sand (ALS)] were centrifuged at 8,000 rpm (11,150 g) for 20 min, and the resulting concentrations of HA were measured using the spectrophotometer at 254 and 400 nm to determine the amount of HA adsorbed for a given equilibrium concentration of HA.

Desorption also was evaluated after completion of the adsorption experiments. Supernatant (37.5 mL) was pipetted and replaced with the same volume (i.e., 37.5 mL) of HA-free 0.01 M NaCl stock solution (pH = 4.0 ± 0.2 or 6.5 ± 0.2). The centrifuge tubes were tumbled at 10 rpm for 48 h at 20 °C. Finally, aliquots of the solutions resulting after tumbling were centrifuged at 11,150 g for 20 min, and the HA concentration was measured at 254 and 400 nm with a spectrophotometer.

After completion of the preliminary phase of the study to evaluate the adsorption and desorption of HA to FES or ALS based on the BESTs, model sorbents were prepared by equilibrating 1800 mL of 0.01 M NaOH (pH = 11.0) containing 0.01 M NaCl and different concentrations of HA with 450 g of either FES or ALS in a 2-L oscillated glass flask for 24 h at 20 °C. The pH was maintained at 4.0 ± 0.2, and HA concentration was measured with time using the spectrophotometer at 254 and 400 nm. After completion of this step, the HA-adsorbed sorbents were rinsed with HA-free 0.01 M NaCl (pH = 6.78) until HA was no longer detected in the effluent based on the absorbance at 254 and 400

nm with a spectrophotometer. Finally, the HA-adsorbed sorbents were dried at room temperature and kept in 0.1-mm-thick low-density polyethylene bags (Dyer Packing, Inc., Willowbrook, IL) for storage until use as sorbents in the BESTs with NNOCs.

3.2.4 Fractionation of HA by Adsorption onto Model Sorbents

The extracted terrestrial HA fraction derived from the commercial peat soil used in this study is a mixture of diverse organic molecules with a wide range of MW linked by hydrogen bonds and hydrophobic interactions (Piccolo 2001, Simpson et al. 2002, Sutton and Sposito 2005, Kelleher and Simpson 2006). If significant preferential binding of certain fractions from a mixture of HA molecules occurs during adsorption onto the mineral surfaces, interpretation of an "average" adsorption behavior using the "average" HA molecules is not valid (Murphy et al. 1990, Van de Weerd et al. 1999). Instead, kinetic adsorption/desorption and the competition between the different HA fractions must be considered (Van de Weerd et al. 1999).

Although NMR spectroscopy has been applied recently to determine the chemical nature of unbound HA fractions in solution and structures of HA adsorbed at the mineral surfaces (Wang and Xing 2005, Feng et al. 2006), NMR spectroscopy could not be applied in this study because the f_{oc} values of HA-mineral complexes were too low ($f_{oc} \leq 0.016\%$). As an alternative, the ratio of absorbance at 465 and 665 nm (E_4/E_6) based on UV-Visible spectroscopy was used to provide indirectly an indication of the fractionation of HA during adsorption onto mineral surfaces (Gu et al. 1996, Wang and Xing 2005). The E_4/E_6 ratio has been correlated with the MW of HA and the contents of O, C, COOH and total acidity in the HA, and has been shown to be independent of HA concentration

(Chen et al. 1977, Stevenson 1994). Since the E_4/E_6 ratio decreases with increasing MW and increases with decreasing MW (Chen et al. 1977, Stevenson 1994), changes in E_4/E_6 ratios relative to original value of HA remaining in the solution indicate preferential adsorption of different fractions of HA molecules.

Thus, based on the E_4/E_6 ratios, the fractionation kinetics of HA at an initial concentration of 40 mg/L onto different model sorbents was investigated at a constant S:L of 1:4 (w/w) for 72 h at 20 °C. The supernatant was sampled with time, and the pH of the solution was adjusted to 8.0 ± 0.2 by adding 0.1 M NaOH (pH = 11.0) containing 0.01 M NaCl at each sampling interval. Then, the E_4/E_6 ratios for HA remaining in the solution were measured with the spectrophotometer.

Also, an experiment involving sequential adsorption of HA at an initial concentration of 200 mg/L onto HA-free model sorbents was conducted at a constant S:L of 1:4 (w/w). In this experiment, HA-free model sorbents and HA solutions were placed in 250-mL centrifuge tubes (Fisher Scientific Co., Pittsburgh, PA), and the centrifuge tubes were tumbled at 10 rpm for 48 h at 20 °C. After tumbling, HA-coated model sorbents were separated from solution by centrifuging at 1,500 g for 20 min, and supernatants were collected. Then, the collected supernatants were placed again in centrifuge tubes with the HA-free model sorbent at approximately the same S:L of 1:4 (w/w) to conduct the sequential adsorption of HA onto HA-free model sorbents. After each sequential adsorption of HA onto HA-free model sorbents, the supernatants were sampled, and the E_4/E_6 ratios for HA remaining in the solution were measured in the same manner as described above. Any changes in the measured values of E_4/E_6 were

considered to be indicative of preferential adsorption of different fractions from HA mixtures occurring during the adsorption process.

3.2.5 Characterization of Model Sorbents

In this study, both the metal (hydr)oxide-coated quartz and the highly amorphous SOM were considered to play important roles in the sorption of NNOCs to metal (hydr)oxide- and HA-coated sand. As indicated by Fig. 3.1, quartz was first modified by precipitating metal (hydr)oxides over the surfaces of sand. Second, the adsorption and desorption of HA to the metal (hydr)oxide-coated sand were performed at desired ionic composition and pHs to produce relatively uniform metal (hydr)oxide- and HA-coated aquifer sands.

The surface topography and mineralogy of the sorbents were characterized using a field emission scanning electron microscopy (JEOL JSM-6500F, JEOL USA Inc. Peabody, MA) integrated with an energy dispersive X-ray spectrometer (Nanotrace LN-Cooled Si(Li) Detector, Thermo Fisher Scientific, Inc., Waltham, MA), SEM/EDS. The specimens were coated with 10-nm-thick layer of gold by a sputter coater, and were placed inside the vacuum chamber of the microscope. The appropriate observation mode, accelerating voltage, probe current, and working distance were adjusted for best results, and two different magnifications (i.e., x400 and x7000) of SEM images for each sorbent were obtained. X-ray microanalysis in SEM/EDS was performed by measuring the energy and intensity distribution of X-ray signals generated by a focused electron beam on the specimen.

Although the SEM/EDS can provide rapid, qualitative, or semi-quantitative

analysis of elemental composition of bulk cross-sectioned specimens, the elemental distributions and chemical states in thin surface coatings on bulk specimens cannot be discerned in terms of various coatings over the quartz (Smith 2002). Thus, as an alternative technique, X-ray photoelectron spectroscopy, XPS (PHI 5800, Physical Electronics, Inc., Chanhassen, MN), was applied to determine the concentrations and chemical states of the elements in thin surface coatings. The XPS experimental procedure commenced with the acquisition of a survey spectrum to identify the elements present in the specimen. After acquiring the survey spectrum, a series of high-resolution spectra were acquired, providing quantitative information about the thin surface coatings. In this study, the X-ray source is a monochromated Al K α ($h\nu = 1486.6$ eV), and XPS experiments were performed at a take-off angle of 25° to increase the further surface sensitivity.

3.3 RESULTS AND DISCUSSION

3.3.1 Kinetics of HA Adsorption at Solid-Water Interfaces

Although adsorption kinetics of HA onto aquifer solids is a complex process depending on the nature of the surface (e.g., hydrophilic versus hydrophobic) and the solution conditions (e.g., pH, ionic strength, and concentration of competing ions), several studies (e.g., Gu et al. 1994, 1995, Avena and Koopal 1998, 1999) have reported that the initial processes of adsorption occur quickly (i.e., within minutes). However, much slower adsorption processes follow this quick adsorption processes due to the presence of electrostatic repulsion or the rearrangements in the adsorbed HA layer either by conformation changes or by exchange of previously adsorbed HA molecules with the

newly adsorbing ones (Avena and Koopal 1999, Van de Weerd et al. 1999, Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2003). Thus, overall sorption kinetics can require several hours (i.e., 6-24 h) to complete (Murphy et al. 1990, 1992, 1994, Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2003), and variations in the adsorption rate depending on the nature of the surface and the solution conditions indicate the dynamics and flexibility of HA molecules (Avena and Koopal 1999).

As shown in Fig. 3.2, the overall adsorption rates of HA onto FES, ALS and uncoated sand at two different equilibrium pHs (i.e., 4.0 ± 0.2 or 6.5 ± 0.2) and a single ionic strength (i.e., 0.01 M NaCl) apparently equilibrated around 4 h at 40-mg/L initial HA concentration, which is relatively slow compared to results from other studies (Gu et al. 1994, 1995, Avena and Koopal 1998, 1999). Additionally, the effect of solution pH (i.e., 4.0 ± 0.2 or 6.5 ± 0.2) on the adsorption rates of HA onto FES and ALS appears to be negligible. Similar to the findings of other studies (Spark et al. 1997, Shen 1999), the adsorption of the HA onto uncoated sand at $\text{pH} = 6.5 \pm 0.2$ was barely measurable such that the adsorption kinetics could not be discerned.

The specific interactions between the carboxylic and phenolic functional groups in the HA molecules and the surface hydroxyl groups of metal (hydr)oxides were found to be a quick (Gu et al. 1994, 1995, Avena and Koopal 1998, 1999). Additionally, electrostatic repulsion is expected to be absent for FES and ALS within the pH ranges investigated due to the typically high zero points of charge, pH_{zpc} (i.e., $7.5 \leq \text{pH}_{\text{zpc}} \leq 9.0$) reported for these metal (hydr)oxides (Ahammed and Chaudhuri 1996, Lukasik et al. 1996). Electrostatic repulsion is also expected to be negligible for the uncoated sand due to medium electrolyte concentration (i.e., 0.01 M NaCl). Thus, the relatively slow

adsorption rates in this study are hypothesized to be attributed to the rearrangement in the adsorbed HA layer either by conformation changes or by exchange of previously adsorbed HA molecules with the newly adsorbing ones. This hypothesis was tested by the fractionation kinetics of HA at initial concentration of 40 mg/L to model sorbents at a constant S:L of 1:4 (w/w) for 72 h at 20 °C.

As shown in Fig. 3.3, the changes in E_4/E_6 ratios for HA remaining in the solution during the adsorption kinetics of HA onto three model sorbents were measured at each sampling event with time. For FES and ALS, the E_4/E_6 ratios decreased sharply within 15 min, gradually increased with time, and apparently achieved steady state around 4 h. This trend in the values of E_4/E_6 with time supports the hypothesis that two phases of adsorption kinetics occurs. That is, the sharp decrease of E_4/E_6 ratios within 15 min suggests fast initial adsorption of lower MW fractions, whereas the gradual increase of E_4/E_6 ratios to 4 h suggests a relatively slow exchange between the adsorbed lower MW fractions and the higher MW fractions of the HA in solution. These results are consistent with those of other studies that indicate a fast initial adsorption of lower MW fractions of HA with more acidic functional groups due to ligand exchange resulting in a modification of the surfaces that subsequently favors hydrophobic interactions and slower replacement with the more hydrophobic, higher MW fractions of the HA (Avena and Koopal 1999, Van de Weerd et al. 1999, Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2003).

However, based on the lower values of E_4/E_6 ratios at steady state relative to those before adsorption, the adsorption of lower MW fractions appears to exceed that of the higher MW fractions. Since the strong binding of lower MW fractions through ligand

exchange between carboxyl/hydroxyl functional groups of HA and metal (hydr)oxides may not be readily replaced with higher MW fractions from solution (Hur and Schlautman 2003, 2004), lower MW fractions were preferentially adsorbed onto metal (hydr)oxides, leaving the higher MW fractions in solution. Additionally, since the relative affinities of lower MW fractions and the extent of exchange of adsorbed lower MW fractions with higher MW fractions may be different between FES and ALS (Namjesnik-Dejanovic et al. 2000), the trend of changes in the E_4/E_6 ratios with time between FES and ALS is different. For uncoated sand, due to negligible formation of complexes between uncoated sand and the functional groups of HA, the substantial changes in E_4/E_6 ratios for HA remaining in the solution during the adsorption kinetics of HA onto uncoated sand were not observed. Thus, the fractionation kinetics of HA onto uncoated sand could not be discerned.

3.3.2 Adsorption and Desorption of HA to Model Sorbents

3.3.2.1 Adsorption and desorption of HA to model sorbents at $\text{pH} = 4.0 \pm 0.2$

The results for adsorption of HA onto FES, ALS, and uncoated sand at $\text{pH} = 4.0 \pm 0.2$ after 48 h are shown in Fig. 3.4. High-affinity adsorption of HA is evident for both metal (hydr)oxide-coated sands at lower equilibrium concentrations, and adsorption maxima are achieved at elevated equilibrium HA concentrations, a behavior that is similar to that previously reported for DOM adsorbing onto (hydr)oxide surfaces (Tipping 1981, Murphy et al. 1990, 1992, 1994, Gu et al. 1994, 1995, 1996, Jones and Tillier 1999, Shen 1999, Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2003, 2004). However, the adsorption of HA onto positively charged metal (hydr)oxide-coated

sands at $\text{pH} = 4.0 \pm 0.2$ was more significant than that onto negatively charged uncoated sand at the same pH. This result is consistent with other studies reporting that the tendency of mineral surfaces to form complexes with acidic functional groups of HA is greater for more basic and proton-accepting iron and aluminum hydroxyls than for more acidic and proton-releasing silica hydroxyls (Spark et al. 1997, Shen 1999). Also, the adsorption of HA onto FES and ALS was statistically different within 95 % confidence intervals. This result may be attributed to the different total surface area (m^2/L) applied, different amounts of metal deposits, and different density and affinity of hydroxylated sites between FES and ALS.

As shown in Fig. 3.4, the Langmuir adsorption model was fitted to the measured data using the least-squares minimization method. The Langmuir model can be written as follows (Langmuir 1918):

$$C_{s,HA} = \frac{C_{s,\max} k C_{e,HA}}{1 + k C_{e,HA}} \quad (3.1)$$

where $C_{s,HA}$ is the amount of HA adsorbed onto sorbent (mg of HA/kg of soil solid), $C_{s,\max}$ is the maximum quantity of HA adsorbed onto sorbent (mg of HA/kg of soil solid), k is adsorption affinity constant (L/mg of HA), and $C_{e,HA}$ is the equilibrium concentration of HA in aqueous phase (mg of HA/L). The empirical Langmuir model has been shown to describe the adsorption of HA onto different mineral surfaces fairly well (Tipping 1981, Murphy et al. 1990, 1992, 1994, Gu et al. 1994, 1995, 1996, Jones and Tiller 1999, Shen 1999, Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2003, 2004), despite some indications that the composition and properties of heterogeneous HA

macromolecules change during adsorption onto mineral surface (Gu et al. 1996, Jones and Tiller 1999, Van de Weerd et al. 1999, Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2003, 2004, Wang and Xing 2005, Feng et al. 2006), and that energetic differences in the adsorption of heterogeneous HA molecules result in different combinations of adsorption mechanisms (Sposito 1989, Gu et al. 1994, Van de Weerd et al. 1999).

The adsorption of HA onto mineral surfaces has been shown to be irreversible due to slow desorption kinetics and multiple binding sites between HA and mineral surfaces (Gu et al. 1994, 1995, Avena and Koopal 1998). For example, Gu et al. (1994) derived a model describing non-equilibrium desorption of HA from mineral surfaces by incorporating a hysteresis coefficient (h) in the desorption term that represents the non-equilibrium desorption hysteresis as follows:

$$C_{s,HA} = \frac{C_{s,max} k C_{e,HA}}{(C_{e,HA} / C_{a,HA})^h + k C_{e,HA}} \quad (3.2)$$

where $C_{a,HA}$ is the equilibrium HA concentration in aqueous phase after adsorption but before starting the desorption tests (mg of HA/L). In Eq. 3.2, the HA concentrations should be $0 < C_{e,HA} \leq C_{a,HA}$ during the desorption tests, and a hysteresis coefficient should be $0 \leq h \leq 1$. When $h = 0$, Eq. 3.2 is reduced to Eq. 3.1, indicating a completely reversible adsorption-desorption process, whereas for $h = 1$, $C_{s,HA}$ becomes independent of $C_{e,HA}$ but dependent on $C_{a,HA}$, indicating a completely irreversible process (Gu et al. 1994).

The results of desorption studies for HA adsorbed onto FES, ALS, and uncoated sand after 72 h at relatively constant pH (i.e., 4.0 ± 0.2) and ionic strength (i.e., 0.01 M

NaCl) are shown in Fig. 3.5. The adsorption and desorption data were fitted by Eqs. 3.1 and 3.2, respectively, using the least-square minimization method. As shown in Fig. 3.5, a significant hysteresis effect occurs for both FES and ALS, indicating that adsorbed HA is not readily desorbed at a given pH and ionic composition due to high-affinity chemical interaction (i.e., ligand exchange) between HA and metal (hydr)oxide-coated sands (Tipping, 1981, Davis 1982, Murphy et al. 1990, 1992, 1994, Gu et al. 1994, 1995, Avena and Koopal 1998), as well as the possible formation of stable inner-sphere complexes between multiple carboxyl groups of HA and surface hydroxyl sites on the sorbents (Murphy et al. 1990, 1992, 1994, Schlautman and Morgan 1993, Spark et al. 1997). In contrast, a weak hysteresis effect is observed for uncoated sand, indicating that the functional groups of HA do not form stable complexes with silica hydroxyls of quartz, since negatively-charged silica hydroxyls dominantly adsorbed HA by the low-affinity chemical interactions (i.e., entropy-driven or hydrophobic interactions) (Spark et al. 1997).

The fitting parameters for adsorption and desorption at $\text{pH} = 4.0 \pm 0.2$, shown in Figs. 3.4 and 3.5, are summarized in Table 3.2. The maximum quantity of HA adsorbed onto a sorbent ($C_{s,max}$) is greater for ALS than for FES, whereas the adsorption affinity constant (k) for ALS is lower than that for FES, reflecting the differences in the distribution, density and intrinsic affinity for HA of hydroxylated sites between FES and ALS. Also, both $C_{s,max}$ and k for uncoated sand were one order of magnitude lower than those for both metal (hydr)oxide-coated sands. These results indicate that positively charged mineral surfaces such as iron or aluminum (hydr)oxides at $\text{pH} = 4.0 \pm 0.2$

strongly adsorb HA, whereas negatively charged mineral surfaces such as quartz weakly adsorb DOM.

Whereas the hysteresis coefficients (h) for FES range from 0.86 to 0.95, those for ALS range from 0.70 to 0.96, indicating that iron and aluminum hydroxyl groups have different site concentrations and different affinity interactions for HA. However, the values for h for both metal (hydr)oxide-coated sands decreased with increase in HA equilibrium concentration in the aqueous phase. This result suggests that high-affinity adsorption occurred initially at low equilibrium HA concentrations, whereas both high-affinity and low-affinity adsorption occurred as the HA concentration increased, i.e., since the relatively low-affinity adsorption fraction is expected to be readily desorbed. Considering that dominant desorption occurs from low-affinity adsorption fraction, the different h values between FES and ALS suggest that adsorption of heterogeneous HA molecules onto these sorbents results in different fractional combinations of adsorption mechanisms (i.e., ligand exchange + hydrophobic interaction).

The hysteresis coefficients (h) for uncoated sand range from 0.41 to 0.78 and are lower than those for FES and ALS, suggesting that silica hydroxyls have low site concentrations and low affinity interactions with HA. However, similar to FES and ALS, the values for h for uncoated sand decreased with increasing HA equilibrium concentration in the aqueous phase. This result also proves high-affinity adsorption occurring dominantly at low equilibrium HA concentrations, and both high-affinity and low-affinity adsorption occurring at high equilibrium HA concentrations. Gu et al. (1994) also reported that values for h derived from adsorption of DOM from a wetland pond onto iron oxide at pH = 4.1 ranged from 0.72 to 0.86. They postulated that the strong

hysteresis in DOM sorption with iron oxide was attributable to the slow desorption kinetics and multiple binding sites between DOM and iron oxide, and that chemisorption between the most active DOM and adsorption sites occurred first, followed by both chemical and physical adsorption onto sites of decreasing activity occurred as the concentration of HA increased.

3.3.2.2 Adsorption and desorption of HA to model sorbents at pH = 6.5 ± 0.2

The results for HA adsorption onto both FES and ALS at pH = 6.5 ± 0.2 after 48 h are shown in Fig. 3.6. Similar to the results for pH = 4.0 ± 0.2, the results for pH = 6.5 ± 0.2 indicate high-affinity adsorption at low equilibrium HA concentrations, and an adsorption maxima that is achieved rapidly as the equilibrium HA concentration increases. However, a significant decrease in the adsorption of HA at pH = 6.5 ± 0.2 compared at pH = 4.0 ± 0.2 was observed, indicating that adsorption of HA onto the metal (hydr)oxide-coated sands is strongly pH-dependent. The decrease in the adsorption of HA with increasing pH can be attributed to the decrease in adsorption sites due to pH-dependent protonation processes of metal (hydr)oxide surfaces (Murphy et al. 1990, 1992, 1994, Gu et al. 1994, 1995, Spark et al. 1997). Also, the adsorption of HA onto FES and ALS is clearly different due to the different total surface area (m²/L) applied, different amounts of metal deposits, and different density and affinity of hydroxylated sites between FES and ALS. Finally, adsorption of HA onto negatively charged uncoated sand was negligible, which is consistent with other studies reporting no proton consumption because of the interaction between the mineral and HA for negatively charged silica surfaces at pH = 6.5 ± 0.2 (Spark et al. 1997, Shen 1999).

As shown in Fig. 3.7, the desorption of HA adsorbed onto FES or ALS after 72 h also was investigated at relatively constant pH (i.e., 6.5 ± 0.2) and ionic strength (i.e., 0.01 M NaCl). A significant hysteresis effect also occurs for both FES and ALS, indicating that HA is not readily desorbed at a given pH and ionic composition due to the slow desorption kinetics and the existence of multiple binding sites between the HA and metal (hydr)oxide-coated sands (Gu et al. 1994, 1995). However, Avena and Koopal (1998) found that the desorption of HA from an iron oxide was fast and reversible when desorption is induced by changing the pH, not by dilution of HA concentration at a constant pH.

The fitting parameters for adsorption and desorption at $\text{pH} = 6.5 \pm 0.2$ as shown in Figs. 3.6 and 3.7 are summarized in Table 3.3. Compared to the results at $\text{pH} = 4.0 \pm 0.2$, the $C_{s,max}$ for HA at $\text{pH} = 6.5 \pm 0.2$ reached 35 % of $C_{s,max}$ for FES and 32 % of $C_{s,max}$ for ALS, suggesting that adsorption of HA onto metal (hydr)oxide is strongly pH-dependent. This decrease in the adsorption of HA onto (hydr)oxide with increasing pH was consistent with a ligand-exchange mechanism, as suggested by others (Murphy et al. 1990, 1992, 1994, Gu et al. 1994, Spark et al. 1997). Since the adsorption of HA onto metal (hydr)oxide by ligand exchange occurs between carboxyl functional groups of HA and the protonated hydroxyl of the metal (hydr)oxide, the degree of protonation which is a function of pH, is partly responsible for the pH-dependent adsorption. Thus, as pH decreases, more protons are available such that a greater amount of HA may complex with the protonated hydroxyl of metal (hydr)oxide. Additionally, increased protonation of any carboxylate sites associated with the HA at lower pH may enhance adsorption by

increasing the possibility for hydrogen bonding with the mineral surfaces (Murphy et al. 1990).

Similar to results at $\text{pH} = 4.0 \pm 0.2$, the Langmuir model parameters ($C_{s,max}$ and k) for both metal (hydr)oxide-coated sands were different, which also illustrates the differences in the distribution, density and affinity for HA of hydroxylated sites between FES and ALS. Compared to the results at $\text{pH} = 4.0 \pm 0.2$, the hysteresis coefficients (h) at $\text{pH} = 6.5 \pm 0.2$ are lower, ranging 0.69 to 0.85 for FES and ranging 0.53 to 0.98 for ALS, reflecting that desorption of HA onto metal (hydr)oxide also is pH-dependent. However, similar to results at $\text{pH} = 4.0 \pm 0.2$, the values for h at $\text{pH} = 6.5 \pm 0.2$ for both metal (hydr)oxide-coated sands decreased with increasing HA equilibrium concentration in the aqueous phase. This result suggests that high-affinity adsorption occurred initially at low equilibrium HA concentrations whereas both high-affinity and low-affinity adsorption occurred as the HA concentration increased, regardless of the pH ranges investigated in this study. Considering that dominant desorption occurs from the low-affinity adsorption fraction, the lower h values at $\text{pH} = 6.5 \pm 0.2$ relative to those at $\text{pH} = 4.0 \pm 0.2$ suggest that adsorption of heterogeneous HA molecules onto these sorbents at $\text{pH} = 6.5 \pm 0.2$ results in lower fractions of high-affinity adsorption than at $\text{pH} = 4.0 \pm 0.2$.

3.3.3 Fractionation of HA by Adsorption onto Model Sorbents

The effect of the sequential HA adsorption onto HA-free mineral surfaces (i.e., FES and ALS) on the E_4/E_6 ratios of the HA remaining in the solution is shown in Fig. 3.8. As the number of sequences in the sequential HA adsorption tests increases, the values for the E_4/E_6 ratios of the HA remaining in the solution decrease gradually for

both HA-free metal hydroxide-coated sands. Also, the decreases in E_4/E_6 ratios were smaller for ALS relative to those for FES. Since the E_4/E_6 ratio decreases with increasing MW (Chen et al. 1977, Stevenson 1994), the decreases in E_4/E_6 ratios relative to original value of HA remaining in the solution indicate the preferential adsorption of certain fractions of HA molecules. From the data presented in Fig. 3.8, HA molecules with relatively lower MW fractions are expected to be preferentially adsorbed onto both metal (hydr)oxide-coated sands, leaving the HA molecules with higher MW fractions in solution. Since the abundance of acidic functional groups is greater for terrestrial HA molecules with lower MW fraction (Hur and Schlautman 2003), the preferential adsorption of lower MW fractions of HA may be associated through ligand exchange dominantly.

As is evident by the changes in E_4/E_6 ratios of HA remaining in the solution during the adsorption kinetics experiments and the sequential adsorption to clean mineral surfaces, the adsorption of heterogeneous HA molecules onto both metal (hydr)oxide-coated sands results from a combination of adsorption mechanisms (i.e., ligand exchange with lower MW fractions of HA + hydrophobic interaction with higher MW fractions of HA). Since E_4/E_6 ratios for HA remaining in the solution decrease gradually for FES and ALS, a greater contribution of ligand exchange may be expected and the adsorption of lower MW fractions may surpass that of higher MW fractions. This result is consistent with that reported by Hur and Schlautman (2003, 2004), who found that purified Aldrich HA of lower MW was preferentially adsorbed to hematite, and postulated that a greater contribution of ligand exchange and electrostatic attraction is associated with lower MW fractions, whereas hydrophobic interactions are associated with higher MW fractions..

Thus, the results of this study indicate that both kinetic adsorption/desorption and the competition between the different HA fractions are important considerations.

3.3.4 Characterization of Model Sorbents

The scanning electron microscope (SEM) images of the model sorbents at two different magnifications (i.e., x400 and x7000) are shown in Fig. 3.9. Whereas the surfaces of uncoated sand appear to be smooth and nonporous, and comprised of only pure quartz, the surfaces of the metal (hydr)oxide-coated sands are rough and coated with metal (hydr)oxide that is hundreds of nm in thickness. Although the SEM investigation of the model sorbents revealed that *in situ* precipitation of metal (hydr)oxide did not completely cover the surface of quartz, most of quartz surface was coated with a relatively uniform and stable metal (hydr)oxide.

The results of microchemical analyses using SEM/EDS for five model sorbents also are shown in Fig. 3.9. Whereas only Si and O are detected on the surfaces of uncoated sand, Fe and Al as well as Si are detected on the surfaces of FES and ALS, respectively (note that the Au is from coating prior to SEM analyses). Additionally, the results of SEM/EDS analyses revealed the presence of substantial amounts of carbon after the adsorption of HA onto both metal (hydr)oxide-coated sands.

As confirmed by the results of the microchemical analyses using XPS shown in Fig. 3.10, significant amounts of Fe [i.e., Fe (2p_{1/2}) and Fe (2p_{3/2})] and Al [i.e., Al (2s) and Al (2p)] in surface compositions are detected, indicating the presence of a thin metal (hydr)oxide coating over the quartz. Although the negligible amount of carbon [i.e., C(1s)] is still detected on the surfaces of FES, ALS, and uncoated sand due to the high

surface sensitivity of XPS, the amount of carbon increased significantly on the surfaces of the metal (hydr)oxide- and HA-coated sands, indicating the presence of HA coating after the adsorption of HA to both metal (hydr)oxide-coated sands.

The chemical structure of metal (hydr)oxide coating also has been investigated using high-resolution XPS. As shown by the results in Fig. 3.11 based on both chemical shift and multiplet splitting effects, distinct spectral characteristics can be described for both metal (hydr)oxides investigated. The peak parameters and regions are optimized using XPS peak fitting program (XPSPEAK 4.1) and the determination of individual chemical states is possible, as shown in Fig. 3.11. Based on the binding energies of the oxide state of Fe (2p_{3/2}) (= 711.4 eV), the iron (hydr)oxide coating appears to be dominated by α -FeO(OH). Based on the binding energies of the oxide state of Al (2p) (= 74.3 eV), the aluminum (hydr)oxide coating appears to be dominated by Al_2O_3 .

3.4 CONCLUSIONS

The preparation procedure and characterization of model sorbents are presented by employing a scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectrometer (EDS) and a X-ray photoelectron spectroscopy (XPS) to quantify the microchemical surface compositions of model sorbents. In addition, the preferential binding of certain fractions from a mixture of HA molecules during adsorption onto the mineral surfaces is evaluated by employing a Ultraviolet (UV)-Visible spectroscopy.

The overall adsorption rates of HA onto FES, ALS and uncoated sand at two different pHs (i.e., 4.0 ± 0.2 or 6.5 ± 0.2) and a single ionic strength (i.e., 0.01 M NaCl) apparently equilibrated around 4 h at 40-mg/L initial HA concentration. The sharp

decrease of E_4/E_6 ratios within 15 min suggests fast initial adsorption of lower MW fractions, whereas the gradual increase of E_4/E_6 ratios to 4 h suggests a relatively slow exchange between the adsorbed lower MW fractions and the higher MW fractions of the HA in solution. These results are consistent with those of other studies that indicate a fast initial adsorption of lower MW fractions of HA with more acidic functional groups due to ligand exchange resulting in a modification of the surfaces that subsequently favors hydrophobic interactions and slower replacement with the more hydrophobic, higher MW fractions of the HA. However, based on the lower values of E_4/E_6 ratios at steady state relative to those before adsorption, the adsorption of lower MW fractions appears to exceed that of the higher MW fractions.

The empirical Langmuir model was found to describe the adsorption of HA onto different mineral surfaces fairly well, despite some indications that the composition and properties of heterogeneous HA macromolecules change during adsorption onto mineral surface and that energetic differences in the adsorption of heterogeneous HA molecules result in different combinations of adsorption mechanisms. The strong hysteresis effects were observed for metal (hydr)oxide-coated sands, suggesting that the adsorbed HA is not readily desorbed at a given pH and ionic composition due to high-affinity chemical interaction (i.e., ligand exchange) between HA and metal (hydr)oxide-coated sands, as well as the possible formation of stable inner-sphere complexes between multiple carboxyl groups of HA and surface hydroxyl sites on the sorbents. In contrast, a weak hysteresis effect was observed for uncoated sand since negatively-charged silica hydroxyls dominantly adsorbed HA by the low-affinity chemical interactions (i.e., entropy-driven or hydrophobic interactions).

As is evident by the changes in E_4/E_6 ratios of HA remaining in the solution during the adsorption kinetics experiments and the sequential adsorption to clean mineral surfaces, the adsorption of heterogeneous HA molecules onto both metal (hydr)oxide-coated sands results from a combination of adsorption mechanisms (i.e., ligand exchange with lower MW fractions of HA + hydrophobic interaction with higher MW fractions of HA). Thus, the results of this study indicate that both kinetic adsorption/desorption and the competition between the different HA fractions are important considerations.

Although the SEM investigation of the model sorbents revealed that *in situ* precipitation of metal (hydr)oxide did not completely cover the surface of quartz, most of quartz surface was coated with a relatively uniform and stable metal (hydr)oxide. Additionally, the results of SEM/EDS analyses revealed the presence of substantial amounts of carbon after the adsorption of HA onto both metal (hydr)oxide-coated sands. As confirmed by the results of the microchemical analyses using XPS, significant amounts of Fe [i.e., Fe (2p_{1/2}) and Fe (2p_{3/2})] and Al [i.e., Al (2s) and Al (2p)] in surface compositions are detected, indicating the presence of a thin metal (hydr)oxide coating over the quartz. The chemical structure of metal (hydr)oxide coating also has been investigated using high-resolution XPS. Based on the binding energies of the oxide state of Fe (2p_{3/2}) (= 711.4 eV), the iron (hydr)oxide coating appears to be dominated by α -FeO(OH). Based on the binding energies of the oxide state of Al (2p) (= 74.3 eV), the aluminum (hydr)oxide coating appears to be dominated by Al_2O_3 .

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Table 3.1 – The E_4/E_6 ratios and elemental compositions of humic acid (HA) extracted from a commercial peat soil (by dialysis with a nominal molecular weight cutoff of 3,500 Daltons).

HA Sample	E ₄ /E ₆ value			Elemental composition (mass %) ^c					Ash content ^c (%)
	E ₄ ^a	E ₆ ^b	E ₄ /E ₆	C	H	N	O	O/C	
HA 1	0.823	0.159	5.18	52.8 ^d	5.25	1.76	34.7	0.658	0.38
HA 2	0.837	0.156	5.37	52.8	5.23	1.81	33.8	0.641	0.44

^a Absorbance at 465 nm

^b Absorbance at 665 nm

^c Based on analyses performed by Huffman Laboratories, Golden, CO

^d $R = f_{om}/f_{oc} = 1/0.528 = 1.89$

Table 3.2 Parameter values from fitting Langmuir adsorption and Langmuir desorption model to measured data ($I = 0.01$ M NaCl and $\text{pH} = 4.0 \pm 0.2$).

Sorbents	Adsorption				Desorption			
	Test	$C_{s,max}$ (mg/kg)	k (L/mg)	r^2	$C_{s,max}$ (mg/kg)	k (L/mg)	C_a^b (mg/L)	h^c
Iron (hydr)oxide-coated	1	246	0.454	0.839	228	0.268	1.85	0.95
	2	229	0.426	0.690			2.06	0.94
	3	228	0.268	0.860			9.89	0.94
	Total ^a	231 (10.1)	0.389 (0.100)	0.742			19.2	0.88
							38.9	0.94
							59.0	0.86
Aluminum (hydr)oxide-coated	1	275	0.145	0.876	258	0.102	4.01	0.96
	2	271	0.122	0.893			9.56	0.91
	3	258	0.102	0.873			11.8	0.95
	Total	265 (8.89)	0.125 (0.022)	0.845			27.4	0.92
							40.3	0.73
							58.9	0.70
Uncoated Quartz	1	18.0	0.025	0.881	18.0	0.025	11.7	0.78
	2	27.8	0.022	0.823			23.0	0.63
	3	17.6	0.070	0.724			25.9	0.41
	Total	20.7 (5.78)	0.032 (0.027)	0.652			41.3	0.47
							50.5	0.37
							64.3	0.41

^aAll data in one plot and numbers in parentheses are one standard deviations

^bHA concentration in aqueous phase after adsorption and before starting the desorption tests

^cHysteresis coefficients for each HA concentration in aqueous phase after adsorption tests

Table 3.3 Parameter values from fitting Langmuir adsorption and Langmuir desorption model to measured data (I = 0.01 M NaCl and pH = 6.5 ± 0.2).

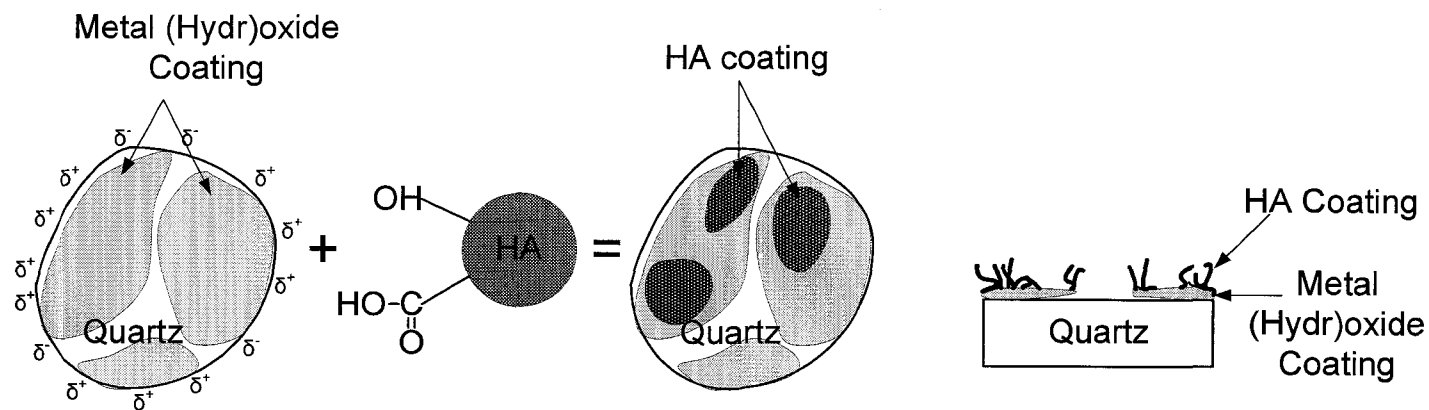
Sorbents	Adsorption				Desorption			
	Test	$C_{s,max}$ (mg/kg)	k (L/mg)	r^2	$C_{s,max}$ (mg/kg)	k (L/mg)	C_a^b (mg/L)	h^c
Iron (hydr)oxide-coated	1	79.6	0.102	0.888	73.0	0.074	7.38	0.81
	2	73.0	0.074	0.853			18.9	0.85
	3	90.5	0.050	0.902			53.2	0.80
	Total ^a	80.4 (8.84)	0.071 (0.026)	0.840			69.9	0.69
							113	0.73
Aluminum (hydr)oxide-coated	1	92.8	0.183	0.738	87.7	0.378	3.75	0.84
	2	95.7	0.241	0.785			9.16	0.98
	3	87.7	0.378	0.859			15.9	0.53
	Total	90.6 (4.04)	0.284 (0.099)	0.769			37.7	0.79
							109	0.66
Uncoated Quartz	N.A. ^d				N.A.			

^aAll data in one plot and numbers in parentheses are standard deviations

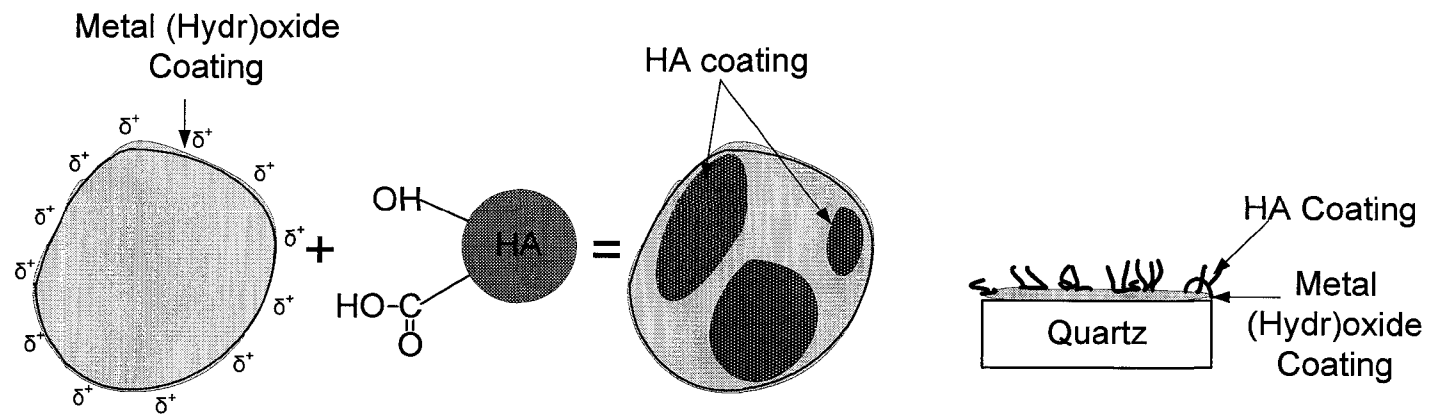
^bHA concentration in aqueous phase after adsorption and before starting the desorption tests

^cHysteresis coefficients for each HA concentration in aqueous phase after adsorption tests

^dNot Available due to the negligible amount of adsorption of HA onto uncoated quartz



(a) Partially-Coated Quartz by Metal (Hydr)oxide



(b) Completely-Coated Quartz by Metal (Hydr)oxide

Fig. 3.1 Schematic diagram of structure of metal (hydr)oxide- and HA- coated sand.

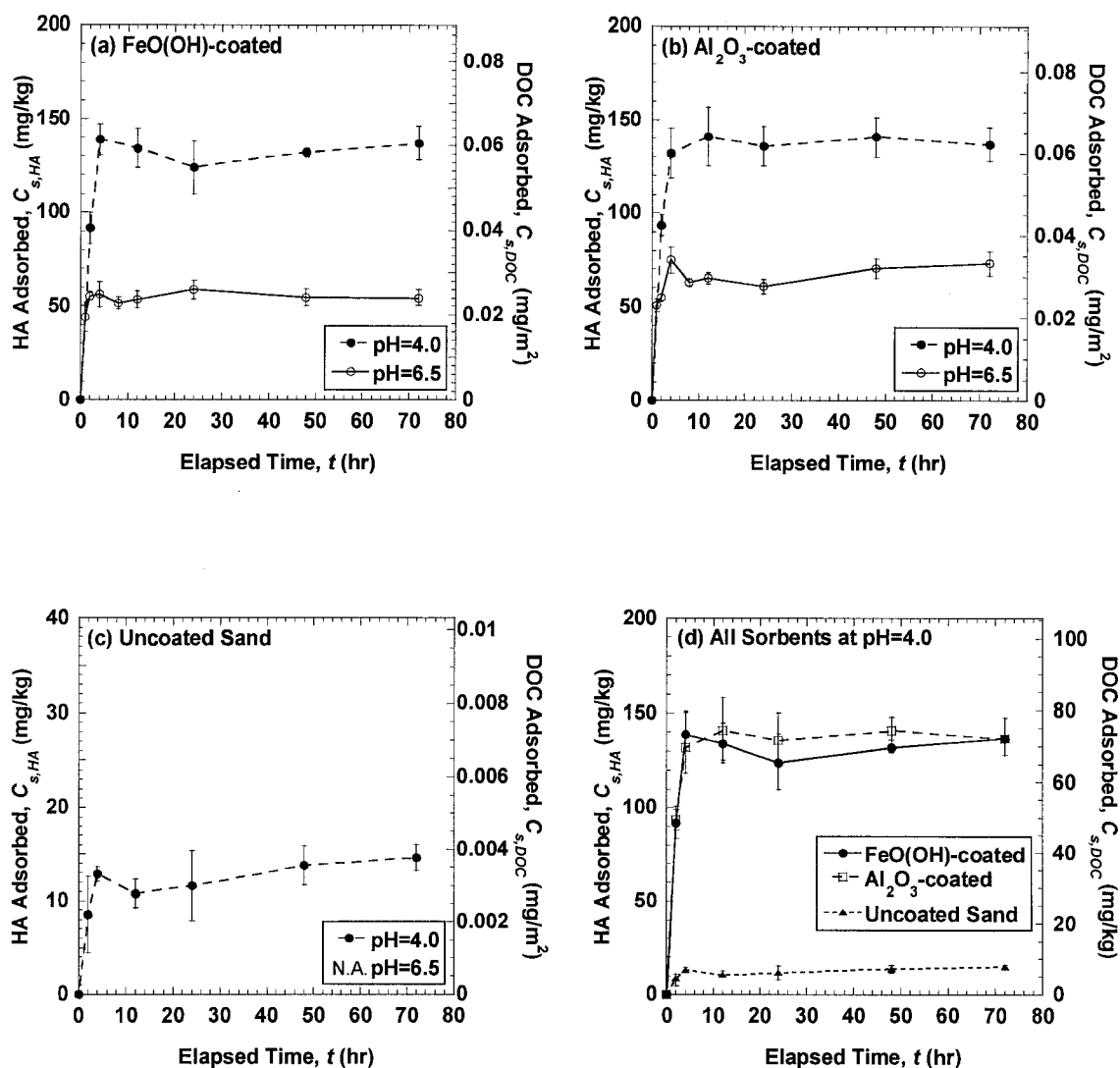


Fig. 3.2 Adsorption kinetics of HA at initial concentration of 40 mg/L onto different model sorbents ($I = 0.01$ M NaCl and $pH = 4.0 \pm 0.2$ or 6.5 ± 0.2).

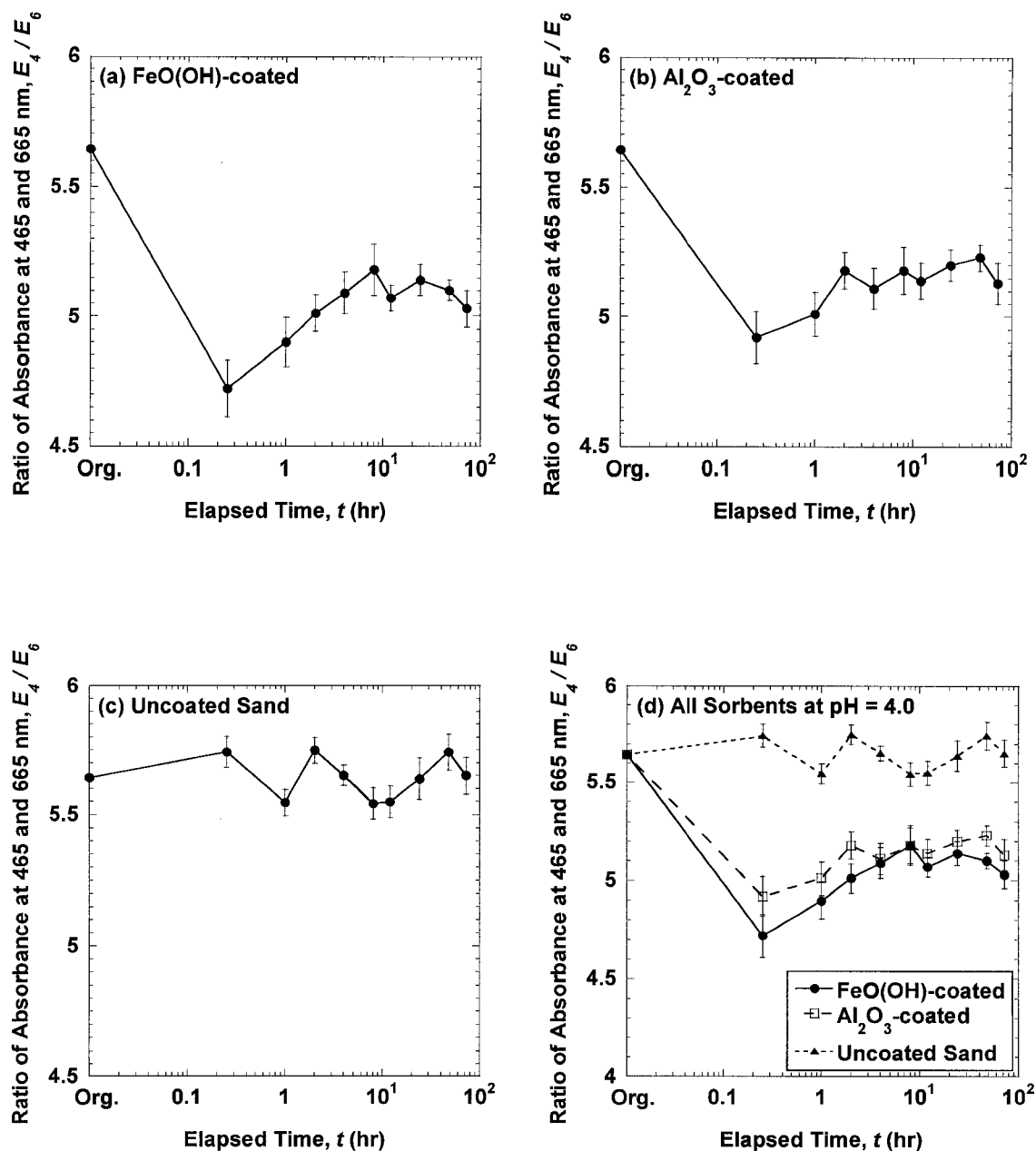


Fig. 3.3 Changes in the ratio of absorbance at 465 and 665 nm (E_4/E_6) over time during the adsorption kinetics of HA at initial concentration of 40 mg/L onto three different model sorbents ($I = 0.01$ M NaCl and $pH = 4.0 \pm 0.2$). (Org. means original HA solution before adsorption onto mineral surfaces).

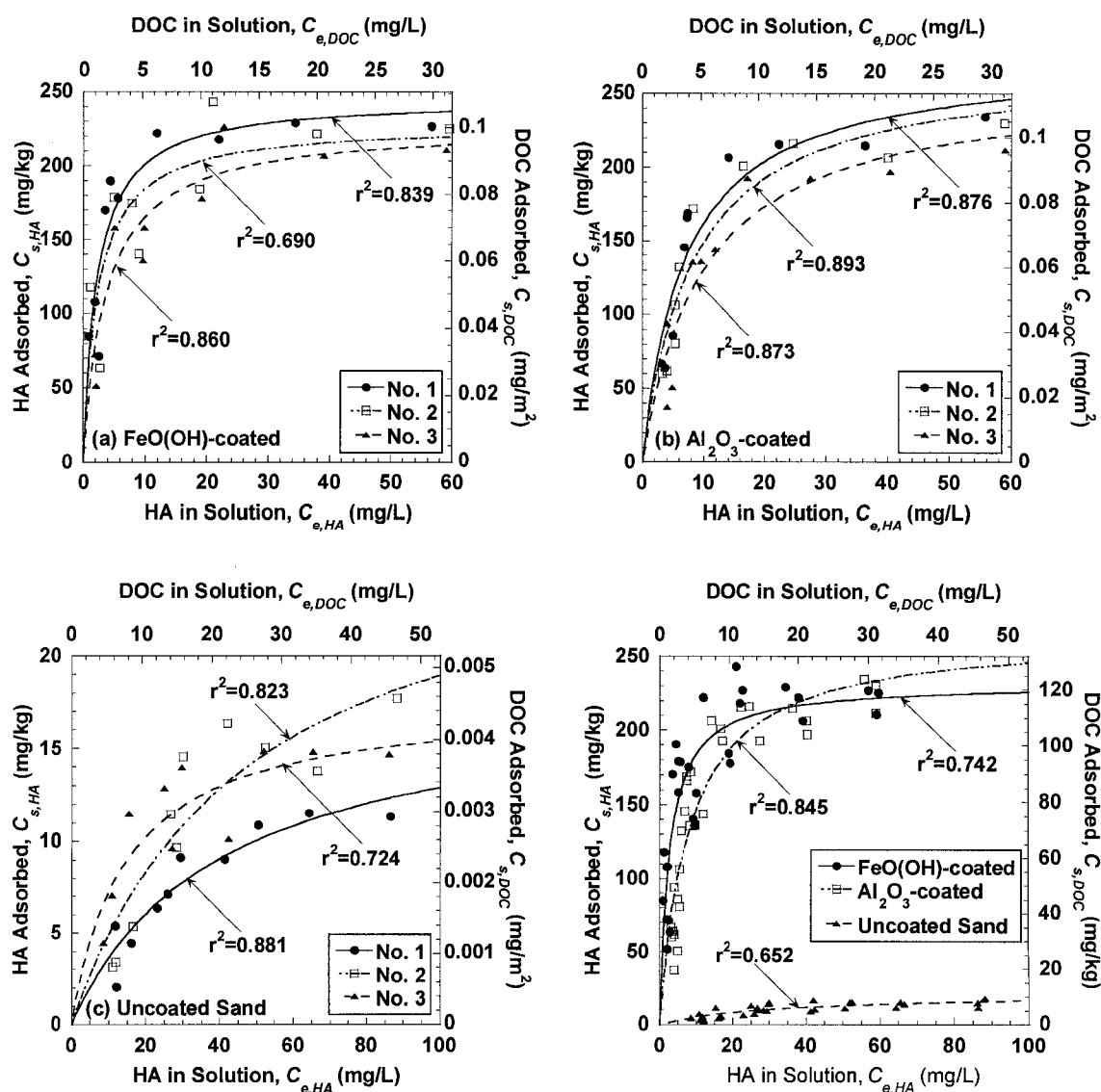


Fig. 3.4 Adsorption isotherm of HA onto different model sorbents after 48 h (I = 0.01 M NaCl and pH = 4.0 ± 0.2). The lines are fits of the data to the Langmuir isotherm model (i.e., Eq. 3.1).

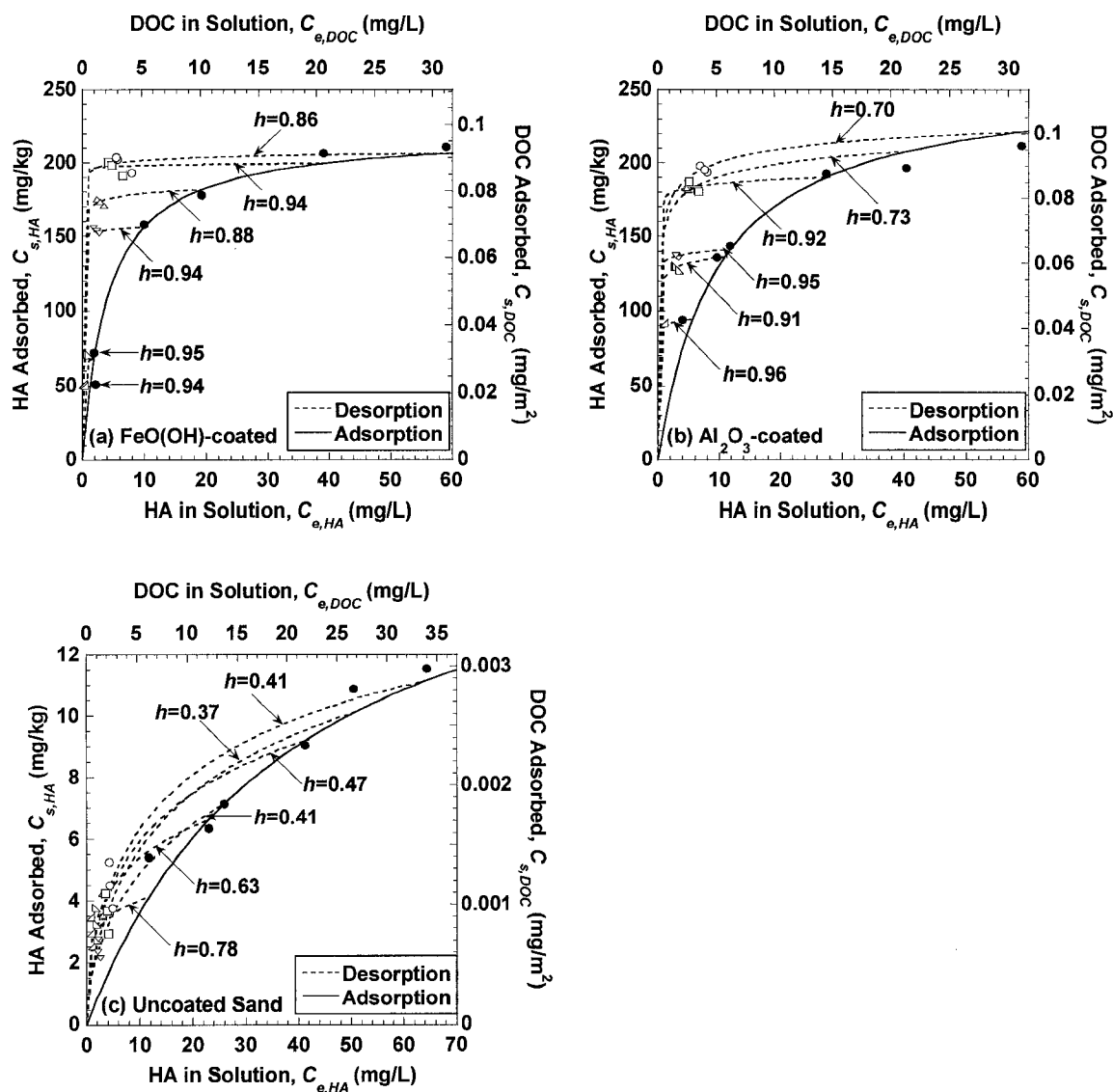


Fig. 3.5 Adsorption and desorption isotherms of HA on different model sorbents after 72 h ($I = 0.01$ M NaCl and $pH = 4.0 \pm 0.2$). Solid and dashed lines are fits of the data to the Langmuir isotherm model (i.e., Eq. 3.1) and desorption model (i.e., Eq. 3.2), respectively.

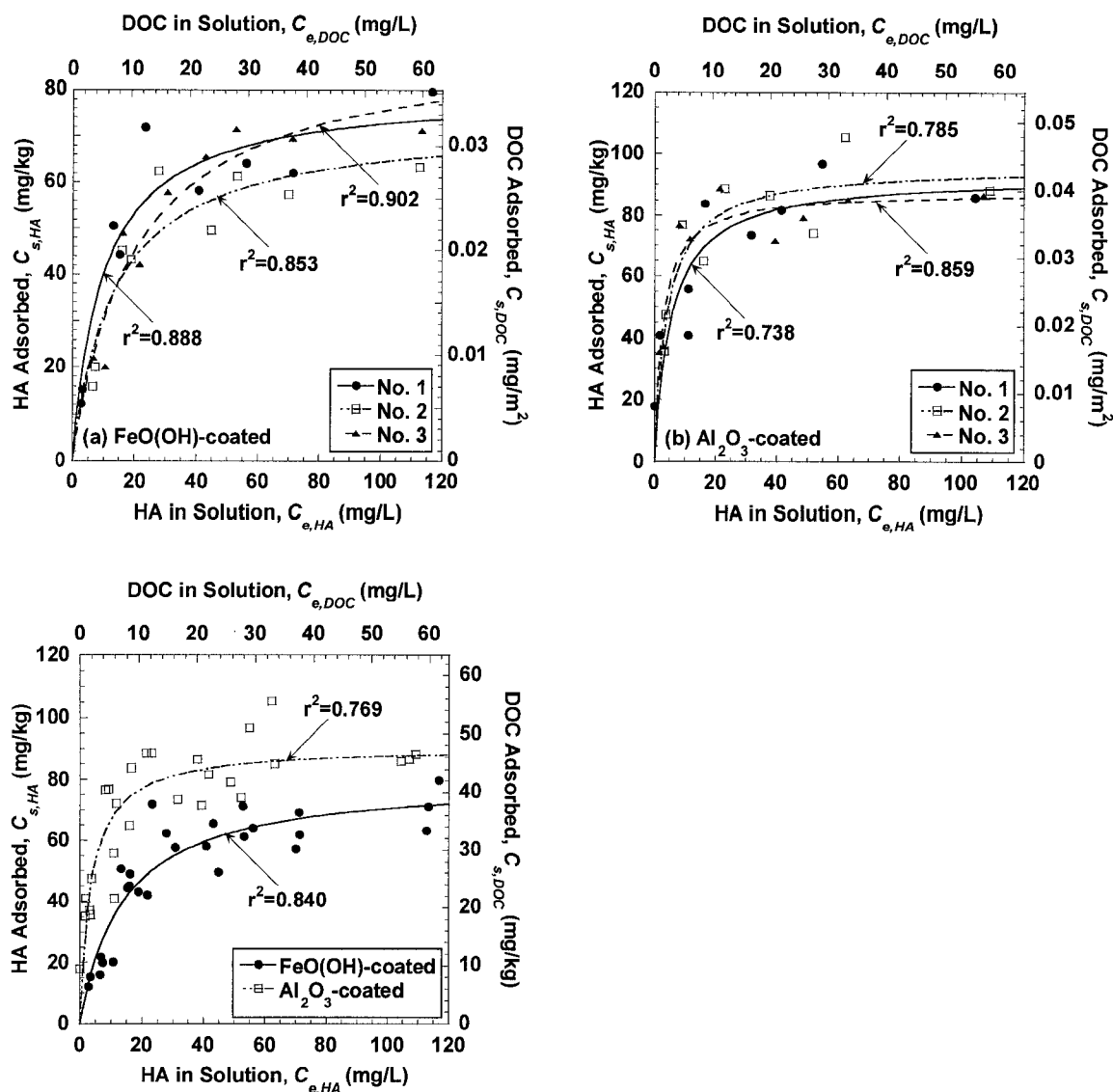


Fig. 3.6 Adsorption isotherm of HA on different model sorbents after 48 h ($I = 0.01$ M NaCl and $pH = 6.5 \pm 0.2$). The lines are fits of the data to the Langmuir isotherm model (i.e., Eq. 3.1). Adsorption isotherm of HA onto uncoated quartz is not available due to negligible amount of adsorption of HA onto uncoated quartz.

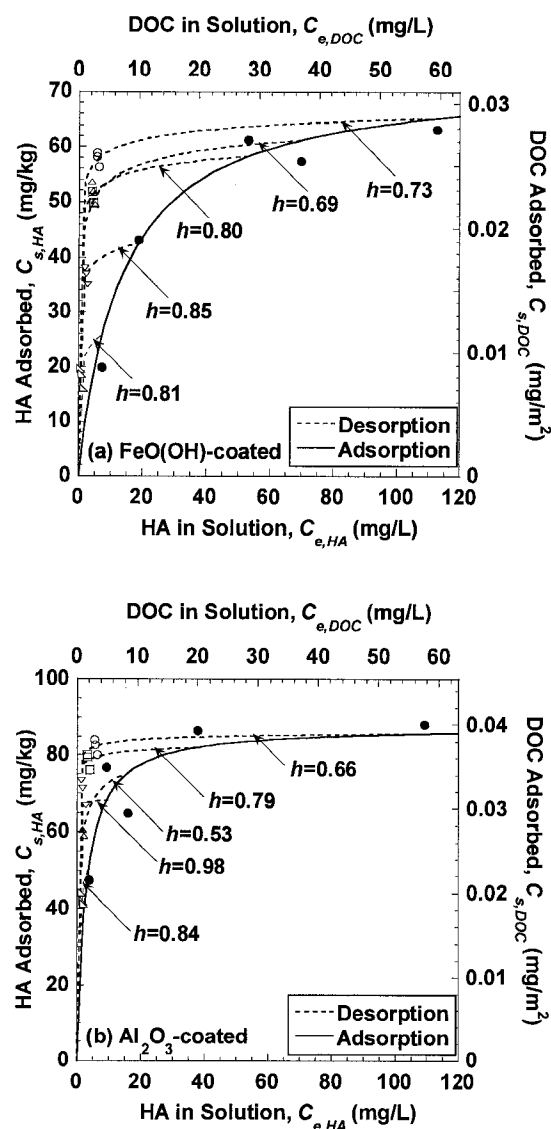


Fig. 3.7 Adsorption and desorption isotherms of HA on different model sorbents after 72 h ($I = 0.01$ M NaCl and $pH = 6.5 \pm 0.2$). Solid and dashed lines were fits of the data to the Langmuir isotherm model (i.e., Eq. 3.1) and desorption model (i.e., Eq. 3.2), respectively.

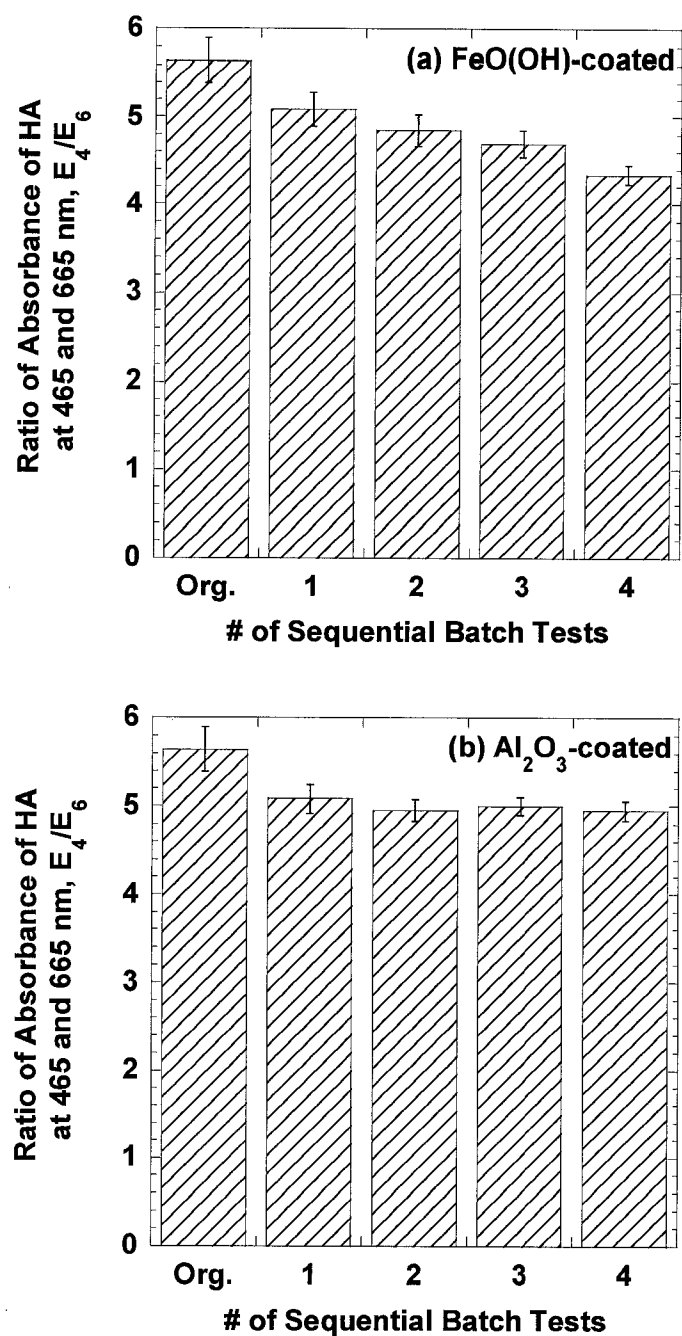


Fig. 3.8 Effect of sequential HA adsorption onto clean mineral surfaces on the ratio of absorbance of HA at 465 and 665 nm (E_4/E_6): (a) iron (hydr)oxide-coated sand, and (b) aluminum (hydr)oxide-coated sand (Org. means original HA solution before adsorption onto mineral surfaces).

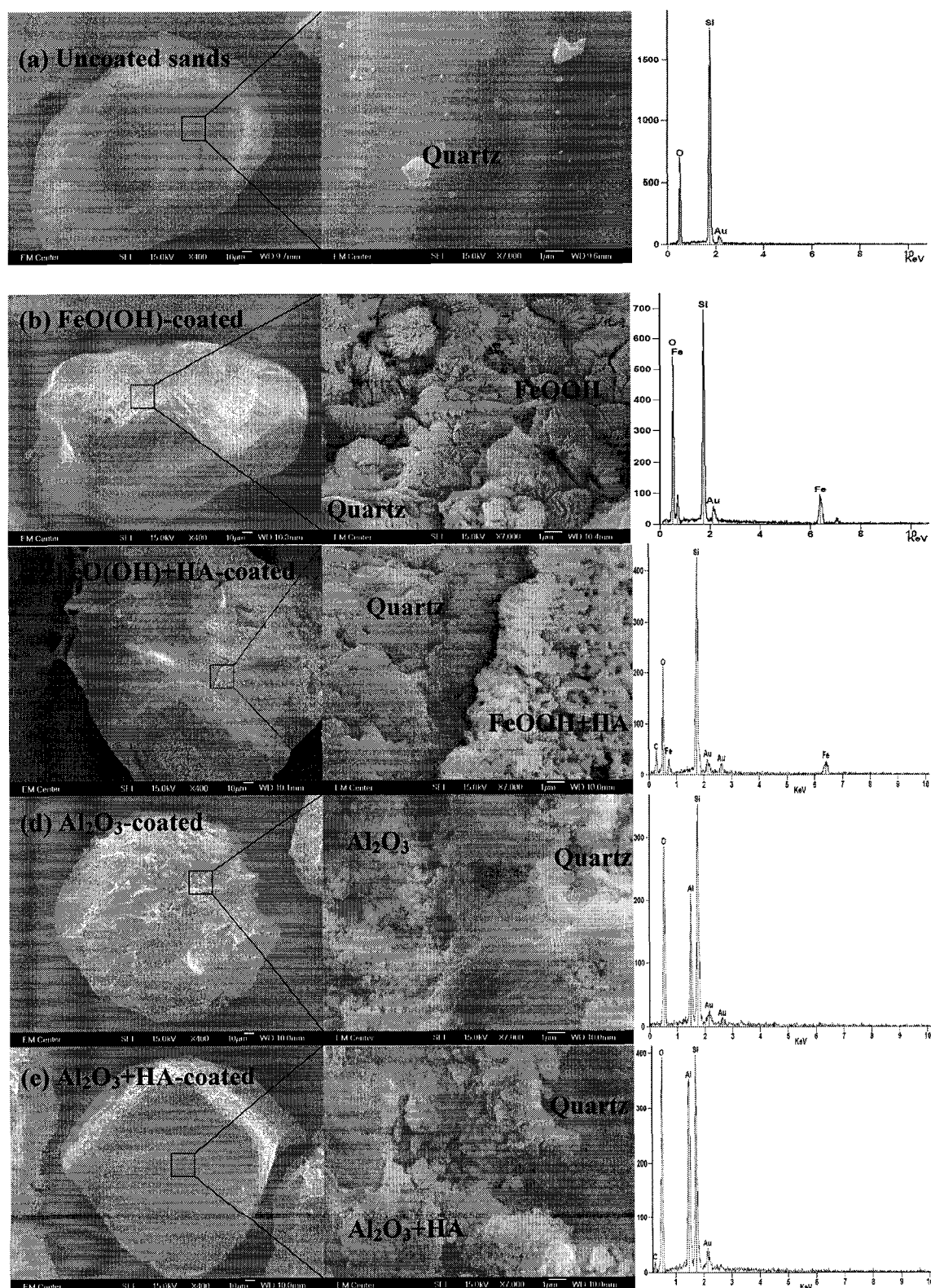


Fig. 3.9 Scanning electron microscopic images at different resolutions (i.e., x400 and x 7000) and associated EDS analyses of model sorbents: (a) uncoated sand; (b) FeO(OH)-coated sand; (c) FeO(OH)+HA- coated sand ($f_{oc} = 0.016\%$); (d) Al₂O₃-coated sand; and (e) Al₂O₃+HA- coated sand ($f_{oc} = 0.014\%$).

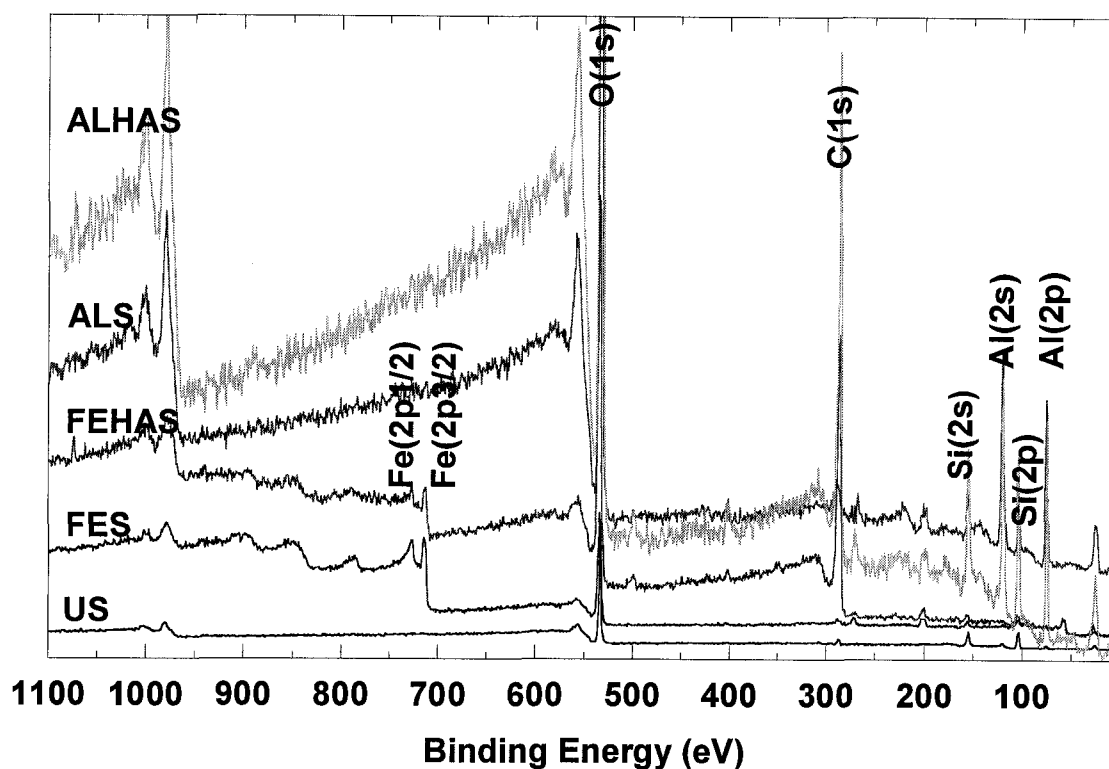


Fig. 3.10 Wide scan energy survey spectra acquired from five model sorbents [i.e., US: uncoated sand; FES: FeO(OH)-coated sand; FEHAS: FeO(OH)+HA- coated sand ($f_{oc} = 0.016\%$); ALS: Al₂O₃-coated sand; ALHAS: Al₂O₃+HA- coated sand ($f_{oc} = 0.014\%$)].

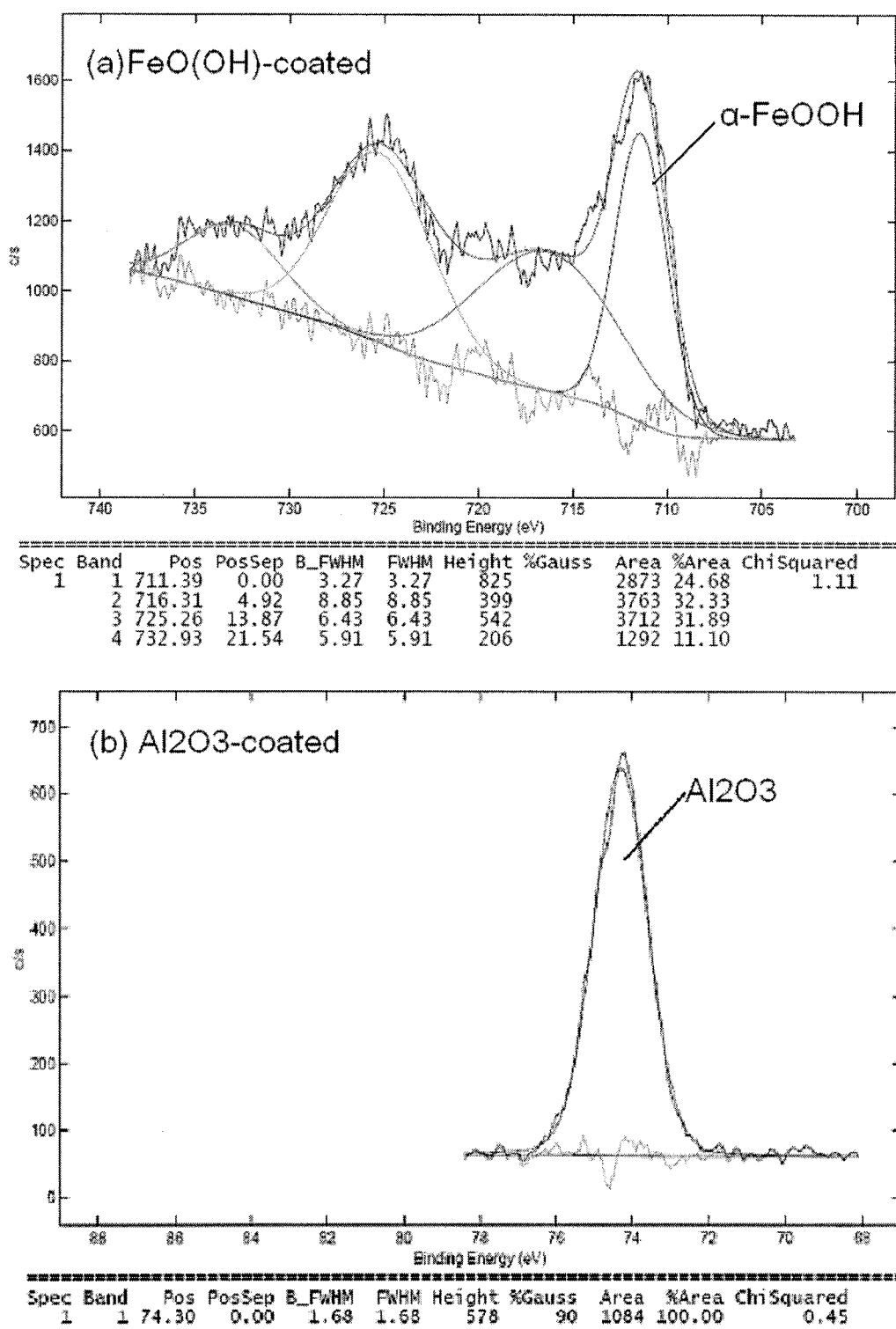


Fig. 3.11 High-resolution XPS spectra acquired from metal hydr(oxide)- coated sands

CHAPTER 4

SORPTION OF NONPOLAR NEUTRAL ORGANIC COMPOUNDS TO METAL (HYDR)OXIDE- AND HUMIC ACID-COATED SANDS

Abstract: The roles of mineral surface and mineral-bound humic acid (HA) in the sorption of six nonpolar neutral organic compounds (1,2,4-trichlorobenzene, 1,4-dichlorobenzene, chlorobenzene, *m*-xylene, toluene, benzene) to HA-mineral complexes with low fractions of organic carbon ($0.006 \% \leq f_{oc} \leq 0.044 \%$) were investigated. Sorption of all six sorbates to metal (hydr)oxide- (i.e., FeO(OH)- or Al₂O₃-) coated sands was nearly linear and increased with increasing hydrophobicity of the sorbates. Sorption of all six sorbates to the HA-mineral complexes was also essentially linear, and resulted from a combination of sorption to both the mineral surface and mineral-bound HA, with the dominance of either contribution depending on the properties of the sorbents (e.g., f_{oc}) and the sorbates (e.g., K_{ow}). Conventional sorption models considering the amended contributions of both the mineral surface and mineral-bound HA provided as good agreement between predicted and measured distribution coefficients as a more complicated, two-component model for sorption considering the mineral fraction. Finally, the reactivity of mineral-bound HA to the sorbates (i.e., K_{oc}^*) were not significantly different between two metal (hydr)oxide- and HA-coated sands evaluated, indicating that the conformational and fractional changes of mineral-bound HA could be similar between two metal (hydr)oxide-coated sands.

Key Words: distribution coefficient, humic acid-mineral complexes, metal (hydr)oxide-coated sands, mineral-bound humic acid, neutral organic compounds, sorption

4.1 INTRODUCTION

Sorption of nonpolar neutral organic compounds (NNOCs) to soil organic matter (SOM)-mineral complexes in subsurface systems has received considerable attention, since mineral-bound SOM can mask physicochemical properties of most underlying minerals and can change surfaces from hydrophilic to hydrophobic. Moreover, SOM may undergo physical and chemical changes (i.e., fractionation by the preferential adsorption and variations in structural and chemical properties) during adsorption onto mineral surfaces (Murphy et al. 1990, 1992, 1994, Gu et al. 1994, 1995, 1996, Jones and Tiller 1999, Van de Weerd et al. 1999, Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2003, 2004, 2006, Wang and Xing 2005, Feng et al. 2006). These complex interactions between SOM and mineral surfaces can complicate the fate and transport of NNOCs in the subsurface.

For instance, Murphy et al. (1990, 1992, 1994) investigated the sorption of anthracene, dibenzothiophene, and carbazole to hematite and kaolinite coated with humic acid (HA) at different fractions of organic carbon, f_{oc} (0.01~0.5 %), and suggested that the orientation and structure of SOM on the mineral surface may affect the surface area of the organic component and the accessibility of hydrophobic domains. Rebhun et al. (1992) studied the sorption of several NNOCs covering a wide range of hydrophobicities on clay and clay-humic complexes representing aquifer-soil systems, and observed that the distribution coefficients of NNOCs to humic fraction were 8-20 times higher than

those to pure clay. Celis et al. (1997) evaluated the sorption behavior of thiazafluron with both calcium montmorillonite and calcium montmorillonite coated with iron species and SOM, and concluded that mineral and organic coatings over clays alter the nature of the surface exposed for sorption of NNOCs, thereby affecting the sorption behavior of colloidal soil particles. Onken and Traina (1997) studied the effect of mineral type (i.e., reagent CaCO_3 , calcite, and montmorillonite) on the sorption of NNOCs to HA-mineral complexes, and reported that mineral surface contribution to sorption was negligible and difficult to assess since HA blocks mineral sorption sites previously available to NNOCs. Laor et al. (1998) prepared HA-mineral complexes using goethite, hematite, and Ca^{2+} - and Cu^{2+} -montmorillonite, and reported that sorption of phenanthrene to these complexes was substantially higher at lower pH, and higher when the HA was associated with montmorillonite rather than goethite and hematite. Jones and Tiller (1999) found that the extent of phenanthrene binding with mineral-bound HA fraction was lower than that with the bulk HA prior to adsorption to mineral surface, and suggested that the conformation of the HA associated with the mineral surface appears to be affecting the level of phenanthrene binding by mineral-bound HA. Shen and Jaffé (2000) prepared HA-coated montmorillonite, aluminum oxide, and kaolinite to estimate the contribution of the mineral surface to the overall sorption of total petroleum hydrocarbons. They concluded that the contribution of the mineral surface to the overall sorption depends on many factors such as the properties and amount of SOM, as well as the surface properties of the sorbents. Hur and Schlautman (2004) observed the variations among the ultrafiltration fractions of purified Aldrich HA in terms of their adsorption onto kaolinite and hematite and their binding of pyrene at the mineral-water interface, and postulated that the

underlying mineral surface can alter the effects of HA heterogeneity on the sorption of NNOCs. Wang and Xing (2005) found that aliphatic fractions of HA extracted from peat were preferentially adsorbed by clay minerals compared to aromatic fractions of HA, and insisted the adsorbed HA fractions have higher sorption linearity and affinity than the source of HA. Finally, Feng et al. (2006) reported that preferential adsorption of polymethylene groups on kaolinite and aromatic moieties on montmorillonite may also contribute to the difference in phenanthrene sorption by peat HA associated with these two types of clay.

Linear hydrophobic partitioning of NNOCs to SOM, whereby the distribution coefficient (K_d) is equal to the product of the fraction of organic carbon (f_{oc}) and the organic carbon partitioning coefficient (K_{oc}) (i.e., $K_d = f_{oc}K_{oc}$), has been shown to be unlikely for sorbents with $f_{oc} < 0.1$ % (Hassett et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Curtis et al. 1986, Kishi et al. 1990, Ball and Roberts 1991, Paya-Perez et al. 1991, Larsen et al. 1992, Rebhun et al. 1992, Onken and Traina 1997, Shen and Jaffé 2000). In particular, measured values of K_{oc} for NNOCs on aquifer solids with low f_{oc} (< 0.1 %) have been shown to deviate significantly from predicted values of K_{oc} based on empirical relationships between K_{oc} and the octanol-water partition coefficient, K_{ow} (Hassett et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Curtis et al. 1986, Murphy et al. 1990, Onken and Traina 1997). These results indicate that the overall sorption is characterized by a combination of sorption to both SOM and mineral surfaces, such that modifications to the linear hydrophobic partitioning concept have been proposed

For example, the two-component model proposed by McCarty et al. (1981)

assumes that sorption to mineral surfaces that is independent of partitioning into organic carbon, whereas the model proposed by Karickhoff (1984) assumes that sorption to mineral surfaces occurs in concert with partitioning into organic carbon (Curtis et al. 1986). Liljestrand and Shimizu (1991) modified the concept of two-component model by incorporating weight fractions of coating solids (e.g., amorphous aluminosilicate gel, iron oxide, and HA) and montmorillonite, and noted that a modified sorption model with blocking parameters effectively explained the sorption of anthracene and 2-aminoanthracene to components in natural solids. Rebhun et al. (1992) proposed that the overall sorption be determined by the balance of sorption to mineral surfaces and partitioning into organic carbon using the fraction of the mineral surface covered by HA. Weber et al. (1992) proposed a composite sorption model with a linear partition contribution and a Freundlich nonlinear adsorption contribution on the basis that physicochemical and structural features of aquifer materials lead to energetic differences between or within individual particles such that different combinations of linear and nonlinear local sorption are likely. Finally, the contribution of the mineral fraction to total sorption of a NNOC has been determined by plotting K_d values versus f_{oc} resulting in an intercept for the sorption of a NNOC to a series of sorbents with different f_{oc} (Kishi et al. 1990, Paya-Perez et al. 1991, Rebhun et al. 1992, Shen and Jaffé 2000).

Recently, experimental observations of K_{oc} (determined after subtraction of mineral contribution) have been found to be affected by the nature of the complexes between SOM and mineral surface (Murphy et al. 1990, 1992, 1994, Schlautman and Morgan 1993, Laor et al. 1998, Jones and Tiller 1999, Hur and Schlautman 2004, 2006, Wang and Xing 2005, Feng et al. 2006). Specifically, the orientation and structure of

mineral-bound dissolved organic matter (DOM) have been shown to be controlled by (i) the configuration of DOM in solution, (ii) the number of attachment points and degree of ionization of carboxylate and hydroxyl sites on DOM, and (iii) the density and reactivity of hydroxyl sites of mineral surface (Murphy et al. 1990, 1992, 1994, Schlautman and Morgan 1993, Laor et al. 1998, Jones and Tiller 1999). Thus, differences in the orientation and structure of the mineral-bound DOM may affect the surface area of the organic phase and the accessibility of hydrophobic domains controlling the sorption of NNOCs (Murphy et al. 1990, 1992, 1994, Schlautman and Morgan 1993, Laor et al. 1998, Jones and Tiller 1999). Additionally, preferential adsorption of different fractions from heterogeneous DOM by different mineral surfaces plays an important role in controlling the sorption of NNOCs (Namjesnik-Dejanovic et al. 2000, Hur and Schlautman 2004, 2006, Wang and Xing 2005, Feng et al. 2006).

For example, Murphy et al. (1990, 1992, 1994) found that the mineral surface apparently affects the interfacial configuration of the DOM, possibly altering the size of hydrophobic domains on the humic molecules or their accessibility to NNOCs. Schlautman and Morgan (1993) postulated that the types of surface complexes between DOM and mineral surfaces greatly influence the ability of the mineral-bound DOM to sorb the NNOCs. Laor et al. (1998) suggested that the possible differences among K_{oc} values obtained with dissolved versus mineral-bound HA were due to steric hindrance arising from the special configuration of the HA on the mineral surface compared to a loose structure of dissolved HA. Jones and Tiller (1999) suggested that the conformation of the HA when adsorbed onto the mineral surfaces appears to be affecting the level of phenanthrene binding by mineral-bound HA. Hur and Schlautman (2004) postulated that

adsorption of well-characterized terrestrial and aquatic HA adsorbed on kaolinite and hematite significantly changed the subsequent K_{oc} values for pyrene relative to their original respective K_{oc} values from dissolved HA. Hur and Schlautman (2006) also reported that the impacts of HA adsorptive fractionation on pyrene sorption isotherm nonlinearity are affected by the source and other biogeochemical characteristics of HA. Wang and Xing (2005) reported that K_{oc} values of mineral-bound HA for the HA-clay complexes could be up to several times higher than those of the source HA, and postulated that this large increase may be attributed to the low polarity of the mineral-bound HA. Finally, Feng et al. (2006) reported that both kaolinite and montmorillonite organo-clay complexes exhibited higher phenanthrene K_{oc} values with decreasing pH, indicating that the coiled configuration of dissolved peat HA provided more favorable sorption conditions than stretched configuration.

Based on the aforementioned considerations, in this study, two hypotheses that (i) overall sorption of NNOCs to HA-mineral complexes is represented by a combination of sorption to both mineral-bound HA and mineral surface, and (ii) experimentally determined K_{oc} values (determined after subtraction of mineral contribution) are influenced by the nature of the complex between mineral surface and HA can be proposed. To test these hypotheses, the roles of mineral-bound HA and mineral surface in the sorption of NNOCs to low-carbon aquifer solids are investigated by using well-characterized mineral surfaces [i.e., FeOOH- or Al₂O₃- coated sands], reference HA, and solution with constant pH and ionic strength. The specific objectives of this study are to: (1) elucidate the contributions of mineral-bound HA and mineral surface to the overall sorption of six individual NNOCs; (2) investigate the effect of the type of mineral

surfaces on the ability of mineral-bound HA to sorb NNOCs (i.e., K_{oc}); and (3) evaluate predictive tools of sorption based on a comparison among four different sorption models.

4.2 MATERIALS AND METHODS

The materials and methods used in this study are described in detail in the Chapters 2 and 3. The description includes (1) the extraction and characterization of HA, (2) the preparation processes and characterization of four different types of model sorbents, (3) the physicochemical properties of the six NNOCs, (4) the analytical methods of the six NNOCs using gas chromatography with a flame ionization detector, (5) the methodology for the batch equilibrium sorption tests (BESTs), (6) the procedures for analyzing the results of BESTs, and (7) the evaluation of the potential effect on the observed sorption coefficients due to desorption of HA from metal (hydr)oxide- and HA-coated sands.

4.2.1 Preparation procedures for the solutions of the individual NNOC

Solutions of each individual NNOC were prepared by adding the exact amount of neat compound to 0.01 M NaCl in a 0.5-L flat-bottom glass flask with a short neck (Pyrex Brand, Fisher Scientific Co., Pittsburgh, PA) to reduce any volatile loss to the gas phase, and by mixing the contents with a magnetic stirrer (Fisher Scientific Co., Pittsburgh, PA) at 600 rpm for 24 h before use. A bacterial inhibitor in the form of 100 mg/L of sodium azide, NaN_3 (Fisher Scientific Co, Pittsburgh, PA), was added to all solutions. Detailed procedures in preparing solution are described in Chapter 2.

4.2.2 Characterization of Model Sorbents

In this study, both the metal (hydr)oxide-coated quartz and mineral-bound HA were considered to play important roles in the sorption of NNOCs to metal (hydr)oxide- and HA-coated sand. As indicated by Fig. 3.1, quartz was first modified by precipitating metal (hydr)oxides over the surface of the sand particles. Second, the adsorption and desorption of HA to the metal (hydr)oxide-coated sand were performed at desired ionic composition and pH to produce relatively uniform metal (hydr)oxide- and HA-coated aquifer solids. Characterization of the sorbents involved measurements of the total organic carbon and the specific surface area.

The total organic carbon (TOC) of each sorbent was determined by Huffman Laboratories (Golden, CO) as the difference between total carbon (TC) and total inorganic carbon (TIC). The detection limits for TC, TIC, and TOC were all 0.005 %. Also, the surface area and intra-particle porosity of the sorbents were determined by Porous Materials, Inc. (Ithaca, NY) via a nitrogen adsorption analysis with a volumetric apparatus (BET Sorptometer, Porous Materials, Inc., Ithaca, NY). The multi-point surface area was determined after low-temperature adsorption data were fitted by the BET method (Brunauer et al. 1938), and the total pore volume was determined. Detailed characterization procedures are described in Chapter 2.

4.3 MODEL DESCRIPTIONS

4.3.1 Sorption Model for Two-Component Aquifer Solids

Mathematical models describing the distribution of NNOCs among multi-component aquifer solids have been developed to assist in explaining contaminant

sorption as a multiple reaction phenomenon (McCarty et al. 1981, Karickhoff 1984, Liljestrand and Shimizu 1991, Weber et al. 1992). For the case where only two particle-scale domains [i.e., mineral-bound HA and metal (hydr)oxide coating] are considered to play dominant roles in the sorption of NNOCs to metal (hydr)oxide- and HA-coated sand, the distribution of a NNOC to two particle-scale domains can be expressed as follows:

$$C_s = f_{om} K_{om} C_e + f_{min} K_{f,min} C_e^{n,min} \quad (4.1)$$

where C_s is the NNOC concentration in the solid-phase at equilibrium ($\mu\text{mol/kg}$ of solid), C_e is the NNOC concentrations in the aqueous phase ($\mu\text{mol/L}$) at equilibrium, f_{om} and f_{min} are the fractional masses of SOM (kg of SOM/ kg of solid) and mineral (kg of mineral/ kg of solid) for metal (hydr)oxide- and HA-coated sand, respectively, K_{om} is the organic-matter-normalized distribution coefficient (L/kg of SOM), and $K_{f,min}$ and n,min are Freundlich capacity coefficient ($(\mu\text{mol/kg of mineral})/(\mu\text{mol/L})^n$) and Freundlich exponent for the mineral component, respectively. Since the ability of mineral-bound HA to sorb NNOCs has been found to be affected by the nature of the complex between HA and the mineral surface (Murphy et al. 1990, 1992, 1994, Schlautman and Morgan 1993, Laor et al. 1998, Jones and Tiller 1999, Hur and Schlautman 2004, 2006, Wang and Xing 2005, Feng et al. 2006), the individual K_{om} values should be determined using Eq. 4.1 with sorption data from which the mineral contribution has been subtracted.

Since hydrophilic mineral surfaces are covered with a layer of chemically adsorbed water molecules overlain by layers of physically adsorbed water molecules (Drost-Hansen 1969, Adamson 1990, Schwarzenbach et al. 1993), NNOCs are sorbed

and enriched in the energetically homogeneous vicinal water region adjacent to the mineral surface, although the sorption is not localized at specific sorption sites on the mineral surfaces. Thus, sorption of NNOCs to hydrophilic mineral surfaces should exhibit linear isotherms since surface coverage is low and energy differences among sites are small due to the coated vicinal water region (Schwarzenbach et al. 1993, Huang et al. 1996, Weber and Huang 1996, Luthy et al. 1997, Mader et al. 1997, Su et al. 2006). For example, linear sorption of NNOCs to non-porous minerals, including α -Al₂O₃, α -Fe₂O₃, quartz, kaolinite, and amorphous SiO₂, from aqueous solution was observed at concentrations as high as 50 % of aqueous solubilities for several NNOCs (Huang et al. 1996, Mader et al. 1997, Su et al. 2006).

In the case where mineral sorption yields near-linear sorption behavior (i.e., $n_{min} \approx 1$), Eq. 4.1 can be further simplified into the composite linear sorption model as follows (McCarty et al. 1981, Karickhoff 1984):

$$\frac{C_s}{C_e} = K_d = f_{om} K_{om} + f_{min} K_{min} \quad (4.2)$$

where K_{min} is the distribution coefficient to the mineral component (L/kg of mineral). (note that Eq. 4.2 is only valid when negligible DOM is present in the aqueous solution and when K_{om} values from each sorption data in sorption isotherm are relatively constant). If only the organic and one mineral component are considered, the sum of f_{om} and f_{min} equals unity (i.e., $f_{om} + f_{min} = 1$). For a given mineral, K_{min} is the product of the specific surface area of the mineral component, S_A (m²/kg of mineral) and the surface-area-normalized distribution coefficient, K_S (L/m²) (Curtis et al. 1986, Huang et al. 1996).

Therefore, since $f_{oc}K_{oc} = f_{om}K_{om}$ and $K_{min} = S_A K_S$, Eq. 4.2 can be rewritten as follows:

$$K_d = f_{oc}K_{oc} + f_{min}S_A K_S \quad (4.3)$$

where K_{oc} is the organic carbon partitioning coefficient (L/kg of organic carbon). However, if sorption by partitioning into organic carbon becomes dominant such that the contribution of the mineral surface is negligible, the overall sorption can be described by the following well-known linear model based on simple hydrophobic partitioning into organic carbon (Chiou et al. 1979, Karickhoff 1984, Schwarzenbach and Westall 1981, Nguyen et al. 2005):

$$K_d = f_{om}K_{om} = f_{oc}K_{oc} \quad (4.4)$$

The contribution of the mineral fraction to overall sorption of NNOCs can be determined by plotting K_d values versus f_{oc} for the sorption of a NNOC to a series of model sorbents with different f_{oc} (Kishi et al. 1990, Paya-Perez et al. 1991, Rebhun et al. 1992, Shen and Jaffé 2000). In this case, K_d can be determined from the following modified linear model with an intercept:

$$K_d = f_{oc}K_{oc}^* + K_{min}^* \quad (4.5)$$

where K_{oc}^* (L/kg of organic carbon) is the slope of the linear regression of K_d plotted against f_{oc} , and K_{min}^* (L/kg of mineral) is the y-intercept at $f_{oc} = 0$. Whereas K_{oc} is the

organic carbon partitioning coefficient including the mineral sorption contribution, K_{oc}^* is the amended organic carbon partitioning coefficient without the mineral sorption contribution. Also, K_{min} is the distribution coefficient to the pure mineral surface, whereas K_{min}^* is the average distribution coefficient to the exposed mineral surface, representing the component of sorption attributed only to the mineral surface. Since K_{min}^* for aquifer solids with low f_{oc} has been found to be significantly greater than zero (Kishi et al. 1990, Paya-Perez et al. 1991, Rebhun et al. 1992, Shen and Jaffé 2000), K_{oc}^* can be determined by subtracting K_{min}^* from K_d .

The K_{oc} values for NNOCs on aquifer solids with low f_{oc} ($< 0.1\%$) have deviated significantly from predictions of K_{oc} based on empirical K_{oc} - K_{ow} relationships, and the K_{oc} values are widely divergent and tend to increase as f_{oc} decreases due to the mineral sorption contribution (Hassett et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Curtis et al. 1986, Murphy et al. 1990, Onken and Traina 1997). Thus, the K_{oc}^* values, representing hydrophobic partitioning of NNOCs to organic carbon without the mineral sorption contribution, are likely to be more accurate than the K_{oc} values in predicting the true hydrophobic partitioning of NNOCs to organic carbon.

The sorption of NNOCs to mineral surface without the organic carbon contribution cannot be directly determined from the results of the batch equilibrium sorption tests (BESTs) in this study, because the f_{oc} values for both metal (hydr)oxide-coated sands are still measurable (i.e., $f_{oc} \geq 0.005\%$). Thus, the sorption of NNOCs to pure mineral surface should be determined by using K_{min}^* in Eq. 4.5, assuming only minor, if any, blocking effect of mineral surfaces by mineral-bound HA due to the extremely low amount of HA covered (i.e., $f_{oc} \leq 0.044\%$). In this case, the K_d for the two-

component model can be written based on Eq. 4.5 as follows:

$$K_d = f_{oc} K_{oc}^* + f_{min} K_{min}^* = \underbrace{f_{oc} K_{oc}^*}_{\text{hydrophobic partitioning}} + \underbrace{(1 - R f_{oc}) K_{min}^*}_{\text{mineral adsorption}} \quad (4.6)$$

where R is the ratio of the fraction of organic matter to the fraction of organic carbon (i.e., $R = f_{om}/f_{oc}$). The available fractions of organic and mineral components can be regarded as unity since blocking of sorption to the mineral component by HA is likely negligible, and vice versa, due to low coverage of the mineral surface by HA (Murphy et al. 1990). Finally, the sorption models evaluated in this study are summarized in Table 4.1.

4.3.2 Critical Organic Fraction

McCarty et al. (1981) proposed the concept of a critical level of the f_{oc} , or f_{oc}^* , that represents the f_{oc} at which sorption to the organic and inorganic components is equal. Based on this concept, the organic component dominates sorption for sorbents with $f_{oc} > f_{oc}^*$, whereas the mineral component dominates sorption for sorbents with $f_{oc} < f_{oc}^*$. The expression for f_{oc}^* proposed by McCarty et al. (1981) depends on S_A and K_{ow} , as follows:

$$f_{oc}^* = \frac{S_A}{200(K_{ow})^{0.84}} \quad (4.7)$$

Predicted values of f_{oc}^* for different NNOCs based on Eq. 4.7 were reported by McCarty et al. (1981).

An alternative definition for f_{oc}^* can be proposed for the special case of the model

sorbents considered in the present study by equating the two terms on the right-hand-side of Eq. 4.6, and solving the resulting expression for f_{oc} ($=f_{oc}^*$) as follows:

$$f_{oc} = f_{oc}^* = \frac{K_{min}^*}{K_{oc}^* + RK_{min}^*} \quad (4.8)$$

Although apparently more applicable in the current study, the expression for f_{oc}^* given by Eq. 4.8 is limited because the available mineral surface area is a function of the fraction of the mineral surface that is covered by HA, or f_{om} , and is expected to be inversely related to f_{om} . Additionally, differences in the orientation and structure of the mineral-bound HA may affect the surface area of the organic phase and the accessibility of hydrophobic domains controlling the sorption of NNOCs.

4.4 RESULTS

4.4.1 Characterization of Model Sorbents

The physical and chemical characterization of the model sorbents are summarized in Table 4.2. Characterization of the sorbents involved measurements of the total organic carbon and the specific surface area. Detailed characterization procedures are described in Chapter 2. Additionally, the scanning electron microscope images of the model sorbents at two different magnifications (i.e., 400X and 7000X), the results of microchemical analyses using the scanning electron microscope equipped with energy-dispersive X-ray spectrometer, and the results of the microchemical analyses using a X-ray photoelectron spectroscopy for model sorbents are shown in Chapter 3.

The total organic carbon (TOC) of each sorbent was determined as the difference

between total carbon (TC) and total inorganic carbon (TIC). The f_{oc} values contributed by the adsorbed HA are low, ranging from 0.009 to 0.044 % for FEHAS and from 0.006 to 0.036 % for ALHAS. These low f_{oc} values are due to the low surface area of the model sorbents and the significant desorption of HA by increasing pH values (4.0 $\rightarrow$ 6.8) during the rinsing processes with HA-free 0.01 M NaCl.

As shown in Table 4.2, the surface areas for both metal (hydr)oxide-coated sands and metal (hydr)oxide- and HA- coated sands are close, although the specific surface area increases slightly with increasing f_{oc} . As f_{oc} increases, the exposed mineral surface area is expected to decrease, but new adsorption surfaces for N₂ become available within the matrix of the HA. Thus, the overall total surface area is a combination of these two opposing trends.

4.4.2 Sorption Rates of NNOCs to Sorbents

The kinetics for sorption of all six NNOCs at an initial aqueous concentration of 150 $\mu\text{mol/L}$ to FeO(OH)-coated sand, FHS ($f_{oc} = 0.006$ %), Al₂O₃-coated sand, ALS ($f_{oc} = 0.005$ %), FeO(OH) and HA -coated sand, FEHAS ($f_{oc} = 0.015$ %), and Al₂O₃- and HA- coated sand, ALHAS ($f_{oc} = 0.012$ %) was evaluated before performance of the BESTs. As shown in Fig. 4.1, the sorption for all six NNOCs to all sorbents approached equilibrium within 4 h. This relatively short (i.e., ≤ 4 h) equilibrium time was expected because (1) diffusion of the NNOCs across the aqueous boundary layer coating these sorbents is considered to be fast (Holmén and Gschwend 1997), (2) the surface diffusion to nonporous and nonaggregated sorbents is also fast (Huang et al. 1996), and (3) the SOM contents are extremely low (i.e., $f_{oc} \leq 0.016$ %). Thus, the mineral-bound HA is

readily accessible to NNOCs such that the associated sorption rates are relatively fast (i.e., ≤ 4 h). This finding is similar to other studies that have reported sorption equilibrium for various NNOCs to HA-mineral complexes in much less than 24 h (Murphy et al. 1990, 1992, 1994, Rebhun et al. 1992, Celis et al. 1997, Onken and Traina 1997, Laor et al. 1998, Jones and Tiller 1999, Shen and Jaffé 2000, Feng et al. 2006).

4.4.3 Sorption Isotherm Results

4.4.3.1 Sorption to Metal (hydr)oxide-coated Sand

The measured equilibrium sorption data and the fitted Freundlich and linear sorption models for the six individual NNOCs are shown in Figs. 4.2 and 4.3 for FES and in Figs. 4.4 and 4.5 for ALS, respectively. The resulting fitted parameter values are summarized in Table 4.3 for FES and in Table 4.4 for ALS. The sorption of all six NNOCs to FES is practically linear up to aqueous equilibrium concentrations (C_e) less than 70 % of NNOCs aqueous solubility (S_w) (i.e., $C_e/S_w < 0.7$), with values of the exponents (n) in the Freundlich sorption model ranging from 0.925 to 1.08. Similarly, the sorption of all six NNOCs to ALS is essentially linear for $C_e/S_w < 0.7$, with n values ranging from 0.905 to 1.02.

As previously reported (Schwarzenbach et al. 1993, Goss and Eisenreich 1996, Huang et al. 1996, Xing et al. 1996, Mader et al. 1997, Su et al. 2006), these weak and linear sorption results can be attributed to the lack of interaction between the NNOCs and surfaces of the metal (hydr)oxide-coated sands due to the coverage of mineral surfaces with an energetically homogeneous vicinal water region (Goss and Eisenreich 1996, Huang et al. 1996, Mader et al. 1997, Xing et al. 1996, Su et al. 2006). For example,

Huang et al. (1996) reported low and linear sorption of phenanthrene to nonporous α -Al₂O₃, quartz, kaolinite, and amorphous SiO₂ from aqueous solution. Mader et al. (1997) found the sorption isotherms for a series of polyaromatic hydrocarbons and chlorobenzenes from aqueous solution to α -Al₂O₃ and α -Fe₂O₃ to be linear to $C_e/S_w < 0.5$. Su et al. (2006) postulated that the reduced adsorptive forces of NNOCs (i.e., 1,2,3-trichlorobenzene, lindane, phenanthrene, and pyrene) with hydrophilic minerals due to physical separation by the water film and the low fractions of the water-film surface covered by NNOCs offer a theoretical basis for linear sorption, low exothermic heats, and no adsorptive competition.

Since the sorption of NNOCs to hydrophilic mineral surfaces has been found to be dependent primarily on the specific surface area of the mineral surfaces (Schwarzenbach et al. 1993, Schlautman and Morgan 1994, Goss and Eisenreich 1996, Mader et al. 1997), the surface-area-normalized distribution coefficient (K_S) values of NNOCs for hydrophilic mineral surfaces were calculated using the specific surface area based on N₂(g) adsorption for both FES and ALS. As shown in Tables 4.3 and 4.4 for FES and ALS, respectively, the K_S values for NNOCs are on the order of 10⁻⁴-10⁻⁵ L/m² and increase with increasing hydrophobicity (i.e., K_{ow}) of the NNOCs. The K_S values increase with increasing hydrophobicity of the NNOCs is expected because sorption of NNOCs to mineral surfaces is promoted by the hydrophobicity of the NNOCs due to the reduced entropy of the bulk water comprising the solvation envelope around the NNOCs (Schwarzenbach et al. 1993). However, the K_S values from this study are greater than K_S values for other NNOCs and sorbents reported in the literature (Schwarzenbach and Westall 1981, Mader et al. 1997). The differences in the K_S values can be attributed, in

part, to differences in solution chemistry, the types of mineral surfaces, and the experimental systems that can result in differences in the structures and volumes of ordered vicinal water (Schlautman and Morgan 1994).

4.4.3.2 Sorption to Metal (hydr)oxide- and HA-coated Sand

The equilibrium sorption data for all six NNOCs are shown together with the fitted Freundlich and linear isotherm models in Figs. 4.6 and 4.7, respectively, for FEHAS sorbents with different average f_{oc} values (i.e., 0.009, 0.015, and 0.041 %) and in Figs. 4.8 and 4.9, respectively, for ALHAS sorbents with different average f_{oc} values (i.e., 0.006, 0.012, and 0.032 %). The average sorption isotherm parameters for all six NNOCs resulting from fitting the measured sorption data with both Freundlich and linear sorption models, as well as the organic carbon partitioning coefficient (K_{oc}), the average f_{oc} , and the pH of aqueous solution at equilibrium, are summarized in Tables 4.5 and 4.6 for FEHAS and ALHAS, respectively.

As shown in Figs. 4.6 through 4.9, the sorption isotherms are essentially linear for both FEHAS ($0.898 \leq n \leq 1.02$) and ALHAS ($0.915 \leq n \leq 1.06$) at $C_e/S_w < 0.7$. Considering the low f_{oc} (≤ 0.044 %) of HA-mineral complexes evaluated in this study, and the negligible fractional coverage of HA over mineral surfaces, the nearly linear sorption behavior of the NNOCs is dominantly attributed to sorption to the energetically homogenous vicinal water region coated over the mineral surfaces.

As the number of sequences in the sequential HA adsorption tests increases, the values for the E_4/E_6 ratios of the HA remaining in the solution decrease gradually for both metal hydroxide-coated sands (see Chapter 3). Since the E_4/E_6 ratio decreases with

increasing aromaticity (Stevenson 1994), the decreases in E_4/E_6 ratios relative to original E_4/E_6 value of HA before adsorption indicate preferential adsorption of relatively aliphatic fractions from a mixture of HA molecules. These aliphatic fractions of HA behave as amorphous organic domains, and account for relatively linear sorption of NNOCs (Wang and Xing 2005, Hur and Schlautman 2006). Additionally, the mineral-bound HA evaluated in this study may have micelle-like structures allowing molecules of NNOCs to penetrate and be trapped in the hydrophobic cores (Engelbrecht and von Wandruszka 1994). Thus, sorption linearity also may be attributed to this partitioning-like behavior of NNOCs to mineral-bound HA for both FEHAS and ALHAS. Similar sorption linearity for sorption of NNOCs to HA-mineral complexes with low f_{oc} has been reported in a number of studies (Rebhun et al. 1992, Onken and Traina 1997, Shen and Jaffé 2000, Wang and Xing 2005, Feng et al. 2006, Hur and Schlautman 2006).

4.5 DISCUSSION

4.5.1 Relationship between K_S versus γ_w^{sat} , K_{ow} , and S_w of the NNOCs

The free energy of sorption of NNOCs to mineral surfaces as represented by K_S has been shown to be inversely related to the free energy of aqueous dissolution of NNOCs (Schwarzenbach et al. 1993, Mader et al. 1997). Accordingly, the log of the average K_S values based on the results for FES and ALS are plotted versus $\log \gamma_w^{sat}$ for the NNOCs in Figs. 4.10a and 4.11a, respectively, where γ_w^{sat} is the aqueous activity coefficient at saturation. As shown in Figs. 4.10a and 4.11a, a linear relationship between the log of the average K_S and $\log \gamma_w^{sat}$ for the NNOCs is apparent, indicating that the free energy of sorption for the NNOCs to both sorbents is inversely related to the free energy

of aqueous dissolution of NNOCs. Although the sorption of NNOCs to FES or ALS can be affected by factors other than the hydrophobicity of the NNOCs in aqueous solution, the use of linear free energy relationships to estimate K_S of NNOCs still appears to be feasible, which is consistent with other studies (Schwarzenbach et al. 1993, Mader et al. 1997). For example, as shown in Figs. 4.10b and 4.11b, the estimated K_S values for both sorbents based on either K_{ow} or S_w of the NNOCs are close ($r^2 = 0.919$) to the measured values.

In order to compare the relationship between K_S and γ_w^{sat} for different mineral surfaces, the log of the average K_S values for various sorbents is plotted versus $\log \gamma_w^{sat}$ for the NNOCs in Fig. 4.12. As shown in Fig. 4.12, the slope and y-intercept of linear regressions among different mineral surfaces are not identical and, therefore, appear to be mineral surface-specific. Therefore, two statistical analyses for a single or multiple factors were performed using the SAS software (SAS® 9.1, Cary, NC) to determine if the type of mineral surface is important in sorption of NNOCs. First, the analysis of variance (ANOVA) F -test was applied to test the null hypotheses H_0 that mean K_S values for different sorbents are equivalent (Ott and Longnecker 2001). Second, multiple comparison procedures (MCPs) were applied to distinguish any differences among mean K_S values for different sorbents evaluated in this study (Westfall et al. 1999) (see Appendix D).

The results of the ANOVA F -test from the SAS output are summarized in Table 4.7. If the value for F_0 , which represents the ratio of the mean square in variability between the sorbents to the mean square in variability within the sorbents, exceeds the critical value of F ($F_{0.05, v1, v2}$) for a given associated probability, α , of 0.05 and two

degrees of freedom, the null hypothesis H_0 of equality of mean K_S values among sorbents is rejected (Ott and Longnecker 2001). Since all the resulting F_0 values are greater than the corresponding $F_{0.05, v1, v2}$ values (see Table 4.7), the null hypothesis H_0 of equality of mean K_S values among sorbents is rejected at the 0.05 ($= \alpha$) level of statistical significance. Thus, at least one of the mean K_S values for the sorbents differs from those of the rest of the sorbents.

The results of the MCPs using the procedure proposed by Tukey (1953) are summarized in Table 4.8. Tukey's procedure for MCPs was designed specifically for pair-wise comparisons based on studentized range of K_S values to distinguish any differences among mean K_S values for four sorbents evaluated in this study. The level of significance represented by p -value is the probability of obtaining a value of the test statistic that is likely to reject H_0 (Ott and Longnecker 2001). Thus, if the p -value is less than α , H_0 is rejected. In contrast, if the p -value is greater than α , then H_0 can not be rejected. As shown in Table 4.8, the p -values among heated, uncoated, and FES sands and the p -values between FES and ALS (see the shaded area) are greater than α ($= 0.05$), whereas the p -values between ALS versus heated sand and uncoated sand are lower than α ($= 0.05$). As a result, the null hypothesis H_0 of equality of mean K_S values among sorbents is rejected at the 0.05 ($= \alpha$) level of statistical significance for between ALS versus both heated sand and uncoated sand.

Since hydrophillic mineral surfaces are completely covered with ordered vicinal water region, a vicinal water region levels out character and heterogeneity in the original mineral surfaces. In this scenario, the surface-area-normalized distribution coefficient (K_S) of a given NNOC should be the same on various mineral surfaces, and the

relationship between K_S and γ_w^{sat} for different mineral surfaces should be identical. However, in this study, the K_S values for a given NNOC are not identical for the various mineral surfaces and the linear relationship between K_S and γ_w^{sat} for different sorbents also is not identical at the 0.05 ($= \alpha$) level of statistical significance. These findings indicate that the type of mineral surface is also important and plays a role in the sorption of neutral NNOCs, although the sorption of NNOCs to mineral surfaces depends primarily on the surface area of the mineral surfaces.

Consistent with this study, Schlutman and Morgan (1994) also noted that the sorption of NNOCs to mineral surfaces depends primarily on the surface area of the mineral surfaces, and proposed that variations in sorption for different types of mineral surfaces are observed as the second-order effects. Goss and Eisenreich (1996) explained how the character of mineral surface influences sorption of NNOCs even when the mineral surface is covered by vicinal water region. Although the different mineral surfaces that are in equilibrium with water molecules must have the same surface free energy by definition, the relative contributions of different forces (i.e., hydrogen bonding, dispersion and dipole interactions) to the overall surface free energy may differ for different mineral surfaces. Similarly, the sorption of a given NNOC onto different mineral surfaces cannot necessarily be expected to be identical due to the different contributions of forces to the total free energy. Finally, Mader et al. (1997) postulated that surface area is an important variable, but noted that the intrinsic sorptive affinity of mineral surfaces also plays a role in the sorption of neutral NNOCs. Thus, they concluded that both γ_w^{sat} and the type of mineral surface are important.

4.5.2 Effect of mineral-bound HA on the sorption of NNOCs

The dependence of the measured K_d values for FEHAS and ALHAS on f_{oc} for the six NNOCs is shown explicitly in Figs. 4.13a and 4.13b, respectively. As f_{oc} increases from 0.006 % to 0.044 %, the K_d values of the three more hydrophobic NNOCs (i.e., 1,2,4-TCB, 1,4-DCB, and *m*-XYL) increase substantially, whereas the K_d values of the three less hydrophobic NNOCs (i.e., CB, TOL, and BZ) slightly increase as the f_{oc} increases. As expected, the greater the hydrophobicity of NNOCs, the greater the dependency of K_d on f_{oc} . These results indicate that mineral-bound HA still enhanced the sorption of NNOCs at f_{oc} values below the commonly cited threshold level of 0.1 %, which is consistent with the findings of other similar studies (Murphy et al. 1990, 1992, 1994, Rebhun et al. 1992, Onken and Traina 1997, Laor et al. 1998, Shen and Jaffé 2000, Wang and Xing 2005, Hur and Schlautman 2006).

4.5.3 Dependence of apparent K_{oc} values for NNOCs on f_{oc}

The apparent K_{oc} for FEHAS and for ALHAS were calculated from each K_d shown in Fig 4.13a and Fig. 4.13b, respectively, according to the relation given by Eq. 4.4 (i.e., $K_{oc} = K_d/f_{oc}$), and the resulting dependence of the apparent K_{oc} values for each NNOC on f_{oc} is shown in Figs. 4.14a and 4.14b for FEHAS and ALHAS, respectively. As f_{oc} increases, the apparent K_{oc} decreases initially significantly and subsequently more gradually. However, the apparent K_{oc} values are widely divergent for each NOC, which is consistent with other studies indicating significant differences between measured and predicted K_{oc} values for NNOCs on aquifer solids with low f_{oc} (< 0.1 %) based on empirical K_{oc} - K_{ow} relationships, due to the significant sorption to mineral surface (Hassett

et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Curtis et al. 1986, Murphy et al. 1990, Onken and Traina 1997). Thus, these results indicate that when f_{oc} is low (e.g., ≤ 0.044 % in this study), sorption of the NNOCs to the aquifer solids likely results from contributions of both mineral surfaces and mineral-bound HA.

4.5.4 Contributions of Mineral-Bound HA and Mineral Surfaces

Linear regressions of plots of K_d versus f_{oc} are shown in Figs. 4.15 and 4.16 for FEHAS and ALHAS, respectively, based on Model 1 and Model 2. A comparison of the coefficients of determination (r^2) for each NNOC based on these regressions indicates that Model 2 fits the data better than Model 1. Thus, in this study, predictions of K_d based on sorption to both HA and mineral surface (i.e., Model 2) appear to be more accurate than those based on only sorption to HA with zero intercept (i.e., Model 1). These observations suggest that, for sorbents with low f_{oc} (< 0.1 %), the contribution of mineral sorption is sufficiently important such that accurate estimates of K_d can be obtained only by determining and using K_{oc}^* and K_{min}^* (i.e., Model 2), as opposed to determining and using K_{oc} (i.e., Model 1). Because the sum of squared residuals ($SS_{residual}$) is greater than total sum of squares (SS_{total}) for some NNOCs based on the regression using Model 1, r^2 [$= (SS_{total} - SS_{residual})/SS_{total}$] is negative.

In addition, the results of the regressions using Model 2 allow for the determination of the amended organic carbon partitioning coefficient (K_{oc}^*) and the mineral-component sorption coefficient (K_{min}^*), respectively (Kishi et al. 1990, Rebhun et al. 1992, Shen and Jaffé 2000). Thus, the overall K_{oc} and K_{oc}^* values considering all sorbents together resulting from the regressions shown in Figs. 4.15 and 4.16 are

summarized in Tables 4.9 and 4.10 for FEHAS and ALHAS, respectively, along with the resulting K_{min}^* values. Similar to other studies (Kishi et al. 1990, Rebhun et al. 1992, Shen and Jaffé 2000), the overall K_{oc} values for all NNOCs are greater than the overall K_{oc}^* values due to the mineral sorption contribution. Thus, the overall K_{oc}^* values, representing hydrophobic partitioning of NNOCs to organic carbon without the mineral sorption contribution, are likely to be more accurate than the overall K_{oc} values in predicting the true hydrophobic partitioning of NNOCs to organic carbon.

The fractional contributions of mineral surfaces to overall sorption of six NNOCs as a function of f_{oc} can be estimated using Model 2 as shown in Figs. 4.17a and 4.17b for FEHAS and ALHAS, respectively. As shown in Figs. 4.17a and 4.17b, the fractional contributions of mineral surfaces to overall sorption are different among NNOCs at given $\log f_{oc}$ values ranging from -6 to -2. Also, the fractional contributions of mineral surfaces for NNOCs with high K_{ow} decrease faster than those for NNOCs with low K_{ow} as f_{oc} increases. These observations suggest that as the hydrophobicity of NNOCs increases, sorption to mineral-bound HA becomes increasingly more dominant such that the significance of the contribution of mineral surface consequently decreases at given $\log f_{oc}$ values ranging from -6 to -2. However, within f_{oc} ranges ($0.005 \% \leq f_{oc} \leq 0.044 \%$) evaluated in this study, the overall sorption for six NNOCs to both FEHAS and ALHAS should be determined by sorption to both mineral-bound HA and mineral surface, and the dominance of either contribution depends on the properties of sorbents (e.g., f_{oc}) and of NNOCs (e.g., K_{ow} and S_w).

4.5.5 Comparison of Models

Based on observation of a composite linear sorption behavior, with pure mineral-phase adsorption at $f_{oc} \approx 0$ represented by K_{min}^* , and the linear sorption at high f_{oc} (i.e., ≥ 0.1 %) given by $K_d = f_{oc}K_{oc}$, the two-component models using both K_{oc} and K_{min} (i.e., Models 1 and 3) and both K_{oc}^* and K_{min}^* (i.e., Models 2 and 4) were used to predict the sorption behavior over the entire range of f_{oc} values for both sorbents. All measured sorption data for six sorbates to each sorbent with different f_{oc} were compared with the predicted sorption behavior using four sorption models as shown in Figs. 4.18 and 4.19 for FEHAS and ALHAS, respectively. Although some of differences in r^2 values are virtually negligible, the agreement between predicted and measured distribution coefficients increases in the order of Model 3 < Model 1 < Model 2 = Model 4. Whereas Models 1 and 3 significantly overpredicts K_d for all the NNOCs and both sorbents, Models 2 and 4 predicts K_d fairly well ($r^2 \geq 0.978$). Thus, relatively accurate estimates of K_d can be obtained in this study only through the use of K_{oc}^* and K_{min}^* . These results indicate that amended contributions of mineral-bound HA and mineral surfaces should be considered to accurately predict the sorption of NNOCs to HA-mineral complexes with low f_{oc} .

Because the sum of squared residuals ($SS_{residual}$) is greater than total sum of squares (SS_{total}) for some NNOCs in Models 1 and 3, $r^2 [= (SS_{total} - SS_{residual})/SS_{total}]$ is negative. Thus, the method of maximum likelihood also was used to discriminate between sorption models for both sorbents. For each sorption model, the values of the log of the likelihood function (LLF) and the proportion of variance explained (PVE, equivalent to r^2) are summarized in Table 4.11 for FEHAS and Table 4.12 for ALHAS. Based on the values of LLF and PVE for each NNOC, both Model 2 and Model 4 provide

better agreement between the predicted and measured K_d values than Model 1 or Model 3. However, Model 2 and Model 4 have the identical LLF and PVE values for all NNOCs for both sorbents. Since the difference between Model 2 and Model 4 is the consideration of mineral fraction (f_{min}) and f_{min} values are close to unity due to low f_{oc} values, Model 4 does not improve the prediction of the measured K_d values for both sorbents. No statistical differences between the predictions based on Model 2 and Model 4 suggest that use of the more conventional sorption models (Models 2) provided as good agreement between predicted and measured K_d values as the more complicated, two-component model for sorption that takes into account mineral fraction (Model 4).

4.5.6 Effect of types of mineral surfaces on K_{oc}^* values

Experimental observations of K_{oc}^* (calculated after subtraction of mineral contribution) have been found to be influenced by the conformational and fractional changes of mineral-bound HA affecting the surface area of the organic phase and the accessibility of hydrophobic domains controlling the sorption of NNOCs (Murphy et al. 1990, 1992, 1994, Schlautman and Morgan 1993, Laor et al. 1998, Jones and Tiller 1999, Hur and Schlautman 2004, Wang and Xing 2005, Feng et al. 2006). Additionally, the K_{oc}^* values are affected by the source and other biogeochemical characteristics of mineral-bound SOM (Hur and Schlautman 2006). Therefore, the K_{oc}^* values from HA associated with FES and ALS were compared to evaluate the effect of the type of mineral surface on the ability of mineral-bound HA to sorb NNOCs.

As shown in Figs. 4.20a, the K_{oc}^* values obtained from FEHAS are not different at the 0.05 ($= \alpha$) level of statistical significance from those for ALHAS within the

NNOCs tested. Additionally, the ratio of K_{oc}^* from FEHAS to K_{oc}^* from ALHAS plotted with the hydrophobicity of NNOCs (i.e., K_{ow}) does not show any trend (see Fig. 4.20b). This result indicates similar mechanisms for adsorption of HA to both FES and ALS (i.e., ligand exchange with lower molecular weight fractions of HA + hydrophobic interaction with higher molecular weight fractions of HA) are likely to occur due to the similarities in density and reactivity of hydroxyl sites between FES and ALS. Also, conformational and fractional (i.e., molecular weight and specific functional groups) changes of mineral-bound HA could be similar between two mineral surfaces. Therefore, the surface area of the organic phase and the accessibility of hydrophobic domains controlling the sorption of NNOCs and the resulting K_{oc}^* values are not significantly different between the two mineral surfaces. However, since the conformational and fractional adsorption of HA have been found to be dependent on sources and nature of HA and types of mineral surface, and this complex nature in organic coating over aquifer solids subsequently complicates the fate and transport of NNOCs in the subsurface, further work is required to characterize the impact of the conformational and fractional adsorption of HA on changes in K_{oc}^* values as a function of (1) the source and biogeochemical characteristics of SOM, (2) the aqueous chemistry in the ground water, and (3) different types of mineral surfaces in aquifer solids.

4.5.7 Critical Organic Carbon Content

Values for the critical organic carbon content, f_{oc}^* , of the six NNOCs calculated using Eq. 4.8 are compared in Fig. 4.21 with calculated values of f_{oc}^* based on Eq. 4.7 from McCarty et al. (1981). The calculations were based on the S_A for FES of 1.194 m²/g

and for ALS of $1.123 \text{ m}^2/\text{g}$ (see Table 4.1), the R (i.e., $R = f_{om}/f_{oc}$) of 1.89, and the values for K_{ow} , K_{oc}^* , and K_{min}^* from Tables 2.4, 4.9, and 4.10. As shown in Fig. 4.21, the f_{oc}^* values based on Eq. 4.7 from McCarty et al. (1981) are from about one to two orders-of-magnitude lower than the f_{oc}^* values for both FEHAS and ALHAS. These differences in f_{oc}^* may result, in part, from the assumptions inherent in the derivation of Eq. 4.7.

For example, McCarty et al. (1981) used the empirical relationship, $K_{oc} = 0.63K_{ow}$, reported by Karickhoff et al. (1979) for a variety of NNOCs. However, many experimental and K_{ow} -derived K_{oc} values for NNOCs reported in the literature fail to explain variations in the structure and composition of SOM (Garbarini and Lion 1986, Grathwohl 1990, Rutherford et al. 1992, Kile et al. 1995). Furthermore, separate correlations between K_{oc} and K_{ow} for individual classes of NNOCs based on molecular structure (e.g., apolar, monopolar, and bipolar NNOCs) are required for more accurate estimation of K_{oc} (Schwarzenbach et al. 1993, Allen-King et al. 2002, Nguyen et al. 2005). As a result, estimates of f_{oc}^* based on the simple relationship of $K_{oc} = 0.63K_{ow}$ instead of class- and SOM-specific linear free energy relationships may not be accurate.

Finally, in developing Eq. 4.7, McCarty et al. (1981) used an expression derived from the free-energy relationship to approximate sorption by silica surfaces. However, since the surface area, pore geometry, and intrinsic sorptive affinity of mineral surfaces have since been shown to play a significant role in the sorption of NNOCs (Huang et al. 1996, Mader et al. 1997), the discrepancy between f_{oc}^* values based on Eq. 4.7 versus those based on the results of this study also may be due, in part, to differences in the pore geometry and intrinsic sorptive affinity of the mineral surfaces with the NNOCs with different molecular sizes and shapes.

4.6 SUMMARY AND CONCLUSIONS

The roles of mineral-bound HA and mineral surface in the sorption of six nonpolar neutral organic compounds (1,2,4-trichlorobenzene, 1,4-dichlorobenzene, chlorobenzene, *m*-xylene, toluene, benzene) to HA-mineral complexes with low fractions of organic carbon (f_{oc}) ranging from 0.006 to 0.044 % were investigated by using well-characterized mineral surfaces [i.e., FeOOH- or Al₂O₃- coated sands], reference HA, and solution with constant pH and ionic strength. Sorption of all six sorbates to both metal (hydr)oxide-coated sands was nearly linear due to the coverage of mineral surfaces with an energetically homogeneous vicinal water region. Although the sorption of sorbates to mineral surfaces depends primarily on the surface area of the mineral surfaces, the type of mineral surface is also important and plays a role in the sorption of sorbates. Sorption of all six sorbates to HA-mineral complexes was also essentially linear, and resulted from a combination of sorption to both mineral-bound HA and the mineral surface, with the dominance of either contribution depending on the properties of the sorbents (e.g., f_{oc}) and the sorbates (e.g., K_{ow}). The reactivity of mineral-bound HA to the sorbates (i.e., K_{oc}^*) were not significantly different between two mineral surfaces, indicating that the conformational and fractional (i.e., molecular weight and specific functional groups) changes of mineral-bound HA could be similar between two mineral surfaces. Finally, the amended contributions of mineral-bound HA and mineral surfaces should be considered to accurately predict the sorption of sorbates to HA-mineral complexes with low f_{oc} . The conventional sorption models considering the contributions of both mineral-bound HA and the mineral surface (i.e., Model 2) provided as good agreement between

predicted and measured distribution coefficients as the more complicated, two-component model for sorption that takes into account mineral fraction (i.e., Model 4).

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Table 4.1 Sorption models evaluated in this study.

Sorption Model	Equation	References
Model 1	$K_d = f_{om} K_{om} = f_{oc} K_{oc}$	Chiou et al. (1979), Schwarzenbach and Westall (1981), Karickhoff (1984), Nguyen et al. (2005)
Model 2	$K_d = f_{oc} K_{oc}^* + K_{min}^*$	Kishi et al. (1990), Rebhun et al. (1992), Shen and Jaffé (2000)
Model 3	$K_d = f_{oc} K_{oc} + (1 - R f_{oc}) K_{min}$	Karickhoff (1984), Curtis et al. (1986)
Model 4	$K_d = f_{oc} K_{oc}^* + (1 - R f_{oc}) K_{min}^*$	This study

- f_{oc} = fractional mass of organic carbon (kg of organic carbon/kg of solid);
 f_{om} = fractional mass of soil organic matter (kg of SOM/kg of solid);
 K_d = mass-averaged distribution coefficient for the summed linear components (L/kg of solid);
 K_{min} = apparent distribution coefficient to the mineral component (L/kg of mineral);
 K_{min}^* = amended distribution coefficient to the exposed mineral surface, representing the component of sorption attributed only to the mineral surface (L/kg of mineral);
 K_{oc} = apparent organic carbon partitioning coefficient (L/kg of organic carbon);
 K_{oc}^* = amended organic carbon partitioning coefficient without the mineral sorption contribution (L/kg of organic carbon);
 K_{om} = organic-matter-normalized distribution coefficient (L/kg of SOM);
 R = f_{om}/f_{oc} (> 1).

Table 4.2 Physical and chemical properties of model sorbents.

Model sorbent		Carbon content ^a (%)			BET ^b surface area using N ₂ (m ² /g)
Type	No.	Replicate	Organic	Inorganic	
Iron (hydr)oxide-coated	1	1	0.006	<0.005	1.194
		2	0.005	<0.005	
		3	0.007	<0.005	
		Average	0.006	<0.005	
Iron (hydr)oxide- and HA- coated	2	1	0.009	<0.005	1.161
		2	0.008	<0.005	
		3	0.010	<0.005	
		Average	0.009	<0.005	
	3	1	0.014	<0.005	1.190
		2	0.015	<0.005	
		3	0.016	<0.005	
		Average	0.015	<0.005	
	4	1	0.038	<0.005	1.321
		2	0.041	<0.005	
		3	0.044	<0.005	
		Average	0.041	<0.005	
Aluminum (hydr)oxide-coated	5	1	0.005	<0.005	1.123
		2	0.005	<0.005	
		3	0.006	<0.005	
		Average	0.005	<0.005	
Aluminum (hydr)oxide- and HA- coated	6	1	0.006	<0.005	1.116
		2	0.007	<0.005	
		3	0.006	<0.005	
		Average	0.006	<0.005	
	7	1	0.012	<0.005	1.793
		2	0.014	<0.005	
		3	0.011	<0.005	
		Average	0.012	<0.005	
	8	1	0.027	<0.005	1.356
		2	0.032	<0.005	
		3	0.036	<0.005	
		Average	0.032	<0.005	

^aMeasured by Huffman Laboratories, Golden, CO^bMeasured by Porous Materials Inc., Ithaca, NY

Table 4.3 Parameter values (average $\pm$ standard deviation) from fitting Freundlich and liner sorption models to measured sorption data for six individual NNOC and FeO(OH)-coated sand.

Compound	Freundlich Model ^a		Linear Model ^a		pH	
	Freundlich Capacity Coefficient, $K_f (\mu\text{mol/kg})/(\mu\text{mol/L})^n$	Freundlich Exponent, n	Distribution Coefficient, $K_d (\text{L/kg})$	Surface-Area-Normalized Distribution Coefficient, K_s^b ($\times 10^{-5} \text{ L/m}^2$)	Range	Average
1,2,4-trichlorobenzene	0.174 ± 0.023	1.005 ± 0.030	0.177 ± 0.009	14.8 ± 0.758	6.4 – 6.8	6.6
1,4-dichlorobenzene	0.124 ± 0.036	1.036 ± 0.054	0.143 ± 0.009	11.9 ± 0.777	6.2 – 6.5	6.4
chlorobenzene	0.124 ± 0.022	0.967 ± 0.021	0.105 ± 0.010	8.81 ± 0.806	6.5 – 6.7	6.6
<i>m</i> -xylene	0.128 ± 0.031	0.988 ± 0.033	0.119 ± 0.010	9.95 ± 0.838	6.3 – 6.4	6.4
toluene	0.105 ± 0.023	0.986 ± 0.054	0.097 ± 0.004	8.14 ± 0.330	6.1 – 6.6	6.4
benzene	0.116 ± 0.024	0.955 ± 0.027	0.093 ± 0.008	7.76 ± 0.678	6.1 – 6.7	6.5

^a Number of observations = 3

^b $K_s = K_d/S_A$ and $S_A = 1.194 \text{ m}^2/\text{g}$ from Table 4.2

Table 4.4 Parameter values (average $\pm$ standard deviation) from fitting Freundlich and liner sorption models to measured sorption data for six individual NNOC and Al₂O₃-coated sand.

Compound	Freundlich Model ^a		Linear Model ^a		pH	
	Freundlich Capacity Coefficient, $K_f (\mu\text{mol/kg})/(\mu\text{mol/L})^n$	Freundlich Exponent, n	Distribution Coefficient, $K_d (\text{L/kg})$	Surface-Area-Normalized Distribution Coefficient, K_s^b ($\times 10^{-5} \text{ L/m}^2$)	Range	Average
1,2,4-trichlorobenzene	0.210 ± 0.054	0.966 ± 0.052	0.176 ± 0.008	15.7 ± 0.748	6.2 – 6.6	6.3
1,4-dichlorobenzene	0.168 ± 0.035	0.967 ± 0.037	0.142 ± 0.008	12.6 ± 0.687	6.4 – 6.6	6.5
chlorobenzene	0.159 ± 0.025	0.945 ± 0.051	0.122 ± 0.012	10.9 ± 1.062	6.7 – 6.8	6.7
<i>m</i> -xylene	0.148 ± 0.025	0.980 ± 0.040	0.133 ± 0.003	11.9 ± 0.238	6.4 – 6.6	6.5
toluene	0.143 ± 0.015	0.954 ± 0.018	0.115 ± 0.003	10.3 ± 0.309	6.5 – 6.6	6.6
benzene	0.127 ± 0.036	0.962 ± 0.035	0.104 ± 0.011	9.27 ± 1.006	6.1 – 6.5	6.4

^a Number of observations = 3

^b $K_s = K_d/S_A$ and $S_A = 1.123 \text{ m}^2/\text{g}$ from Table 4.2

Table 4.5 Parameter values (average $\pm$ standard deviation) from fitting Freundlich and liner sorption models to measured sorption data for six individual NNOC and FeO(OH)- and HA- coated sand with different f_{oc} .

Compound	Average Organic Carbon Content, f_{oc}	Linear Model ^a		Freundlich Model ^a		pH	
		Distribution Coefficient, K_d (L/kg)	Organic Carbon Partitioning Coefficient, K_{oc} (L/kg) ^b	Freundlich Capacity Coefficient, K_f ($\mu\text{mol/kg}/(\mu\text{mol/L})^n$)	Freundlich Exponent, n	Range	Average
1,2,4-trichloro benzene	0.00009	0.181 $\pm$ 0.003	2029 $\pm$ 192	0.289 $\pm$ 0.046	0.899 $\pm$ 0.033	6.2 – 6.4	6.3
	0.00015	0.242 $\pm$ 0.014	1618 $\pm$ 17.5	0.233 $\pm$ 0.129	1.029 $\pm$ 0.103	6.2 – 6.5	6.3
	0.00041	0.576 $\pm$ 0.018	1409 $\pm$ 68.8	0.523 $\pm$ 0.135	1.027 $\pm$ 0.062	6.3 – 6.8	6.5
1,4-dichloro benzene	0.00009	0.142 $\pm$ 0.002	1596 $\pm$ 160	0.227 $\pm$ 0.031	0.901 $\pm$ 0.030	6.2 – 6.4	6.3
	0.00015	0.175 $\pm$ 0.006	1169 $\pm$ 42.5	0.252 $\pm$ 0.064	0.926 $\pm$ 0.062	6.2 – 6.4	6.4
	0.00041	0.350 $\pm$ 0.006	857 $\pm$ 49.7	0.404 $\pm$ 0.079	0.971 $\pm$ 0.050	6.4 – 6.8	6.5
chlorobenzene	0.00009	0.109 $\pm$ 0.007	1214 $\pm$ 60.8	0.111 $\pm$ 0.051	1.023 $\pm$ 0.099	6.2 – 6.6	6.5
	0.00015	0.118 $\pm$ 0.004	786 $\pm$ 27.6	0.151 $\pm$ 0.028	0.948 $\pm$ 0.045	6.5 – 6.7	6.5
	0.00041	0.206 $\pm$ 0.007	504 $\pm$ 19.5	0.218 $\pm$ 0.039	0.989 $\pm$ 0.032	6.2 – 6.7	6.4
<i>m</i> -xylene	0.00009	0.121 $\pm$ 0.005	1357 $\pm$ 112	0.134 $\pm$ 0.029	0.981 $\pm$ 0.040	6.1 – 6.2	6.2
	0.00015	0.143 $\pm$ 0.004	955 $\pm$ 34.8	0.148 $\pm$ 0.038	0.996 $\pm$ 0.061	6.2 – 6.6	6.4
	0.00041	0.261 $\pm$ 0.024	636 $\pm$ 25.0	0.400 $\pm$ 0.149	0.913 $\pm$ 0.099	6.1 – 6.7	6.4
toluene	0.00009	0.098 $\pm$ 0.001	1095 $\pm$ 114	0.117 $\pm$ 0.024	0.964 $\pm$ 0.045	6.3 – 6.5	6.4
	0.00015	0.110 $\pm$ 0.005	732 $\pm$ 17.4	0.126 $\pm$ 0.020	0.972 $\pm$ 0.033	6.2 – 6.5	6.3
	0.00041	0.197 $\pm$ 0.011	481 $\pm$ 9.81	0.222 $\pm$ 0.099	0.993 $\pm$ 0.133	6.4 – 6.7	6.5
benzene	0.00009	0.093 $\pm$ 0.004	1045 $\pm$ 74.4	0.127 $\pm$ 0.009	0.934 $\pm$ 0.021	6.2 – 6.6	6.3
	0.00015	0.103 $\pm$ 0.002	687 $\pm$ 31.9	0.151 $\pm$ 0.056	0.928 $\pm$ 0.098	6.2 – 6.5	6.4
	0.00041	0.162 $\pm$ 0.013	397 $\pm$ 24.8	0.204 $\pm$ 0.059	0.956 $\pm$ 0.065	6.4 – 6.6	6.5

^a Number of observations = 3

^b $K_{oc} = K_d/f_{oc}$

Table 4.6 Parameter values (average $\pm$ standard deviation) from fitting Freundlich and liner sorption models to measured sorption data for six individual NNOC and Al₂O₃- and HA- coated sand with different f_{oc} .

Compound	Average Organic Carbon Content, f_{oc}	Linear Model ^a		Freundlich Model ^a		pH	
		Distribution Coefficient, K_d (L/kg)	Organic Carbon Partitioning Coefficient, K_{oc} (L/kg) ^b	Freundlich Capacity Coefficient, K_f ($\mu\text{mol/kg}/(\mu\text{mol/L})^n$)	Freundlich Exponent, n	Range	Average
1,2,4-trichloro benzene	0.00006	0.176 $\pm$ 0.006	2796 $\pm$ 190	0.190 $\pm$ 0.098	1.004 $\pm$ 0.113	6.2 – 6.3	6.3
	0.00012	0.224 $\pm$ 0.010	1830 $\pm$ 145	0.256 $\pm$ 0.067	0.976 $\pm$ 0.074	6.4 – 6.6	6.5
	0.00032	0.519 $\pm$ 0.021	1659 $\pm$ 223	0.423 $\pm$ 0.173	1.06 $\pm$ 0.100	6.2 – 6.5	6.4
1,4-dichloro benzene	0.00006	0.146 $\pm$ 0.003	2321 $\pm$ 164	0.179 $\pm$ 0.005	0.957 $\pm$ 0.004	6.3 – 6.5	6.3
	0.00012	0.171 $\pm$ 0.004	1401 $\pm$ 133	0.152 $\pm$ 0.027	1.028 $\pm$ 0.043	6.3 – 6.5	6.3
	0.00032	0.341 $\pm$ 0.039	1081 $\pm$ 40.5	0.568 $\pm$ 0.292	0.909 $\pm$ 0.160	6.4 – 6.7	6.6
chlorobenzene	0.00006	0.122 $\pm$ 0.003	1933 $\pm$ 130	0.154 $\pm$ 0.030	0.952 $\pm$ 0.045	6.1 – 6.4	6.2
	0.00012	0.133 $\pm$ 0.003	1087 $\pm$ 108	0.166 $\pm$ 0.035	0.956 $\pm$ 0.049	6.3 – 6.6	6.4
	0.00032	0.191 $\pm$ 0.009	610 $\pm$ 72.4	0.179 $\pm$ 0.096	1.04 $\pm$ 0.147	6.2 – 6.7	6.4
<i>m</i> -xylene	0.00006	0.133 $\pm$ 0.005	2104 $\pm$ 134	0.172 $\pm$ 0.043	0.952 $\pm$ 0.058	6.2 – 6.5	6.4
	0.00012	0.149 $\pm$ 0.004	1222 $\pm$ 119	0.140 $\pm$ 0.055	1.026 $\pm$ 0.089	6.2 – 6.5	6.3
	0.00032	0.258 $\pm$ 0.010	824 $\pm$ 98.8	0.356 $\pm$ 0.038	0.928 $\pm$ 0.021	6.3 – 6.4	6.4
toluene	0.00006	0.115 $\pm$ 0.006	1828 $\pm$ 111	0.151 $\pm$ 0.021	0.942 $\pm$ 0.041	6.3 – 6.6	6.4
	0.00012	0.124 $\pm$ 0.004	1017 $\pm$ 95.5	0.136 $\pm$ 0.020	0.983 $\pm$ 0.036	6.3 – 6.5	6.4
	0.00032	0.182 $\pm$ 0.014	579 $\pm$ 39.2	0.277 $\pm$ 0.073	0.912 $\pm$ 0.080	6.1 – 6.4	6.2
benzene	0.00006	0.104 $\pm$ 0.003	1650 $\pm$ 99.4	0.130 $\pm$ 0.020	0.953 $\pm$ 0.032	6.3 – 6.6	6.4
	0.00012	0.113 $\pm$ 0.004	924 $\pm$ 82.3	0.133 $\pm$ 0.027	0.968 $\pm$ 0.049	6.3 – 6.4	6.3
	0.00032	0.158 $\pm$ 0.006	503 $\pm$ 55.6	0.194 $\pm$ 0.156	1.01 $\pm$ 0.198	6.1 – 6.6	6.4

^a Number of observations = 3

^b $K_{oc} = K_d/f_{oc}$

Table 4.7 Results of the analysis of variance (ANOVA) for a single or multiple factors using statistical software (SAS® 9.1, Cary, NC)

Model	Source of Variation	Degree of Freedom	Sum of Squares	Mean Square	F_0 value ^a	$F_{0.05,v1,v2}$ ^b	p -value ^c	Conclusion
$\log K_d = f(\log \gamma_w^{sat})$	Between sorbents	1	0.068	0.068	17.65	4.30	0.0004	Reject H_0 ^d
	Within sorbents	22	0.086	0.0039				
	Total	23	0.154					
$\log K_d = f(\log \gamma_w^{sat}, \text{sorbents})$	Between sorbents	4	0.122	0.031	17.93	2.90	< 0.0001	Reject H_0
	Within sorbents	19	0.032	0.0017				
	Total	23	0.154					
$\log K_d = f(\log \gamma_w^{sat}, \text{sorbents}, \log \gamma_w^{sat} \times \text{sorbents})$	Between sorbents	7	0.144	0.021	33.83	2.66	< 0.0001	Reject H_0
	Within sorbents	16	0.010	0.0006				
	Total	23	0.154					

^a F_0 value = mean square between NNOCs/mean square within NNOCs.

^b $F_{0.05,v1,v2}$ value = the critical value of F from Ott and Longnecker (2001) for $\alpha = 0.05$ and two different degree of freedom.

If $F_{0.05,v1,v2}$ value < F_0 value, then reject H_0 .

^cLevel of significance. If the p -value $\leq \alpha$ ($=0.05$), then reject H_0 .

^dNull hypothesis H_0 = mean ψ values for all six NNOCs are equivalent

Table 4.8 The multiple-comparison output using Tukey's procedure in statistical software (SAS® 9.1, Cary, NC)

<i>p</i> -value ^a for $H_0 : \text{LSM}^b \psi (i) = \text{LSM} \psi (j)$				
i/j (<i>p</i>-value)	Heated	Uncoated	Fe(OH) ₃ -coated	Al(OH) ₃ -coated
Heated		0.9992	0.2139	0.0007
Uncoated	0.9992		0.1723	0.0006
FeO(OH)-coated	0.2139	0.1723		0.0590
Al ₂ O ₃ -coated	0.0007	0.0006	0.0590	

^aLevel of significance. If the *p*-value $\leq \alpha$ (=0.05), then reject H_0 .

^bLeast squares means

Table 4.9 Organic-carbon and mineral-component distribution coefficients for sorption of six NNOCs to FeO(OH)- and HA- coated sand with different f_{oc} .

Compound	Linear Regression with zero Intercept		Linear Regression with Intercept		
	K_{oc}^a (L/kg)	r^2	K_{oc}^{*b} (L/kg)	K_{min}^{*c} (L/kg)	r^2
1,2,4-trichlorobenzene	1477	0.889	1182.6	0.084	0.988
1,4-dichlorobenzene	942.9	0.544	617.8	0.093	0.984
chlorobenzene	583.6	-0.447	299.1	0.081	0.977
<i>m</i> -xylene	724.0	0.192	424.2	0.086	0.981
toluene	552.4	-0.140	299.9	0.072	0.982
benzene	472.7	-1.64	206.4	0.076	0.976

^a Overall organic carbon partitioning coefficient from Fig. 4.15a

^b Overall amended organic carbon partitioning coefficient from Fig. 4.15b

^c Y-intercept at $f_{oc}=0$ from Fig. 4.15b

Table 4.10 Organic-carbon and mineral-component distribution coefficients for sorption of six NNOCs to Al₂O₃- and HA- coated sand with different f_{oc} .

Compound	Linear Regression with zero Intercept		Linear Regression with Intercept		
	K_{oc}^a (L/kg)	r^2	K_{oc}^{*b} (L/kg)	K_{min}^{*c} (L/kg)	r^2
1,2,4-trichlorobenzene	1717	0.800	1298	0.093	0.960
1,4-dichlorobenzene	1189	0.522	771.4	0.093	0.982
chlorobenzene	737.8	-3.92	264.2	0.105	0.946
<i>m</i> -xylene	935.6	-0.462	477.0	0.102	0.967
toluene	702.4	-3.37	263.2	0.098	0.978
benzene	615.8	-4.95	207.4	0.091	0.951

^a Overall organic carbon partitioning coefficient from Fig. 4.16a

^b Overall amended organic carbon partitioning coefficient from Fig. 4.16b

^c Y-intercept at $f_{oc}=0$ from Fig. 4.16b

Table 4.11 Comparison of model representations of experimental data for FeO(OH)- and HA- coated sand with different f_{oc} using the log of the likelihood function (LLF) and proportion of variance explained (PVE).

Model	1,2,4-TCB		1,4-DCB		CB		<i>m</i> -XYL		TOL		BZ	
	LLF ^a	PVE ^b	LLF	PVE	LLF	PVE	LLF	PVE	LLF	PVE	LLF	PVE
Model 1	23.2	0.882	22.8	0.557	24.5	0	23.7	0.223	26.6	0	25.9	0
Model 2	32.0	0.964	42.9	0.970	48.8	0.946	43.3	0.943	55.6	0.976	55.2	0.949
Model 3	5.79	0	10.4	0	16.0	0	13.7	0	16.7	0	17.5	0
Model 4	32.1	0.964	42.9	0.970	48.8	0.946	43.3	0.943	55.6	0.976	55.2	0.949

^a Estimate the log of the likelihood function using SAS (GENMOD Procedure)

^b Equivalent to the r^2 and negative r^2 is treated as $r^2 = 0$

Table 4.12 Comparison of model representations of experimental data for Al_2O_3 - and HA- coated sand with different f_{oc} using the log of the likelihood function (LLF) and proportion of variance explained (PVE).

Model	1,2,4-TCB		1,4-DCB		CB		<i>m</i> -XYL		TOL		BZ	
	LLF ^a	PVE ^b	LLF	PVE	LLF	PVE	LLF	PVE	LLF	PVE	LLF	PVE
Model 1	20.7	0.784	22.8	0.575	21.3	0	21.7	0	22.4	0	23.5	0
Model 2	30.0	0.938	41.7	0.966	53.8	0.942	48.2	0.962	49.0	0.876	58.7	0.949
Model 3	5.68	0	10.3	0	13.0	0	11.6	0	13.2	0	15.3	0
Model 4	30.0	0.938	41.7	0.966	53.8	0.942	48.2	0.962	49.0	0.876	58.7	0.949

^a Estimate the log of the likelihood function using SAS (GENMOD Procedure)

^b Equivalent to the r^2 and negative r^2 is treated as $r^2 = 0$

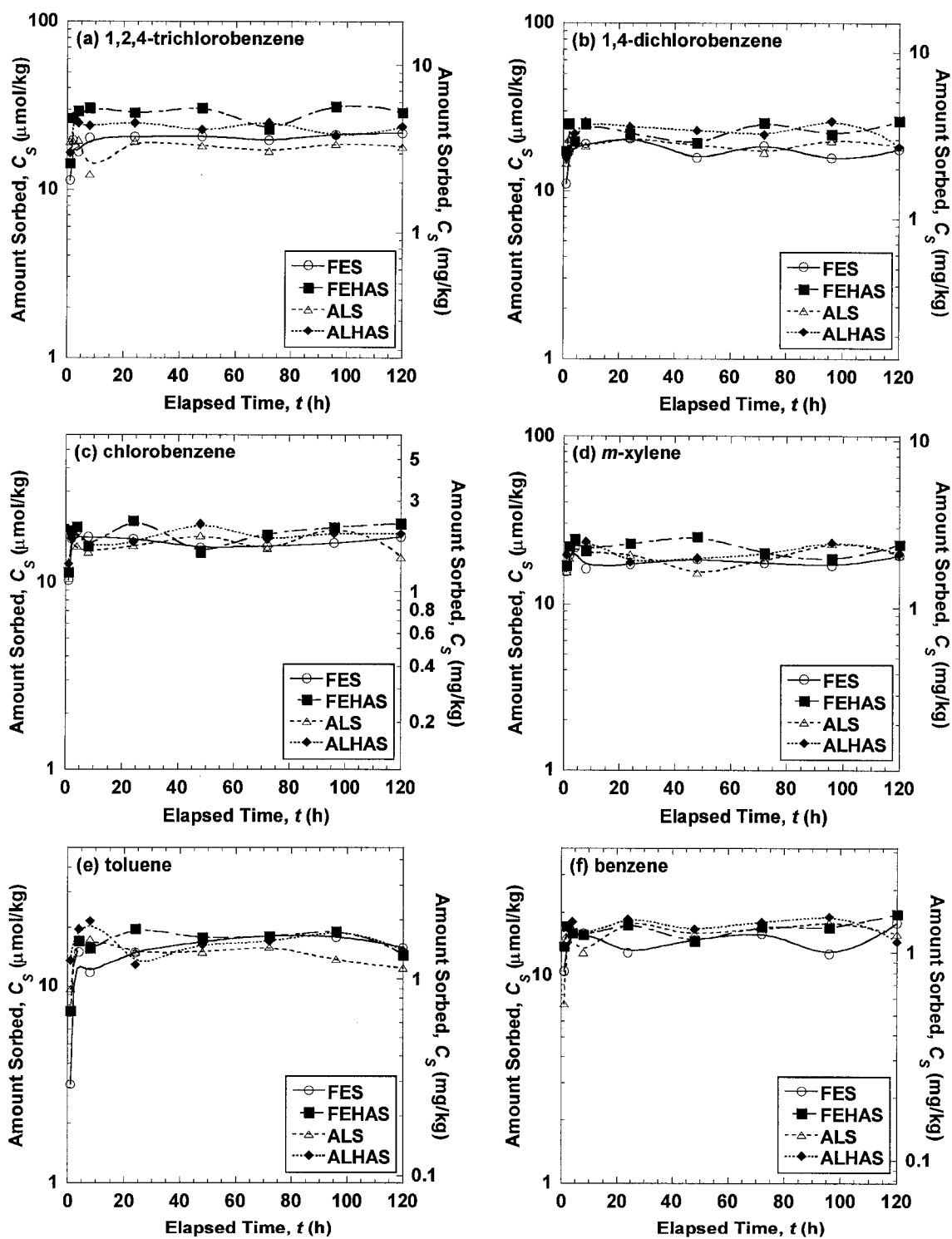


Fig. 4.1 Sorption kinetics for six NNOCs to FeO(OH)-coated, FES ($f_{oc} = 0.006\%$), Al_2O_3 -coated, ALS ($f_{oc} = 0.005\%$), FeO(OH)- and HA-coated, FEHAS ($f_{oc} = 0.015\%$), and Al_2O_3 - and HA-coated, ALHAS ($f_{oc} = 0.012\%$) sands at initial aqueous concentration of $150\ \mu\text{mol/L}$.

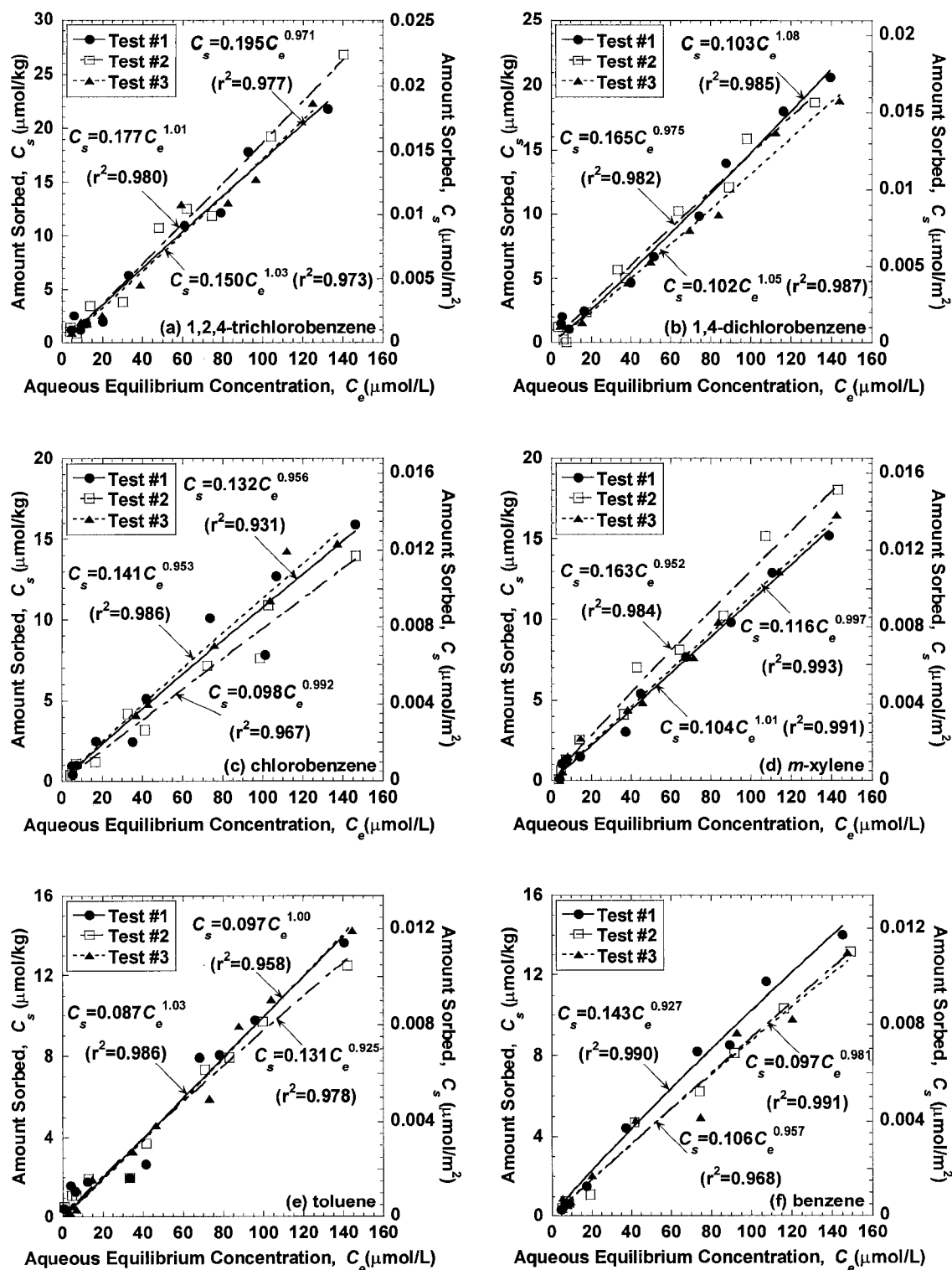


Fig. 4.2 Measured and nonlinearly fitted sorption data for six individual NNOCs and FeO(OH)-coated sand ($f_{oc} = 0.006\%$).

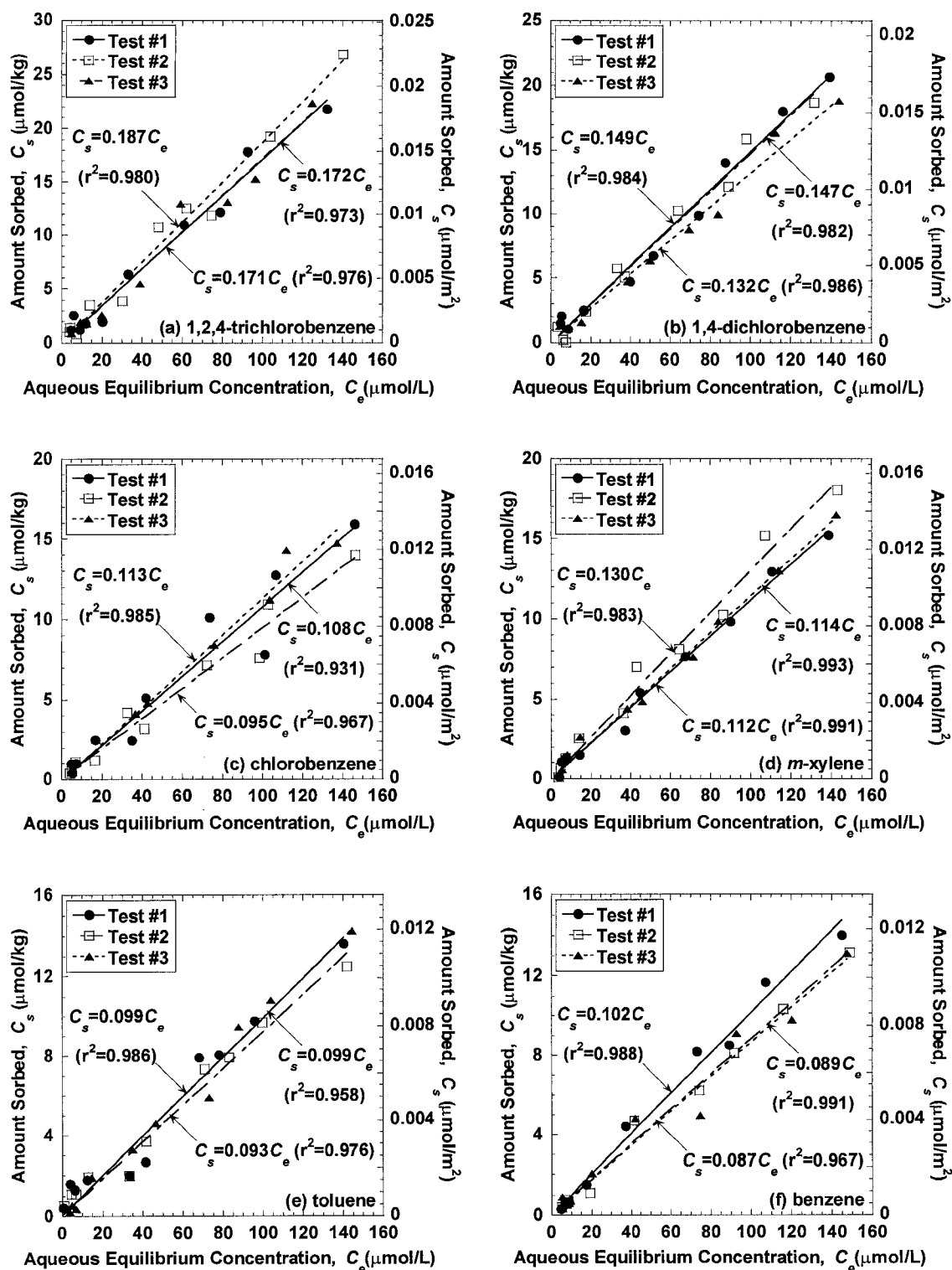


Fig. 4.3 Measured and linearly fitted sorption data for six individual NNOCs and FeO(OH)-coated sand ($f_{oc} = 0.006\%$).

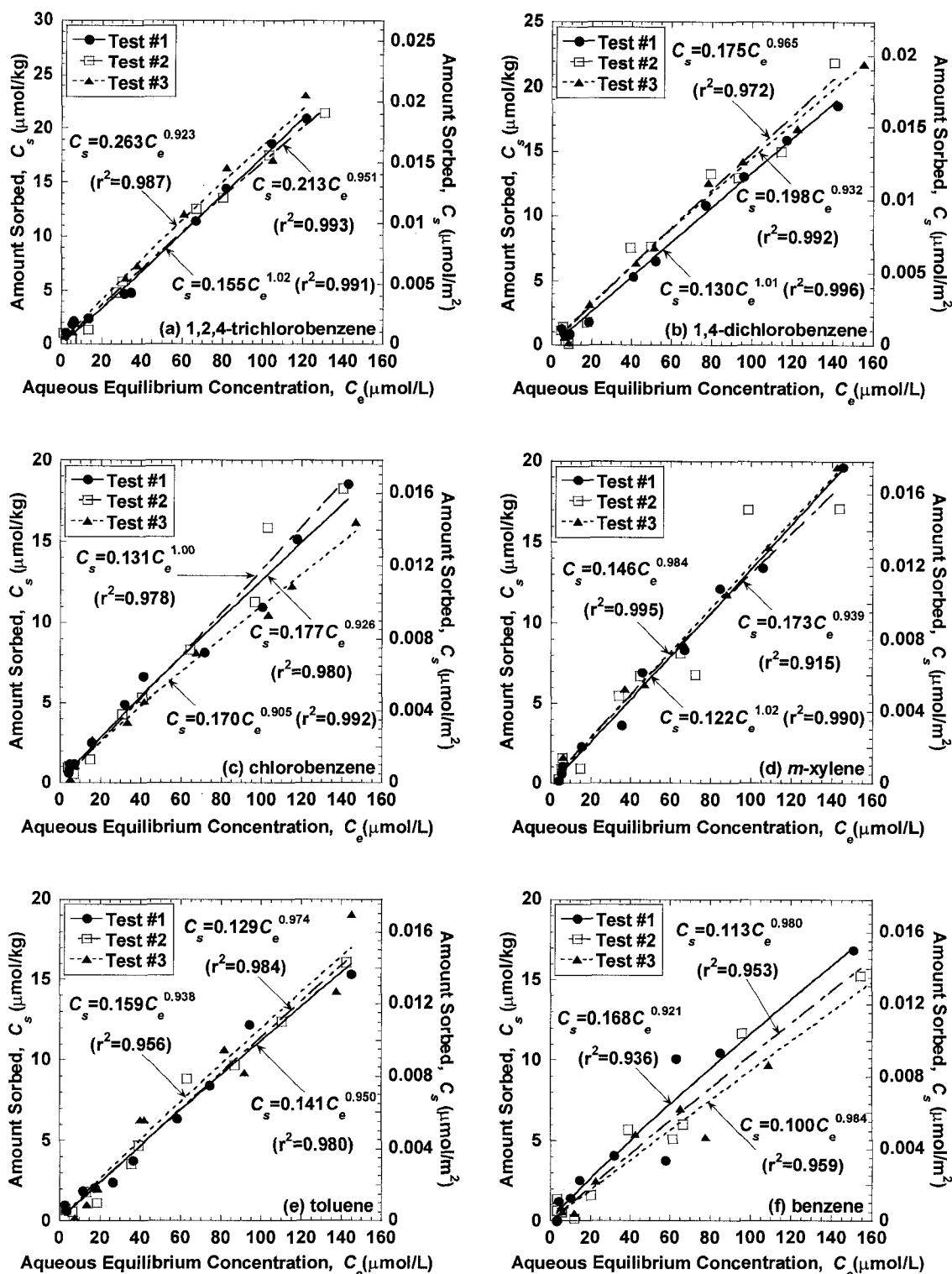


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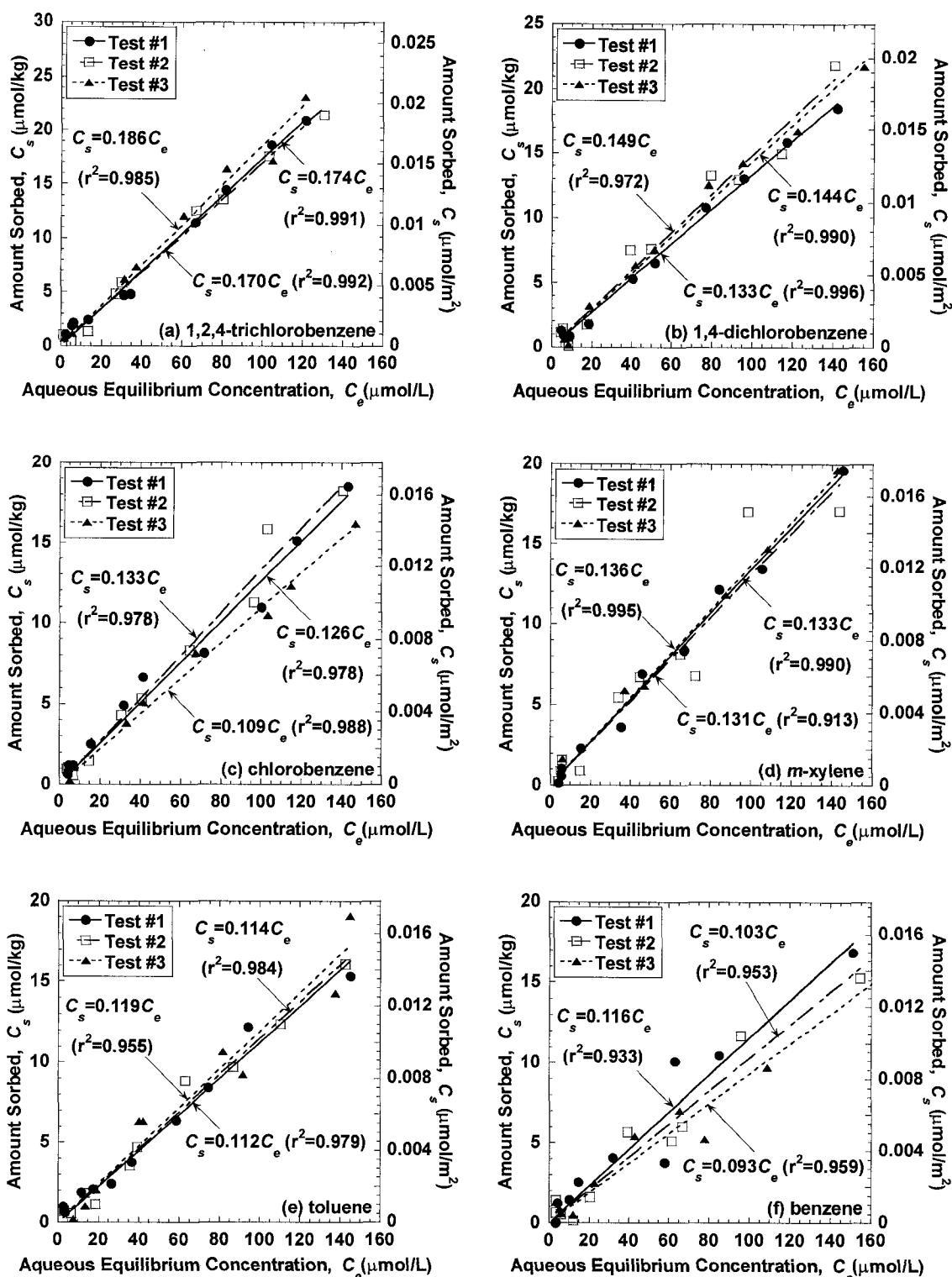


Fig. 4.5 Measured and linearly fitted sorption data for six individual NNOCs and Al_2O_3 -coated sand ($f_{oc} = 0.005\%$).

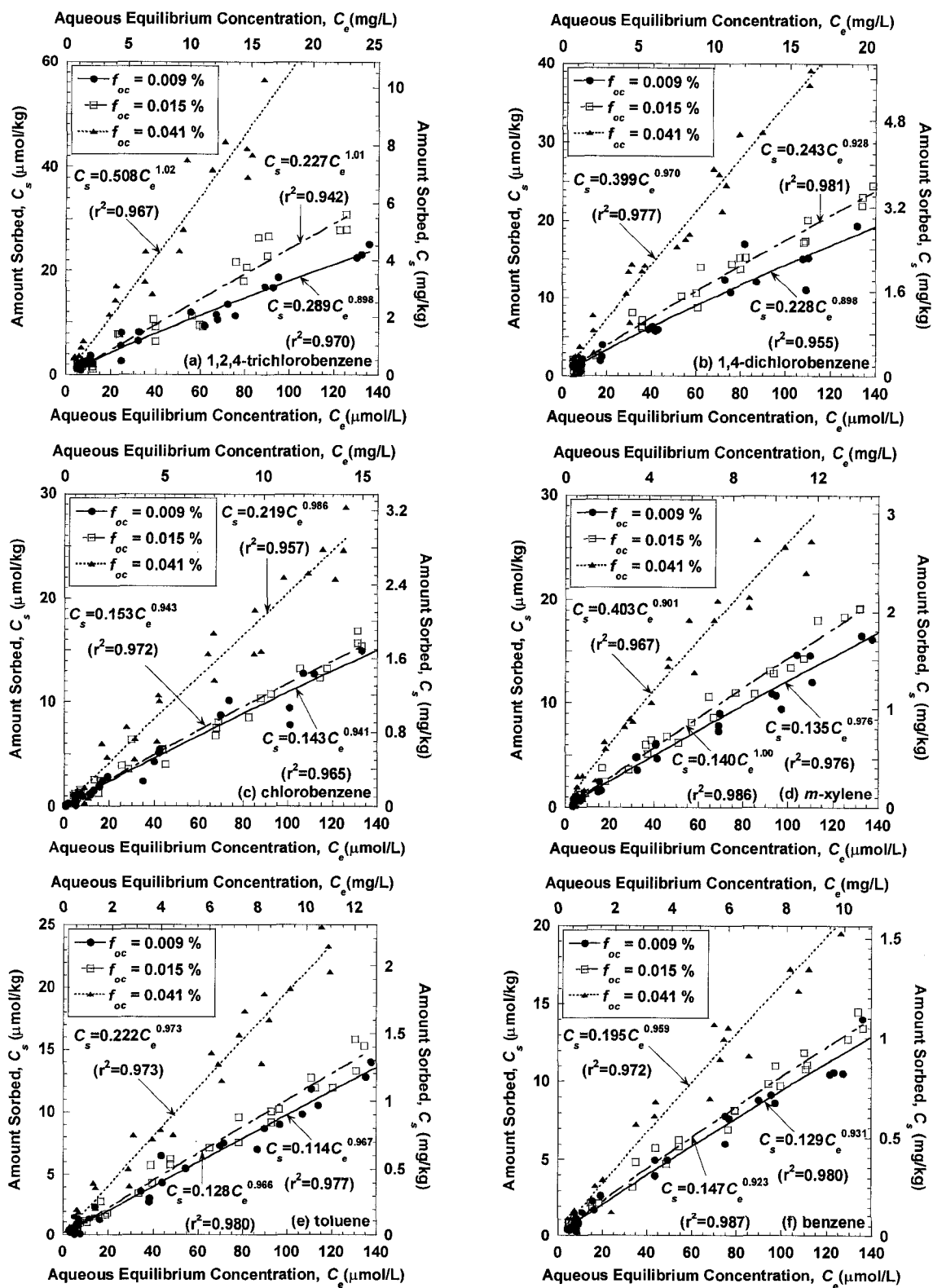


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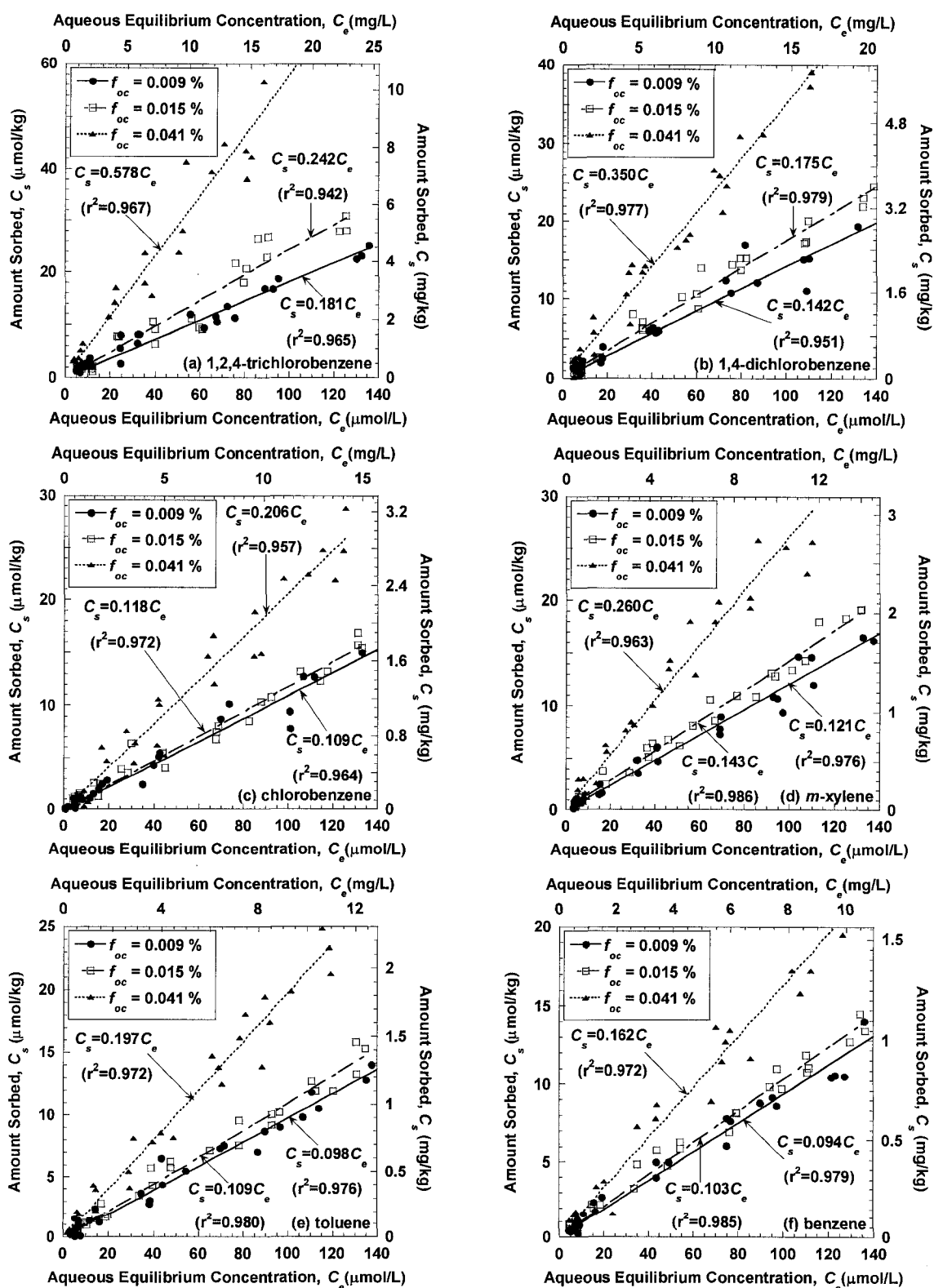


Fig. 4.7 Measured and linearly fitted sorption data for six NNOCs to FeO(OH)- and HA-coated sand with different f_{oc} .

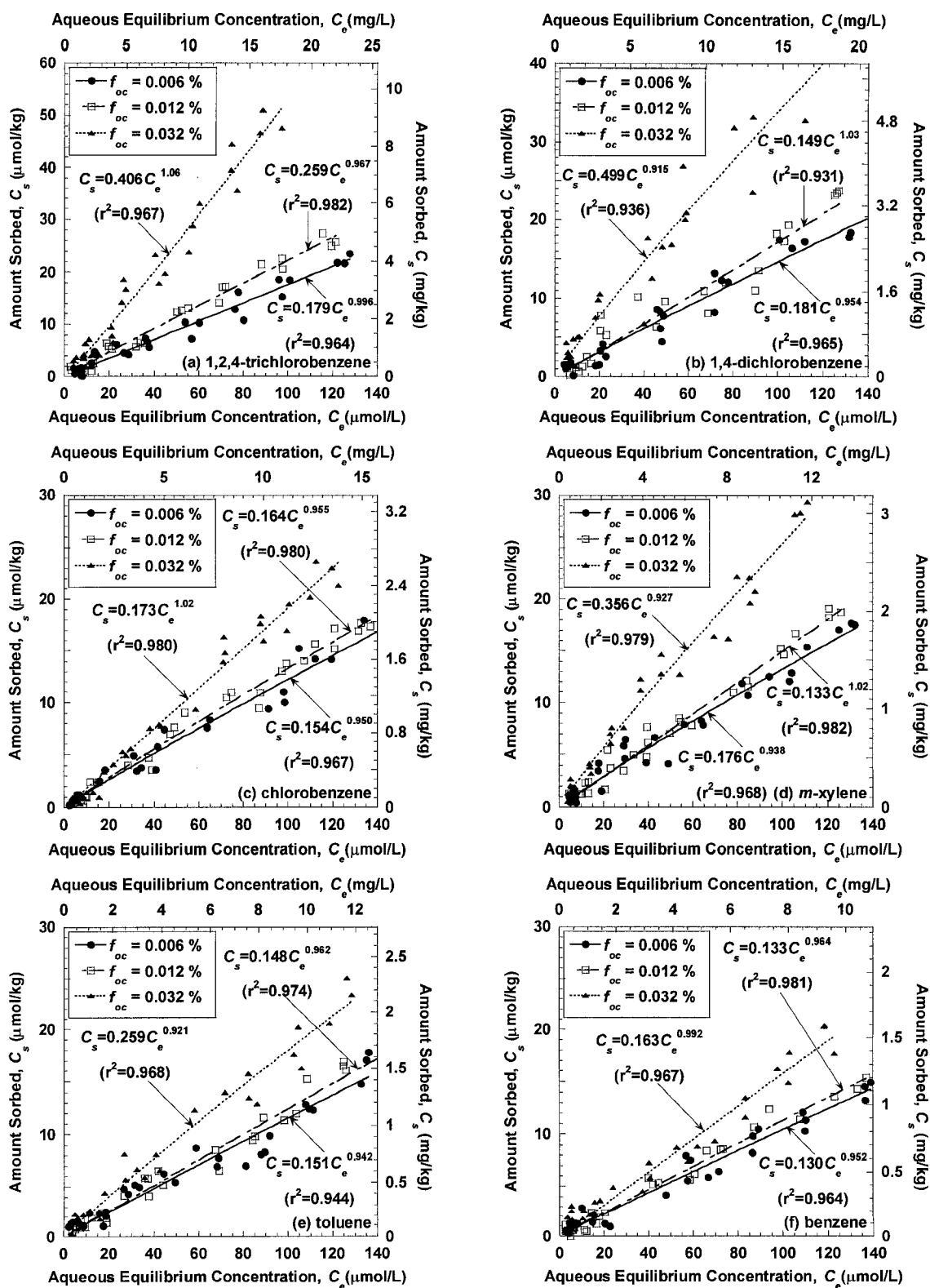


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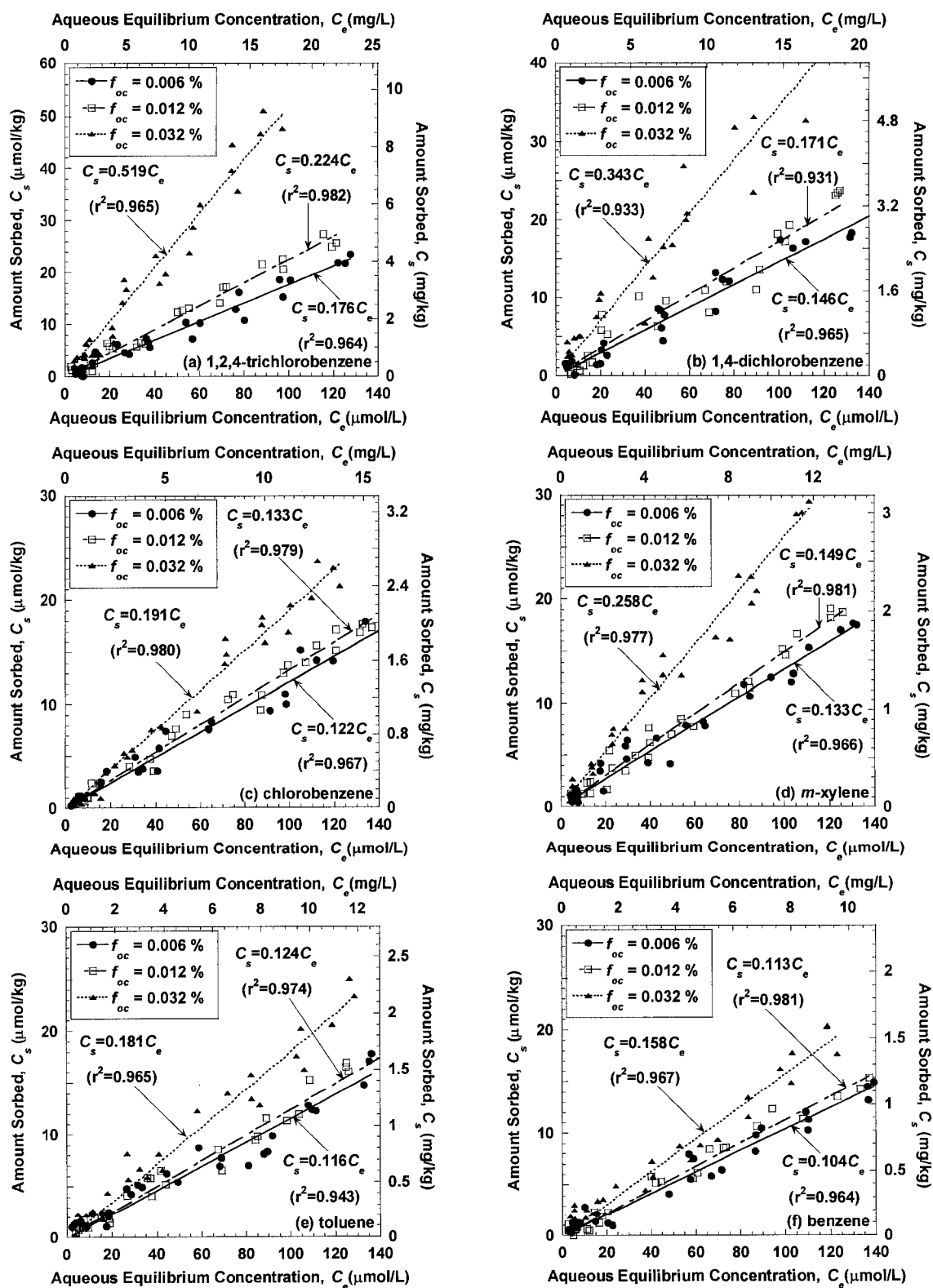


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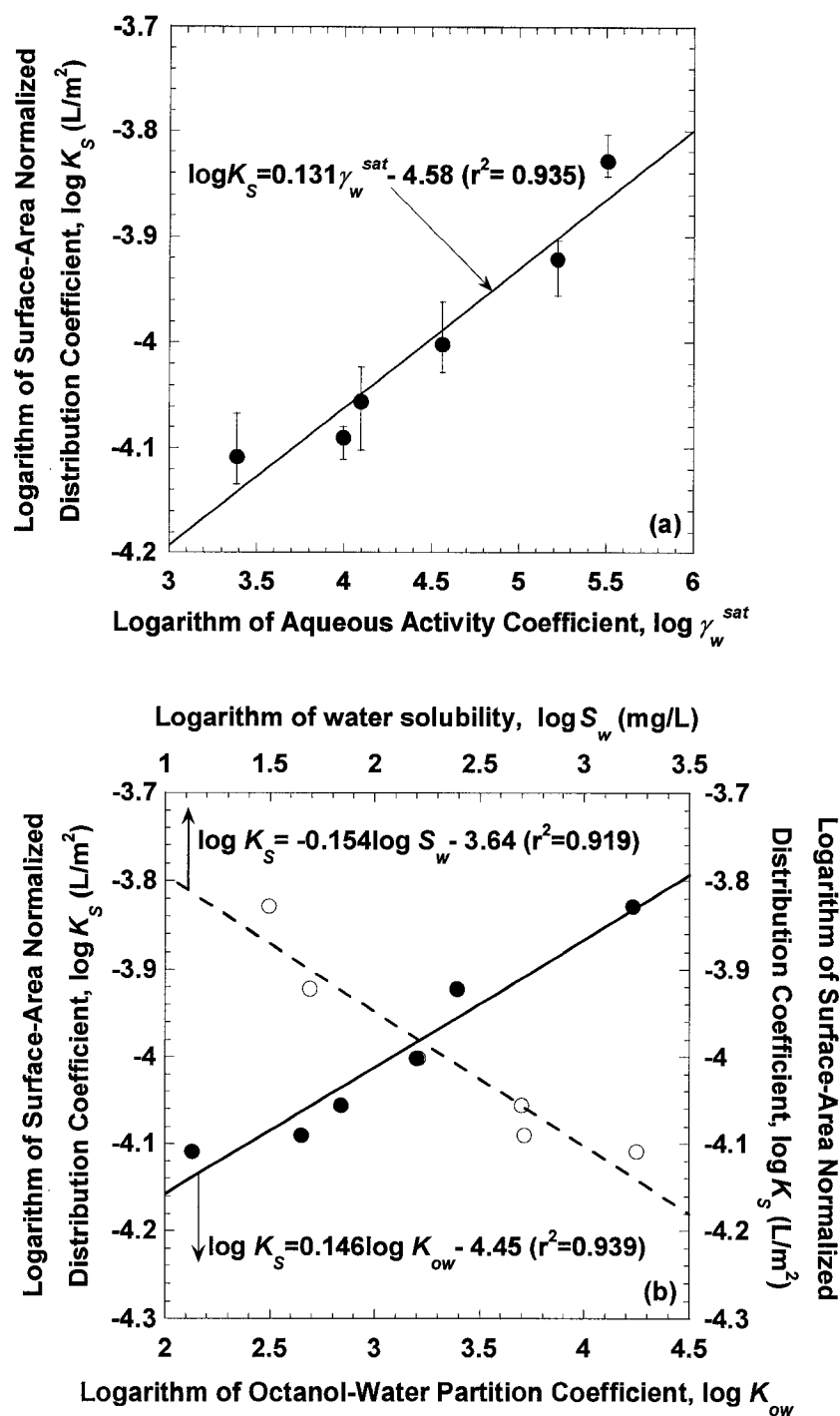


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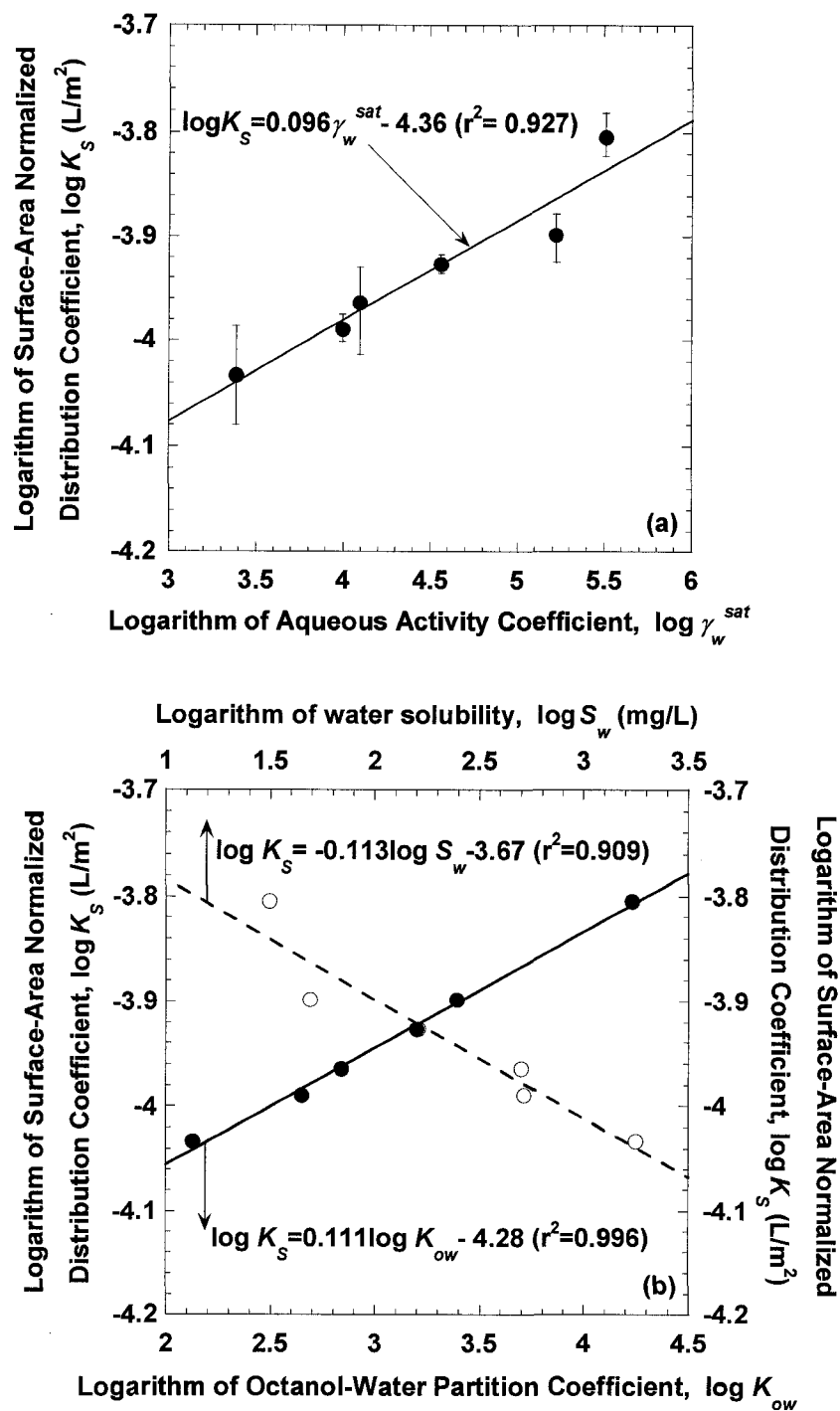


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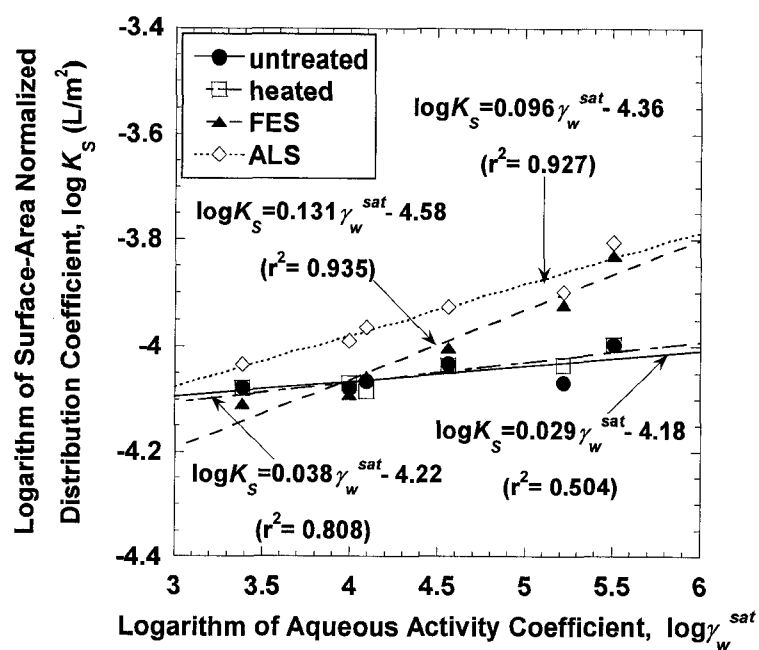


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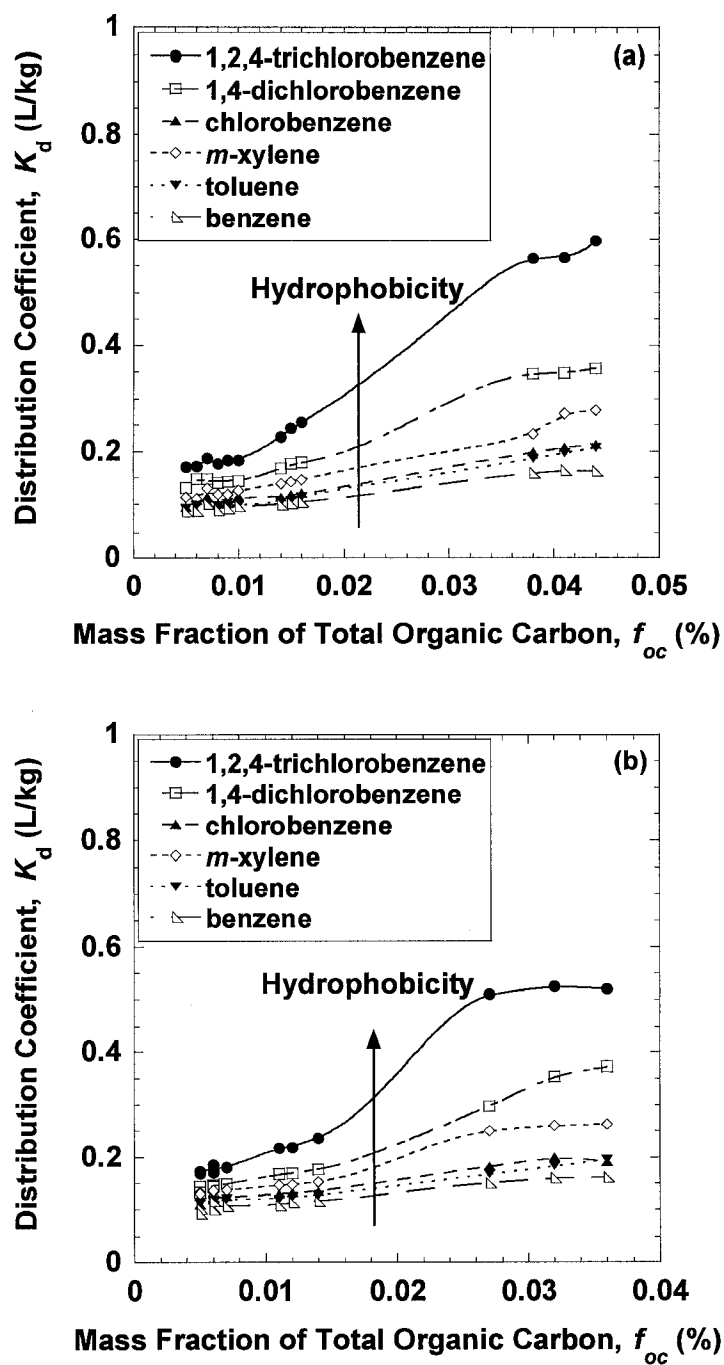


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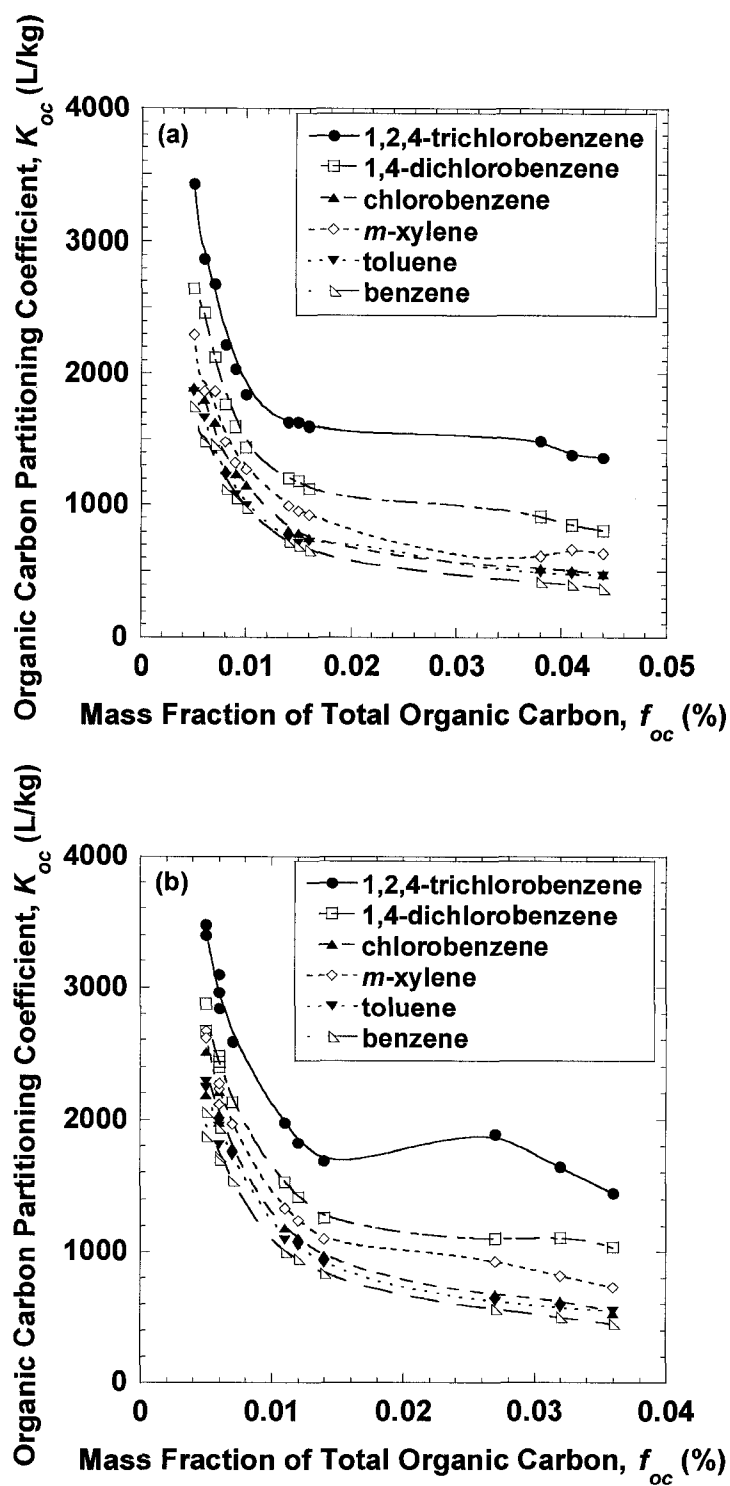


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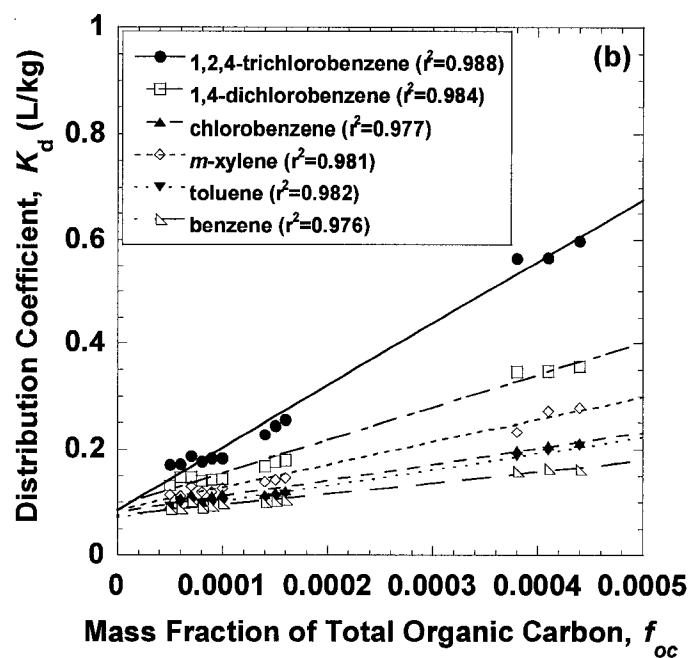
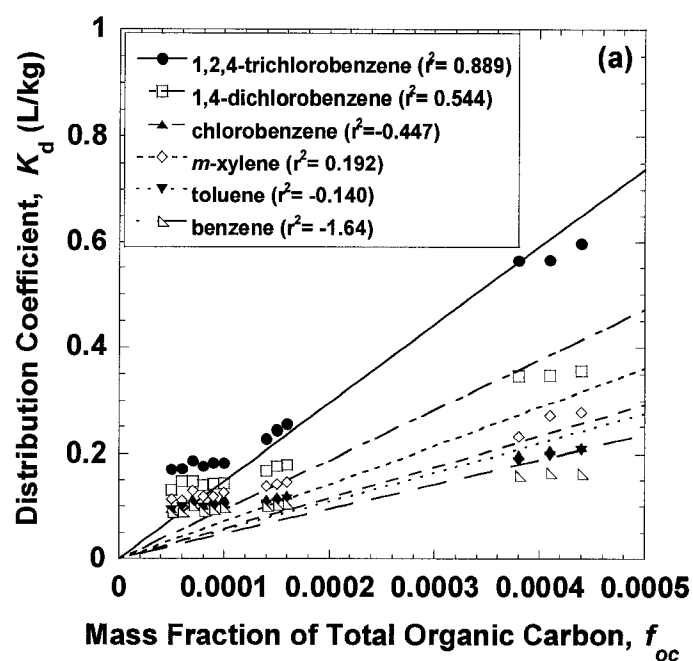


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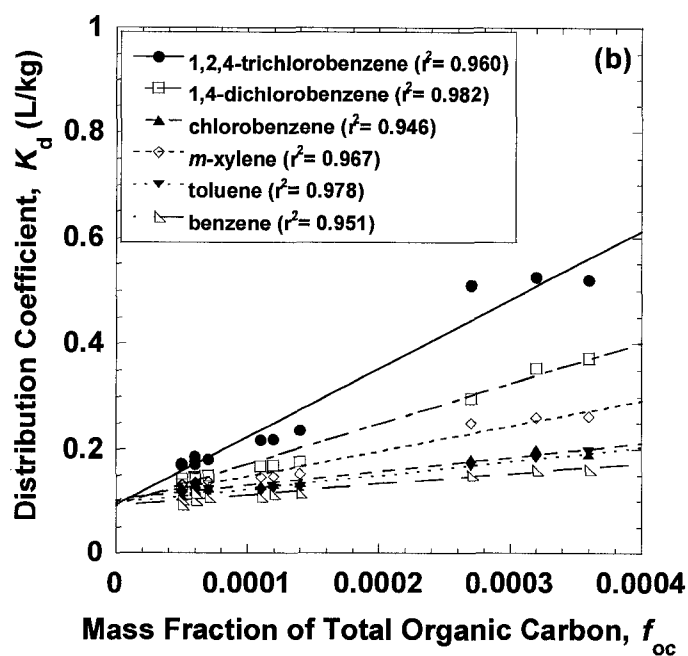
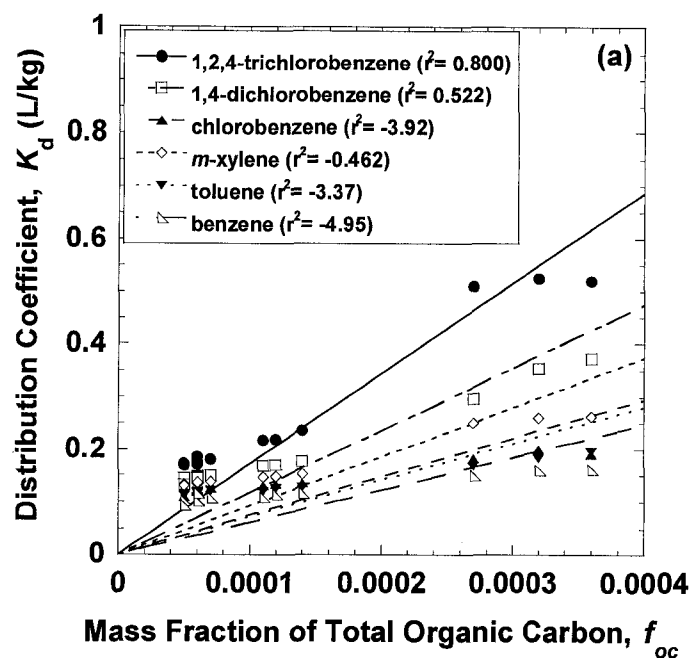


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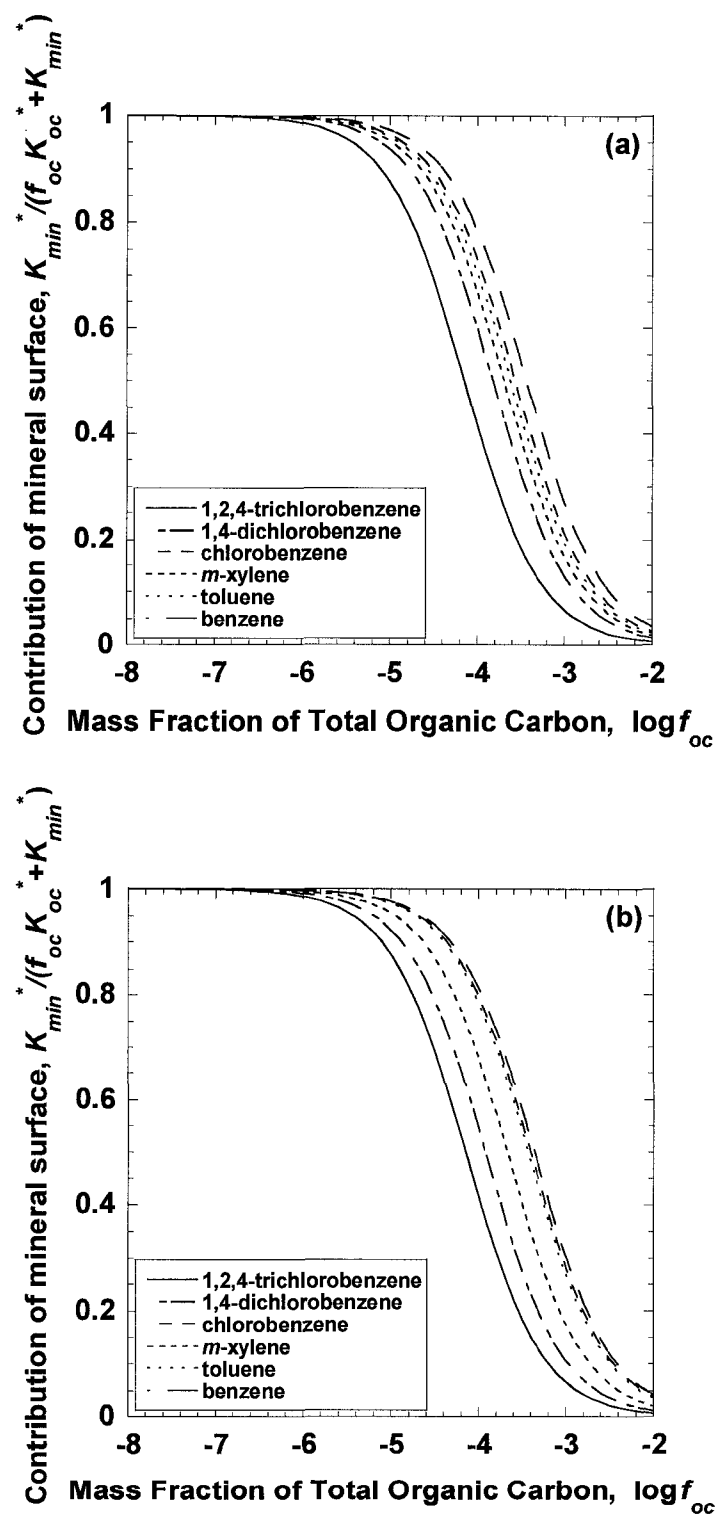


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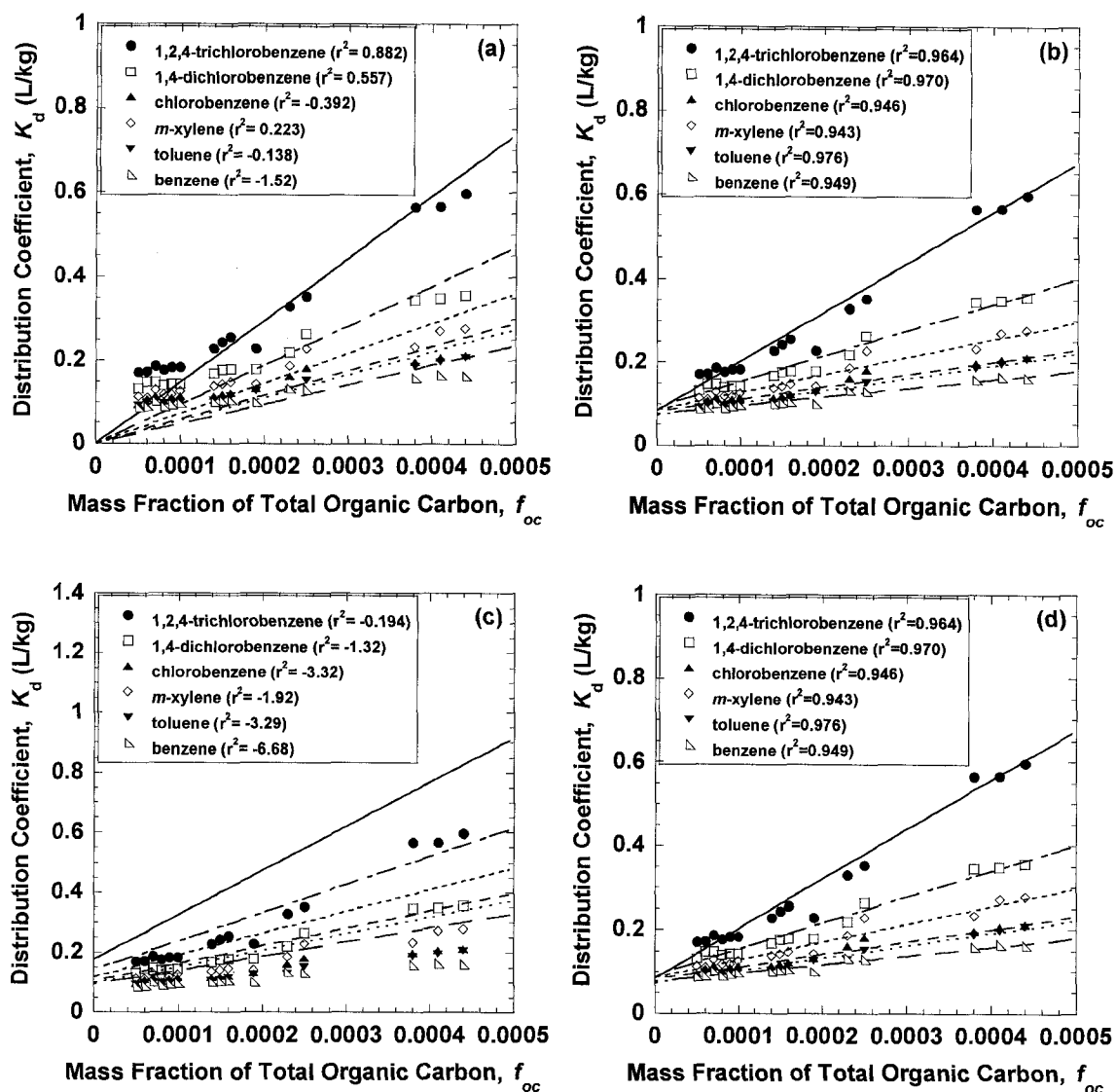


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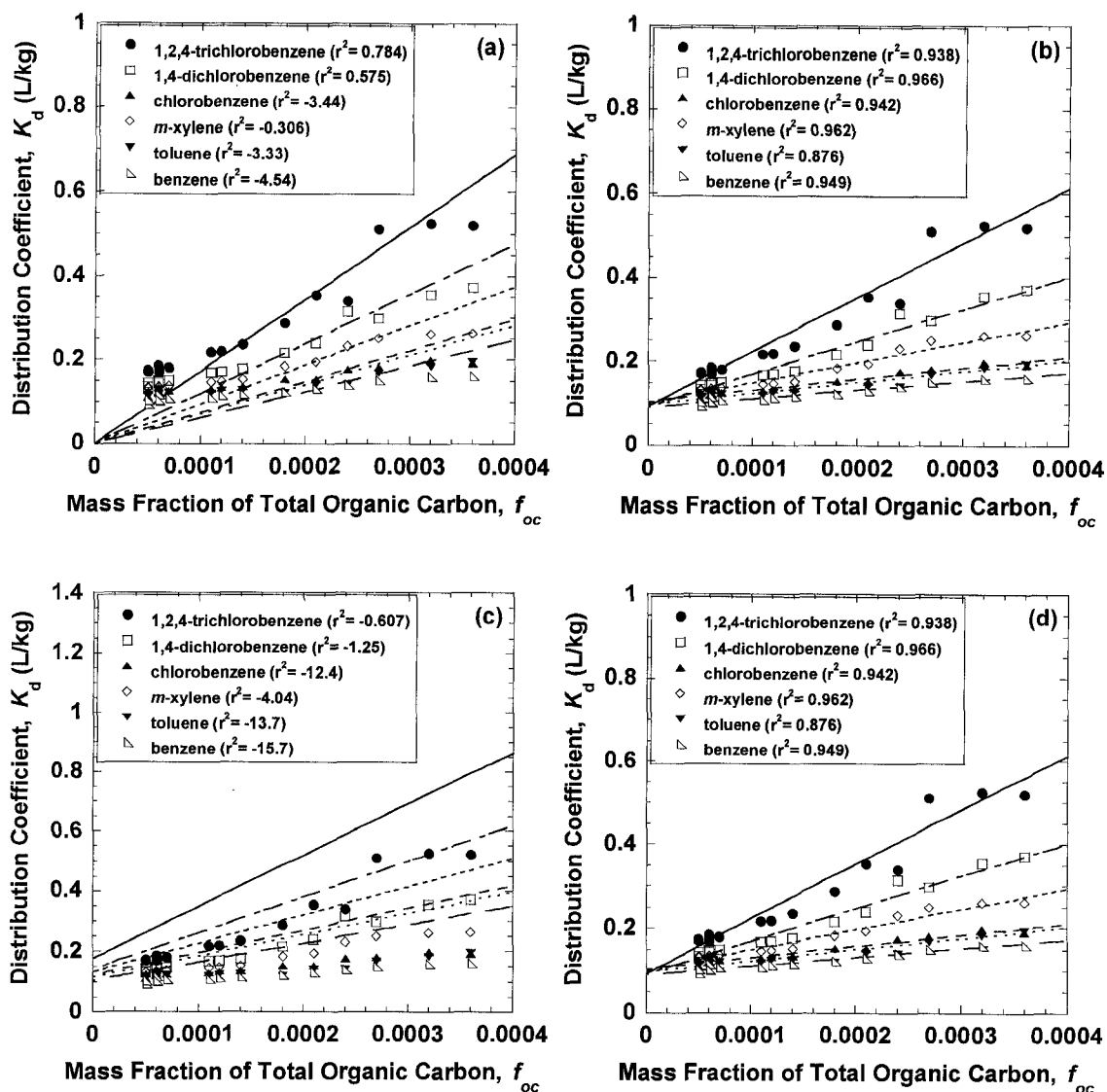


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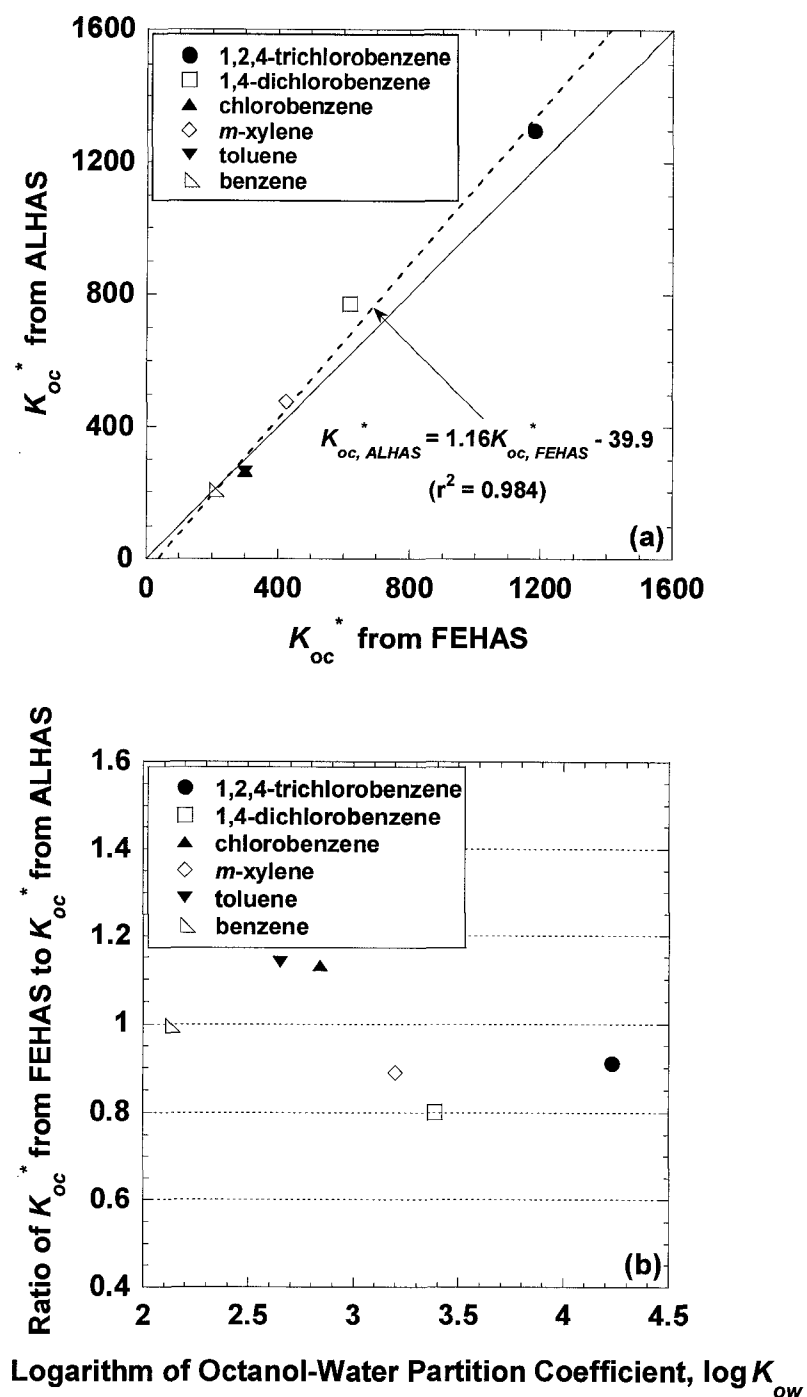


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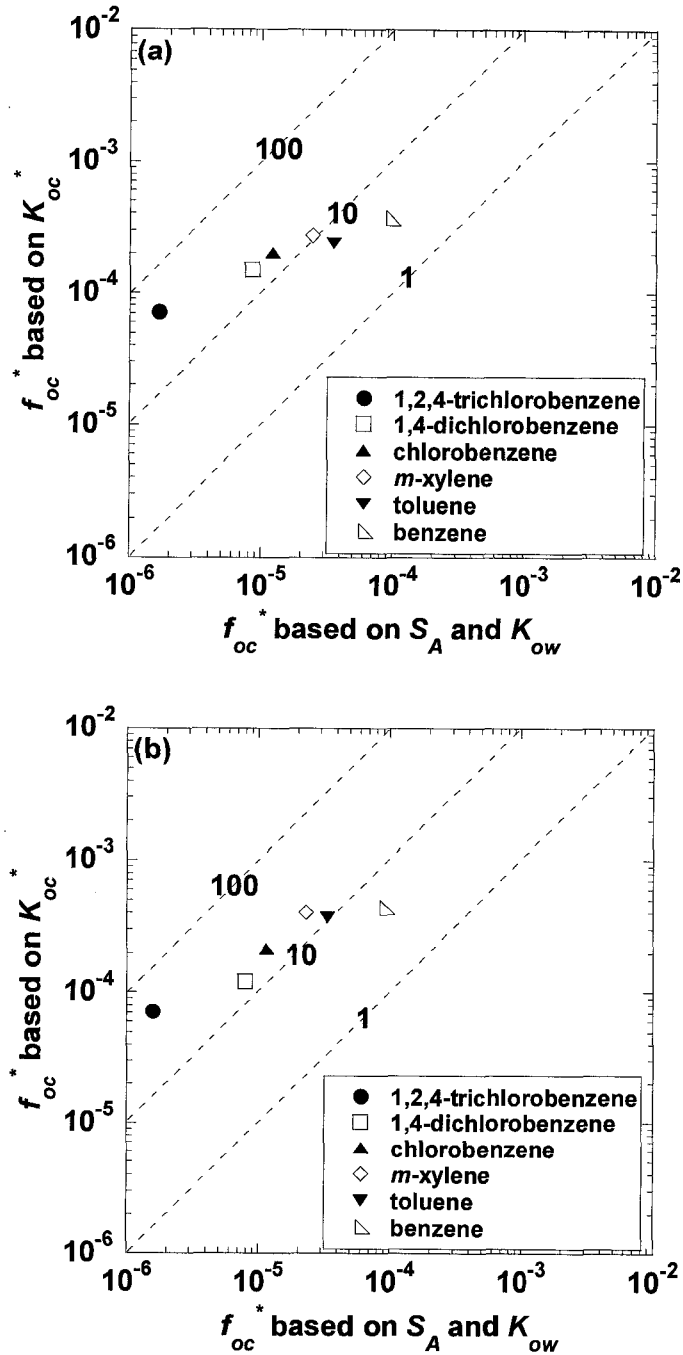


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DISSERTATION

**LUMPED APPROACH FOR SORPTION OF ORGANIC
CONTAMINANT MIXTURES TO SIMULATED AQUIFER
SORBENTS**

Volume II

(Chapters 5-8)

Submitted by

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CHAPTER 5

SORPTION OF NEUTRAL ORGANIC COMPOUNDS IN MIXTURES TO MINERAL SURFACES AND HUMIC ACID-MINERAL COMPLEXES

Abstract: In order to characterize both complex interactions and collective effects among sorbates at relatively low concentrations from either the same or the different neutral organic compound classes, the batch equilibrium sorption tests using neutral organic compounds in single-sorbate, three-sorbate, and 12-sorbate systems to both hydrophilic mineral surfaces (i.e., uncoated, FeOOH-coated, and Al₂O₃-coated sands) and humic acid-mineral complexes with different f_{oc} values (i.e., 0.051, 0.119, and 0.221 %) were performed. In sorption to hydrophilic mineral surfaces, mixture effects were not statistically significant ($\alpha = 0.05$) for nonpolar compounds whereas the suppression in the sorption of some polar compounds was found to be statistically significant but in a complex and selective manner. Similarly, in sorption to humic acid-mineral complexes, mixture effects were not statistically significant for nonpolar compounds whereas mixture effects were statistically significant for some polar compounds but in a complex and selective manner. Thus, sorption of polar compounds in mixtures to model sorbents evaluated in this study is more subject to variation with concentrations and compositions in mixtures, and is more complex and difficult to predict, compared to sorption of nonpolar compounds to simulated aquifer sorbents.

Key Words: batch equilibrium sorption tests, humic acid-mineral complexes, mineral surfaces, mixture effects, neutral organic compound

5.1 INTRODUCTION

Structurally and physicochemically different components of geosorbents, such as amorphous versus condensed soil organic matter (SOM) and high-surface-area carbonaceous material (HSACM), macroporous versus meso- and micro-porous mineral matrices, and interlayer surfaces of swelling clays, have been found to interact differently with neutral organic compounds (NOCs) in terms of binding energies and rates of associated sorption and desorption (Chiou et al. 1979, 1983, McCarthy et al. 1981, Schwarzenbach and Westall 1981, Karickhoff 1984, Ball and Roberts 1991, Weber et al. 1992, Huang et al. 1996, Weber and Huang 1996, Xing et al. 1996, Luthy et al. 1997, Mader et al. 1997, Chiou and Kile 1998, Xia and Ball 1999, Li and Werth 2001, Allen-King et al. 2002, Weber et al. 2002, Ju and Young 2004, Cornelissen et al. 2005, Nguyen and Ball 2006, Pignatello et al. 2006, Su et al. 2006). In addition, the fractionation and variations in structural and chemical properties of SOM, and the mineral surface blockage by SOM in SOM-mineral complexes contribute to the distinct sorption reactivities for NOCs (Karickhoff 1984, Kishi et al. 1990, Murphy et al. 1994, Liljestrand and Shimizu 1991, Rebhun et al. 1992, Onken and Traina 1997, Laor et al. 1998, Jones and Tiller 1999, Shen and Jaffé 2000, Hur and Schlautman 2004, Wang and Xing 2005, Feng et al. 2006). As a result, the overall sorption of NOCs by natural geosorbents has been found to be

represented by the sum of the contributions of several active components in heterogeneously combined geosorbents.

In mineral components, the sorption of nonpolar neutral organic compounds (NNOCs) to hydrophilic macroporous surfaces is typically linear and reversible with equilibrium being attained instantaneously, whereas that to interlayer surfaces of swelling clays is generally nonlinear and irreversible with equilibrium being attained relatively slow due to the differences in accessibility of each mineral surface to NNOCs, as affected by near-surface geometric effects and by the preferential adsorption of water molecules onto hydrophilic mineral surfaces (Drost-Hansen 1969, Huang et al. 1996, Xing et al. 1996, Mader et al. 1997, Su et al. 2006). However, the unsuppressed adsorption of polar neutral organic compounds (PNOCs) on certain minerals by water molecules leads to nonlinear sorption, and the nonlinearity is a complex function of the polarity and the H-bonding ability of the PNOCs (Southworth and Keller 1986, Bishop et al. 1990, Xing et al. 1996).

In organic components, the highly amorphous (soft) SOM domain exhibits linear sorption of NNOCs, relatively rapid rates of sorption and desorption, no sorbate-sorbate competition, sorption reversibility, and greater bioavailability of sorbed NNOCs (Chiou et al. 1979, 1983, Karickhoff 1984, Schwarzenbach et al. 1993, Nguyen et al. 2005). In contrast, the condensed (hard) SOM domain or HSACM exhibits nonlinear sorption of NNOCs, relatively slow rates of sorption and desorption, sorbate-sorbate competition, sorption irreversibility, and significantly reduced bioavailability of sorbed NNOCs (Weber et al. 1992, Weber and Huang 1996, Xing et al. 1996, Luthy et al. 1997, Chiou and Kile 1998, Li and Werth 2001,

Allen-King et al. 2002, Weber et al. 2002, Ju and Young 2004, Cornelissen et al. 2005, Nguyen and Ball 2006, Pignatello et al. 2006). However, the hydrophilic specific interactions of PNOCs with active sites of SOM lead to nonlinear sorption at relatively low concentrations, and the nonlinearity is a complex function of the polarity of the PNOCs and the nature of the hydrophilic specific interactions (Isaacson and Frink 1984, Senesi 1992, Spurlock and Biggar 1994, Chiou and Kile 1998).

Although numerous studies have been focused on characterizing the interactions of NOCs with various geosorbents comprised of different inorganic and organic components, the majority of these studies have involved single-sorbate systems to reveal sorption mechanisms for each component and to reconcile models for heterogeneous natural geosorbents. However, environmental contamination usually results in the presence of mixtures of compounds (e.g., gasoline, fuel hydrocarbon/chlorinated solvents, pesticides, and landfill leachates) in the subsurface. Although model development can be approached mechanistically from the study of simpler systems (i.e., single-sorbate systems), single-sorbate interactions with specific components of sorbents may be significantly altered by the presence and the quantity of other sorbates due to the complex interactions (e.g., competitive or synergistic effect) among sorbates in mixtures. Thus, complex interactions among sorbates in mixtures may contribute to significant errors in predicting the fate and transport of NOCs in mixtures based on models developed from single-sorbate systems. Therefore, both systematic characterization and

quantification of potential interactions among sorbates within mixtures may be required for such predictions.

Both competitive and non-competitive sorption has been found for NOCs. Competitive sorption has been found to exist when sorbates with similar size and polarity compete for a limited number of sorption sites at aqueous equilibrium concentrations (C_e) that are low relative to the solubility of the NOCs (S_w) (i.e., $C_e/S_w \leq 0.02$ for NNOCs and $C_e/S_w \leq 0.1$ for PNOCs) (Isaacson and Frink 1984, Bishop et al. 1990, Senesi 1992, Weber et al. 1992, Spurlock and Biggar 1994, Weber and Huang 1996, Xing et al. 1996, Luthy et al. 1997, Chiou and Kile 1998, Xia and Ball 1999, Li and Werth 2001, Allen-King et al. 2002, Weber et al. 2002, Ju and Young 2004, Cornelissen et al. 2005, Nguyen and Ball 2006, Pignatello et al. 2006). Both isotherm nonlinearity and competition have been attributed to the presence and quantity of the condensed SOM domain for NNOCs and to site specific interactions with both mineral surfaces and SOM for PNOCs.

In contrast, non-competitive, linear sorption has been found for NNOCs at $C_e/S_w \leq 0.5$, and attributed to the dominance of the amorphous SOM or to the suppressed adsorption onto hydrophilic mineral surfaces by strongly chemisorbed water molecules (Drost-Hansen 1969, Chiou et al. 1979, 1983, Schwarzenbach and Westall 1981, Karickhoff 1984, Huang et al. 1996, Xing et al. 1996, Mader et al. 1997, Nguyen et al. 2005, Su et al. 2006). In addition, a coexisting PNOC has been reported to strongly suppresses the nonlinear sorption of the other PNOCs, whereas a coexisting NNOC has a small effect, indicating that different mechanistic

processes between PNOCs and NNOCs are operative (Xing et al. 1996, Chiou and Kile 1998).

Overall, all of these complex interactions among sorbates in terms of binding energies and rates of associated sorption and desorption can depend on several factors, including (1) the dominant sorption process (i.e., absorption vs. adsorption), (2) the character and quantity of sorbates, (3) the nature of the SOM (i.e., amorphous vs. condensed SOM or HSACM), and (4) the nature of the mineral surface (i.e., macroporous mineral surfaces vs. interlayer surfaces of swelling clays) (Chiou and Kile 1998, Weber et al. 2002). However, the vast majority of studies on sorption in mixtures has involved sorbents with relatively high fractions of organic carbon, f_{oc} ($> 0.5\%$), whereas only a few studies have been reported for systems with low f_{oc} ($< 0.1\%$), which is more common for aquifer sorbents (Ball and Roberts 1991, Larsen et al. 1992).

Since f_{oc} typically is $< 0.1\%$ in natural aquifer systems, sorption of NOCs to aquifer sorbents likely results from sorption to both mineral surfaces and SOM (e.g., Schwarzenbach and Westall 1981, Karickhoff 1984, Curtis et al. 1986, Ball and Roberts 1991, Larsen et al. 1992, Onken and Traina 1997, Shen and Jaffé 2000). Thus, if sorption to SOM does not lower the amount of mineral sorption to a level controlled by the f_{oc} of the sorbents, the complex interactions among sorbates in mixtures in terms of sorption to both mineral surfaces and SOM would be expected.

However, little evidence is available pertaining to mixture effects for mixtures with more than two sorbates from either the same or different NOC classes at relatively low concentrations (i.e., $C_e/S_w < 0.3$). However, the collective effect of

multiple classes of NOCs with different structures and physicochemical properties at low C_e/S_w on the sorption of individual NOCs may be significant. Therefore, characterizing both complex interactions and collective effects among sorbates at relatively low concentrations from either the same or the different NOC classes, similar to mixtures in downstream from the contaminant source zone, is critical for risk assessment and management. Thus, the specific objectives of this study were to (1) investigate the complex interactions in mixtures (i.e., competitive or synergistic effect) among either the same or the different NOC classes within environmental concentration ranges in terms of sorption to various model sorbents with low f_{oc} ($\leq 0.221\%$), and to (2) elucidate the effects of type of mineral surface and quantity of SOM on the complex interactions among NOCs with either similar or different physicochemical properties.

5.2 MATERIALS AND METHODS

5.2.1 Humic Acid

The humic acid (HA) used in this study was extracted from a commercial peat soil (Voluntary Purchasing Groups, Inc., Bonham, TX) using the method recommended by International Humic Substances Society (Swift 1996). Both the detailed extraction procedures and the characterization of HA were previously described in Chapter 2.

5.2.2 Simulated Aquifer Sorbents

Ottawa sand (F-95, U.S. Silica, Berkeley Springs, WV) was used as the reference aquifer sand prior to any surface modification or treatment because Ottawa sand is absent of any impurities, such as other minerals or SOM (see Table 2.2). Both the detail preparation procedures and characterization of HA-coated sands and metal (hydr)oxide-coated sands were described in Chapters 2 and 3, respectively. Overall, four different types of model sorbents were used in this study, viz., (1) uncoated sand, (2) FeO(OH)-coated sand (FES), (3) Al₂O₃-coated sand (ALS), and (4) HA-coated sand with different f_{oc} (HAS). The physical and chemical properties of the model sorbents are summarized in Table 5.1.

5.2.3 Mixtures of Organic Compounds

Organic compounds used in this study were selected based on priority hazardous compounds as listed by the Agency for Toxic Substances and Disease Registry (ATSDR 2005). Mixtures of organic compounds are comprised of 12 NOCs, six of which are considered to be polar (hydrophilic) with polar functional groups (i.e., oxygen atom), and six of which are considered to be nonpolar (hydrophobic) without any polar functional groups. The six polar compounds include acetone (ACE), 2-butanone (2-BUT), 2-hexanone (2-HEX), phenol (PHE), *p*-cresol (*p*-CRE), and 2,4-dimethyl phenol (2,4-DMP). The six nonpolar compounds include benzene (BZ), toluene (TOL), *m*-xylene (*m*-XYL), chlorobenzene (CB), 1,4-dichlorobenzene (1,4-DCB), and 1,2,4-trichlorobenzene (1,2,4-TCB). All NOCs were obtained from Sigma-Aldrich Co. (St. Louis, MO) and

Fisher Scientific Co. (Pittsburgh, PA), and were of the highest available purity. Selected properties of all NOCs are summarized in Table 5.2.

In addition to single-sorbate sorption, the sorption of each sorbate in mixtures (i.e., 3 sorbates from the same NOC class and 12 sorbates from both the same and different NOC classes with various compositions) were also determined according to Fig. 5.1 and Table 5.3. Detailed procedures in preparing the solutions are described in Chapter 2. Based on Table 5.3, the solutions of NOC mixtures were prepared by adding the exact amount of neat compound to nanopure water (Barnstead/Thermolyne, Dubuque, IA) and by mixing the contents with a magnetic stirrer for 24 hrs before use.

5.2.4 Analytical Method

The concentration of each sorbate in mixtures was measured using gas chromatography (GC) (HP 5890 II, Hewlett-Packard Co., Inc) with a mass selective detector (MSD) and a flame ionization detector (FID). For BZ, TOL, *m*-XYL, CB, 1,4-DCB, and 1,2,4-TCB, aqueous samples are extracted as follows: 1.25 mL of aqueous sample are mixed with 0.75 mL of methyl tertiary butyl ether (MTBE-HPLC grade, 99.9 % purity) in 2-mL auto-sampler glass vial (National Scientific Co., Duluth, GA) sealed with a Teflon[®]-lined septa. The vial then is placed on a rotary extraction shaker for 30 min to allow for partitioning of NNOCs to MTBE phase. Then, the MTBE layer is transferred to a 2.0-mL vial containing a 100- μ L insert and then analyzed using a GC equipped with a MSD (HP 5971A, Hewlett-Packard Co., Inc) and an autosampler (Agilent Technologies, Inc., Santa Clara, CA).

The NNOCs are separated on a 30 m x 0.25 mm x 1 μ m HP-5MS column (Agilent Technologies, Inc., Santa Clara, CA). High-purity helium flows through the column at 1 mL/min, and the temperatures of inlet and detector are 250 and 280 °C, respectively. The oven temperature is maintained at an initial value of 40 °C for 5 min, raised at 8 °C/min to 180 °C, then increased at 40 °C/min to 260 °C, and finally held at 260 °C for 2 min.

For ACE, 2-BUT, 2-HEX, PHE, *p*-CRE, and 2,4-DMP, aqueous samples were placed in a 2-mL auto-sampler glass vial and sealed with Teflon[®]-lined septa. Then, the optimum injected volume (i.e., 1.0 μ L/s) was injected and then analyzed using a GC equipped with a FID and an autosampler. The PNOCs are separated on a 30 m x 0.53 mm x 1.5 μ m EQUITY[™]-5 column (Supelco, Inc., Bellefonte, PA). The flow rates for the gases were 3 mL/min for high-purity helium, 27 mL/min for non-flammable nitrogen gas, 40 mL/min for hydrogen gas, and 400 mL/min for compressed air. The temperatures of the inlet and detector were 225 °C and 250 °C, respectively. The oven temperature was held at an initial value of 40 °C for 4 min, raised at 6 °C/min to 180 °C, then increased at 20 °C/min to 200 °C, and finally held at 200 °C for 1 min.

In order to facilitate the qualitative identifications and quantitative determination of each sorbate, the external standard curves were prepared for each sorbate. Also, in order to correct for the loss of sorbates during sample preparation or sample inlet process, the internal standard (i.e., *o*-xylene or 2-hexone) was used for calibration by determining the ratio of the peak area of sorbate to the peak area of an internal standard.

5.2.5 Batch Sorption Methodology

Detailed batch equilibrium sorption tests (BESTs) procedures are described in Chapter 2. Diluted solutions of sorbates with different initial concentrations (i.e., $\leq 150 \mu\text{mol/L}$) were added to sorbents and sealed immediately with a Teflon[®]-lined Mininert[®] valve (Valco Instruments Co. Inc., Houston, TX) without headspace. The tube then was initially vortex mixed using a vortexer (VWR, West Chester, PA) for 20 s, and subsequently mixed end-over-end at 10 rpm and 20 °C during the entire experimental period to minimize the abrasion of sorbents. After the equilibrium time was pre-determined for each sorbate-sorbent system, the tube was centrifuged at 450 g for 20 min, and 2-mL aliquots of the supernatant were transferred to 2-mL auto-sampler glass vial with gas-tight glass syringe (5 mL Purge and Trap Syringe, Hamilton Co., Reno, NV). The collected samples were stored at 4 °C in a refrigerator and analyzed within one week after sampling. All BESTs for each sorbent were performed at least three times in both single-sorbate systems and mixtures. The concentration of any HA in the supernatant resulting from the desorption of HA from HA-coated sand during the BESTs was measured at 254 nm with the spectrophotometer (DU[®] 640, Beckman Instruments, Inc., Fullerton, CA) after sampling, since partitioning of sorbates to dissolved HA decreases the observed sorption coefficient (Gschwend and Wu 1985).

5.2.6 Sorption Model

The Freundlich isotherm model was used to describe and interpret all sorption isotherm data in this study. The Freundlich isotherm model has the form

$$C_s = K_f C_e^n \quad (5.1)$$

where C_s ($\mu\text{mol/kg}$) and C_e ($\mu\text{mol/L}$) represent the equilibrium solid-phase and solution-phase concentrations, respectively. The parameter K_f [$(\mu\text{mol/kg})/(\mu\text{mol/L})^n$] is the Freundlich unit sorption capacity, and n (dimensionless) is the joint measure of the relative magnitude and diversity of energies (Weber et al. 1992). Although Freundlich model is often considered empirical, this model has been widely applied to describe the overall sorption for heterogeneous sorbents since the Freundlich model results from the summation of several Langmuir-type sorption phenomena representing different interaction energies and sorption capacities (Weber et al. 1992).

5.2.7 Statistical Analyses

Since the two sorption parameters in the Freundlich sorption model (K_f and n) are dependent parameters, confidence regions for joint parameters using the linear approximation method are represented by an ellipse indicating potential combinations of sorption parameters that fall within the confidence regions. However, in all cases, the resulting confidence regions at the 0.05 ($= \alpha$) level of statistical significance for the single-sorbate systems evaluated in this study overlapped those for the mixtures evaluated in this study, indicating no effect of the

mixtures for any of the sorbates. Nonetheless, previous studies have evaluated the effect of mixtures on the sorption of NOCs on the basis that two Freundlich sorption parameters (K_f and n) in log-linearized Freundlich model are assumed to be independent parameters based on their physical meaning (e.g., Xing et al. 1996, Weber et al. 2002). Based on this precedent, the confidence intervals for each sorption parameter were compared individually in this study to evaluate the mixture effects among NOCs. The comparison was based at the 0.05 ($= \alpha$) level of statistical significance using Dunnett's procedure (Dunnett 1955) as contained within the statistical software (SAS® 9.1, Cary, NC) (see Appendix E).

5.3 RESULTS AND DISCUSSION

5.3.1 Sorption Rates of NOCs in Mixtures to various Sorbents

As shown in Fig. 5.2, the sorption for six NNOCs to uncoated, FES, and ALS approached equilibrium within 4 h, whereas sorption equilibrium was not achieved in the case of the HAS until about 12 h. The time required to attain apparent sorption equilibrium for the sorbates to three mineral surfaces was expected to be relatively short (i.e., ≤ 4 h) because: (1) diffusion of the sorbates across the aqueous boundary layer coating these sorbents is considered to be fast (Holmén et al. 1997); (2) the pore volumes from intraparticle porosity of the sorbents are low (i.e., ≤ 2.7 mm³/g); and (3) the SOM contents are very low (i.e., $f_{oc} \leq 0.006$ %). This result also is similar to that of previous studies indicating that the sorption rates of NNOCs to nonporous mineral surfaces are relatively fast (i.e., ≤ 4 h), and intra-

particle diffusion in nonporous mineral surfaces does not affect overall sorption rates (Huang et al. 1996).

However, in the case of the HA-coated sand ($f_{oc} = 0.119\%$), longer times were required to attain sorption equilibrium of some NNOCs, suggesting that diffusion of NNOCs within SOM matrices is the rate-limiting sorption process in the non-aggregated sorbents. Since the HA coating is relatively thin, not present as isolated aggregates on the surface (see Fig. 2.3), and highly hydrated and flexible, the domain represented by the amorphous HA coating likely is readily accessible to NNOCs such that the associated sorption rates are relatively fast (i.e., ≤ 12 h) compared to those (i.e., days to months) for condensed SOM (Weber and Huang 1996, Luthy et al. 1997, Allen-King et al. 2002). This finding is similar to that of Burris et al. (1991), who reported that sorption equilibrium of tetrachloroethylene to HA-coated silica ($f_{oc} = 0.073\%$) required as much as 24 h.

As shown in Fig. 5.3, no significant increase in sorption of PNOCs to uncoated, FES, ALS, and HAS was observed between 1 h and 120 h despite the instability in the amount sorbed to the model sorbents. This instability is attributed to the weak sorption, especially for 2-BUT and ACE. Since small concentration differences (C_e without sorbent vs. with sorbent) of some of the PNOCs are within the GC measurement error ranges (i.e., $\leq 4\%$), discerning any significant differences in amount sorbed between 1 h and 120 h is difficult for some PNOCs. However, these kinetic results clearly showed that the sorption rates of PNOCs to model sorbents used in this study are faster than those of NNOCs, and the determination of the equilibration time of 48 h for the BESTs is sufficient to reach

equilibrium of all NOCs in mixtures.

5.3.2 Sorption to Mineral Surface

Equilibrium sorption of each 12 NOCs in both single-sorbate systems and mixtures to uncoated sand, FeO(OH)-coated sand (FES), and Al₂O₃-coated sand (ALS) was investigated according to Table 5.3 and Fig. 5.1. For all sorption isotherms presented herein, the solid lines indicate the best-fit Freundlich sorption model for data set obtained from single-sorbate systems, and the dashed lines denote the corresponding 95 % confidence intervals for the associated Freundlich sorption model.

5.3.2.1 Sorption of Nonpolar Neutral Organic Compounds to Mineral Surface

The equilibrium sorption isotherms of NNOCs in both single-sorbate systems and mixtures to uncoated sand, FES, and ALS are presented in Figs. 5.4, 5.5, and 5.6, respectively. The least-squares mean Freundlich sorption parameters (i.e., K_f and n) of NNOCs in both single-sorbate systems and mixtures to uncoated sand, FES, and ALS in terms of experimental conditions are summarized in Tables 5.4, 5.5, and 5.6, respectively.

As shown in Figs. 5.4, 5.5, and 5.6 and Tables 5.4, 5.5, and 5.6, the equilibrium sorption isotherms of all NNOCs in single-sorbate systems to three hydrophilic mineral surfaces are nearly linear (i.e., $0.906 \leq n \leq 1.04$), and none showed evidence of a saturation plateau within the concentration ranges tested (i.e., $C_e/S_w \leq 0.6$). This near linear sorption can be attributed to preferential adsorption of

chemically adsorbed water molecules onto the hydrophilic mineral surfaces within the vicinal water region, since NNOC molecules cannot effectively compete with strongly chemisorbed water molecules (Drost-Hansen 1969, Schwarzenbach et al. 1993, Goss and Eisenreich 1996, Huang et al. 1996, Xing et al. 1996, Huang and Weber 1997, Mader et al. 1997, Su et al. 2006). Instead, sorbed NNOC molecules replace the weakly physisorbed water molecules overlying the chemisorbed water molecules in the vicinal water region (Schwarzenbach et al. 1993, Huang et al. 1996). Thus, strongly chemisorbed water molecules over hydrophilic mineral surfaces may reduce the heterogeneous adsorption potential caused by surface irregularity, resulting in the practically linear sorption of NNOCs to energetically homogeneous vicinal water region (Schwarzenbach et al. 1993, Huang et al. 1996, Xing et al. 1996, Mader et al. 1997, Su et al. 2006). This observation is consistent with that of several other studies where linear sorption of several NNOCs (e.g., chlorobenzenes, trichloroethene, and PAHs) to water saturated hydrophilic mineral surfaces (e.g., mineral oxides and kaolinite) has been observed (Huang et al. 1996, Xing et al. 1996, Mader et al. 1997, Su et al. 2006).

Based on the comparison of sorption isotherms of NNOCs between single-sorbate systems and three-sorbate mixtures (i.e., Tests #1 and 2) presented in Figs. 5.4, 5.5, and 5.6, sorption of a given NNOC was not affected by the presence of NNOCs with similar structure and physicochemical properties. Also, based on the comparison of sorption isotherms of NNOCs between single-sorbate systems and 12-sorbate mixtures (i.e., Tests #5, 6, 7, 8, and 9) presented in Figs. 5.4, 5.5, and 5.6, sorption of a given NNOC was not affected by the presence of NOCs with various

structure and physicochemical properties. These results indicate that there appear to be little, if any, mixture effects for sorption of NNOCs to hydrophilic mineral surfaces in the C_e ranges evaluated in this study. Also, the effect of changes in mixture composition on sorption of NNOCs to hydrophilic mineral surfaces was found to be insignificant.

This noncompetitive sorption of NNOCs within mixtures can be attributed to the accumulation of NNOCs in the vicinal water region without competition for the specific sorption sites with other NNOCs. Additionally, NNOCs cannot compete with PNOCs and water for the specific sorption sites on these hydrophilic mineral surfaces and, therefore, sorb further away from the surface due to an incapability of H-bonding (Huang et al. 1996, Xing et al. 1996). In contrast, the slightly enhanced sorption for *m*-XYL, TOL and BZ was observed for uncoated sand (see Fig. 5.4). This result may be attributed to an increase in the accumulative hydrocarbonaceous fraction within the vicinal water region (Brusseau 1991, Onken and Traina 1997), allowing more NNOCs sorbing to more hydrophobic vicinal water region.

The variations and 95 % confidence limits of the least-squares mean Freundlich sorption parameters of the NNOCs with the uncoated sand, FES, and ALS are presented in Figs. 5.7, 5.8, and 5.9, respectively, and the comparison of sorption parameters between single-sorbate systems and mixtures for the uncoated sand, FES, and ALS using Dunnett's procedure is summarized in Tables 5.7, 5.8, and 5.9, respectively. As evident by Figs. 5.7, 5.8, and 5.9 and Tables 5.7, 5.8, and 5.9, the 95 % confidence limits of the least-squares mean Freundlich sorption parameters between single-sorbate systems and mixtures overlapped in most cases.

Thus, least-squares mean Freundlich sorption parameters for the NNOCs between single-sorbate systems and mixtures were not significantly different ($\alpha = 0.05$). This result indicates that mixture effects were not involved with respect to the sorption of most NNOCs to three hydrophilic mineral surfaces. However, mixture effects were statistically significant with respect to the sorption of some NNOCs (e.g., *m*-XYL, TOL, and BZ) to uncoated sands.

In order to quantify the changes in least-squares mean Freundlich sorption parameters for the NNOCs in mixtures, Freundlich sorption parameters for the uncoated sand, FES, and ALS in mixtures were normalized against those from single-sorbate systems. As shown in Fig. 5.10, 5.11, and 5.12, K_f values in mixtures increased to 55 % or decreased to 44 % relative to those in single-sorbate systems whereas n values in mixtures increased to 15 % or decreased to 11 % relative to those in single-sorbate systems, indicating that the sorption capacity (K_f) was more readily affected than the diversity of energies (n) in the mixtures. This result suggests that relative magnitude and diversity of energies associated with the sorption process between single-sorbate systems and mixtures was not significantly different. Although sorption capacity changed readily, those changes in sorption capacity were not statistically significant ($\alpha = 0.05$) for most cases.

In summary, this lack of mixture effects for sorption of NNOCs to hydrophilic mineral surfaces evaluated in this study can be attributed to the reduced sorption of NNOCs with hydrophilic mineral surfaces due to the separation by vicinal water region. Under this scenario, isosteric heat during the sorption of NNOCs to hydrophilic mineral surfaces is near-zero, and changes slightly as surface

loadings of NNOCs increase (Huang and Weber 1997). This result implies that the sorbed NNOCs was at a discrete molecular state rather than at a condensed state on hydrophilic mineral surfaces (Su et al. 2006). Thus, near-linear and noncompetitive sorption of NNOCs in mixtures to hydrophilic mineral surfaces was expected at low surface coverage, where the molecules of NNOCs were at a discrete molecular state.

Although the enhanced sorption for *m*-XYL, TOL and BZ in mixtures to uncoated sands relative to that in single-sorbate systems is statistically significant ($\alpha = 0.05$) in some cases (see Table 5.7), enhanced sorption was not consistent even in same mineral surface. Additionally, there was no consistent enhancement on sorption of same NNOCs under the identical mixture composition to different mineral surfaces. These results indicate that enhanced sorption was dependent on the composition of sorbate mixtures (i.e., concentration and polarity of NOCs) and the type of mineral surface (i.e., specific volume of vicinal water region). However, the observed enhanced sorption in this study was not significant in terms of a practical perspective.

5.3.2.2 Sorption of Polar Neutral Organic Compounds to Mineral Surface

The equilibrium sorption isotherms for the PNOCs in both single-sorbate systems and mixtures to uncoated sand, FES, and ALS are presented in Figs. 5.13, 5.14, and 5.15, respectively. The least-squares mean Freundlich sorption parameters (i.e., K_f and n) for the PNOCs in both single-sorbate systems and mixtures to uncoated sand, FES, and ALS in terms of experimental conditions are summarized in Tables 5.4, 5.5, and 5.6, respectively.

The equilibrium sorption isotherms for all of the PNOCs in single-sorbate systems to three hydrophilic mineral surfaces are more nonlinear (i.e., $0.584 \leq n \leq 0.897$) than those for the NNOCs, and none of the isotherms showed evidence of a saturation plateau within the concentration ranges tested (i.e., $C_e/S_w \leq 0.005$). Furthermore, sorption capacities of hydrophilic mineral surfaces for PNOCs are lower than those for NNOCs by a factor ranging from three to more than an order of magnitude. This nonlinear sorption of PNOCs in single-sorbate systems is due to the greater contribution from hydrophilic specific interactions, presumably H-bonding with surface hydroxyls or with strongly chemisorbed water molecules, than that from hydrophobic nonspecific interactions (Karickhoff 1984, Southworth and Keller 1986, Xing et al. 1996). Also, sorption of the PNOCs in the single-sorbate systems to the three hydrophilic mineral surfaces becomes progressively nonlinear with increasing PNOC polarity, suggesting that the nonlinear sorption of the PNOCs was related to sorbate polarity. Since the solution pHs were all less than 7.5 and lower than the pK_a of methyl phenol group (i.e., PHE, *p*-CRE, and 2,4-DMP) by more than two log units (i.e., $pK_a - pH \geq 2$), the contribution of the protonated species of this group to the overall sorption likely was negligible.

Based on the comparison of sorption isotherms of PNOCs between single-sorbate systems and three-sorbate mixtures (i.e., Tests #3 and 4) presented in Figs. 5.13, 5.14, and 5.15, sorption of a given PNOC was affected by the presence of PNOCs with similar structure and physicochemical properties. Also, based on the comparison of sorption isotherms of PNOCs between single-sorbate systems and 12-sorbate mixtures (i.e., Tests #5, 6, 7, 8, and 9) presented in Figs. 5.13, 5.14, and 5.15,

sorption of a given PNOC was affected by the presence of NOCs with various structure and physicochemical properties. These results indicate that there appears to be mixture effects for sorption of PNOCs to hydrophilic mineral surfaces in the C_e ranges evaluated in this study.

As shown in Figs. 5.13, 5.14 and 5.15, the sorption of *p*-CRE, PHE and, 2-HEX decreased and became more linear in the presence of the other NOCs relative to that in the single-sorbate system; however, a decrease in sorption was not apparent for 2,4-DMP, 2-BUT, and ACE. This observation suggests that the decreased and linearized sorption of a PNOC within a mixture of NOCs occurs in a complex and selective manner, which is consistent with the findings of other studies (Xing et al. 1996, Chiou and Kile 1998). However, since sorption of 2-BUT and ACE was weak, the small concentration differences (C_e without sorbent vs. with sorbent) were within the measurement error (i.e., $\leq 4\%$) of the GC making the discernment of any significant differences in sorption behavior between single-sorbate systems and mixtures difficult.

The variations and 95 % confidence limits of the least-squares mean Freundlich sorption parameters of PNOCs with the uncoated sand, FES, and ALS are presented in Figs. 5.16, 5.17, and 5.18, respectively, and the comparison of sorption parameters between single-sorbate systems and mixtures for the uncoated sand, FES, and ALS using Dunnett's procedure is summarized in Tables 5.7, 5.8, and 5.9, respectively. Based on lower K_f values and higher n values for *p*-CRE, PHE, and 2-HEX in mixtures relative to single-sorbate systems, the suppressed sorption of *p*-CRE, PHE, and 2-HEX by other NOCs is statistically apparent ($\alpha =$

0.05) in some cases (i.e., shaded areas in Tables 5.7, 5.8, and 5.9). In contrast, the sorption of 2,4-DMP, 2-BUT, and ACE as single sorbate or within mixtures was not statistically different ($\alpha = 0.05$) in any case.

In order to quantify the changes in least-squares mean Freundlich sorption parameters for the PNOCs in mixtures, Freundlich sorption parameters for the uncoated sand, FES, and ALS in mixtures were normalized against those from single-sorbate systems as shown in Figs. 5.19, 5.20, and 5.21, respectively. As shown in Figs. 5.19, 5.20, and 5.21, K_f values of *p*-CRE and 2-HEX in three-sorbate mixtures (i.e, Tests #3 and 4) decreased to 62 % and 42 %, respectively, relative to those in single-sorbate systems, whereas n values of *p*-CRE and 2-HEX in three-sorbate mixtures increased to 31 % and 12 %, respectively, relative to those in single-sorbate systems. This result shows that both sorption capacity and sorption nonlinearity decreased for *p*-CRE and 2-HEX in the presence of PNOCs with similar structure and physicochemical properties. However, the nonlinear sorption of 2,4-DMP, PHE, 2-BUT and ACE in three-sorbate mixtures was not significantly suppressed ($\alpha = 0.05$) in any case.

On the other hand, K_f values of *p*-CRE, PHE, and 2-HEX in 12-sorbate mixtures (i.e., Tests #5, 6, 7, 8, and 9) decreased to 60 %, 67 %, and 39 %, respectively, relative to those in single-sorbate systems whereas n values of *p*-CRE, PHE, and 2-HEX in 12-sorbate mixtures increased to 27 %, 30 %, and 14 %, respectively, relative to those in single-sorbate systems. This result suggests that both sorption capacity and sorption nonlinearity decreased for *p*-CRE, PHE, and 2-HEX in the 12-sorbate mixtures with both similar and different structure and

physicochemical properties. However, the nonlinear sorption of 2,4-DMP, 2-BUT and ACE in 12-sorbate mixtures was not significantly suppressed ($\alpha = 0.05$) in any case.

Because the nonlinear sorption of PHE was suppressed in the 12-sorbate mixtures but not in the three-sorbate mixtures, sorption of the PNOCs in mixtures to hydrophilic mineral surfaces occurs in a complex and selective manner. Based on the aforementioned results, the higher polarity of PHE relative to that for 2,4-DMP and *p*-CRE in the three-sorbate mixtures favors PHE sorption to the hydrophilic specific sites relative to that for either 2,4-DMP or *p*-CRE. However, in 12-sorbate mixtures, the PNOCs with higher polarity (i.e., 2-BUT and ACE) than PHE suppress the nonlinear interactions of PHE with hydrophilic specific sites such that both sorption capacity and sorption nonlinearity decreased for PHE (i.e., relative to those in both single-sorbate and three-sorbate systems). Thus, both sorption capacity and sorption nonlinearity for the PNOCs to the hydrophilic mineral surfaces were affected to different extents depending on the mixture composition. These results suggest that sorption of the PNOCs in mixtures to hydrophilic mineral surfaces is more complex and difficult to predict than that of NNOCs.

In summary, the complex mixture effects for sorption of PNOCs to hydrophilic mineral surfaces evaluated in this study can be attributed to the mutual competition for hydrophilic specific sorption sites. Under this scenario, the suppression of nonlinear sorption for a given PNOC was likely due to the existence of other PNOCs versus other NNOCs in mixtures. Also, the presence and magnitude of mutual competition was subject to variation and depended on both the

composition of mixtures (i.e., concentration and polarity of PNOCs) and the type of mineral surface (i.e., specific volume of vicinal water region and availability of hydrophilic specific sorption sites). Thus, where accurate estimates in sorption behaviors of PNOCs in mixtures are needed, direct measurements of sorption distribution of target PNOCs in mixtures should be made instead of using sorption distributions in single-sorbate systems.

5.3.3 Sorption to HA-mineral Complexes

Equilibrium sorption of each 12 NOCs in both single-sorbate systems and mixtures to HA-coated sand with different f_{oc} values (HAS) was investigated according to Table 5.3 and Fig. 5.1. All statistical analyses were performed in the same manner described in sorption to mineral surfaces.

5.3.3.1 Effect of f_{oc} on Sorption of Nonpolar Neutral Organic Compounds

The equilibrium sorption isotherms of NNOCs for both single-sorbate systems and mixtures to HA-coated sands (HAS) with average f_{oc} values of 0.051 (i.e., HAS1), 0.119 (i.e., HAS2), and 0.221 % (i.e., HAS3) are presented in Figs. 5.22, 5.23, and 5.24, respectively. The least-squares mean Freundlich sorption parameters (i.e., K_f and n) for the NNOCs in both single-sorbate systems and mixtures to all HAS in terms of experimental conditions are summarized in Tables 5.10, 5.11, and 5.12, respectively.

The equilibrium sorption isotherms for all NNOCs in single-sorbate systems to all HASs are nearly linear (i.e., $0.877 \leq n \leq 1.07$) and without a saturation plateau

within the concentration ranges tested (i.e., $C_e/S_w \leq 0.5$). The near-linear sorption can be attributed to both absorptive partitioning into HA and the suppression of adsorption onto mineral surface by vicinal water region, and is thermodynamically expected where sorption sites are sufficiently homogeneous to give constant differential enthalpy of sorption (Chiou et al. 1979, Ball and Roberts 1991).

Sorption of the NNOCs to the HAS can be promoted by the several mechanisms, including linear and noncompetitive absorption (partitioning) into amorphous domains of HA and adsorption onto hydrophilic mineral surfaces (Chiou et al. 1979, 1983, Karickhoff 1984, Schwarzenbach et al. 1993, Huang et al. 1996, Mader et al. 1997, Nguyen et al. 2005, Su et al. 2006), and nonlinear and competitive adsorption or hole filling onto condensed domains of HA or HASCM (Chiou and Kile 1998, Xia and Ball 1999, Allen-King et al. 2002, Weber et al. 2002, Ju and Young 2004, Cornelissen et al. 2005, Nguyen and Ball 2006, Pignatello et al. 2006). Therefore, isotherm nonlinearity and competition may be attributed to the presence and quantity of condensed domains of HA or HASCM. For the HA used in this study, substantial condensed domains of HA or HASCM, such as charcoal and soot, likely do not exist based on the high oxygen/carbon ratio (see Table 2.1) for the HA and the low surface areas of the HAS (see Table 5.1). Thus, molecules of NNOCs primarily partition into loosely knit macromolecules of HA, relegating the role of adsorption or hole filling onto tightly knit macromolecules of HA or HSACM as insignificant even at low concentration ranges ($C_e/S_w < 0.05$). As a result, strong sorbate adsorption was not likely, such that linear sorption behavior in single-sorbate systems with low f_{oc} sorbents was expected.

Based on the comparison of sorption isotherms of NNOCs between single-sorbate systems and three-sorbate mixtures (i.e., Tests #1 and 2) presented in Figs. 5.22, 5.23, and 5.24, sorption of a given NNOC was not affected by the presence of NNOCs with similar structure and physicochemical properties. Also, based on the comparison of sorption isotherms of NNOCs between single-sorbate systems and 12-sorbate mixtures (i.e., Tests #5, 6, 7, 8, and 9) presented in Figs. 5.22, 5.23, and 5.24, sorption of a given NNOC was not affected by the presence of NOCs with various structure and physicochemical properties. These results indicate that there appeared to be little, if any, mixture effects for sorption of NNOCs to all of the HASs within the concentration ranges tested (i.e., $C_e/S_w \leq 0.5$). Also, the effect of changes in mixture composition on sorption of NNOCs to HAS was found to be insignificant.

As indicated by the near-linear and noncompetitive sorption isotherms of most of the NNOCs to all of the HASs in both single-sorbate and mixtures, the absence of mixture effects can be attributed to the dominance of partitioning of NNOCs into loosely knit macromolecules of HA, relative to the adsorption or hole-filling of NNOCs onto tightly knit macromolecules of HA or HSACM. Additionally, NNOCs cannot compete effectively with PNOCs and water for the oxygen- and hydroxyl-containing functional groups of the HA (Karickhoff 1984, Spurlock and Biggar 1994, Xing et al. 1996, Chiou and Kile 1998). Although the existence of nonlinear sorption isotherms for some of the sorbates in the single-sorbate systems (e.g., $n = 0.892$ for CB and $n = 0.877$ for TOL) may infer the possibility of

competitive sorption in the mixtures, such competition was found to be statistically insignificant at the 0.05 ($= \alpha$) level of statistical significance.

The variations and 95 % confidence limits of the least-squares mean Freundlich sorption parameters of the NNOCs with HAS1, HAS2, and HAS3 are shown in Figs. 5.25, 5.26, and 5.27, respectively, and the comparison of sorption parameters between single-sorbate systems and mixtures for HAS1, HAS2, and HAS3 using Dunnett's procedure is summarized in Tables 5.13, 5.14, and 5.15, respectively. The 95 % confidence limits of the least-squares mean Freundlich sorption parameters between the single-sorbate systems and mixtures overlapped in all cases. Thus, the differences in the least-squares mean Freundlich sorption parameters for the NNOCs between single-sorbate systems and mixtures were not significant ($\alpha = 0.05$). This result indicates that mixture effects were not involved with respect to the sorption of all NNOCs to three HASs.

In order to quantify the changes in least-squares mean Freundlich sorption parameters for the NNOCs in mixtures, Freundlich sorption parameters for three HASs in mixtures were normalized against those from single-sorbate systems. As shown in Figs. 5.28, 5.29, and 5.30, K_f values for the NNOCs in the mixtures increased to 38 % or decreased to 32 % relative to those in single-sorbate systems, whereas n values in mixtures increased to 13 % or decreased to 12 % relative to those in single-sorbate systems, indicating that sorption capacity (K_f) was more readily affected than the diversity of energies (n) in the mixtures. This result suggests that relative magnitude and diversity of energies associated with the sorption process between single-sorbate systems and mixtures were not significantly

different. Although the sorption capacity changed, such changes in sorption capacity were not statistically significant ($\alpha = 0.05$) for all cases.

However, in some cases (see CB and TOL in Fig. 5.29), both the sorption capacity and nonlinearity for CB and TOL decrease in mixtures relative to the single-sorbate systems. As higher affinity adsorption regions become saturated by other NOCs with greater hydrophobicity, the sorption of CB and TOL was expected to be increasingly confined to lower affinity partitioning domains, such that the adsorption affinity was reduced resulting in more linear sorption behavior for these compounds (McGinley et al. 1993, 1996, Chiou and Kile 1998, Xia and Ball 2000). A slight mixture competition among the NOCs over the condensed domains of HA or HASCM can be expected because the HA is not completely in an amorphous state.

In summary, mixture effects were not statistically significant ($\alpha = 0.05$) in terms of the sorption of all NNOCs to three HASs with different f_{oc} . This lack of apparent mixture effects can be attributed to noncompetitive partitioning of the NNOCs into amorphous domains of HA dominating the competitive adsorption of the NNOCs onto condensed domains of HA or HSACM. Thus, the single-sorbate interactions for the NNOCs with the HAS were not significantly altered by the presence and quantity of other sorbates evaluated in this study. This conclusion suggests that single-sorbate sorption coefficients would be adequate for use in environmental modeling of the NNOCs in mixtures. However, the collective effect of multiple classes of NOCs on the sorption of a given NNOC to HA-mineral complexes may not be ignored if the competitive adsorption of NOCs onto condensed domains of HA or HSACM is significant.

5.3.3.2 Effect of f_{oc} on Sorption of Polar Neutral Organic Compounds

The equilibrium sorption of the six PNOCs in both single-sorbate systems and mixtures to HAS with different f_{oc} values are presented in Figs. 5.31, 5.32, and 5.33, respectively, and the least-squares mean Freundlich sorption parameters (i.e., K_f and n) are summarized in Tables 5.10, 5.11, and 5.12, respectively.

As shown in Figs. 5.31, 5.32, and 5.33 and Tables 5.10, 5.11, and 5.12, the equilibrium sorption isotherms of all PNOCs in single-sorbate systems to three HASs are more nonlinear (i.e., $0.666 \leq n \leq 0.854$) than those of NNOCs, and none showed evidence of a saturation plateau within the concentration ranges tested (i.e., $C_e/S_w \leq 0.005$). Also, except for ACE, the amount of sorbed PNOC increased with increasing f_{oc} up to some threshold value which depended on the specific PNOC. Thus, soil organic carbon above the threshold f_{oc} contributes to the sorption of PNOCs to HAS.

The nonlinear sorption isotherms of PNOCs in single-sorbate systems to HAS were observed with nonlinearity at lower C_e but relative linearity at higher C_e . Such nonlinear sorption for PNOCs has been attributed to the energetic and site-specific hydrophilic specific interactions, such as H-bonding with the functional groups of HA and surface hydroxyls of mineral surfaces (Isaacson and Frink 1984, Spurlock and Biggar 1994). Additionally, sorption of PNOCs in single-sorbate systems to HAS became progressively nonlinear with increasing polarity of PNOCs, implying that the sorption nonlinearity of the PNOCs is a complex function of both the polarity and the H-bonding ability of the PNOCs with HA and mineral surfaces.

Based on the comparison of sorption isotherms of PNOCs between single-sorbate systems and three-sorbate mixtures (i.e., Tests #3 and 4) presented in Figs. 5.31, 5.32, and 5.33, sorption of a given PNOC was affected by the presence of PNOCs with similar structure and physicochemical properties. Also, based on the comparison of sorption isotherms of PNOCs between single-sorbate systems and 12-sorbate mixtures (i.e., Tests #5, 6, 7, 8, and 9) presented in Figs. 5.31, 5.32, and 5.33, sorption of a given PNOC was affected by the presence of NOCs with various structure and physicochemical properties. These results indicate that there appears to be mixture effects for sorption of PNOCs to HAS in the C_e ranges evaluated in this study.

The variations and 95 % confidence limits of the least-squares mean Freundlich sorption parameters of PNOCs to HAS1, HAS2, and HAS3 are presented in Figs. 5.34, 5.35, and 5.36, respectively, and the comparison of sorption parameters between single-sorbate systems and mixtures to HAS1, HAS2, and HAS3 using Dunnett's procedure is summarized in Tables 5.13, 5.14, and 5.15, respectively. Based on lower K_f values and higher n values for 2,4-DMP, *p*-CRE, PHE, and 2-HEX in mixtures relative to single-sorbate systems, the suppressed sorption of 2,4-DMP, *p*-CRE, PHE, and 2-HEX by other NOCs is statistically apparent ($\alpha = 0.05$) in some cases (i.e., shaded areas in Tables 5.13, 5.14, and 5.15). In contrast, the sorption of 2-BUT and ACE as single sorbate or within mixtures was not statistically different ($\alpha = 0.05$) in any case.

In order to quantify the changes in least-squares mean Freundlich sorption parameters for the PNOCs in mixtures, Freundlich sorption parameters for the HAS

in mixtures were normalized against those from single-sorbate systems, and were shown in Figs. 5.37, 5.38, and 5.39, respectively. As shown in Figs. 5.37, 5.38, and 5.39, K_f values of 2,4-DMP and 2-HEX in three-sorbate mixtures (i.e, Tests #3 and 4 in HAS1) decreased to 40 % and 57 %, respectively, relative to those in single-sorbate systems, whereas n values of 2,4-DMP and 2-HEX in three-sorbate mixtures (i.e, Tests #3 and 4 in HAS1) increased to 15 % and 12 %, respectively, relative to those in single-sorbate systems. This result clearly shows that capacity-decreased and linearized sorption is apparent for 2,4-DMP and 2-HEX in the presence of PNOCs with similar structure and physicochemical properties. However, the nonlinear sorption of *p*-CRE, PHE, 2-BUT and ACE in three-sorbate mixtures was not significantly suppressed ($\alpha = 0.05$) in any case.

On the other hand, K_f values of 2,4-DMP, *p*-CRE, PHE, and 2-HEX in 12-sorbate mixtures (i.e., Tests #5, 6, 7, 8, and 9) decreased to 46 %, 55 %, 57 %, and 46 % respectively, relative to those in single-sorbate systems whereas n values of 2,4-DMP, *p*-CRE, PHE, and 2-HEX in 12-sorbate mixtures increased to 15 %, 31 %, 24 %, and 16 %, respectively, relative to those in single-sorbate systems. This result suggests that capacity-decreased and linearized sorption is apparent for *p*-CRE, PHE, PHE, and 2-HEX in 12-sorbate mixtures with both similar and different structure and physicochemical properties. However, both the sorption capacities and nonlinearity of the PNOCs in mixtures are differently affected by the changes in mixtures compositions. These results suggest that the sorption of the PNOCs in mixtures is affected to a greater extent by variation in concentrations and compositions in mixtures than is the sorption of NNOCs in the same mixtures.

However, the effect of these mixture factors on the sorption of the PNOCs to HAS decreased with increasing f_{oc} . This trend indicates that the relative contribution of hydrophobic nonspecific interactions to hydrophilic specific interactions dominates the sorption of PNOCs at high f_{oc} . In contrast, the nonlinear sorption of 2-BUT and ACE in 12-sorbate mixtures was not significantly suppressed ($\alpha = 0.05$) in any case. Thus, the suppression in the nonlinear sorption of a given PNOC by various NOCs appears to occur in a complex and selective manner.

Sorption of PNOCs may not be strongly influenced by NNOCs due to the differentiated sorption domains and lack of competition between NNOCs and PNOCs for specific sites of both mineral surface and HA (Karickhoff 1984, Xing et al. 1996, Chiou and Kile 1998). Instead, substantial suppression of PNOCs occurs only if other PNOCs compete for specific sites of both mineral surfaces and HA. Thus, the sorption behavior for PNOCs in mixtures likely is subject to variations in concentration and composition of the PNOCs in mixtures. Additionally, the suppression in the sorption of a given PNOC by other PNOCs may be a complex function of polarity and hydrophilic specific interactions (Isaacson and Frink 1984, Spurlock and Biggar 1994, Xing et al. 1996, Chiou and Kile 1998). For example, 2-BUT and ACE in this study may have the greater suppressive power relative to other PNOCs due to the greater H-bonding ability with mineral surface and the functional groups of HA.

In summary, the complex mixture effect for sorption of PNOCs to HA-coated sand with different f_{oc} values can be attributed to mutual competition for hydrophilic specific sites of both mineral surfaces and HA. Thus, the presence and

magnitude of competitive effect may be dependent on the composition of mixtures (i.e., concentration and polarity of NOCs) and the type of sorbents (i.e., availability of hydrophilic specific sites). Consistent with this study, complex interactions between various PNOCs with different size, structure, polarity, and H-bonding ability and the hydrophilic specific interaction sites of mineral surfaces and HA has been reported (Isaacson and Frink 1984, Karickhoff 1984, Southworth and Keller 1986, Spurlock and Biggar 1994, Xing et al. 1996, Chiou and Kile 1998). Therefore, sorption of PNOCs in mixtures to HAS is more subject to variation with concentrations and compositions in mixtures, and is more complex and difficult to predict, compared to sorption of NNOCs.

5.4 SUMMARY AND CONCLUSIONS

In order to characterize both complex interactions and collective effects among sorbates at relatively low concentrations from either the same or the different neutral organic compound classes, the batch equilibrium sorption tests using neutral organic compounds in single-sorbate, three-sorbate, and 12-sorbate systems to both hydrophilic mineral surfaces and humic acid-mineral complexes with different f_{oc} values were performed.

In sorption to hydrophilic mineral surfaces, the following conclusions can be drawn:

- Mixture effects were not statistically significant ($\alpha = 0.05$) with respect to the sorption of most nonpolar neutral organic compounds to the three hydrophilic mineral surfaces, since nonpolar neutral organic compounds are

not adsorbed directly on the specific sites on the mineral surfaces, but rather are accumulated in the vicinal water region. This result has an important implication on the transport of nonpolar neutral organic compounds in mixtures through the subsurface.

- Mixture effects were statistically significant ($\alpha = 0.05$) with respect to the sorption of some polar neutral organic compounds (e.g., *p*-cresol, phenol, and 2-hexanone) to the three hydrophilic mineral surfaces, since the sorption capacity of a given polar neutral organic compound was suppressed by the presence of other polar neutral organic compounds in a complex and selective manner.
- The presence and magnitude of competitive sorption effects among polar neutral organic compounds was dependent on the composition of mixtures (i.e., concentration and polarity of polar neutral organic compounds) and the type of mineral surface (i.e., specific volume of vicinal water region and availability of hydrophilic specific interaction sites).

In sorption to humic acid-mineral complexes, the following conclusions can be drawn:

- Mixture effects were not statistically significant ($\alpha = 0.05$) with respect to the sorption of all nonpolar neutral organic compounds to three humic acid-coated sands with different f_{oc} values (i.e., 0.051, 0.119, and 0.221 %), indicating that the noncompetitive partitioning of nonpolar neutral organic compounds into amorphous domains of humic acid dominated the

competitive adsorption of nonpolar neutral organic compounds onto condensed domains of humic acid or high-surface-area carbonaceous material. This result suggest that single-sorbate sorption coefficients are adequate for use in environmental modeling of the nonpolar neutral organic compounds in mixtures.

- The suppression of the sorption of a given polar neutral organic compound (e.g., 2,4-dimethyl phenol, *p*-cresol, phenol, and 2-hexanone) to humic acid-coated sands by other polar neutral organic compounds was found to be significant but in a complex and selective manner, depending on the composition of mixtures (i.e., concentration and polarity of polar neutral organic compounds) and the type of sorbents (i.e., specific volume of vicinal water region and availability of hydrophilic specific interaction sites). Thus, sorption of polar neutral organic compounds in mixtures to humic acid-coated sands is more subject to variation with concentrations and compositions in mixtures, and is more complex and difficult to predict, compared to sorption of nonpolar neutral organic compounds to humic acid-coated sands.

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Table 5.1 Physical and chemical properties of model sorbents.

Model Sorbent		Carbon Content (%)^a		BET Surface Area, S_A^b (m²/g)
Type	No.	Organic	Inorganic	
Untreated sand	1	0.006	<0.005	2.045
FeO(OH)-coated sand	2	0.006	<0.005	1.194
Al ₂ O ₃ -coated sand	3	0.005	<0.005	1.123
Humic acid-coated sand	4	0.051	<0.005	2.058
	5	0.119	<0.005	2.089
	6	0.221	<0.005	2.840

^aMeasured by Huffman Laboratories, Golden, CO^bMeasured by Porous Materials Inc., Ithaca, NY

Table 5.2 Physical and chemical properties of 12 neutral organic compounds.

Compound			Aqueous ^a Solubility (mg/L)	Log ^b γ_w^{sat}	Log ^c K_{oc}	Log ^d K_{ow}	ATSDR ^e
Name	Formula	Molecular Weight					
1,2,4-trichlorobenzene	C ₆ H ₃ Cl ₃	181.45	31.3 at 25 °C	5.51	3.16	4.23	203
1,4-dichlorobenzene	C ₆ H ₄ Cl ₂	147.00	49 at 22 °C	5.22	2.89	3.39	159
chlorobenzene	C ₆ H ₅ Cl	112.56	500 at 20 °C	4.09	2.52	2.84	105
<i>m</i> -xylene	C ₈ H ₁₀	106.17	161.91 at 20 °C	4.56	2.54	3.20	59
toluene	C ₇ H ₈	92.14	515 at 20 °C	3.99	2.18	2.65	71
benzene	C ₆ H ₆	78.11	1780 at 20 °C	3.38	1.96	2.13	6
2,4-dimethyl phenol	C ₈ H ₁₀ O	122.17	4,200 at 20 °C	3.21	1.87	2.30	189
<i>p</i> -cresol	C ₇ H ₈ O	108.14	19,400 at 20 °C	2.49	1.69	1.67	169
phenol	C ₆ H ₆ O	94.11	67,000 at 25 °C	1.89	1.24	1.46	183
2-hexanone	C ₆ H ₁₂ O	100.16	35,200 at 25 °C	2.20	1.63	1.38	72
2-butanone	C ₄ H ₈ O	72.11	270,000 at 20 °C	1.17	0.09	0.26	209
acetone	C ₃ H ₆ O	58.08	All proportions	NA ^f	-0.43	-0.24	181

^aAqueous solubility from Montgomery (1996)^bCalculated activity coefficient in water at saturation by using aqueous solubility from Montgomery (1996)^cOrganic carbon partitioning coefficient from Montgomery (1996) and Delle Site (2001)^dOctanol-water partitioning coefficient from Montgomery (1996)^eAgency for Toxic Substances and Disease Registry (2005 Ranking in Priority List of Hazardous Substances)^fNot available

Table 5.3 Summary of experimental conditions for sorption of neutral organic compounds in mixtures to all sorbents

Sorbates	Experimental Conditions								
	Concentration of Each Stock Solution ($\mu\text{mol/L}$) ^a								
	Test Number								
	1	2	3	4	5	6	7	8	9
1,2,4-trichlorobenzene	150	0	0	0	50	100	50	68	60
1,4-dichlorobenzene	150	0	0	0	50	50	50	21	56
chlorobenzene	150	0	0	0	50	50	50	28	35
<i>m</i> -xylene	0	150	0	0	50	50	50	35	62
Toluene	0	150	0	0	50	50	50	89	34
Benzene	0	150	0	0	50	50	50	28	71
2,4-dimethyl phenol	0	0	150	0	50	50	50	50	52
<i>p</i> -cresol	0	0	150	0	50	50	50	16	36
phenol	0	0	150	0	50	50	50	82	54
2-hexanone	0	0	0	150	50	50	50	44	24
2-butanone	0	0	0	150	50	50	50	30	89
acetone	0	0	0	150	50	50	100	71	64
SUM	450	450	450	450	600	650	650	562	637

^a Stock solutions were diluted as the same mole fraction for eight bottle point sorption isotherm (sorption isotherm was constructed over a range of three order magnitude in sorbate concentration)

Table 5.4 Summary of least-squares mean Freundlich sorption parameters of 12 neutral organic compounds in mixtures to untreated sand ($f_{oc} = 0.006\%$) based on the different initial aqueous concentration displayed in Table 5.3. (No. of observation = 3)

	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
K_{fs}^a	0.305	0.218	0.171	0.290	0.268	0.169	0.111	0.106	0.095	0.066	0.054	0.082
K_{f1}	0.221	0.228	0.152	NA	NA	NA	NA	NA	NA	NA	NA	NA
K_{f2}	NA ^a	NA	NA	0.330	0.177	0.149	NA	NA	NA	NA	NA	NA
K_{f3}	NA	NA	NA	NA	NA	NA	0.084	0.069	0.094	NA	NA	Na
K_{f4}	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.043	0.060	0.069
K_{f5}	0.202	0.188	0.212	0.244	0.267	0.211	0.091	0.063	0.049	0.066	0.051	0.088
K_{f6}	0.308	0.259	0.233	0.314	0.352	0.244	0.072	0.060	0.056	0.073	0.059	0.083
K_{f7}	0.293	0.253	0.226	0.329	0.262	0.250	0.073	0.057	0.045	0.058	0.057	0.079
K_{f8}	0.268	0.222	0.238	0.293	0.265	0.224	0.078	0.061	0.075	0.061	0.082	0.096
K_{f9}	0.255	0.260	0.230	0.234	0.305	0.255	0.086	0.055	0.064	0.074	0.060	0.088
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
n_s^a	0.918	0.954	1.02	0.908	0.906	1.01	0.802	0.724	0.719	0.827	0.733	0.685
n_1	0.986	0.962	1.02	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	0.904	1.01	1.02	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.883	0.784	0.736	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.914	0.722	0.661
n_5	0.936	0.957	0.969	0.964	0.938	0.956	0.888	0.834	0.828	0.828	0.714	0.725
n_6	0.918	0.947	0.945	0.941	0.935	0.916	0.884	0.854	0.800	0.739	0.777	0.779
n_7	0.929	0.943	0.958	0.932	0.963	0.970	0.848	0.828	0.835	0.873	0.734	0.768
n_8	0.939	1.06	0.936	0.970	0.928	0.978	0.831	0.835	0.755	0.830	0.752	0.666
n_9	0.958	0.983	0.982	1.04	0.914	0.939	0.849	0.813	0.802	0.817	0.746	0.662

^a Not available

Table 5.5 Summary of least-squares mean Freundlich sorption parameters of 12 neutral organic compounds in mixtures to FeO(OH)-coated sand ($f_{oc} = 0.006\%$) based on the different initial aqueous concentration displayed in Table 5.3. (No. of observation = 3)

	1,2,4-TCB	1,4-DCB	CB	<i>m</i>-XYL	TOL	BZ	2,4-DMP	<i>p</i>-CRE	PHE	2-HEX	2-BUT	ACE
K_{fs}	0.174	0.124	0.124	0.128	0.105	0.116	0.128	0.260	0.131	0.080	0.210	0.173
$K_{f,1}$	0.155	0.104	0.125	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,2}$	NA ^a	NA	NA	0.134	0.112	0.098	NA	NA	NA	NA	NA	NA
$K_{f,3}$	NA	NA	NA	NA	NA	NA	0.075	0.095	0.103	NA	NA	NA
$K_{f,4}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.046	0.113	0.144
$K_{f,5}$	0.204	0.167	0.173	0.198	0.102	0.182	0.098	0.166	0.077	0.062	0.191	0.168
$K_{f,6}$	0.189	0.097	0.140	0.113	0.110	0.135	0.119	0.164	0.084	0.054	0.176	0.139
$K_{f,7}$	0.213	0.163	0.126	0.140	0.111	0.137	0.080	0.105	0.044	0.053	0.118	0.155
$K_{f,8}$	0.163	0.175	0.149	0.156	0.094	0.111	0.095	0.148	0.055	0.060	0.221	0.216
$K_{f,9}$	0.240	0.199	0.115	0.181	0.146	0.130	0.088	0.128	0.053	0.049	0.163	0.222
	1,2,4-TCB	1,4-DCB	CB	<i>m</i>-XYL	TOL	BZ	2,4-DMP	<i>p</i>-CRE	PHE	2-HEX	2-BUT	ACE
n_s	1.00	1.04	0.967	0.988	0.986	0.955	0.854	0.730	0.717	0.851	0.634	0.668
n_1	0.994	0.985	0.990	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	0.942	0.992	1.00	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.850	0.912	0.755	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.950	0.744	0.687
n_5	0.956	0.945	0.943	0.950	1.03	0.907	0.897	0.841	0.821	0.819	0.676	0.604
n_6	0.954	1.03	0.899	1.06	0.939	0.970	0.806	0.843	0.800	0.966	0.669	0.734
n_7	0.946	0.928	0.962	0.970	1.00	0.990	0.825	0.926	0.928	0.925	0.782	0.692
n_8	1.03	0.986	1.04	0.984	1.02	0.971	0.929	0.837	0.891	0.816	0.644	0.649
n_9	0.928	0.933	0.974	0.887	0.942	0.957	0.810	0.898	0.872	0.930	0.683	0.627

^a Not available

Table 5.6 Summary of least-squares mean Freundlich sorption parameters of 12 neutral organic compounds in mixtures to Al₂O₃-coated sand ($f_{oc} = 0.005\%$) based on the different initial aqueous concentration displayed in Table 5.3. (No. of observation = 3)

	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
$K_{f,s}^a$	0.210	0.168	0.160	0.147	0.143	0.127	0.083	0.305	0.150	0.101	0.205	0.098
$K_{f,1}$	0.222	0.125	0.114	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,2}$	NA ^a	NA	NA	0.132	0.149	0.141	NA	NA	NA	NA	NA	NA
$K_{f,3}$	NA	NA	NA	NA	NA	NA	0.095	0.166	0.125	NA	NA	NA
$K_{f,4}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.080	0.270	0.117
$K_{f,5}$	0.256	0.162	0.159	0.175	0.117	0.183	0.094	0.186	0.111	0.062	0.196	0.099
$K_{f,6}$	0.193	0.185	0.175	0.146	0.171	0.152	0.079	0.185	0.078	0.091	0.165	0.197
$K_{f,7}$	0.209	0.183	0.197	0.225	0.203	0.122	0.076	0.143	0.066	0.061	0.192	0.103
$K_{f,8}$	0.145	0.216	0.199	0.156	0.180	0.145	0.101	0.109	0.083	0.086	0.189	0.180
$K_{f,9}$	0.232	0.209	0.145	0.157	0.179	0.133	0.085	0.154	0.089	0.069	0.321	0.095
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
n_s^b	0.966	0.967	0.945	0.980	0.954	0.962	0.886	0.648	0.658	0.912	0.694	0.767
n_1	0.952	1.01	0.977	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	0.940	0.962	0.968	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.860	0.848	0.680	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.939	0.661	0.750
n_5	0.938	0.953	0.903	0.961	1.03	0.909	0.852	0.823	0.790	0.824	0.643	0.728
n_6	0.939	0.962	0.961	0.966	0.953	1.04	0.843	0.812	0.806	0.833	0.660	0.595
n_7	0.912	0.965	0.947	0.932	0.930	0.978	0.877	0.815	0.789	0.942	0.611	0.739
n_8	0.999	0.912	0.980	0.921	0.922	1.03	0.816	0.895	0.761	0.849	0.705	0.674
n_9	0.993	0.963	0.987	0.939	0.951	0.983	0.905	0.830	0.761	0.960	0.614	0.702

^a Not available

Table 5.7 Summary of the comparison of parameters from control (i.e., single-sorbate systems) to those from treatments (i.e., mixtures) using Dunnett's procedure in statistical software (SAS® 9.1, Cary, NC) for untreated sand ($f_{oc} = 0.006\%$).

p-value^a for H_0: LSM^b (control) = LSM (treatment)												
	1,2,4-TCB	1,4-DCB	CB	<i>m</i>-XYL	TOL	BZ	2,4-DMP	<i>p</i>-CRE	PHE	2-HEX	2-BUT	ACE
$K_{f,s}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,1}$	0.160	0.998	0.925	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,2}$	NA	NA	NA	0.454	0.011	0.900	NA	NA	NA	NA	NA	NA
$K_{f,3}$	NA	NA	NA	NA	NA	NA	0.248	0.129	1.00	NA	NA	NA
$K_{f,4}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.032	0.999	0.835
$K_{f,5}$	0.061	0.732	0.347	0.314	1.00	0.297	0.523	0.049	0.009	1.00	1.00	0.990
$K_{f,6}$	1.00	0.461	0.073	0.850	0.018	0.021	0.051	0.039	0.027	0.854	0.999	1.00
$K_{f,7}$	0.999	0.618	0.129	0.487	0.999	0.011	0.052	0.027	0.005	0.812	1.00	0.999
$K_{f,8}$	0.838	1.00	0.059	1.00	1.00	0.111	0.115	0.045	0.405	0.967	0.459	0.757
$K_{f,9}$	0.609	0.454	0.099	0.172	0.499	0.008	0.301	0.022	0.046	0.714	0.999	0.994
	1,2,4-TCB	1,4-DCB	CB	<i>m</i>-XYL	TOL	BZ	2,4-DMP	<i>p</i>-CRE	PHE	2-HEX	2-BUT	ACE
n_s	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_1	0.358	0.999	1.00	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	1.00	0.011	0.999	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.077	0.248	0.982	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.131	1.00	0.999
n_5	0.995	1.00	0.906	0.419	0.761	0.614	0.075	0.010	0.008	1.00	0.999	0.986
n_6	1.00	0.999	0.657	0.854	0.830	0.143	0.091	0.003	0.056	0.131	0.972	0.641
n_7	0.999	0.999	0.806	0.959	0.263	0.829	0.547	0.016	0.005	0.672	1.00	0.742
n_8	0.987	0.050	0.539	0.331	0.936	0.929	0.882	0.010	0.669	1.00	0.999	0.999
n_9	0.819	0.918	0.977	0.008	0.999	0.355	0.527	0.043	0.049	0.999	1.00	0.999

^aLevel of significance. If the p -value $\leq \alpha$ ($= 0.05$), then reject the null hypothesis, H_0 .^bLeast squares means

Table 5.8 Summary of the comparison of parameters from control (i.e., single-sorbate systems) to those from treatments (i.e., mixtures) using Dunnett's procedure in statistical software (SAS® 9.1, Cary, NC) for FeO(OH)-coated sand ($f_{oc} = 0.006\%$).

p -value ^a for $H_0 : \text{LSM}^b(\text{control}) = \text{LSM}(\text{treatment})$												
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
K_{fs}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
K_{f1}	0.921	0.975	1.00	NA	NA	NA	NA	NA	NA	NA	NA	NA
K_{f2}	NA	NA	NA	0.999	0.999	0.908	NA	NA	NA	NA	NA	NA
K_{f3}	NA	NA	NA	NA	NA	NA	0.331	0.021	0.656	NA	NA	NA
K_{f4}	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.005	0.099	0.957
K_{f5}	0.670	0.607	0.305	0.051	1.00	0.058	0.811	0.278	0.031	0.185	0.886	1.00
K_{f6}	0.971	0.901	0.977	0.972	0.999	0.853	0.999	0.259	0.048	0.029	0.792	0.911
K_{f7}	0.422	0.687	1.00	0.990	0.999	0.813	0.417	0.031	0.007	0.024	0.121	0.995
K_{f8}	0.994	0.439	0.849	0.693	0.991	0.999	0.763	0.152	0.016	0.109	0.998	0.804
K_{f9}	0.065	0.143	0.998	0.169	0.278	0.959	0.595	0.075	0.017	0.011	0.549	0.715
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
n_s	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_1	0.999	0.944	0.993	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	0.916	1.00	0.757	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	1.00	0.007	0.962	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.039	0.236	0.999
n_5	0.832	0.636	0.989	0.963	0.968	0.627	0.953	0.120	0.034	0.843	0.820	0.930
n_6	0.806	1.00	0.563	0.698	0.941	0.999	0.919	0.114	0.040	0.016	0.903	0.916
n_7	0.712	0.477	1.00	0.999	0.999	0.933	0.991	0.004	0.011	0.155	0.069	0.999
n_8	0.976	0.951	0.465	1.00	0.975	0.998	0.683	0.143	0.018	0.787	0.999	0.999
n_9	0.471	0.527	1.00	0.364	0.954	1.00	0.945	0.013	0.029	0.120	0.711	0.991

^aLevel of significance. If the p -value $\leq \alpha$ ($= 0.05$), then reject the null hypothesis, H_0 .

^bLeast squares means

Table 5.9 Summary of the comparison of parameters from control (i.e., single-sorbate systems) to those from treatments (i.e., mixtures) using Dunnett's procedure in statistical software (SAS® 9.1, Cary, NC) for Al₂O₃-coated sand ($f_{oc} = 0.005\%$).

$p\text{-value}^a$ for $H_0 : \text{LSM}^b(\text{control}) = \text{LSM}(\text{treatment})$												
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
K_{fs}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
K_{f1}	0.998	0.852	0.417	NA	NA	NA	NA	NA	NA	NA	NA	NA
K_{f2}	NA	NA	NA	0.985	0.999	0.961	NA	NA	NA	NA	NA	NA
K_{f3}	NA	NA	NA	NA	NA	NA	0.937	0.036	0.318	NA	NA	NA
K_{f4}	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.864	0.655	0.991
K_{f5}	0.656	1.00	1.00	0.819	0.777	0.088	0.959	0.079	0.056	0.357	1.00	1.00
K_{f6}	0.992	0.998	0.983	1.00	0.741	0.727	0.999	0.076	0.001	0.995	0.932	0.096
K_{f7}	1.00	0.999	0.607	0.066	0.125	0.999	0.998	0.013	0.001	0.345	0.999	1.00
K_{f8}	0.337	0.791	0.536	0.999	0.513	0.899	0.743	0.003	0.001	0.958	0.999	0.204
K_{f9}	0.976	0.873	0.989	0.999	0.533	0.999	1.00	0.021	0.003	0.536	0.171	1.00
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
n_s	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_1	0.999	0.924	0.936	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	0.847	1.00	1.00	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.978	0.006	0.988	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.998	0.986	0.999
n_5	0.978	0.999	0.834	0.993	0.476	0.758	0.927	0.015	0.032	0.999	0.915	0.969
n_6	0.981	1.00	0.997	0.998	1.00	0.398	0.831	0.023	0.016	0.765	0.986	0.068
n_7	0.741	1.00	1.00	0.743	0.988	0.998	0.999	0.020	0.033	0.996	0.600	0.994
n_8	0.959	0.802	0.913	0.575	0.957	0.571	0.446	0.001	0.114	0.887	1.00	0.508
n_9	0.982	1.00	0.828	0.839	1.00	0.994	0.996	0.011	0.113	0.961	0.650	0.793

^aLevel of significance. If the $p\text{-value} \leq \alpha (= 0.05)$, then reject the null hypothesis, H_0 .^bLeast squares means

Table 5.10 Summary of least-squares mean Freundlich sorption parameters of 12 organic compounds in mixtures to HA-coated sand ($f_{oc} = 0.051\%$) based on the different initial aqueous concentration displayed in Table 5.3. (No. of observation = 3)

	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
$K_{f,s}$	1.09	0.561	0.268	0.330	0.257	0.142	0.157	0.075	0.092	0.049	0.049	0.120
$K_{f,1}$	0.909	0.395	0.246	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,2}$	NA ^a	NA	NA	0.454	0.212	0.187	NA	NA	NA	NA	NA	NA
$K_{f,3}$	NA	NA	NA	NA	NA	NA	0.094	0.056	0.082	NA	NA	NA
$K_{f,4}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.021	0.057	0.126
$K_{f,5}$	0.948	0.458	0.308	0.373	0.323	0.206	0.118	0.062	0.043	0.062	0.065	0.111
$K_{f,6}$	0.974	0.444	0.298	0.362	0.222	0.176	0.111	0.053	0.058	0.059	0.059	0.144
$K_{f,7}$	1.05	0.438	0.227	0.330	0.315	0.224	0.103	0.077	0.040	0.034	0.037	0.149
$K_{f,8}$	0.946	0.533	0.248	0.269	0.312	0.153	0.084	0.034	0.042	0.065	0.067	0.158
$K_{f,9}$	0.794	0.476	0.229	0.337	0.266	0.179	0.100	0.044	0.056	0.052	0.070	0.168
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
n_s	0.968	0.960	0.986	1.01	0.978	1.08	0.805	0.823	0.734	0.838	0.759	0.723
n_1	0.978	0.987	0.975	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	0.922	0.979	0.951	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.922	0.905	0.799	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.938	0.755	0.681
n_5	1.00	0.965	0.926	0.930	0.942	0.973	0.911	0.876	0.892	0.859	0.743	0.779
n_6	0.976	0.990	0.967	0.952	0.984	1.02	0.874	0.871	0.859	0.879	0.720	0.767
n_7	0.949	0.996	0.965	0.942	0.978	0.949	0.871	0.856	0.912	0.917	0.801	0.799
n_8	0.973	0.912	0.915	1.02	0.928	1.04	0.926	1.08	0.904	0.888	0.681	0.809
n_9	1.03	1.01	1.00	0.997	1.01	0.993	0.888	0.992	0.862	0.822	0.823	0.643

^a Not available

Table 5.11 Summary of least-squares mean Freundlich sorption parameters of 12 organic compounds in mixtures to HA-coated sand ($f_{oc} = 0.119\%$) based on the different initial aqueous concentration displayed in Table 5.3. (No. of observation = 3)

	1,2,4-TCB	1,4-DCB	CB	<i>m</i>-XYL	TOL	BZ	2,4-DMP	<i>p</i>-CRE	PHE	2-HEX	2-BUT	ACE
K_{fs}	2.16	1.03	0.612	0.676	0.569	0.277	0.289	0.208	0.175	0.140	0.085	0.135
K_{f1}	2.63	1.14	0.657	NA	NA	NA	NA	NA	NA	NA	NA	NA
K_{f2}	NA ^a	NA	NA	0.641	0.479	0.212	NA	NA	NA	NA	NA	NA
K_{f3}	NA	NA	NA	NA	NA	NA	0.183	0.158	0.189	NA	NA	NA
K_{f4}	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.121	0.056	0.199
K_{f5}	2.32	0.903	0.589	0.643	0.516	0.276	0.236	0.163	0.125	0.144	0.089	0.140
K_{f6}	2.03	0.904	0.576	0.631	0.411	0.297	0.214	0.173	0.079	0.109	0.068	0.119
K_{f7}	2.00	1.08	0.483	0.699	0.406	0.334	0.183	0.123	0.099	0.133	0.085	0.139
K_{f8}	2.49	1.14	0.417	0.536	0.386	0.236	0.193	0.124	0.133	0.158	0.091	0.146
K_{f9}	1.99	1.19	0.470	0.520	0.404	0.230	0.227	0.151	0.147	0.120	0.096	0.152
	1,2,4-TCB	1,4-DCB	CB	<i>m</i>-XYL	TOL	BZ	2,4-DMP	<i>p</i>-CRE	PHE	2-HEX	2-BUT	ACE
n_s	0.970	0.959	0.897	0.948	0.879	0.968	0.842	0.811	0.762	0.859	0.706	0.668
n_1	0.949	0.956	0.932	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	0.953	0.943	0.999	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.940	0.849	0.801	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.897	0.838	0.673
n_5	0.988	0.988	0.960	0.970	0.942	0.997	0.872	0.856	0.851	0.880	0.740	0.751
n_6	0.940	0.984	0.953	0.942	0.969	0.941	0.872	0.831	0.844	0.859	0.765	0.688
n_7	0.959	0.971	0.974	1.02	0.992	0.955	0.855	0.888	0.936	0.911	0.777	0.701
n_8	0.937	0.928	0.965	0.992	0.975	0.943	0.882	0.975	0.871	0.895	0.751	0.777
n_9	0.971	0.938	0.937	0.928	0.948	0.974	0.894	0.821	0.84	0.886	0.694	0.728

^a Not available

Table 5.12 Summary of least-squares mean Freundlich sorption parameters of 12 organic compounds in mixtures to HA-coated sand ($f_{oc} = 0.221\%$) based on the different initial aqueous concentration displayed in Table 5.3. (No. of observation = 3)

	1,2,4-TCB	1,4-DCB	CB	<i>m</i>-XYL	TOL	BZ	2,4-DMP	<i>p</i>-CRE	PHE	2-HEX	2-BUT	ACE
$K_{f,s}$	2.97	1.35	0.958	0.673	0.346	0.363	0.586	0.449	0.201	0.229	0.244	0.158
$K_{f,1}$	3.75	1.41	0.814	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,2}$	NA ^a	NA	NA	0.799	0.338	0.244	NA	NA	NA	NA	NA	NA
$K_{f,3}$	NA	NA	NA	NA	NA	NA	0.505	0.333	0.247	NA	NA	NA
$K_{f,4}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.181	0.202	0.183
$K_{f,5}$	3.58	1.57	0.824	0.711	0.371	0.278	0.430	0.376	0.176	0.160	0.283	0.185
$K_{f,6}$	3.43	1.41	0.725	0.758	0.403	0.241	0.452	0.371	0.153	0.189	0.237	0.208
$K_{f,7}$	3.49	1.52	0.710	0.681	0.349	0.243	0.522	0.327	0.092	0.149	0.174	0.133
$K_{f,8}$	3.18	1.33	0.686	0.737	0.252	0.293	0.526	0.251	0.127	0.176	0.208	0.124
$K_{f,9}$	3.67	1.60	0.713	0.628	0.420	0.311	0.413	0.377	0.157	0.123	0.244	0.192
	1,2,4-TCB	1,4-DCB	CB	<i>m</i>-XYL	TOL	BZ	2,4-DMP	<i>p</i>-CRE	PHE	2-HEX	2-BUT	ACE
n_s	0.973	0.978	0.958	1.01	0.987	0.949	0.829	0.817	0.823	0.800	0.735	0.686
n_1	0.943	0.996	0.955	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	0.974	0.968	1.02	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.868	0.917	0.757	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.869	0.793	0.701
n_5	0.969	0.951	0.936	0.977	0.938	0.941	0.856	0.824	0.835	0.843	0.713	0.720
n_6	0.959	0.942	0.963	0.968	0.945	0.999	0.862	0.871	0.840	0.839	0.826	0.779
n_7	0.939	0.911	0.927	1.01	0.974	0.922	0.847	0.871	0.959	0.921	0.789	0.757
n_8	1.04	1.04	1.04	0.932	1.04	0.958	0.877	0.831	0.859	0.882	0.778	0.726
n_9	0.969	0.953	0.987	0.991	0.943	0.948	0.907	0.876	0.866	0.927	0.759	0.647

^a Not available

Table 5.13 Summary of the comparison of parameters from control (i.e., single-sorbate systems) to those from treatments (i.e., mixtures) using Dunnett's procedure in statistical software (SAS® 9.1, Cary, NC) for HA-coated sand ($f_{oc} = 0.051\%$).

p -value ^a for $H_0 : \text{LSM}^b(\text{control}) = \text{LSM}(\text{treatment})$												
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
$K_{f,5}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,1}$	0.635	0.070	0.936	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,2}$	NA	NA	NA	0.059	0.674	0.778	NA	NA	NA	NA	NA	NA
$K_{f,3}$	NA	NA	NA	NA	NA	NA	0.047	0.220	0.981	NA	NA	NA
$K_{f,4}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.047	0.954	1.00
$K_{f,5}$	0.809	0.403	0.576	0.849	0.315	0.480	0.446	0.553	0.049	0.715	0.518	0.999
$K_{f,6}$	0.903	0.285	0.817	0.953	0.844	0.916	0.294	0.122	0.081	0.875	0.876	0.940
$K_{f,7}$	0.999	0.242	0.532	1.00	0.426	0.249	0.175	1.00	0.034	0.571	0.749	0.876
$K_{f,8}$	0.803	0.994	0.956	0.600	0.473	0.999	0.040	0.002	0.043	0.546	0.364	0.710
$K_{f,9}$	0.204	0.580	0.577	1.00	0.999	0.888	0.141	0.016	0.068	0.999	0.236	0.492
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
n_5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_1	0.999	0.966	0.999	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	0.238	1.00	0.346	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.039	0.549	0.514	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.563	1.00	0.984
n_5	0.941	1.00	0.470	0.320	0.938	0.524	0.068	0.870	0.011	0.999	0.999	0.946
n_6	1.00	0.946	0.992	0.649	1.00	0.921	0.345	0.912	0.051	0.982	0.966	0.982
n_7	0.996	0.882	0.988	0.482	1.00	0.333	0.394	0.981	0.005	0.760	0.956	0.825
n_8	1.00	0.711	0.314	0.999	0.789	0.994	0.032	0.002	0.007	0.954	0.628	0.747
n_9	0.622	0.643	0.991	0.999	0.986	0.716	0.201	0.043	0.045	0.999	0.781	0.791

^aLevel of significance. If the p -value $\leq \alpha$ ($= 0.05$), then reject the null hypothesis, H_0 .

^bLeast squares means

Table 5.14 Summary of the comparison of parameters from control (i.e., single-sorbate systems) to those from treatments (i.e., mixtures) using Dunnett's procedure in statistical software (SAS® 9.1, Cary, NC) for HA-coated sand ($f_{oc} = 0.119\%$).

p -value ^a for $H_0 : \text{LSM}^b(\text{control}) = \text{LSM}(\text{treatment})$												
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
$K_{f,s}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,1}$	0.261	0.868	0.979	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,2}$	NA	NA	NA	0.997	0.544	0.280	NA	NA	NA	NA	NA	NA
$K_{f,3}$	NA	NA	NA	NA	NA	NA	0.042	0.409	0.994	NA	NA	NA
$K_{f,4}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.993	0.381	0.210
$K_{f,5}$	0.965	0.821	0.999	0.998	0.907	1.00	0.507	0.508	0.391	1.00	0.999	1.00
$K_{f,6}$	0.981	0.827	0.994	0.989	0.099	0.983	0.204	0.729	0.025	0.929	0.818	0.987
$K_{f,7}$	0.962	0.997	0.387	0.999	0.085	0.395	0.055	0.048	0.090	1.00	1.00	1.00
$K_{f,8}$	0.594	0.893	0.091	0.432	0.055	0.708	0.069	0.049	0.550	0.994	0.998	0.998
$K_{f,9}$	0.957	0.926	0.301	0.334	0.079	0.577	0.359	0.270	0.865	0.989	0.969	0.988
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
n_s	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_1	0.985	1.00	0.849	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	1.00	0.472	0.909	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.285	0.932	0.882	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.973	0.126	1.00
n_5	0.991	0.928	0.366	0.997	0.489	0.926	0.978	0.880	0.234	0.998	0.977	0.832
n_6	0.924	0.965	0.478	1.00	0.183	0.955	0.999	0.997	0.298	1.00	0.797	0.998
n_7	0.999	0.999	0.198	0.620	0.068	0.999	0.936	0.478	0.005	0.904	0.650	0.997
n_8	0.887	0.908	0.299	0.922	0.142	0.965	0.828	0.022	0.101	0.978	0.922	0.629
n_9	1.00	0.985	0.769	0.998	0.402	1.00	0.999	0.999	0.341	0.994	0.999	0.950

^aLevel of significance. If the p -value $\leq \alpha$ ($= 0.05$), then reject the null hypothesis, H_0 .

^bLeast squares means

Table 5.15 Summary of the comparison of parameters from control (i.e., single-sorbate systems) to those from treatments (i.e., mixtures) using Dunnett's procedure in statistical software (SAS® 9.1, Cary, NC) for HA-coated sand ($f_{oc} = 0.221\%$).

p -value ^a for $H_0 : \text{LSM}^b(\text{control}) = \text{LSM}(\text{treatment})$												
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
$K_{f,5}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,1}$	0.295	0.994	0.460	NA	NA	NA	NA	NA	NA	NA	NA	NA
$K_{f,2}$	NA	NA	NA	0.428	1.00	0.106	NA	NA	NA	NA	NA	NA
$K_{f,3}$	NA	NA	NA	NA	NA	NA	0.813	0.375	0.651	NA	NA	NA
$K_{f,4}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.527	0.826	0.954
$K_{f,5}$	0.518	0.444	0.523	0.991	0.992	0.342	0.266	0.772	0.966	0.228	0.865	0.929
$K_{f,6}$	0.740	0.997	0.100	0.440	0.774	0.097	0.399	0.726	0.648	0.702	1.00	0.564
$K_{f,7}$	0.648	0.693	0.075	1.00	1.00	0.101	0.918	0.325	0.049	0.138	0.419	0.955
$K_{f,8}$	0.988	1.00	0.056	0.908	0.344	0.521	0.934	0.049	0.257	0.456	0.895	0.844
$K_{f,9}$	0.381	0.326	0.079	0.980	0.568	0.763	0.191	0.779	0.712	0.032	1.00	0.841
	1,2,4-TCB	1,4-DCB	CB	<i>m</i> -XYL	TOL	BZ	2,4-DMP	<i>p</i> -CRE	PHE	2-HEX	2-BUT	ACE
n_5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_1	0.967	0.997	1.00	NA	NA	NA	NA	NA	NA	NA	NA	NA
n_2	NA	NA	NA	0.912	0.996	0.691	NA	NA	NA	NA	NA	NA
n_3	NA	NA	NA	NA	NA	NA	0.733	0.083	0.730	NA	NA	NA
n_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.855	0.558	0.999
n_5	1.00	0.978	0.985	0.931	0.807	1.00	0.923	1.00	0.999	0.980	0.984	0.950
n_6	0.999	0.918	1.00	0.852	0.879	0.904	0.847	0.548	0.999	0.986	0.178	0.277
n_7	0.950	0.504	0.936	1.00	0.999	0.925	0.988	0.560	0.135	0.416	0.619	0.523
n_8	0.580	0.515	0.299	0.393	0.705	1.00	0.561	0.998	0.970	0.751	0.793	0.913
n_9	1.00	0.983	0.950	0.992	0.861	1.00	0.150	0.464	0.936	0.371	0.978	0.921

^aLevel of significance. If the p -value $\leq \alpha$ ($= 0.05$), then reject the null hypothesis, H_0 .

^bLeast squares means

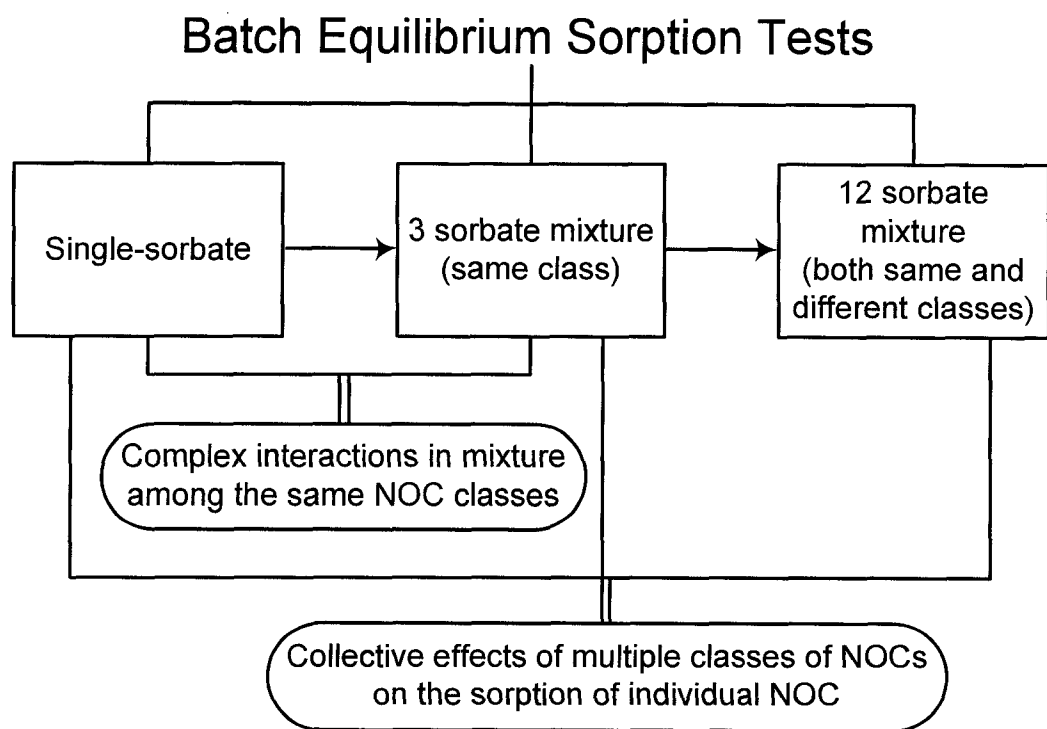


Fig. 5.1 Schematic plan of batch equilibrium sorption tests to investigate the complex interactions and collective effects among sorbates from either the same or different neutral organic compound (NOC) classes to model sorbents used in this study.

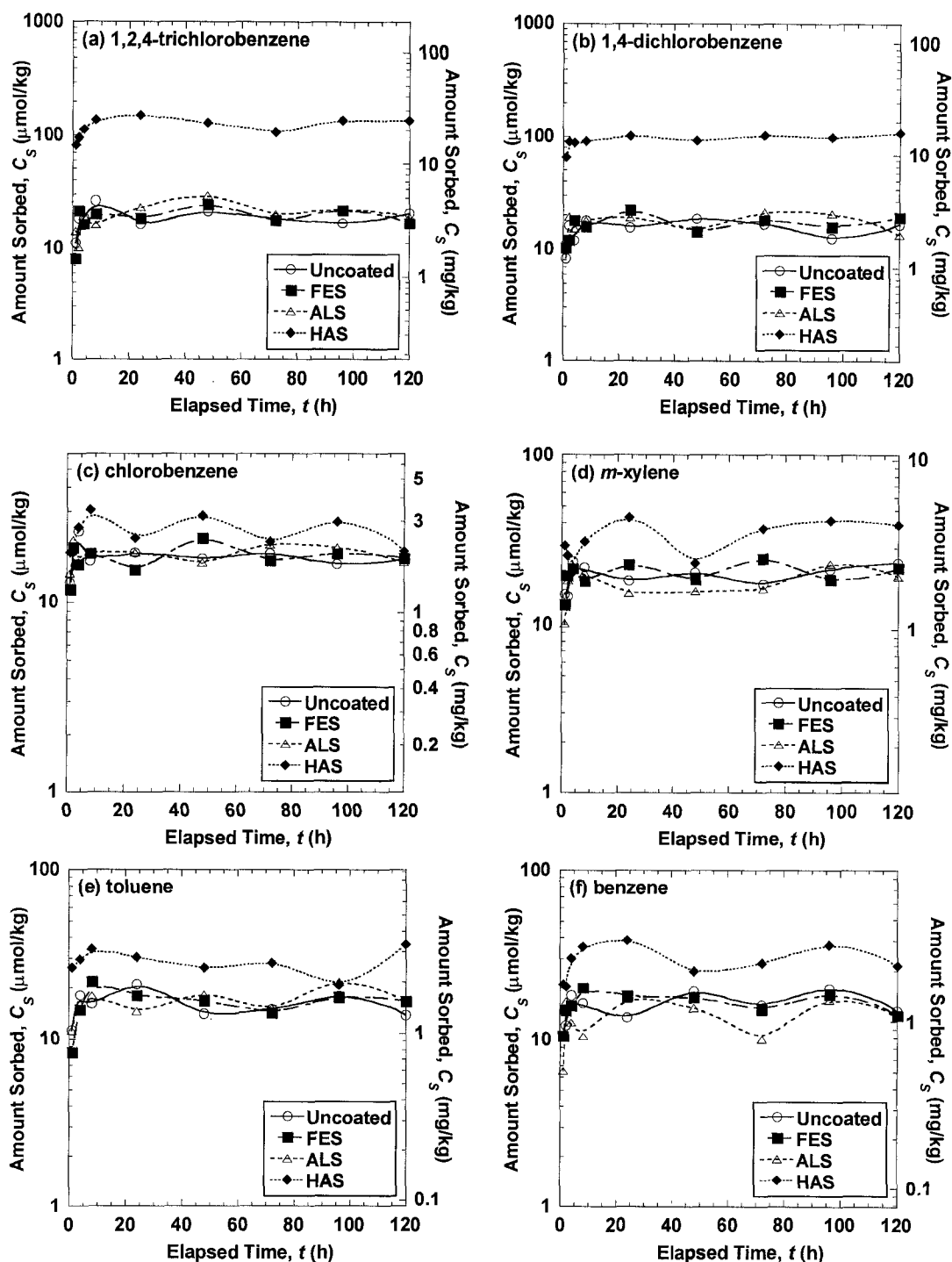


Fig. 5.2 Sorption kinetics for six NNOCs in mixtures to uncoated ($f_{oc} = 0.006\%$), FeO(OH)-coated, FES ($f_{oc} = 0.006\%$), Al_2O_3 -coated, ALS ($f_{oc} = 0.005\%$), and HA-coated sands, HAS ($f_{oc} = 0.119\%$) at initial aqueous concentration of $150\ \mu\text{mol/L}$.

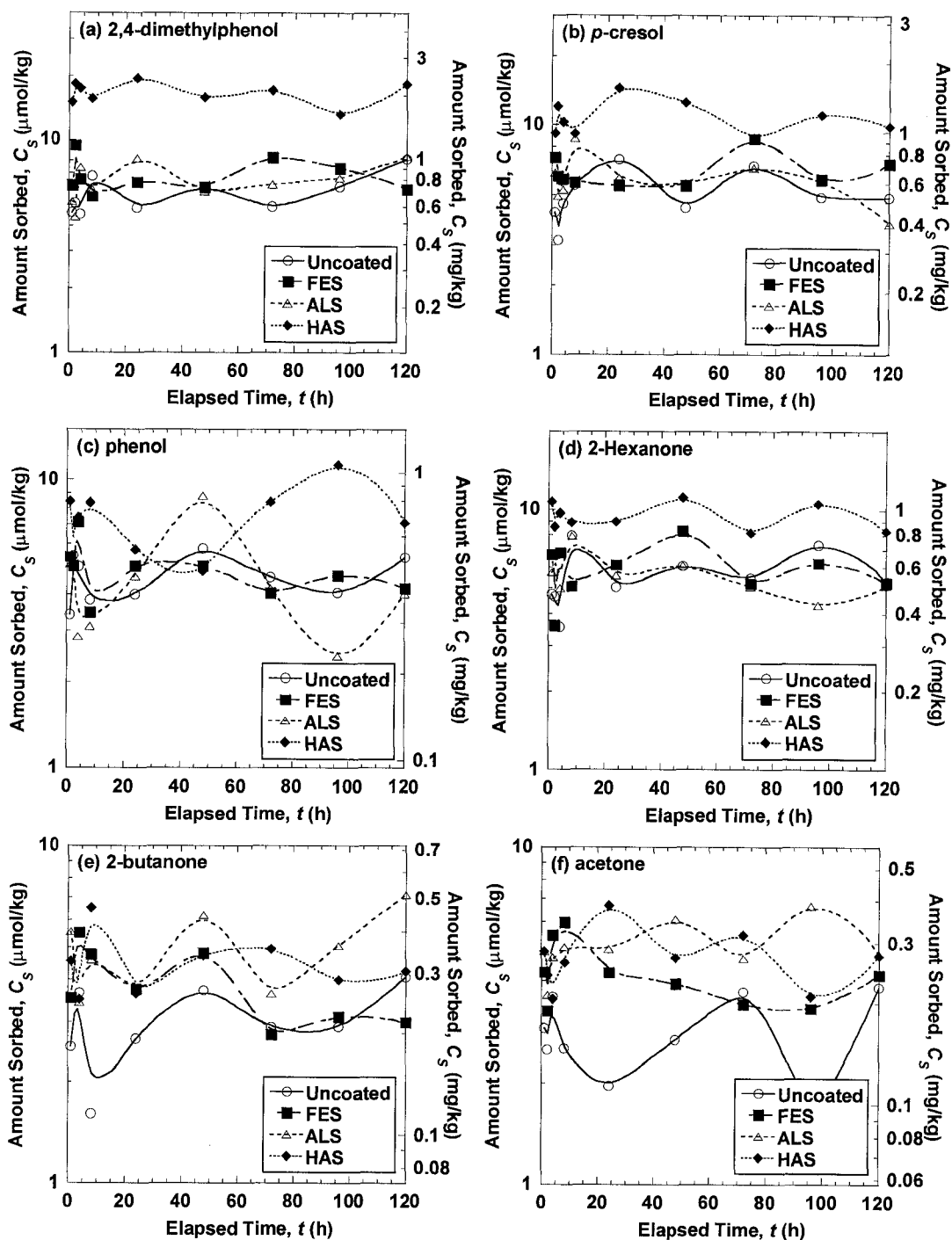


Fig. 5.3 Sorption kinetics for six PNOCs in mixtures to uncoated ($f_{oc} = 0.006\%$), FeO(OH)-coated, FES ($f_{oc} = 0.006\%$), Al₂O₃-coated, ALS ($f_{oc} = 0.005\%$), and HA-coated sands, HAS ($f_{oc} = 0.119\%$) at initial aqueous concentration of 150 μmol/L.

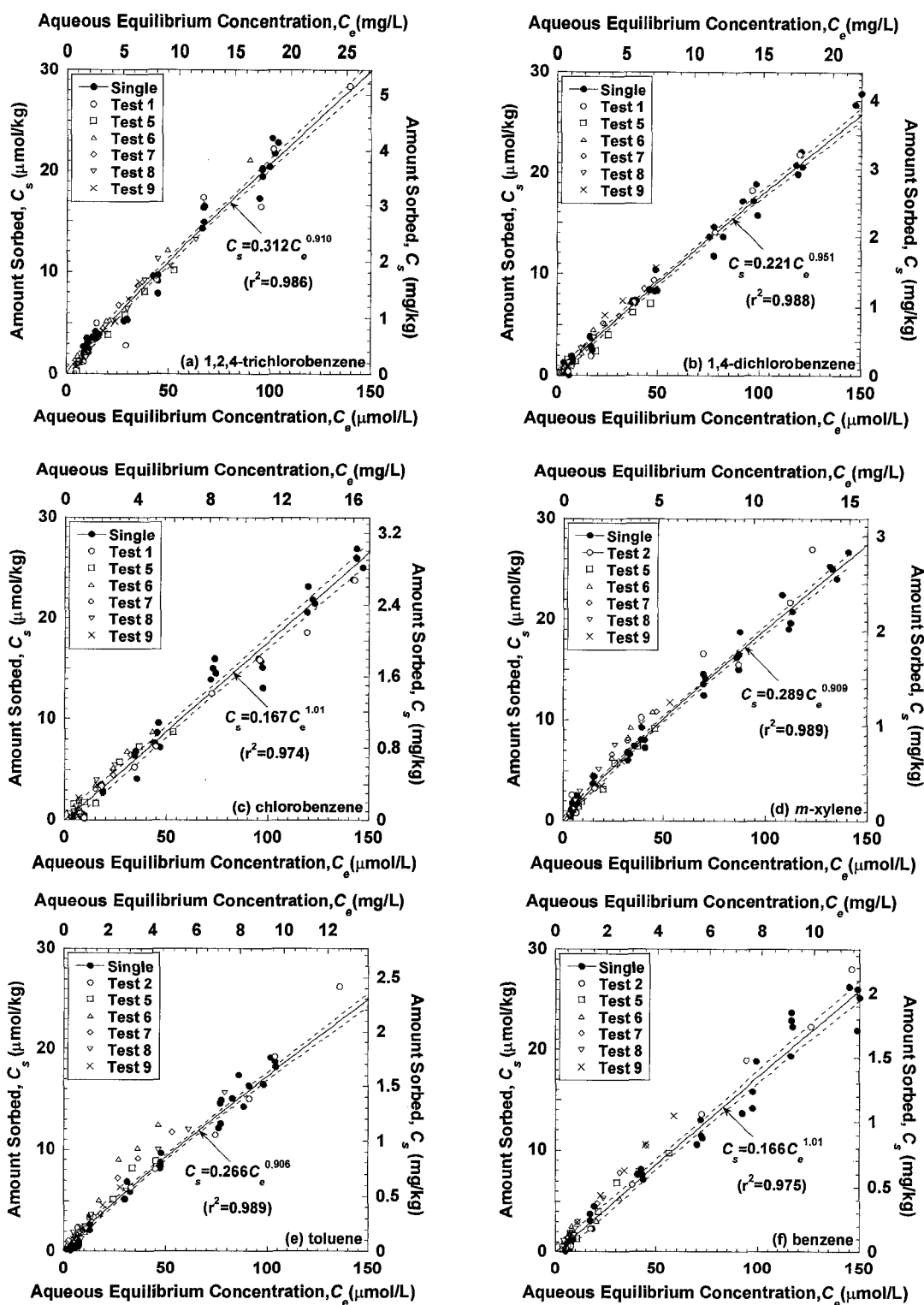


Fig. 5.4 Sorption isotherms of nonpolar neutral organic compounds in single-sorbate systems and in mixtures to uncoated sand. The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.

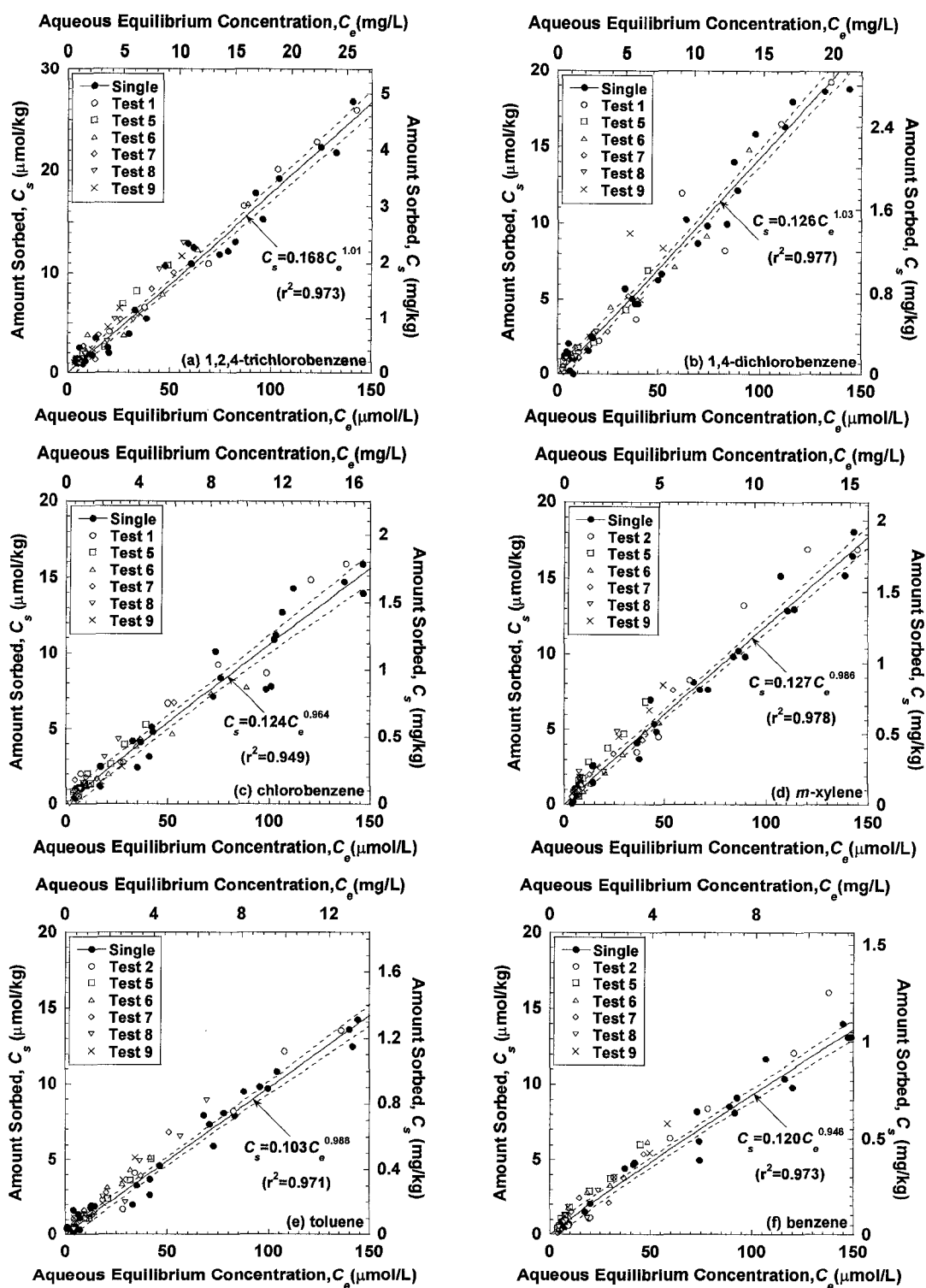


Fig. 5.5 Sorption isotherms of nonpolar neutral organic compounds in single-sorbate systems and in mixtures to FeO(OH)-coated sand. The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.

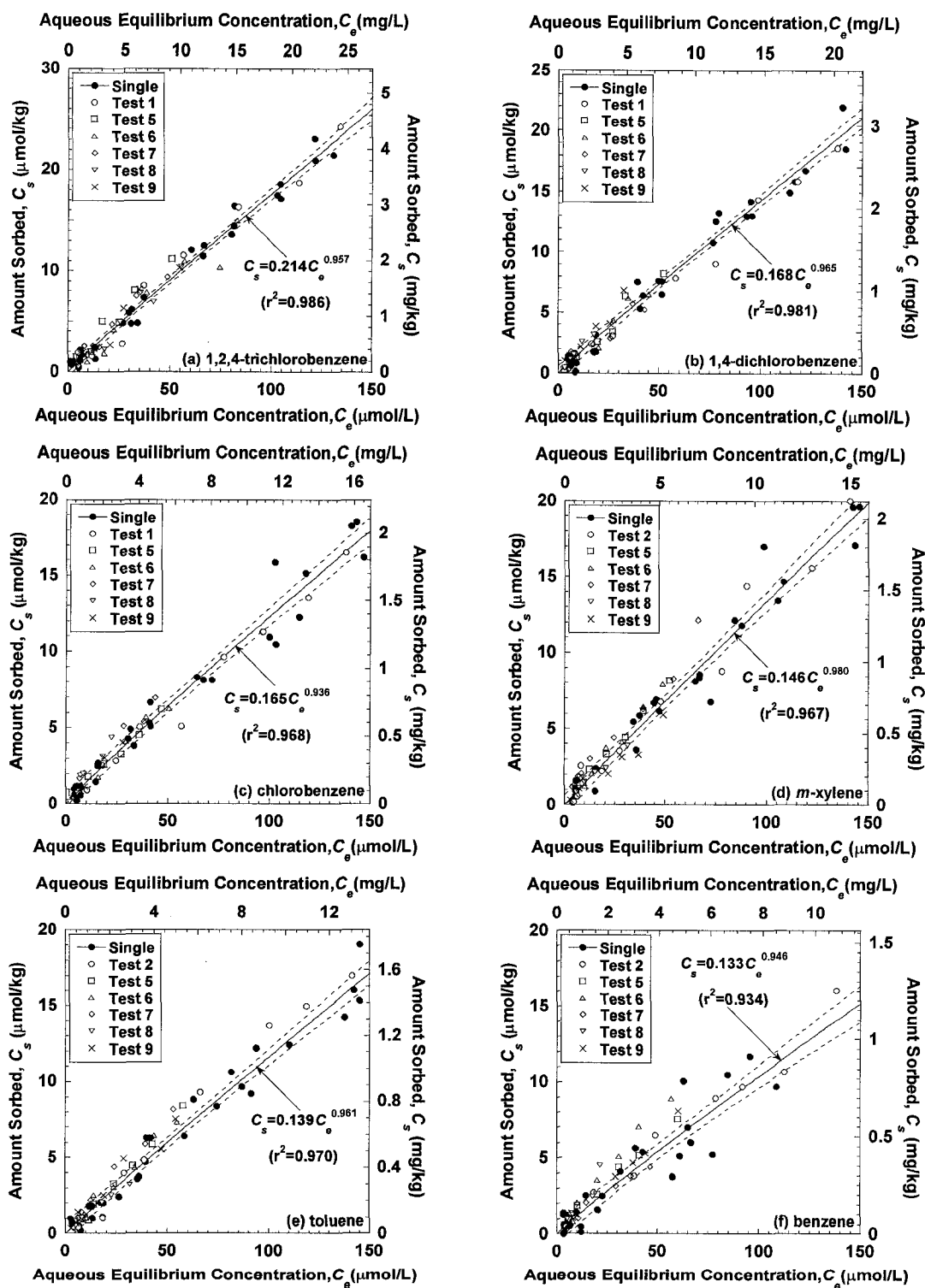


Fig. 5.6 Sorption isotherms of nonpolar neutral organic compounds in single-sorbate systems and in mixtures to Al_2O_3 -coated sand. The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.

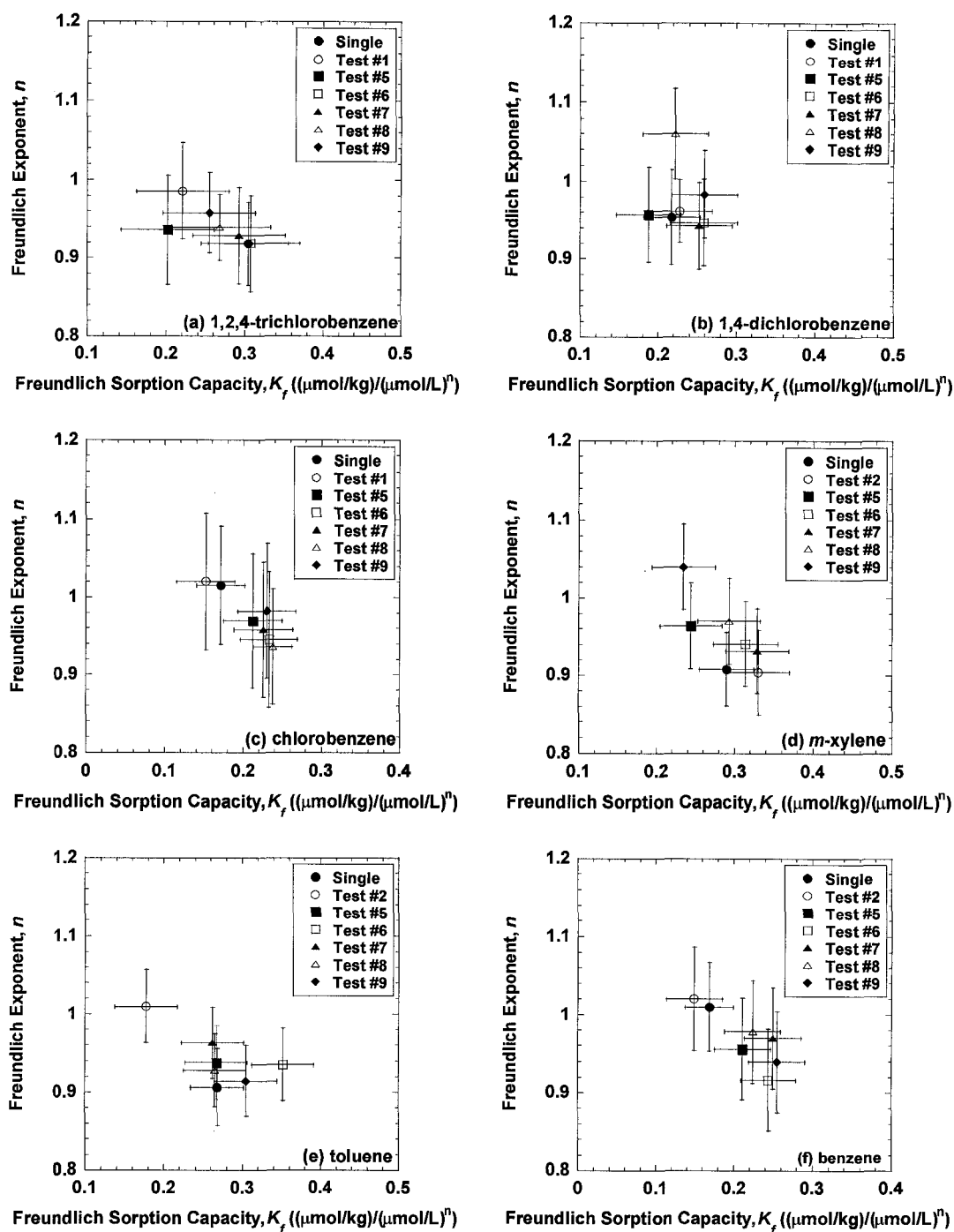


Fig. 5.7 Variations of Freundlich sorption parameters (K_f and n) for nonpolar neutral organic compounds to uncoated sand in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

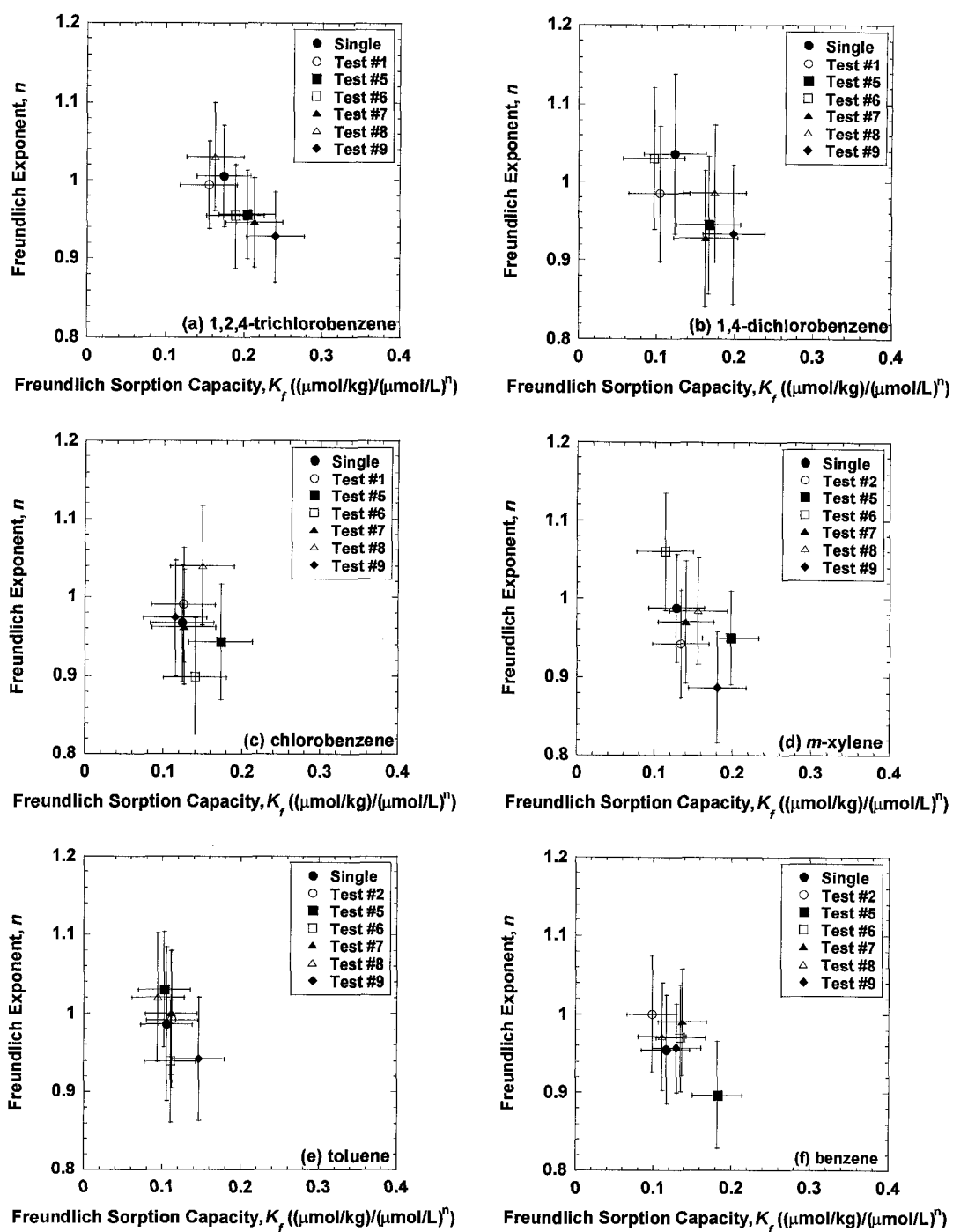


Fig. 5.8 Variations of Freundlich sorption parameters (K_f and n) for nonpolar neutral organic compounds to FeO(OH)-coated sand in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

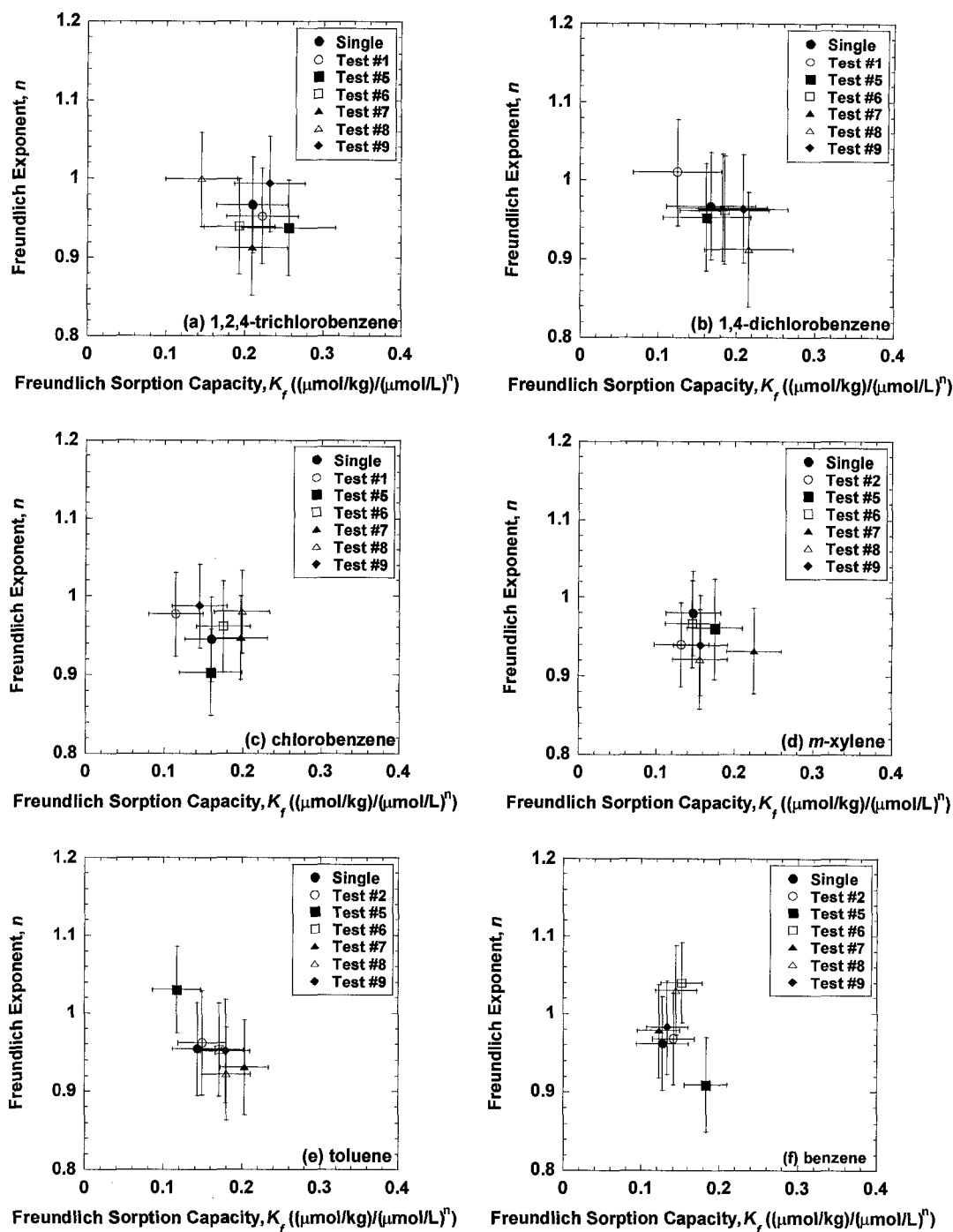


Fig. 5.9 Variations of Freundlich sorption parameters (K_f and n) for nonpolar neutral organic compounds to Al_2O_3 -coated sand in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

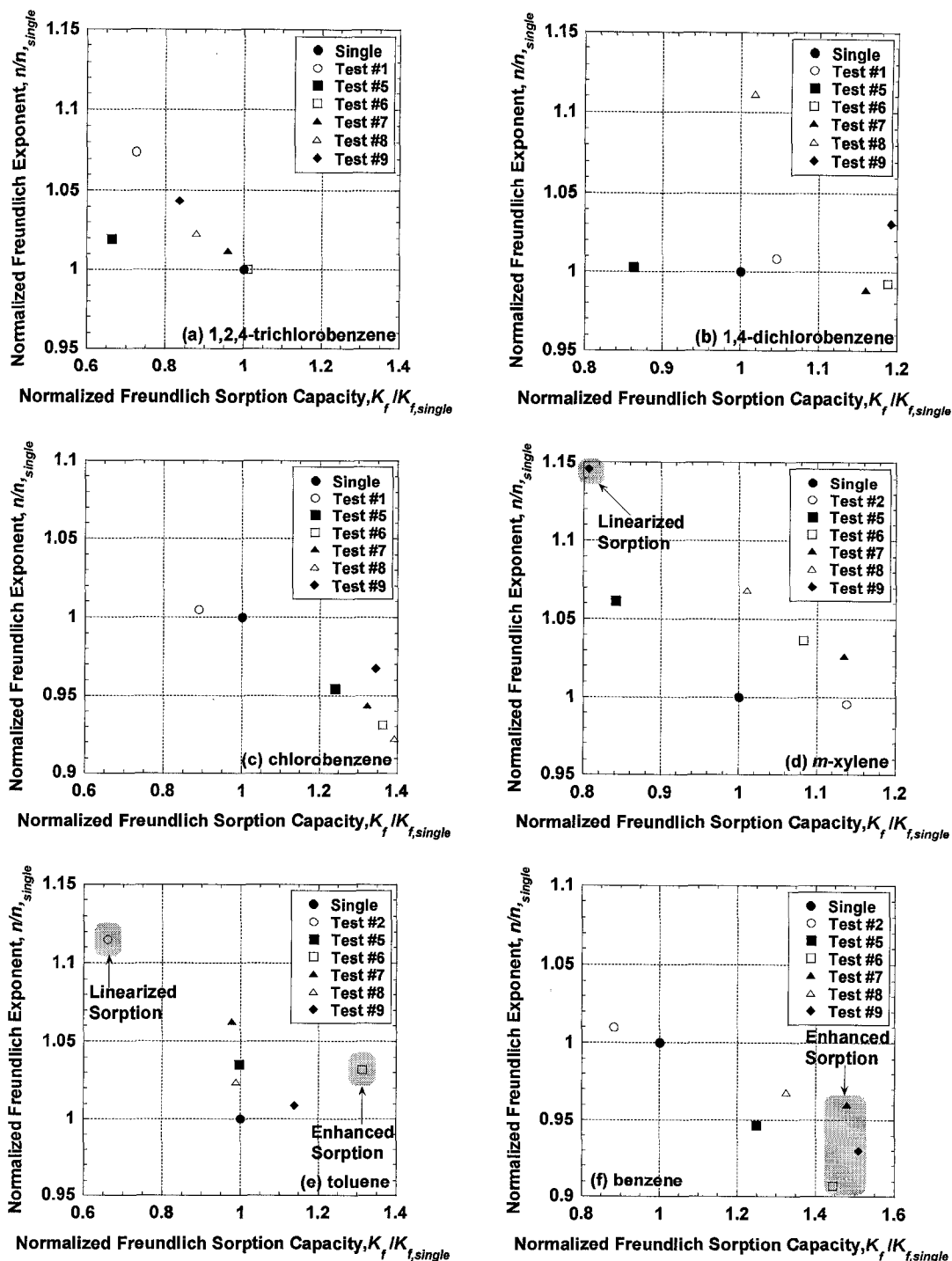


Fig. 5.10 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for nonpolar neutral organic compounds to uncoated sand in terms of experimental conditions.

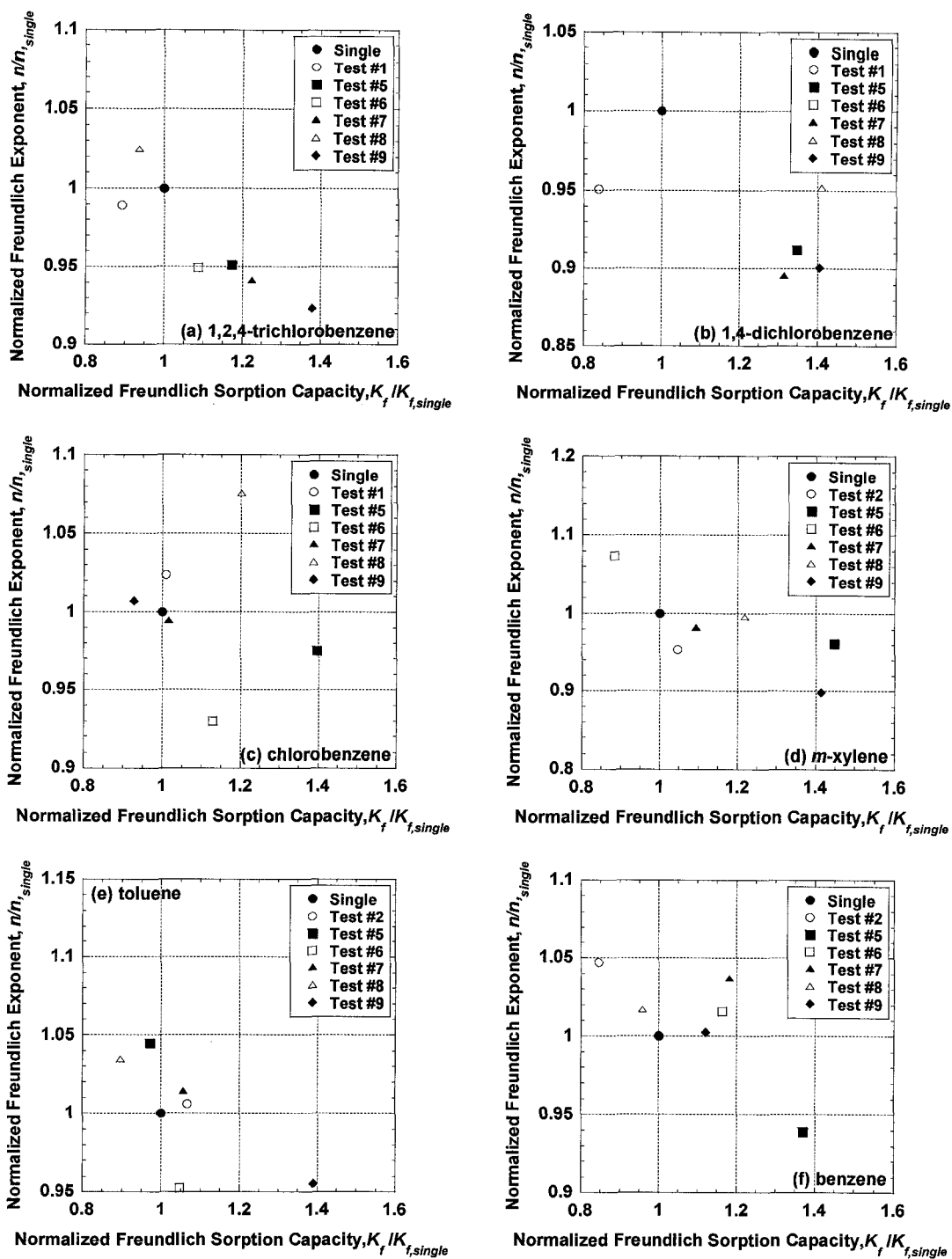


Fig. 5.11 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for nonpolar neutral organic compounds to FeOOH-coated sand in terms of experimental conditions.

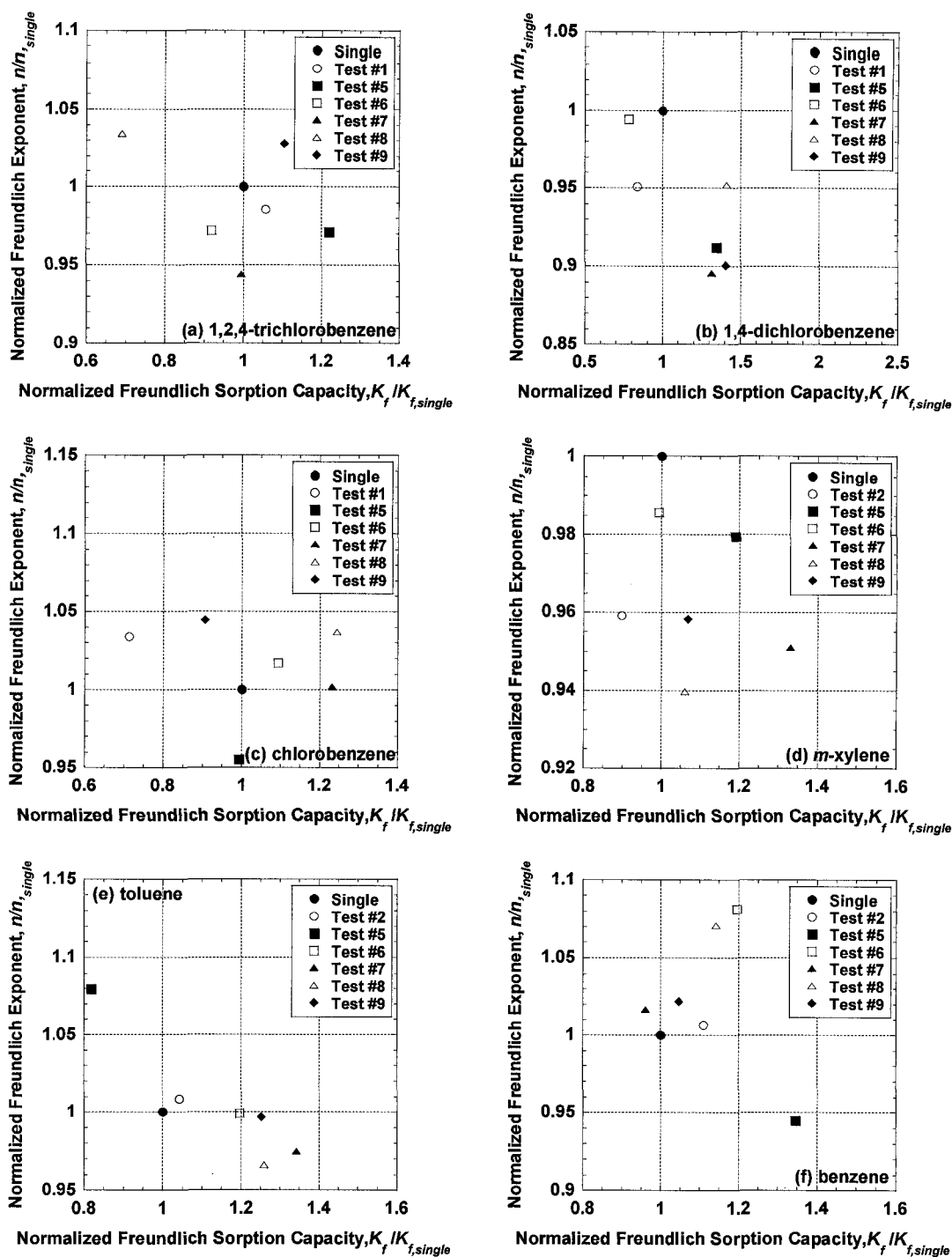


Fig. 5.12 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for nonpolar neutral organic compounds to Al_2O_3 -coated sand in terms of experimental conditions.

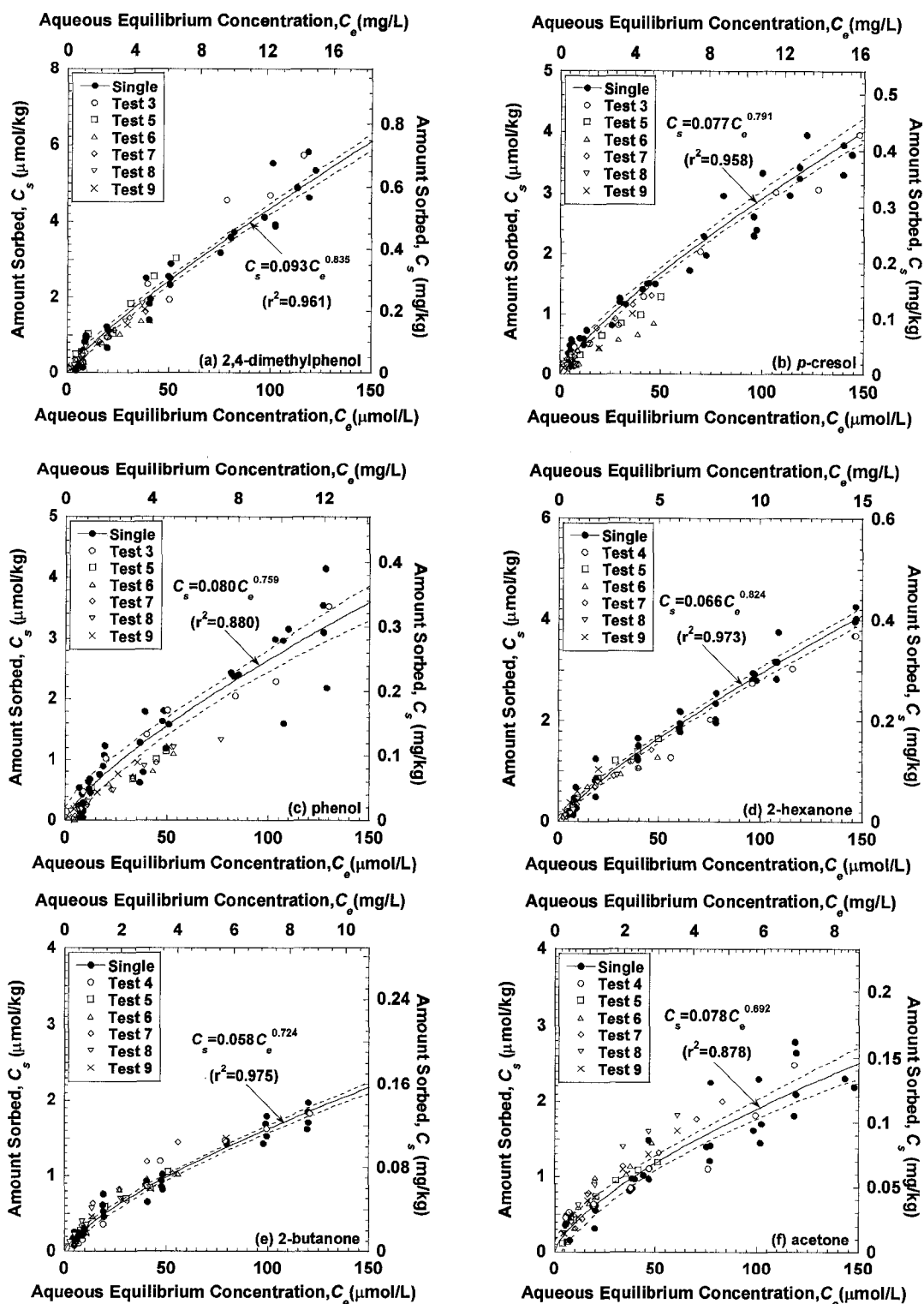


Fig. 5.13 Sorption isotherms of polar neutral organic compounds in single-sorbate systems and in mixtures to uncoated sand. The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.

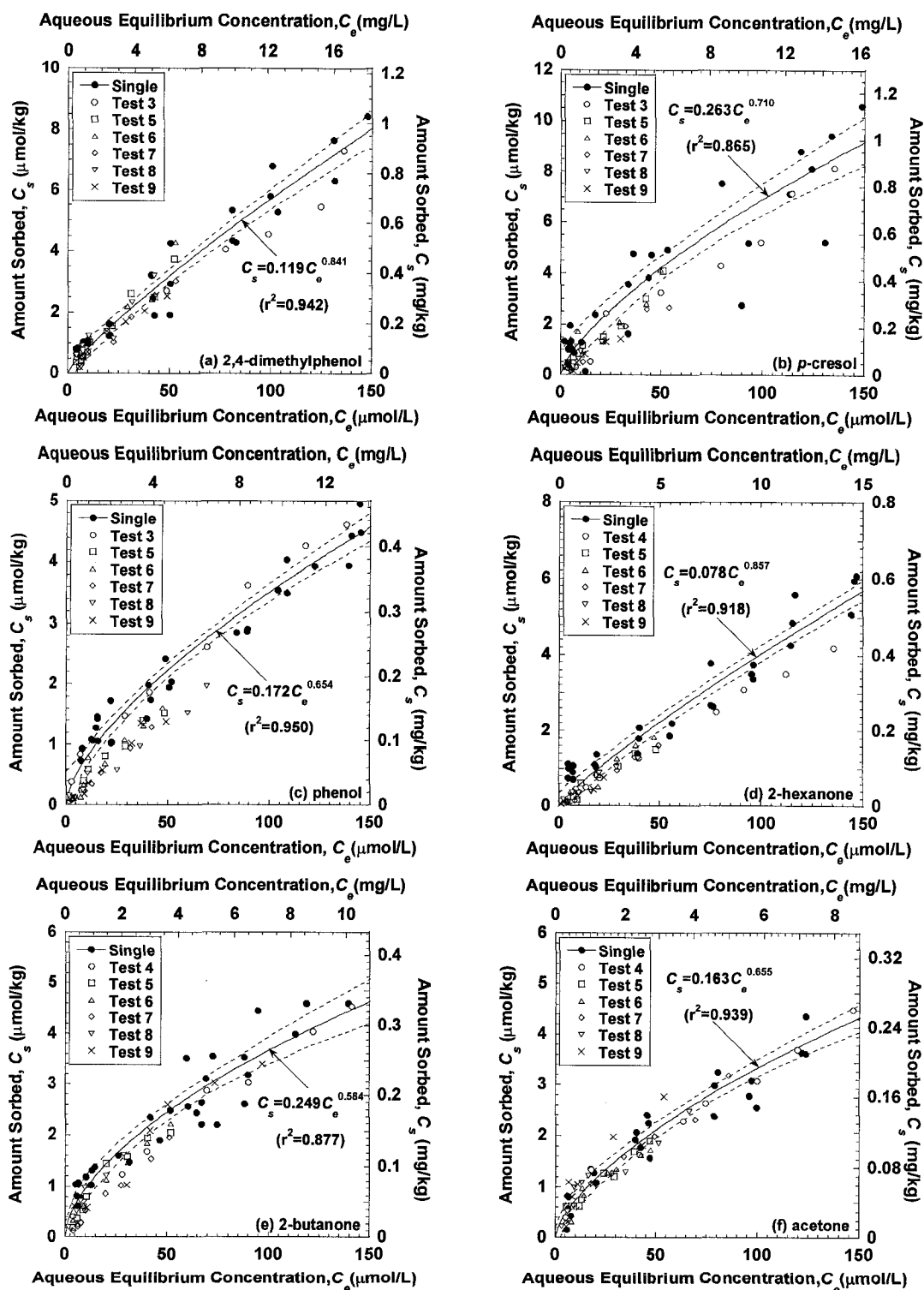


Fig. 5.14 Sorption isotherms of polar neutral organic compounds in single-sorbate systems and in mixtures to FeO(OH)-coated sand. The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.

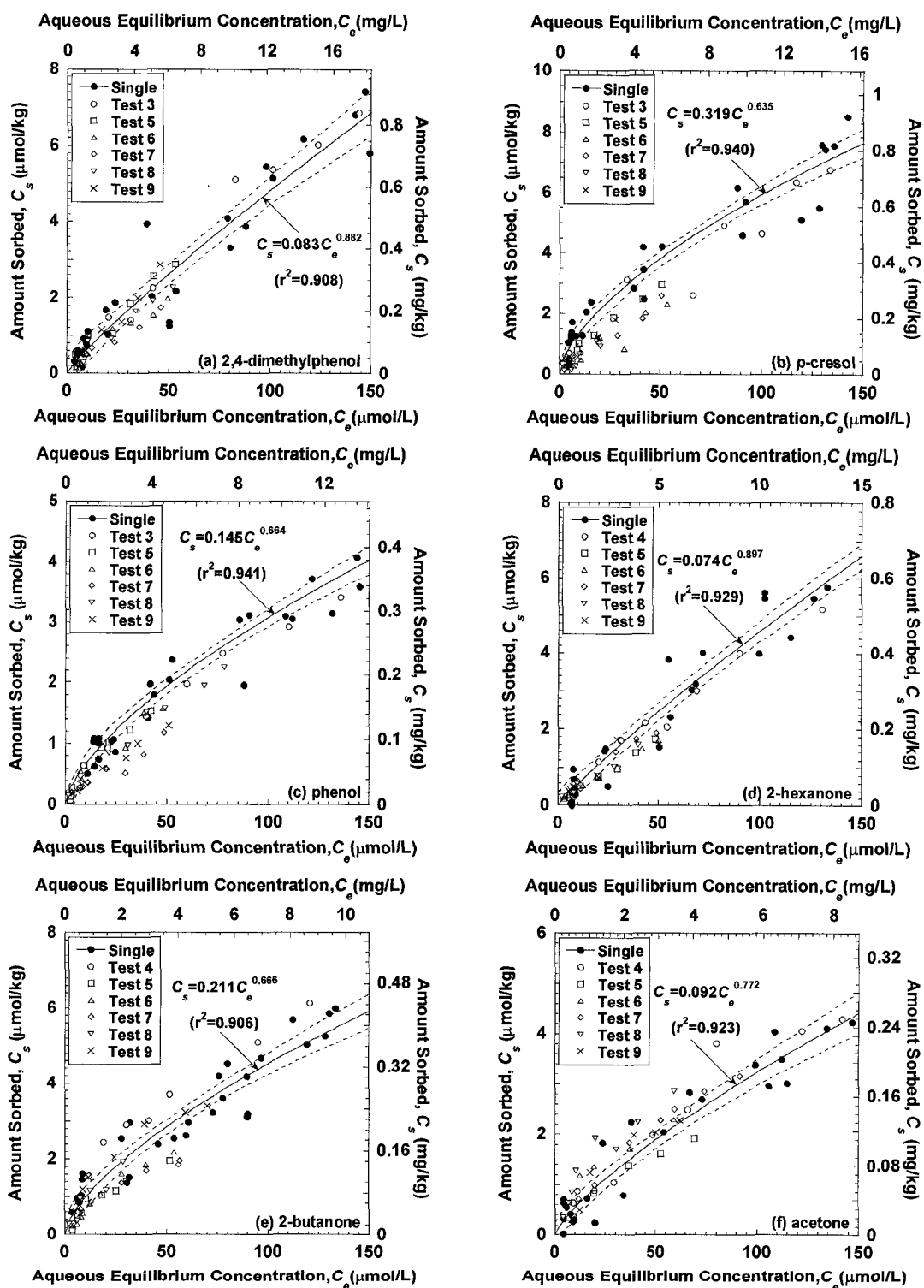


Fig. 5.15 Sorption isotherms of polar neutral organic compounds in single-sorbate systems and in mixtures to Al_2O_3 -coated sand. The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.

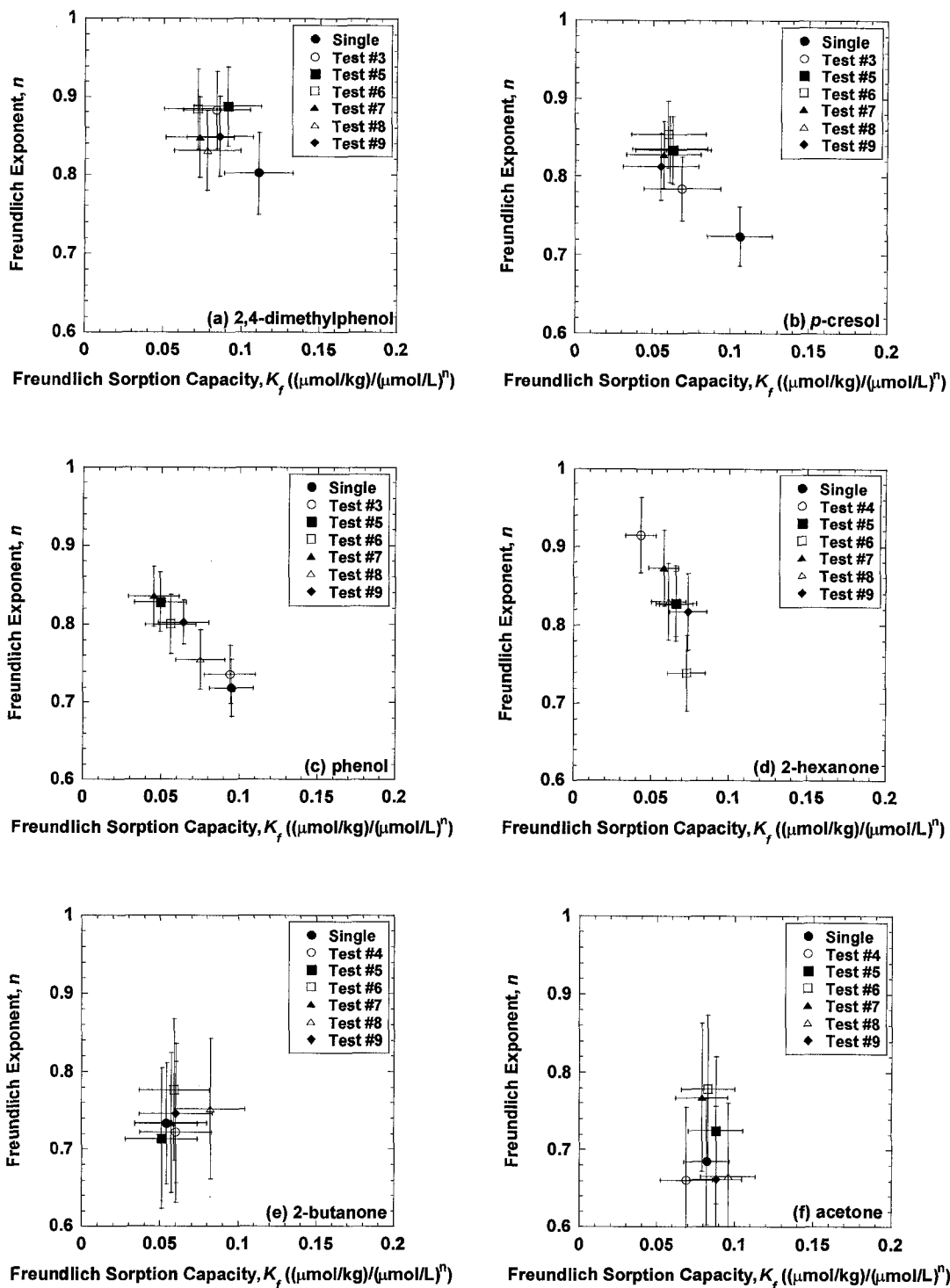


Fig. 5.16 Variations of Freundlich sorption parameters (K_f and n) for polar neutral organic compounds to uncoated sand in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

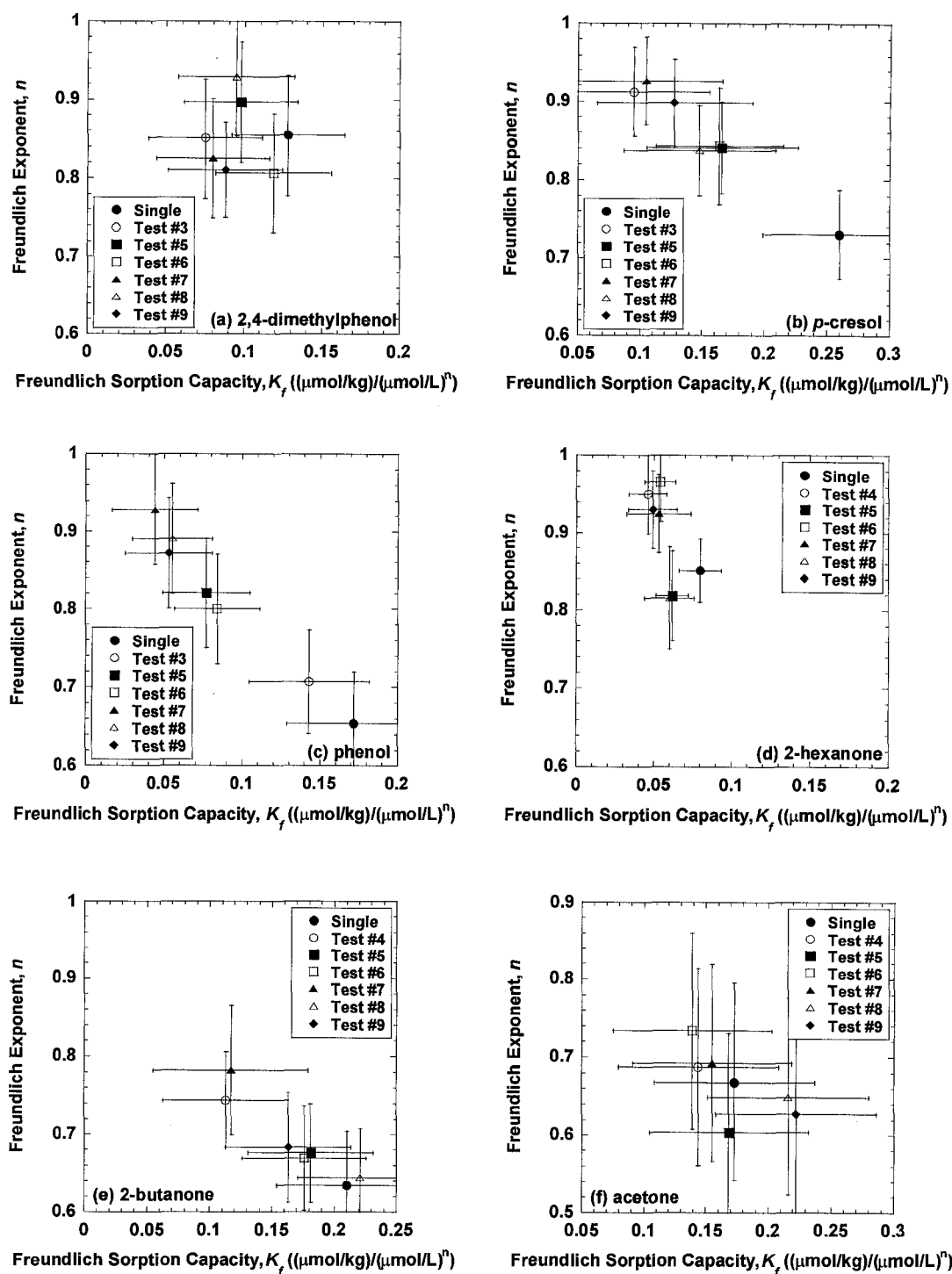


Fig. 5.17 Variations of Freundlich sorption parameters (K_f and n) for polar neutral organic compounds to FeO(OH)-coated sand in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

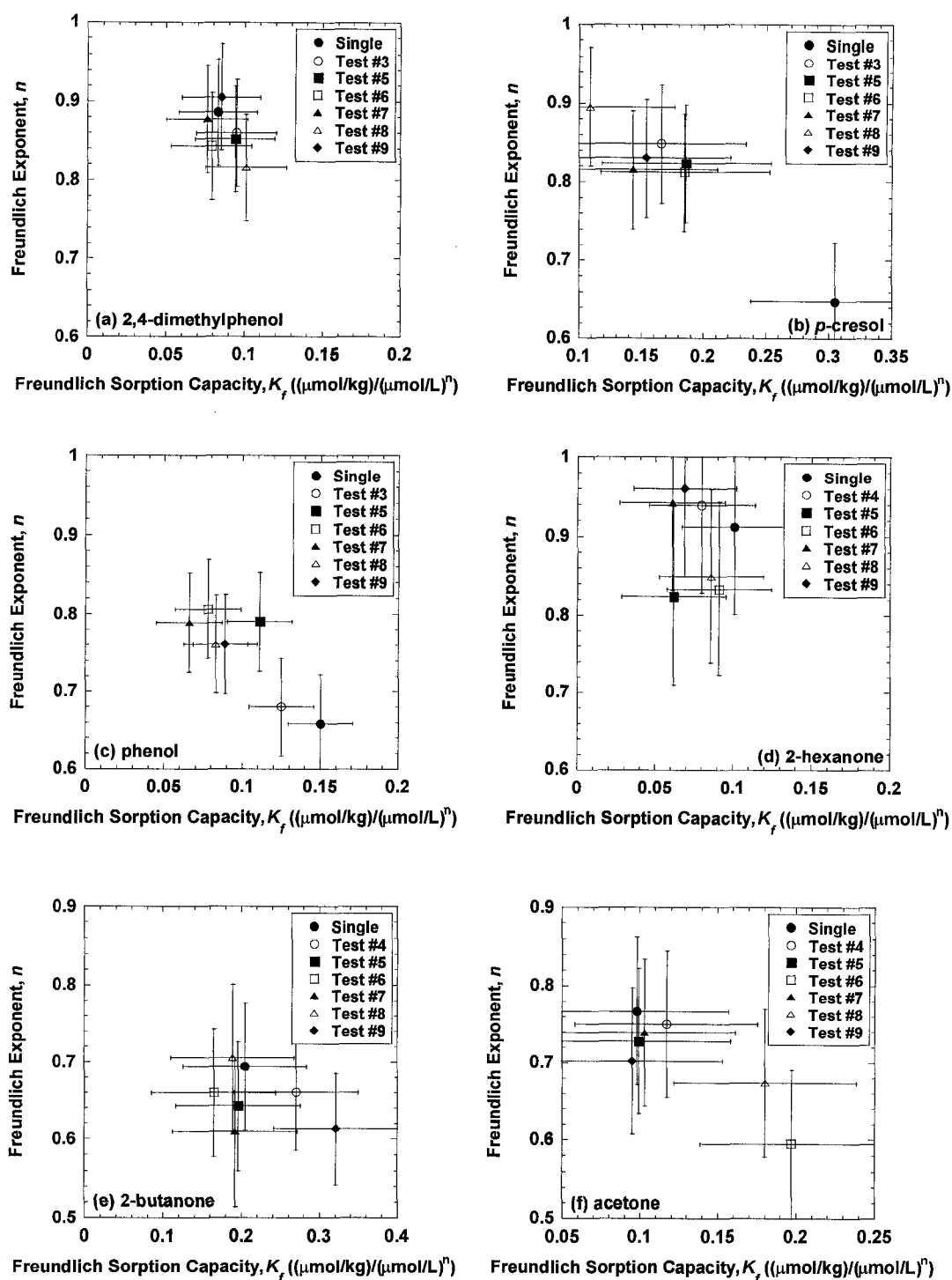


Fig. 5.18 Variations of Freundlich sorption parameters (K_f and n) for polar neutral organic compounds to Al_2O_3 -coated sand in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

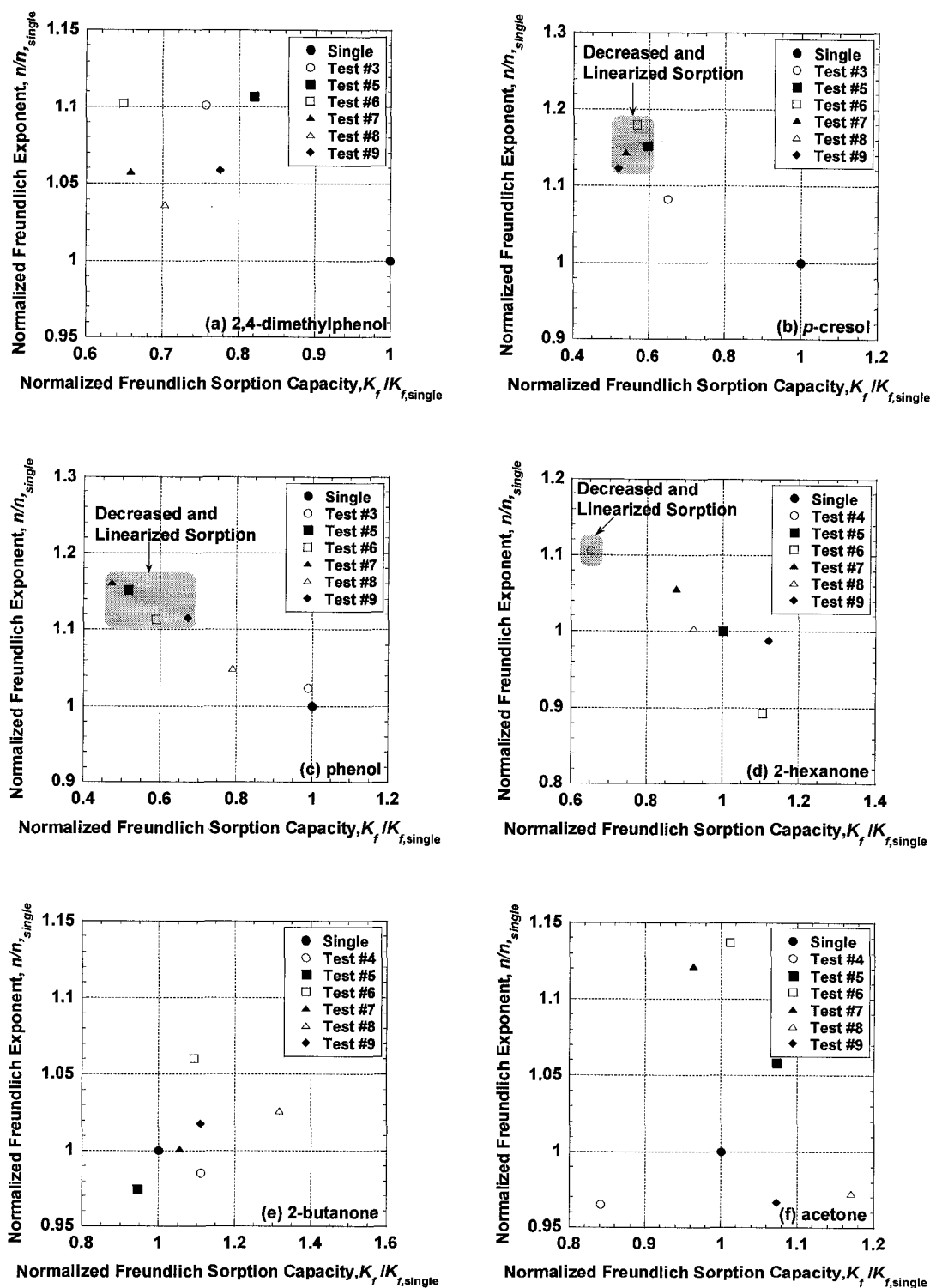


Fig. 5.19 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for polar neutral organic compounds to uncoated sand in terms of experimental conditions.

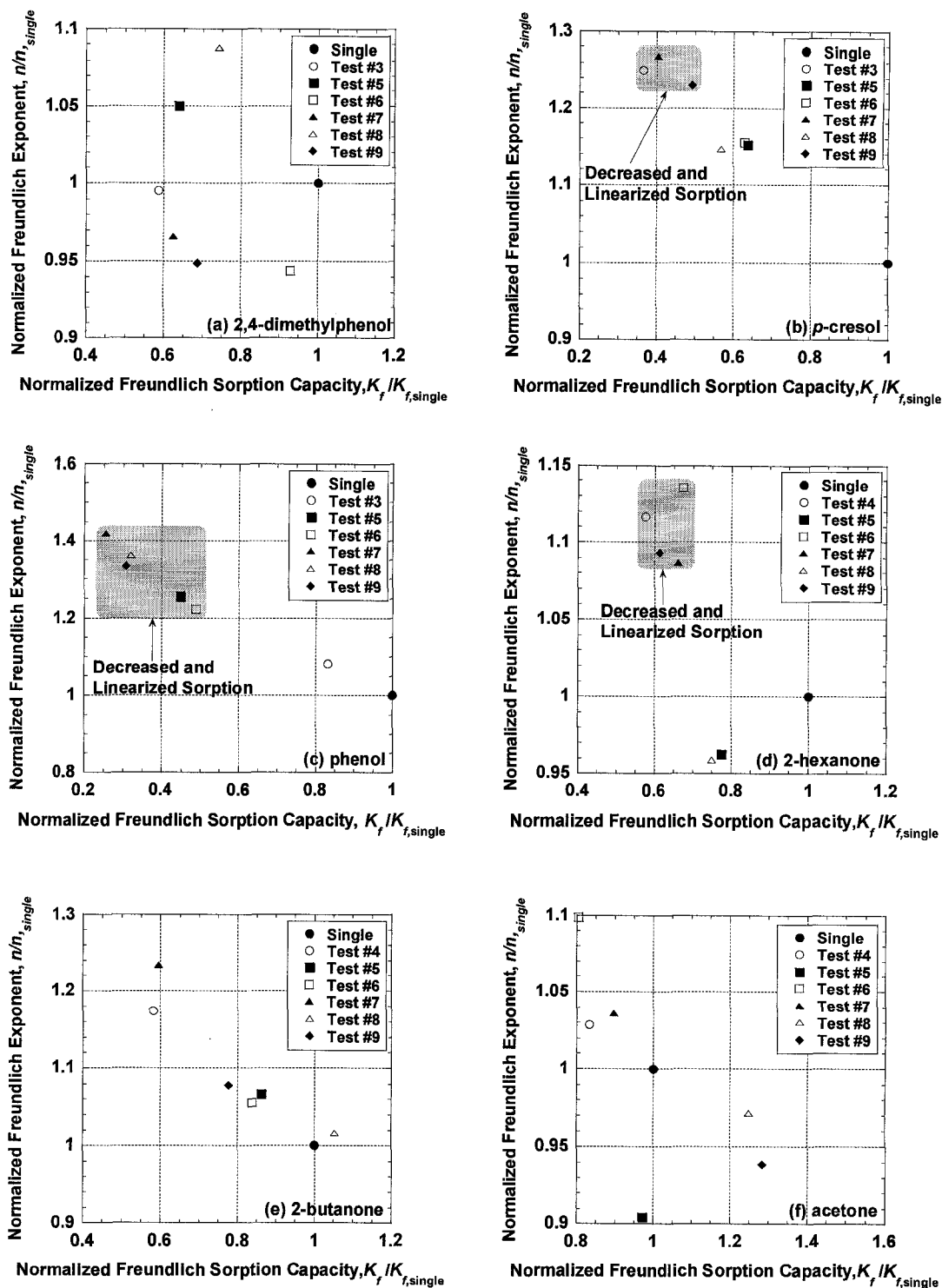


Fig. 5.20 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for polar neutral organic compounds to FeO(OH)-coated sand in terms of experimental conditions.

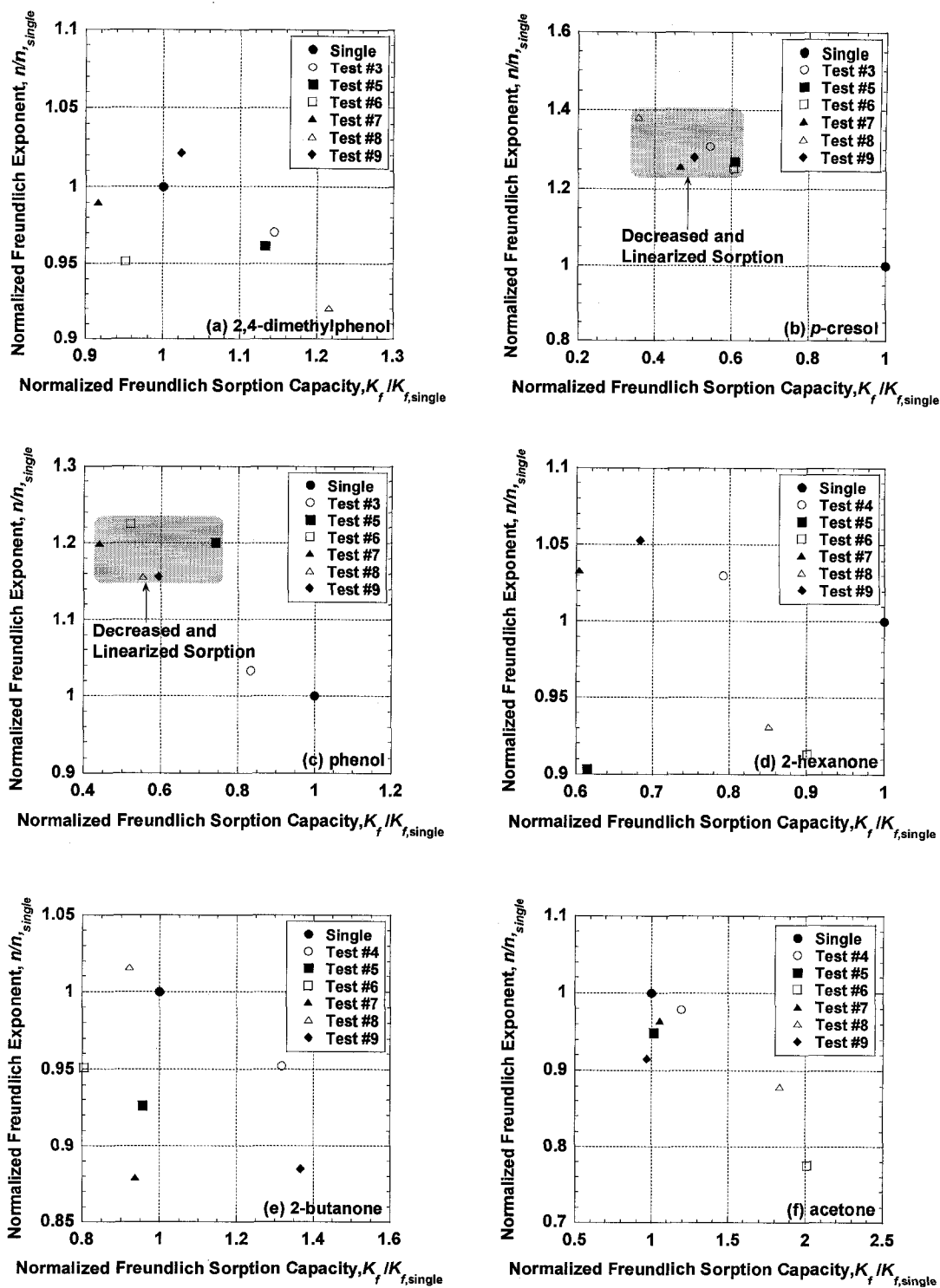


Fig. 5.21 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for polar neutral organic compounds to Al_2O_3 -coated sand in terms of experimental conditions.

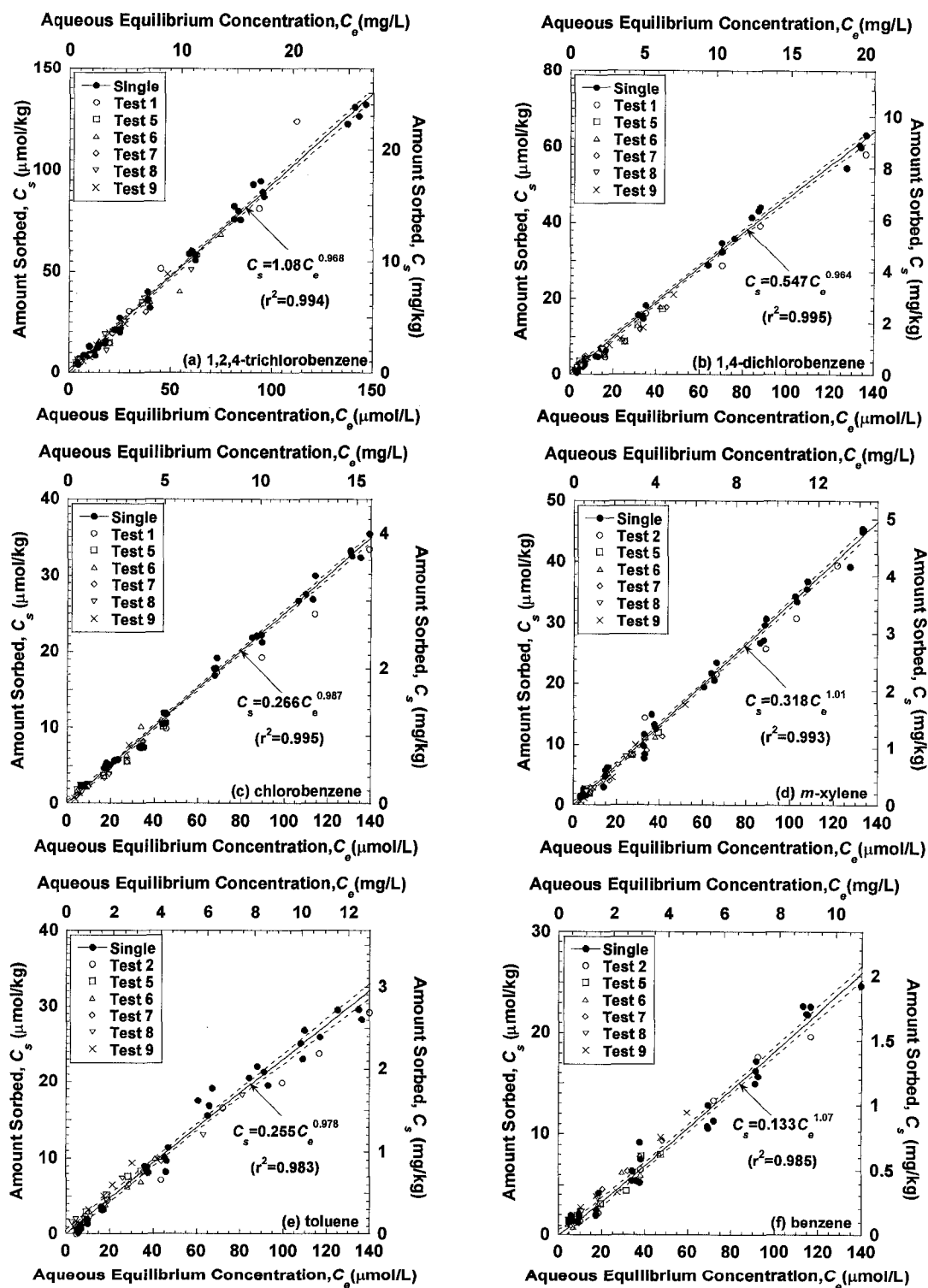
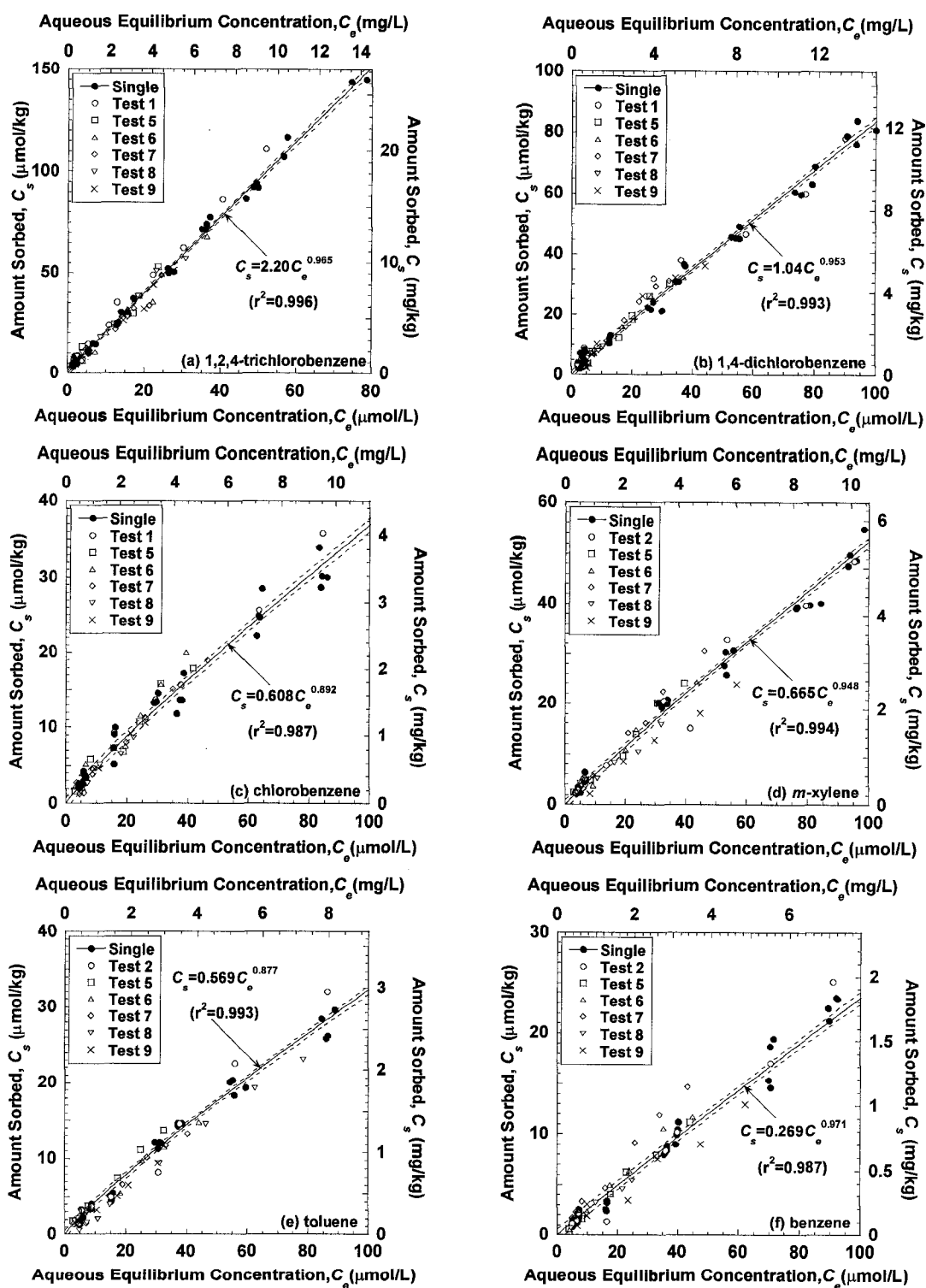


Fig. 5.22 Sorption isotherms of nonpolar neutral organic compounds in single-sorbate systems and in mixtures to HA-coated sand ($f_{oc} = 0.051\%$). The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.



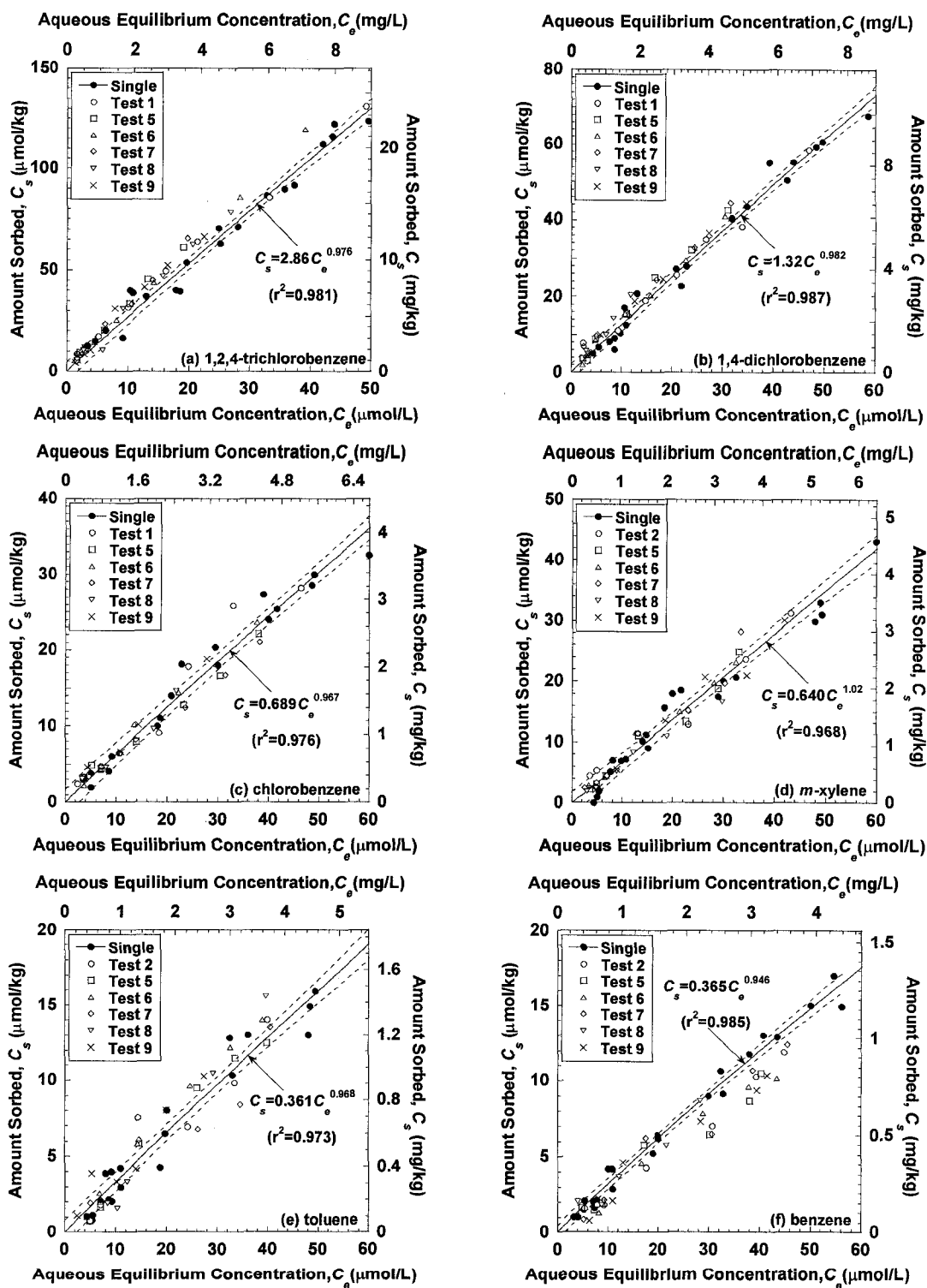


Fig. 5.24 Sorption isotherms of nonpolar neutral organic compounds in single-sorbate systems and in mixtures to HA-coated sand ($f_{oc} = 0.221\%$). The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.

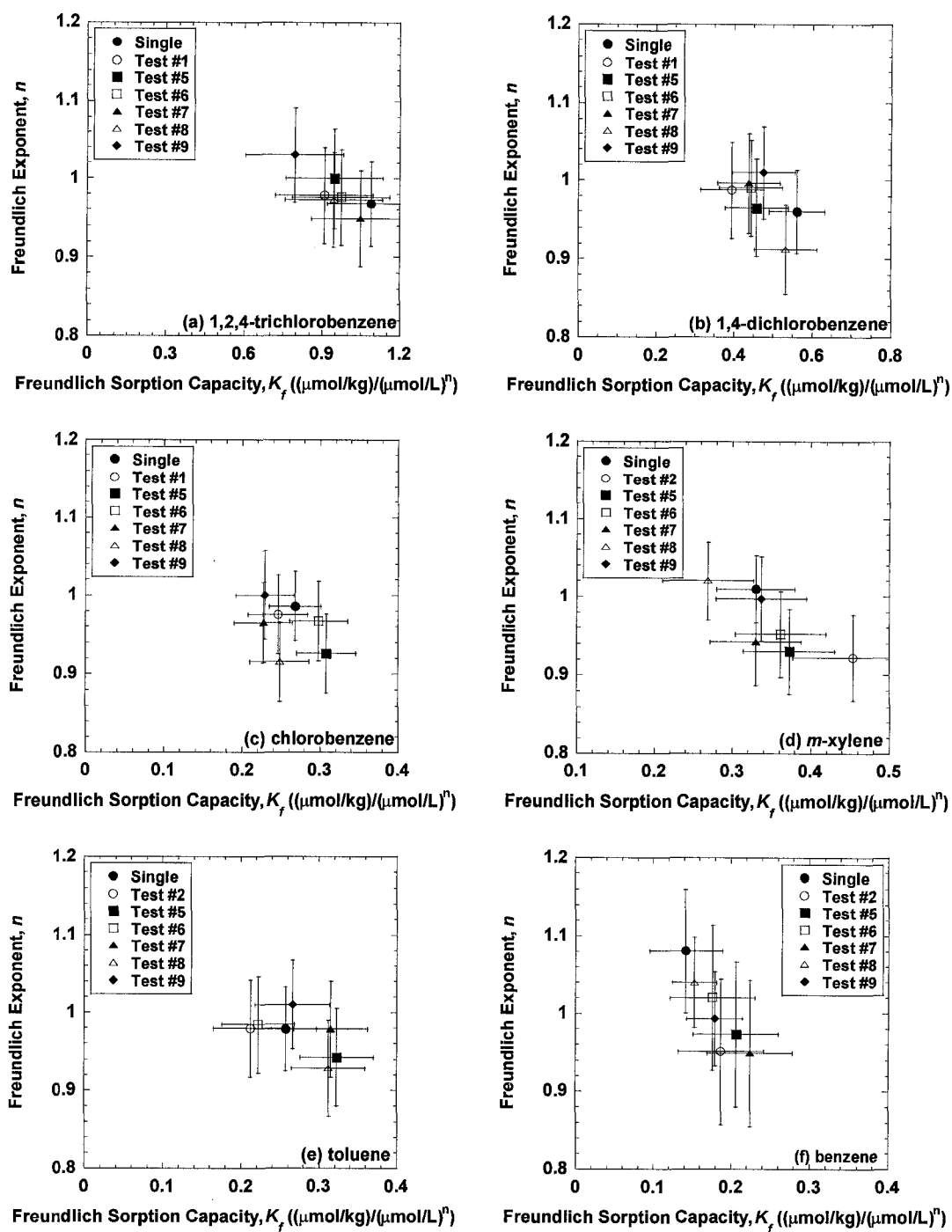


Fig. 5.25 Variations of Freundlich sorption parameters (K_f and n) for nonpolar neutral organic compounds to HA-coated sand ($f_{oc} = 0.051\%$) in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

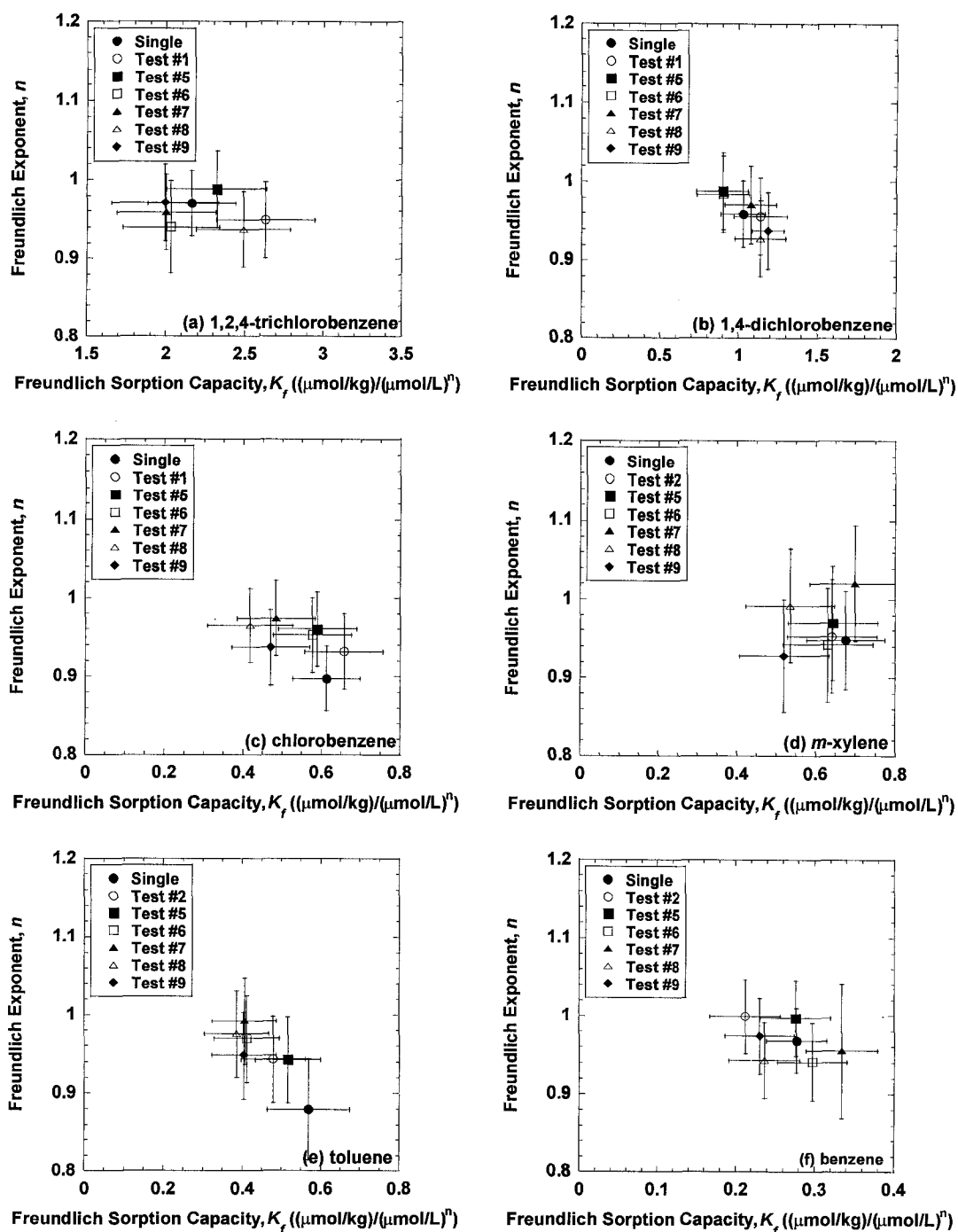


Fig. 5.26 Variations of Freundlich sorption parameters (K_f and n) for nonpolar neutral organic compounds to HA-coated sand ($f_{oc} = 0.119\%$) in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

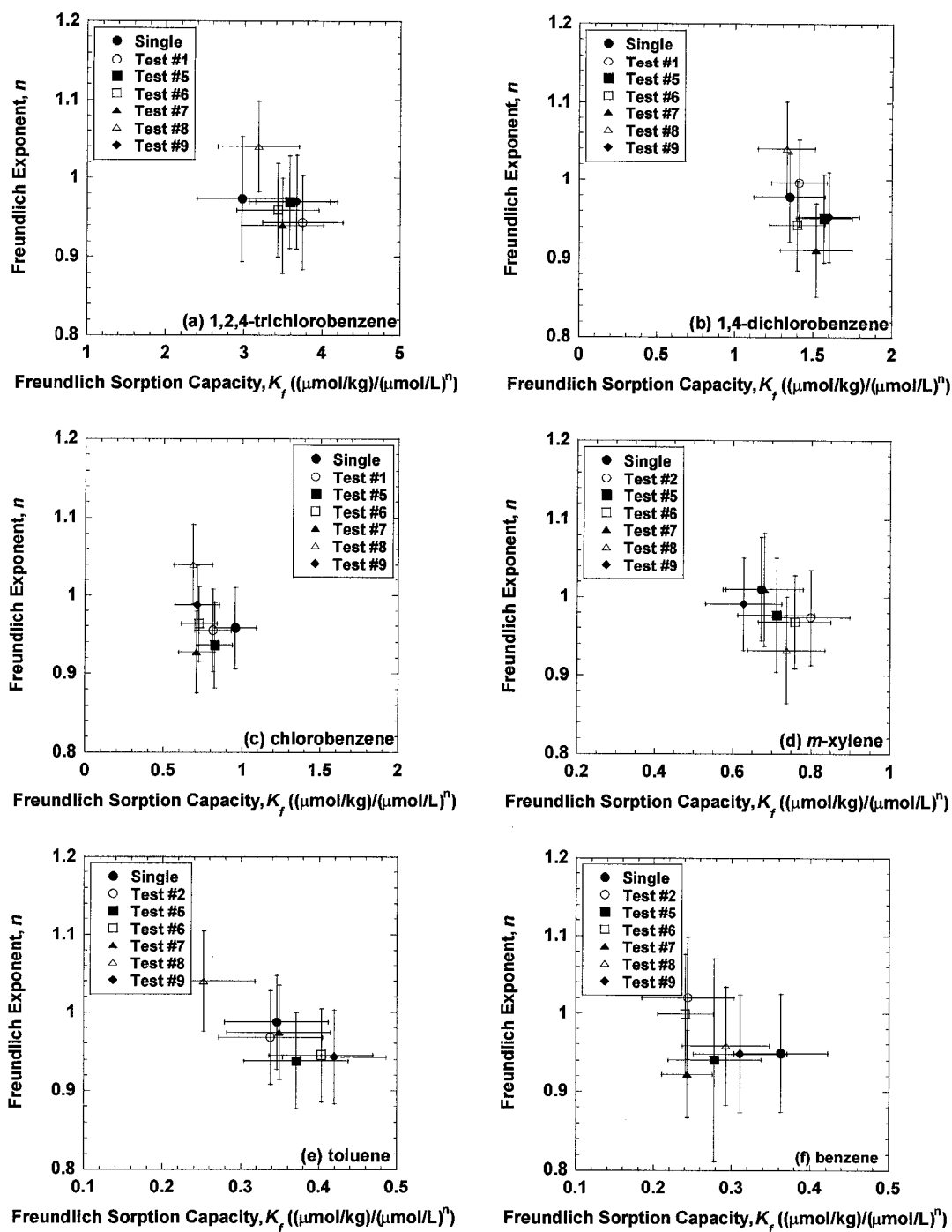


Fig. 5.27 Variations of Freundlich sorption parameters (K_f and n) for nonpolar neutral organic compounds to HA-coated sand ($f_{oc} = 0.221\%$) in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

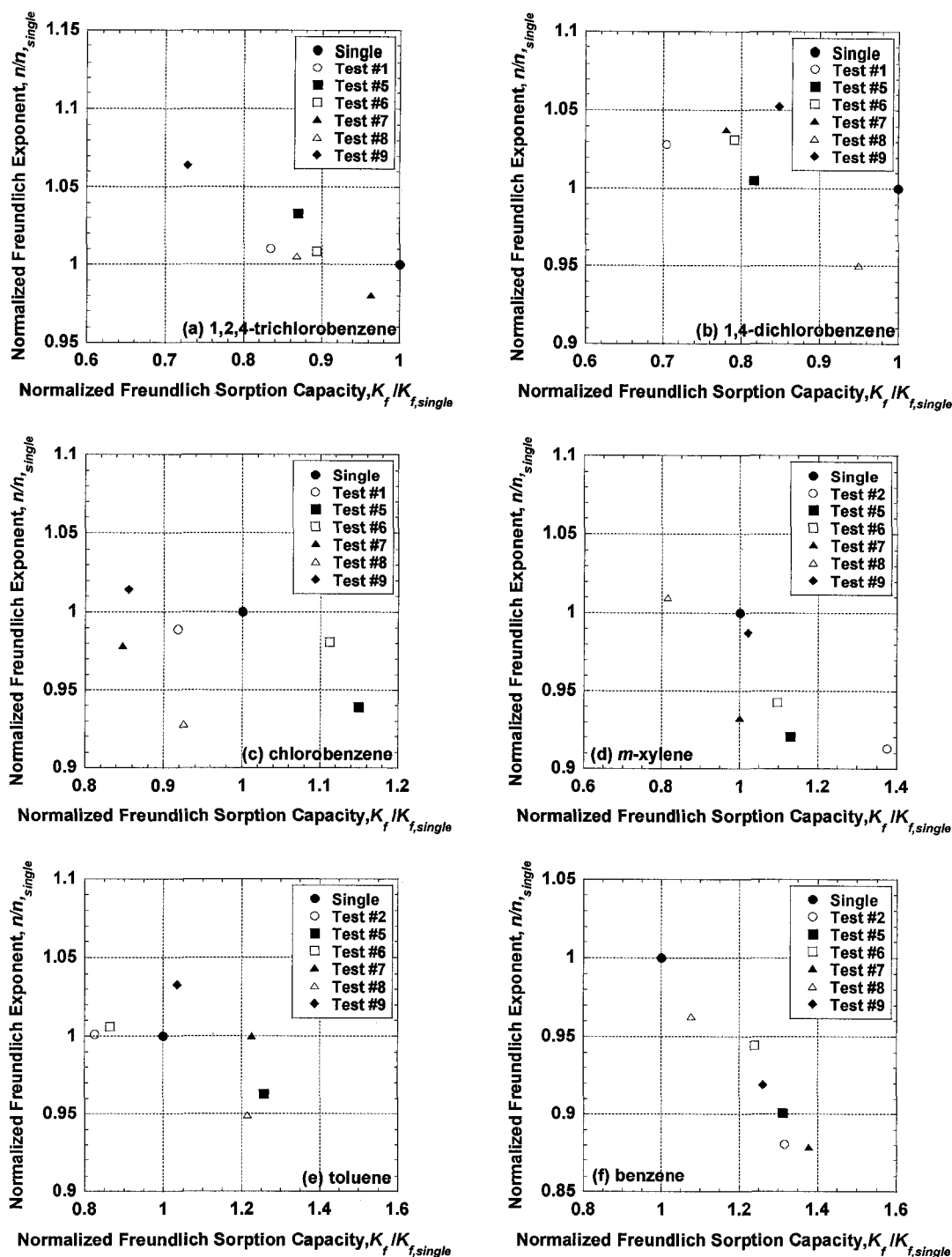


Fig. 5.28 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for nonpolar neutral organic compounds to HA-coated sand ($f_{oc} = 0.051\%$) in terms of experimental conditions.

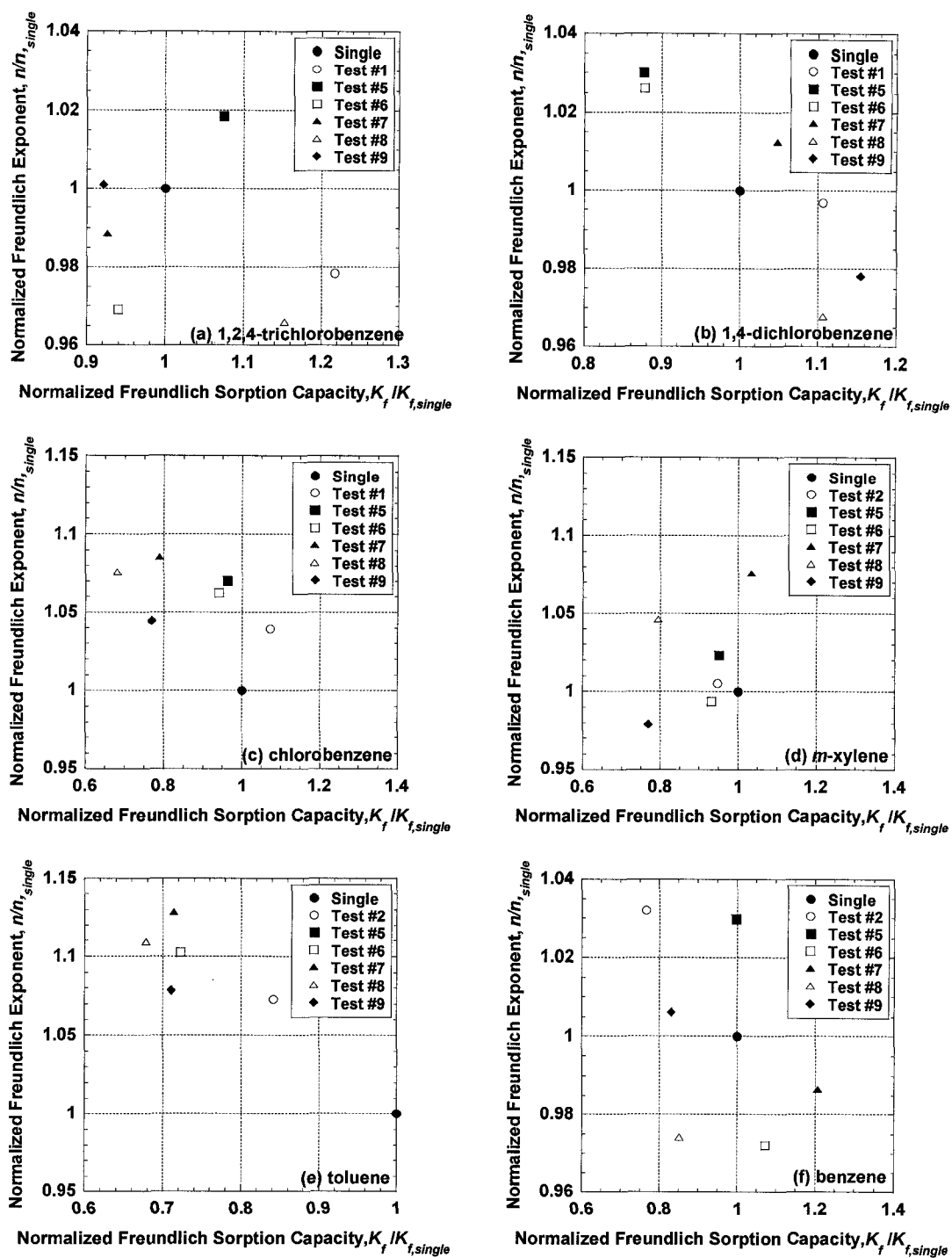


Fig. 5.29 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for nonpolar neutral organic compounds to HA-coated sand ($f_{oc} = 0.119\%$) in terms of experimental conditions.

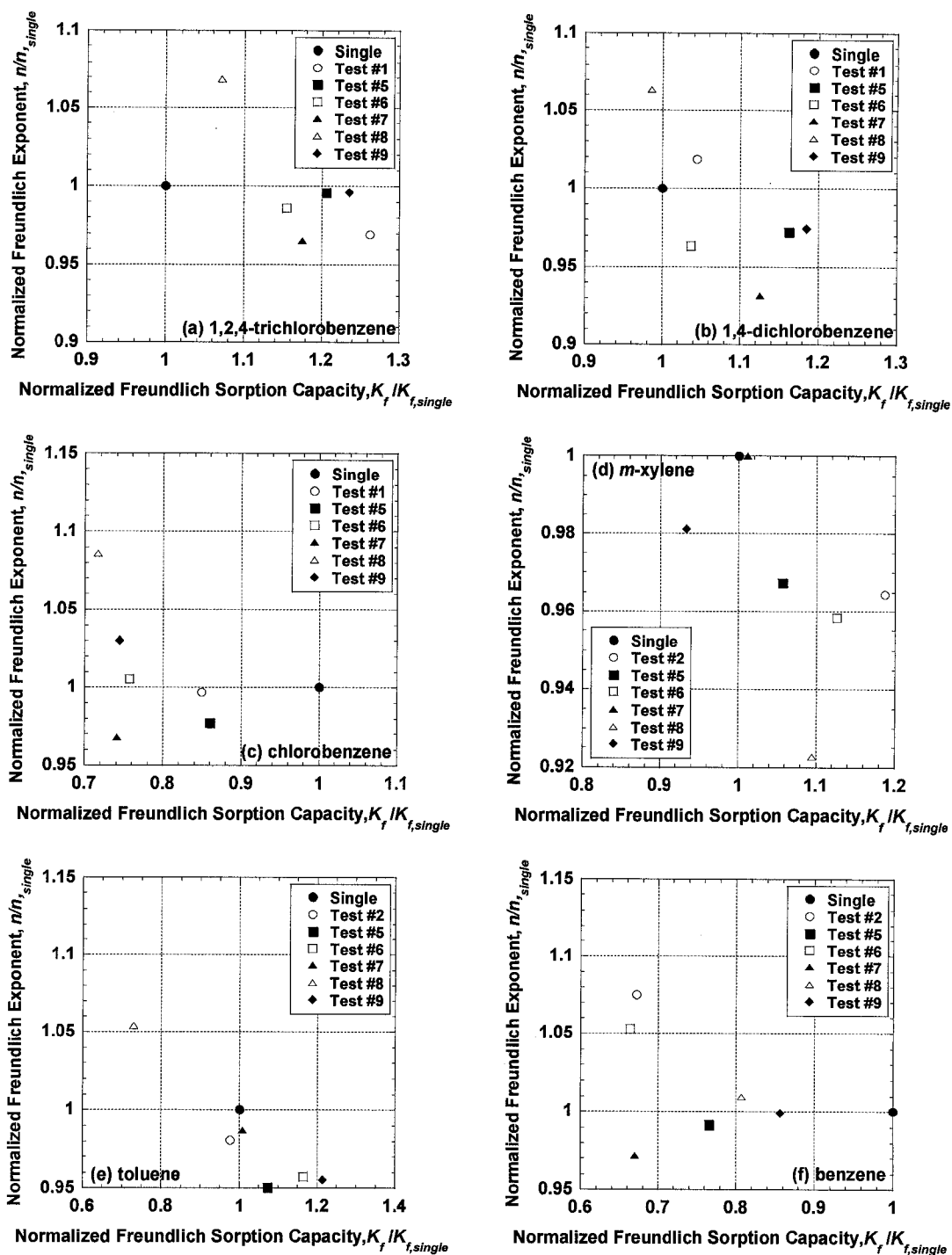


Fig. 5.30 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for polar neutral organic compounds to HA-coated sand ($f_{oc} = 0.221\%$) in terms of experimental conditions.

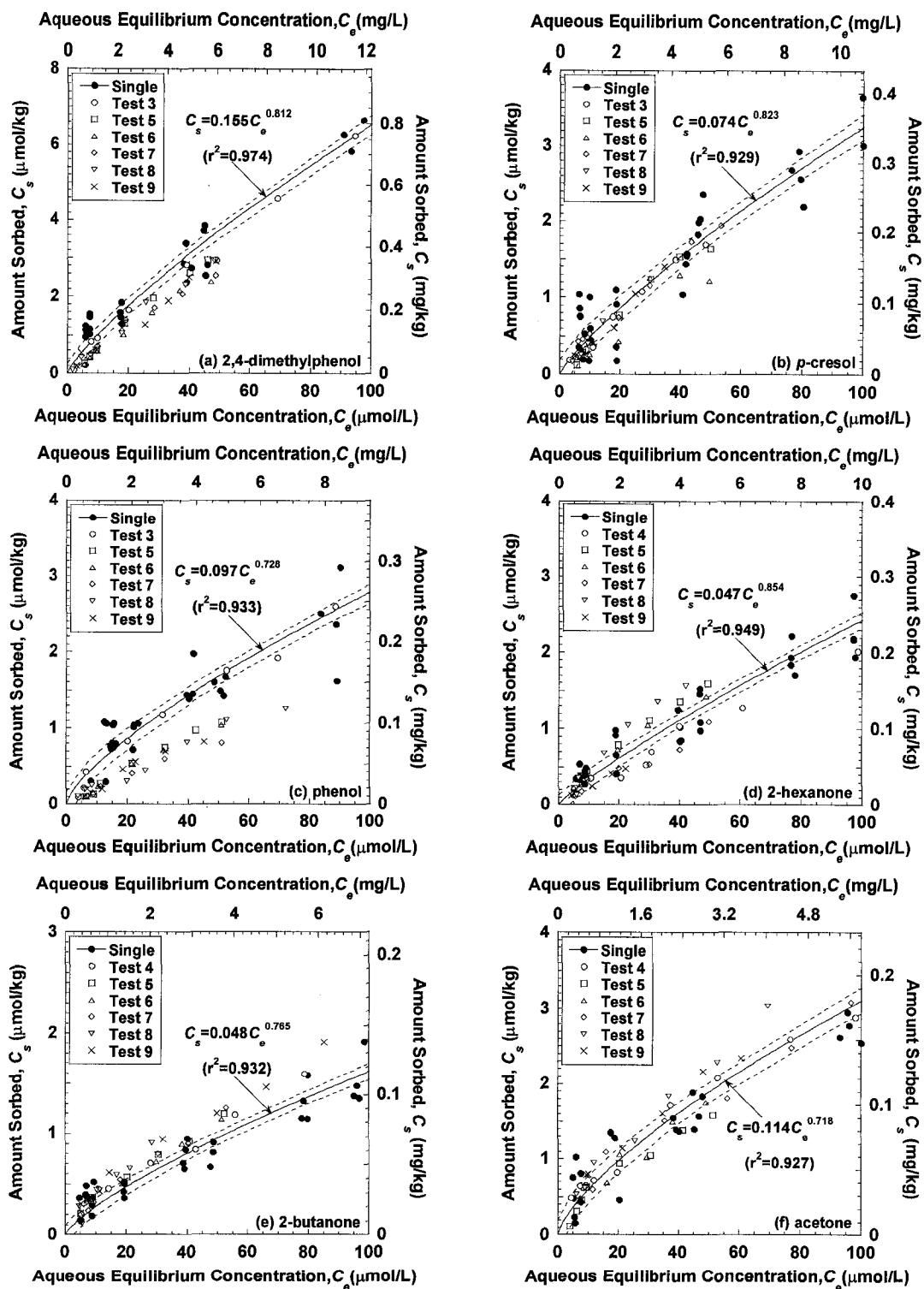


Fig. 5.31 Sorption isotherms of polar neutral organic compounds in single-sorbate systems and in mixtures to HA-coated sand ($f_{oc} = 0.051\%$). The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.

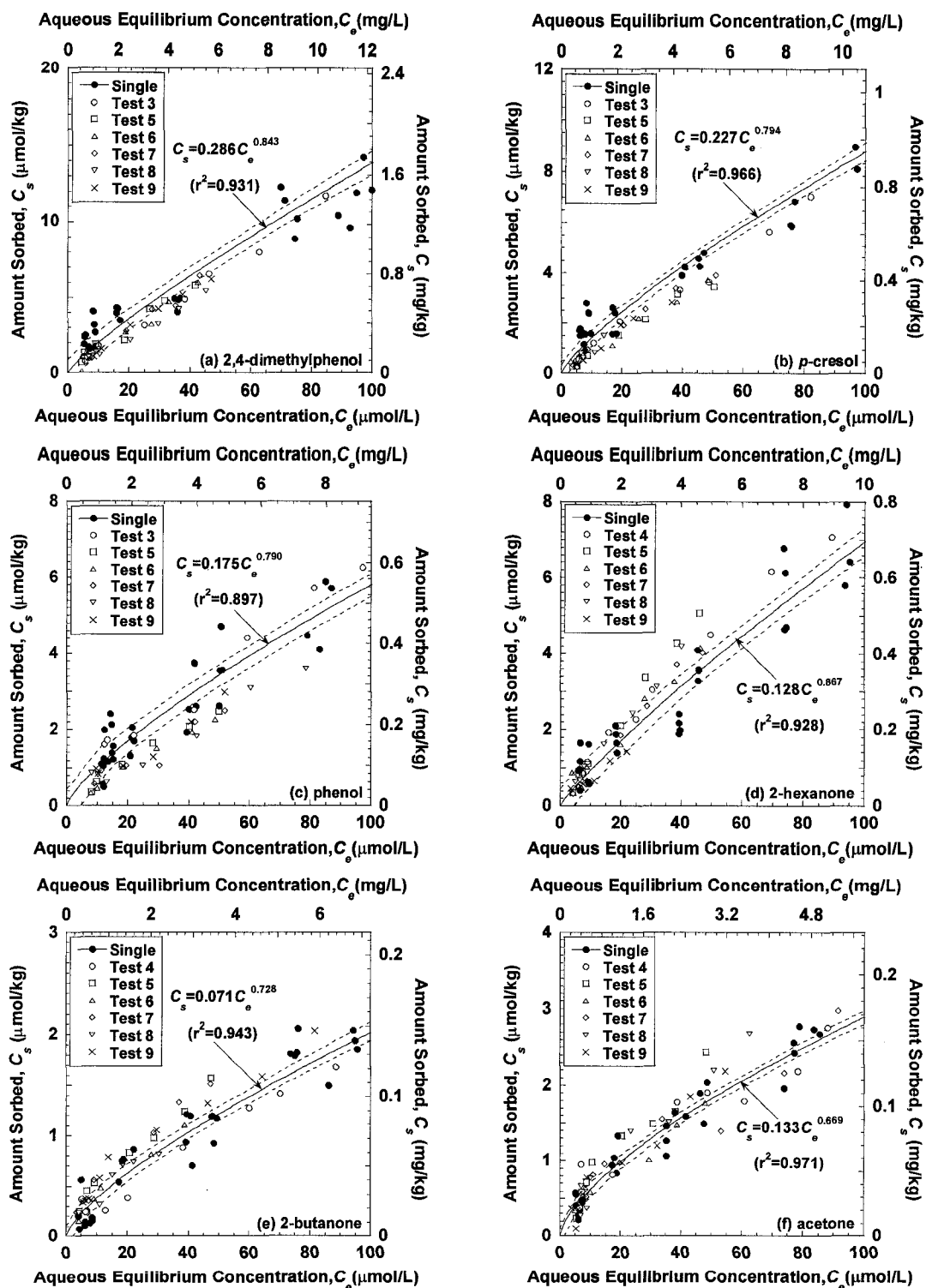


Fig. 5.32 Sorption isotherms of polar neutral organic compounds in single-sorbate systems and in mixtures to HA-coated sand ($f_{oc} = 0.119\%$). The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.

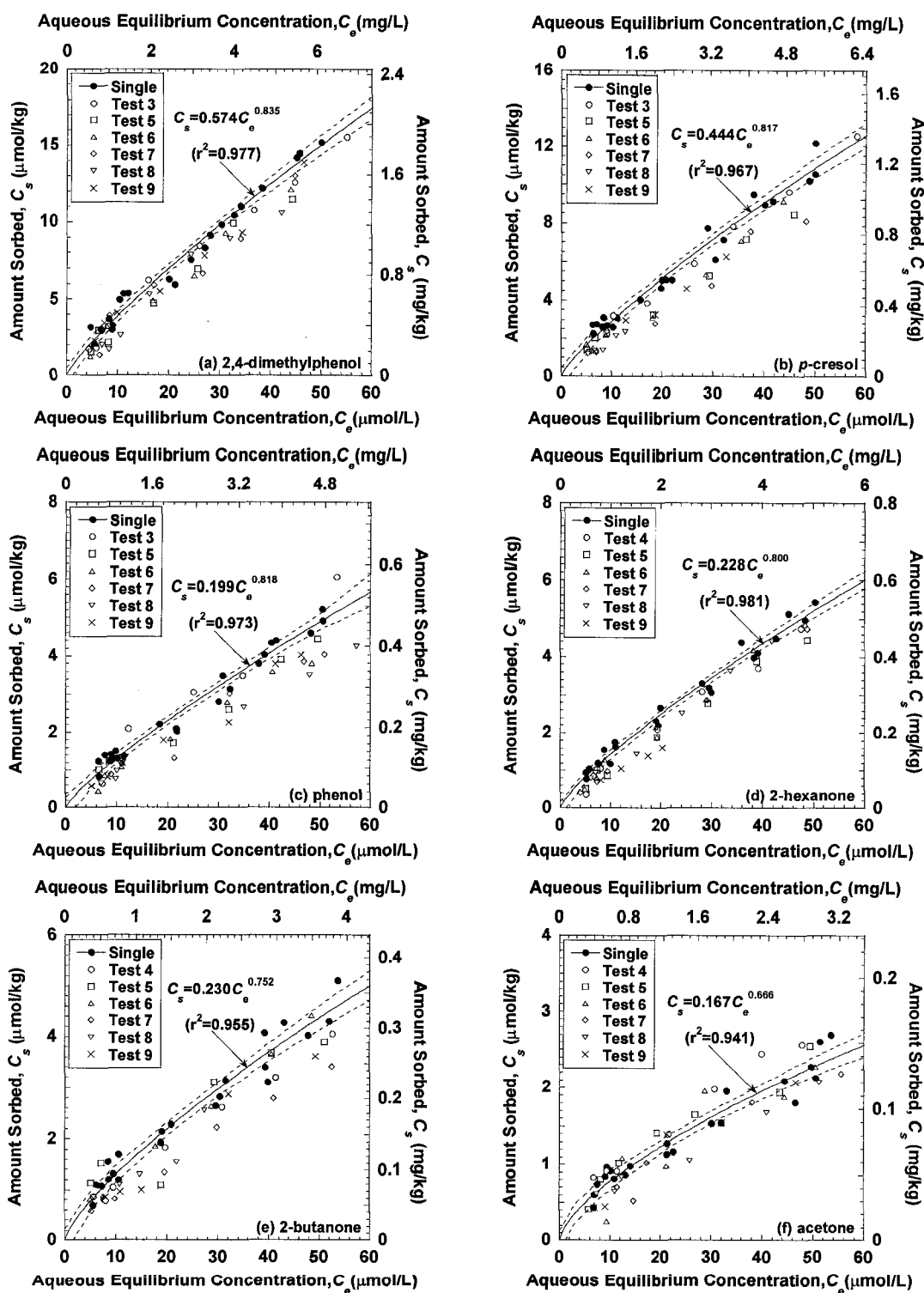


Fig. 5.33 Sorption isotherms of polar neutral organic compounds in single-sorbate systems and in mixtures to HA-coated sand ($f_{oc} = 0.221\%$). The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for data set obtained from single-sorbate systems.

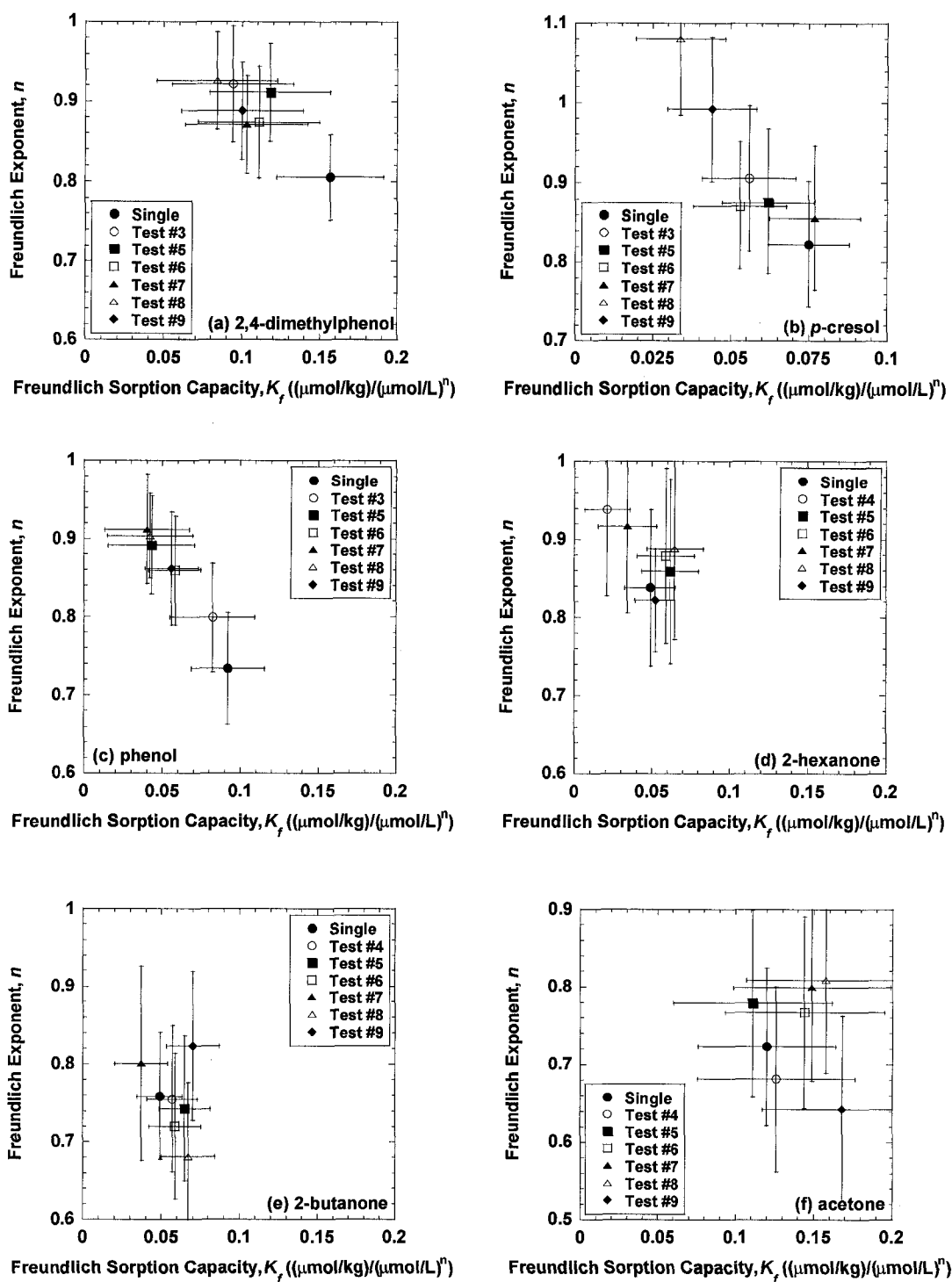


Fig. 5.34 Variations of Freundlich sorption parameters (K_f and n) for polar neutral organic compounds to HA-coated sand ($f_{oc} = 0.051\%$) in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

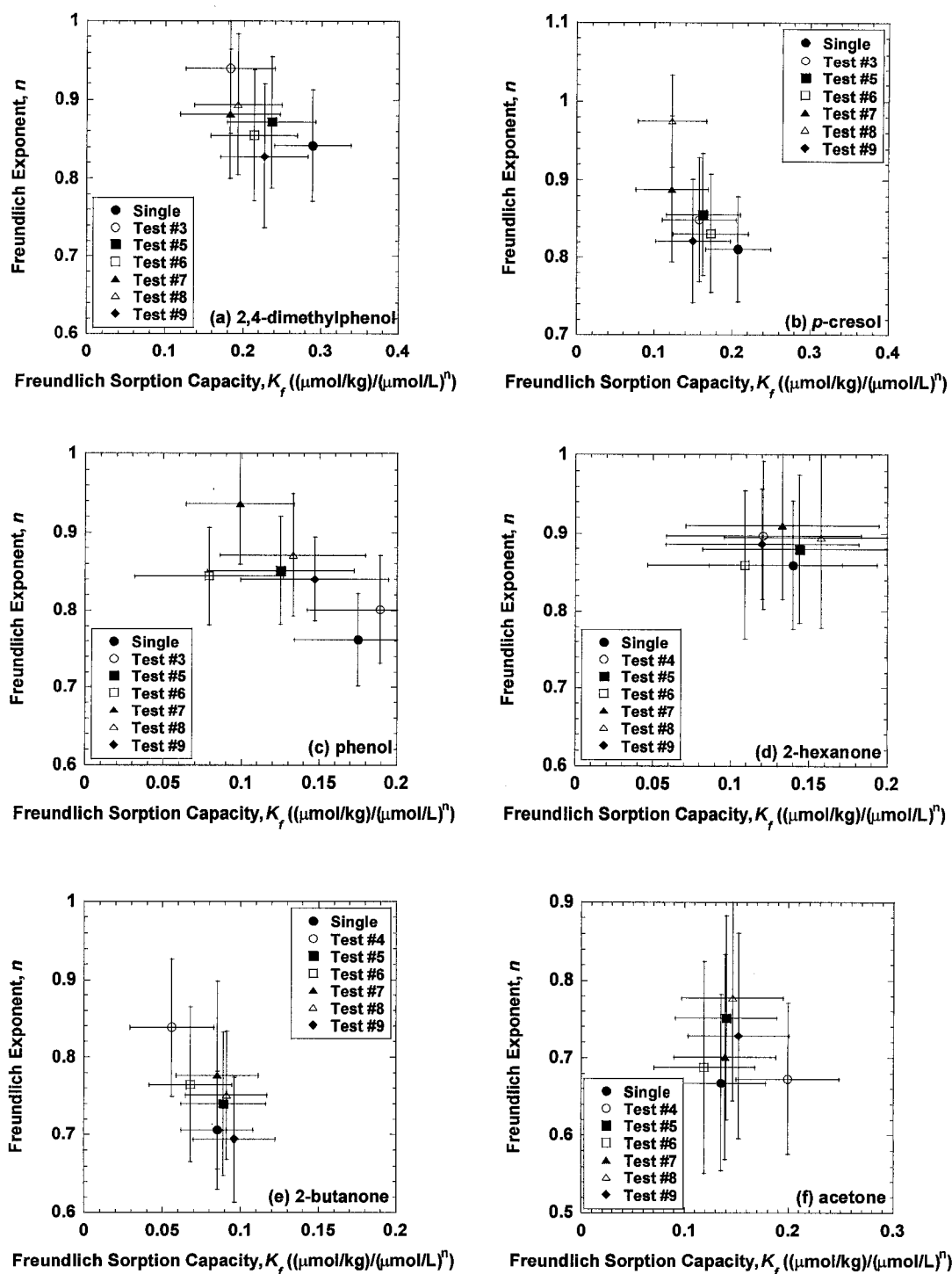


Fig. 5.35 Variations of Freundlich sorption parameters (K_f and n) for polar neutral organic compounds to HA-coated sand ($f_{oc} = 0.119\%$) in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

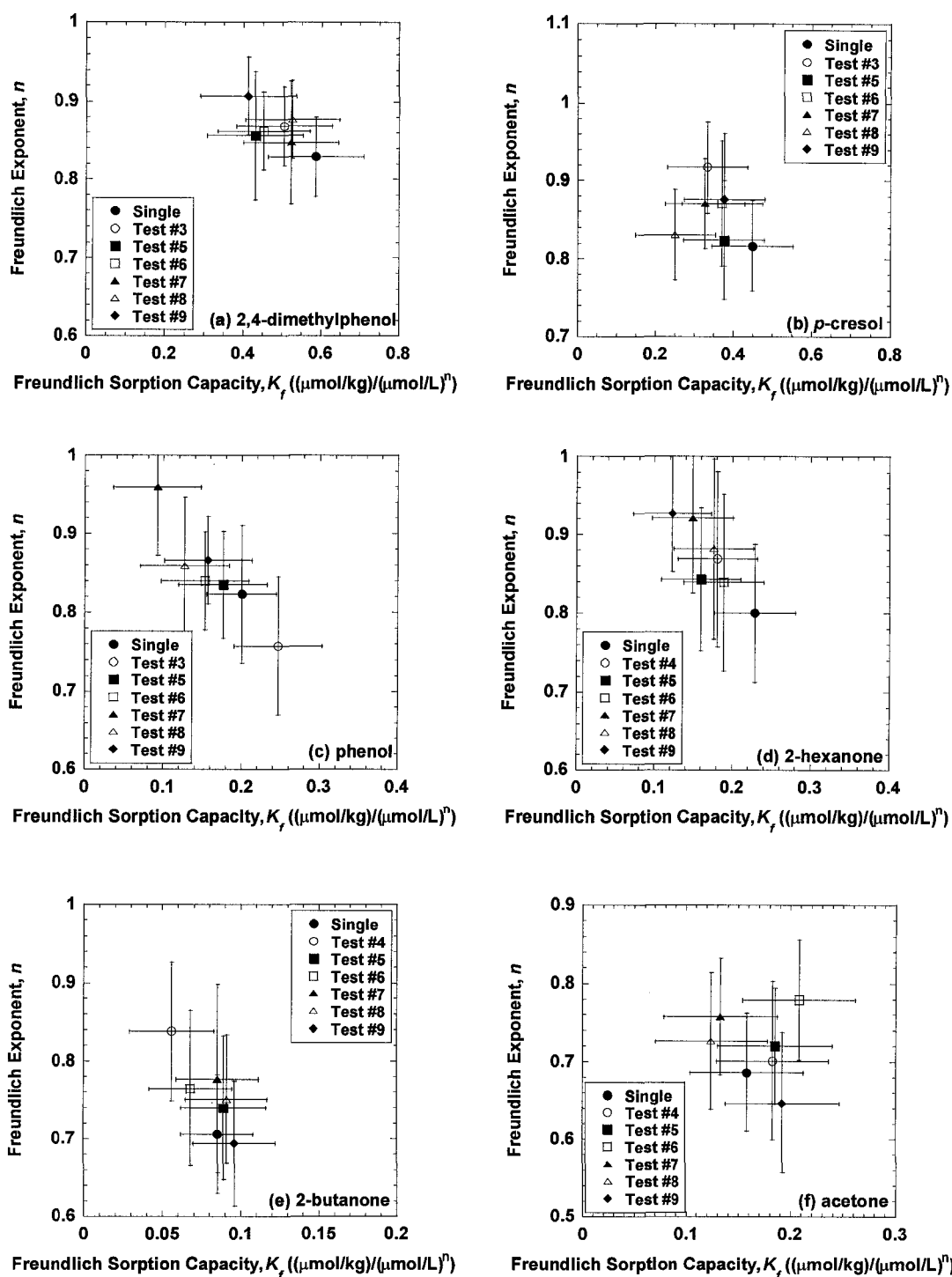


Fig. 5.36 Variations of Freundlich sorption parameters (K_f and n) for polar neutral organic compounds to HA-coated sand ($f_{oc} = 0.221\%$) in terms of experimental conditions. The error bars indicate 95 % confidence limits of least-squares means for Freundlich sorption parameters (K_f and n) using the statistical software (SAS® 9.1, Cary, NC).

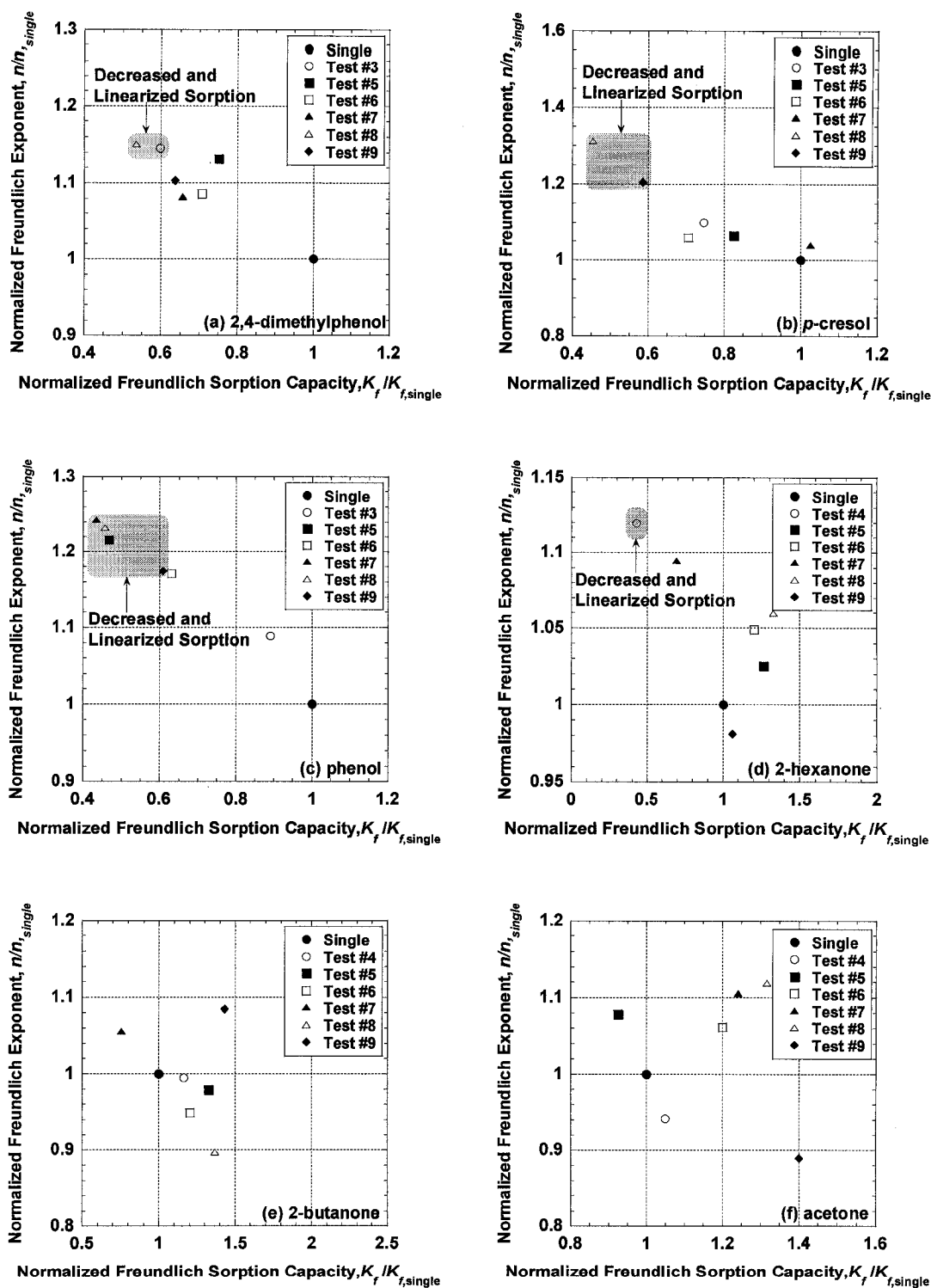


Fig. 5.37 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for polar neutral organic compounds to HA-coated sand ($f_{oc} = 0.051\%$) in terms of experimental conditions.

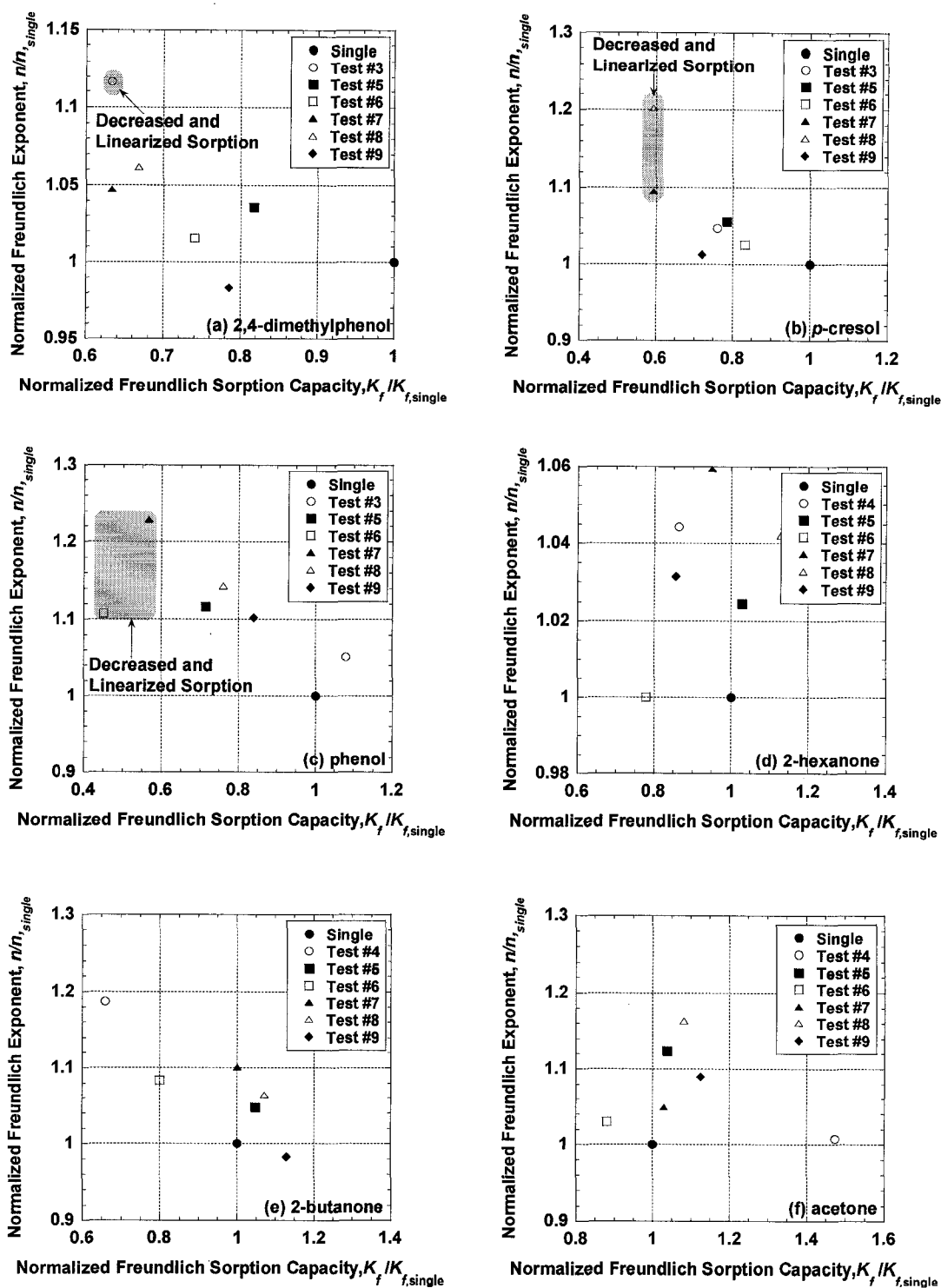


Fig. 5.38 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for polar neutral organic compounds to HA-coated sand ($f_{oc} = 0.119\%$) in terms of experimental conditions.

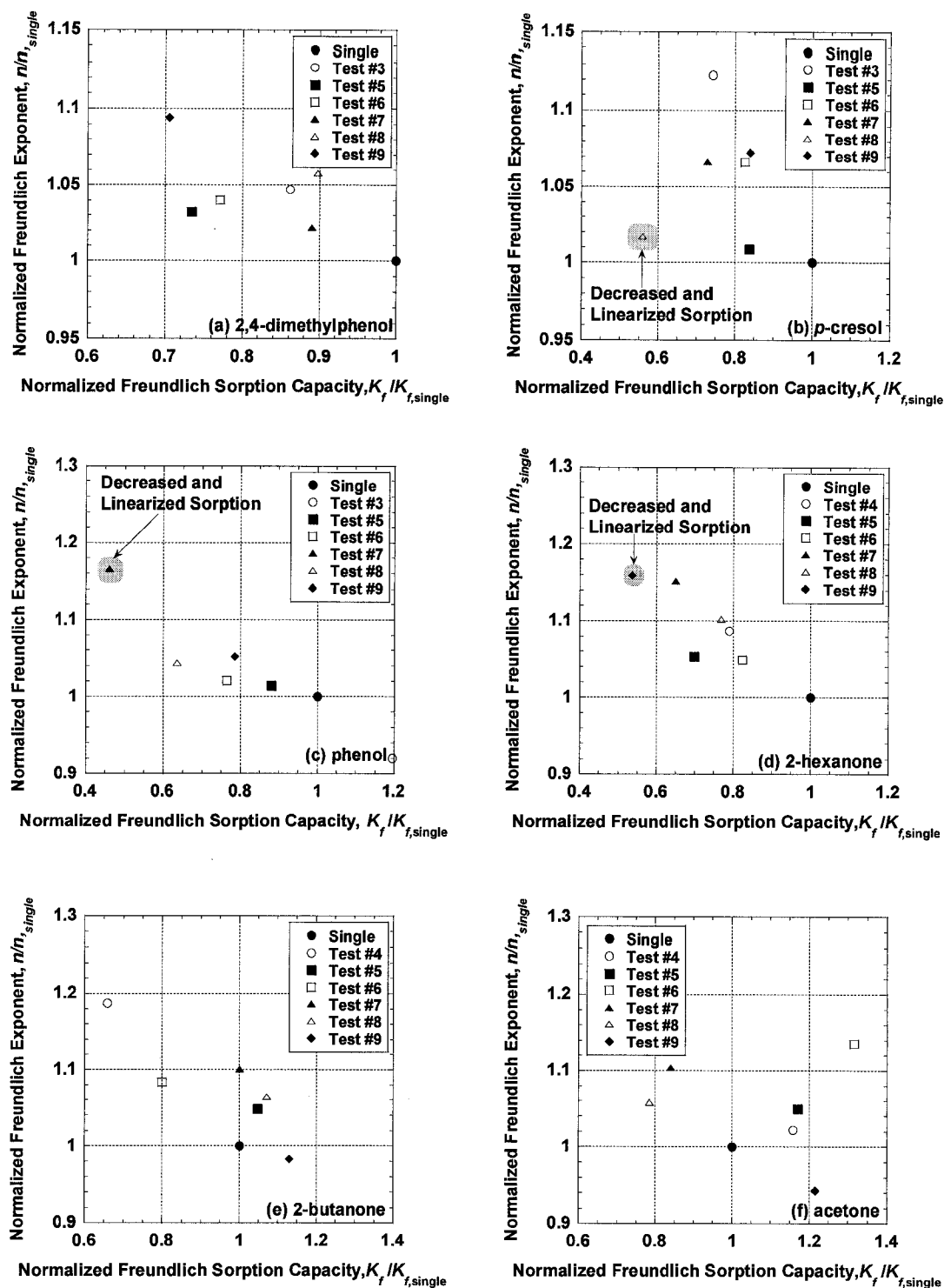


Fig. 5.39 Variations of normalized Freundlich sorption parameters (K_f and n) against those from single-sorbate systems for polar neutral organic compounds to HA-coated sand ($f_{oc} = 0.221\%$) in terms of experimental conditions.

CHAPTER 6

LUMPED APPROACH FOR SORPTION OF NEUTRAL ORGANIC COMPOUNDS IN MIXTURES TO SIMULATED AQUIFER SORBENTS

Abstract: Both feasibility and accuracy of lumped approach to group 12 neutral organic compounds in mixtures into a fewer number of pseudocompounds in sorption processes were evaluated using mixtures containing neutral organic compounds with a wide range of hydrophobicities (i.e., $-0.24 \leq \log K_{ow} \leq 4.23$) and various types of low-surface-area simulated aquifer sorbents. The lumped approach for sorption to simulated aquifer sorbents was guided by cluster analysis from statistics. Both feasibility and accuracy of the lumped approach using both base case and random mixtures of neutral organic compounds in terms of different type of mineral surfaces and HA-mineral complexes with different organic carbon content (f_{oc}) were confirmed by the relatively consistent lumping schemes for each sorbent and the acceptable approximation of sorption behavior of compounds mixtures. Besides the experimentally derived lumping criteria (i.e., sorption parameters), the possible theoretical lumping criteria (i.e., aqueous activity coefficient at saturation and organic carbon partitioning coefficient) were obtained to provide the theoretical lumping schemes. Finally, the assignment of the Freundlich sorption parameters of pseudocompounds using single-sorbate Freundlich sorption parameters of components led to inaccuracy of sorption prediction.

Key Words: simulated aquifer sorbents, cluster analysis, lumped approach, mixtures, neutral organic compounds, pseudocompounds, sorption

6.1 INTRODUCTION

Research over the last three decades has revealed that structurally and physicochemically different components of geosorbents, such as amorphous versus condensed soil organic matter (SOM) and high surface area carbonaceous material (HSACM), macroporous versus meso- and micro-porous mineral matrices, and interlayer surfaces of swelling clays, interact differently with neutral organic compounds (NOCs) in terms of binding energies and the rates of associated sorption and desorption (Karickhoff 1984, Weber et al. 1992, Xing et al. 1996, Luthy et al. 1997, Chiou and Kile 1998, Allen-King et al. 2002, Cornelissen et al. 2005, Nguyen and Ball 2006, Pignatello et al. 2006, Su et al. 2006). In addition, the fractionation and variations in structural and chemical properties of SOM, and the mineral surface blockage by SOM in SOM-mineral complexes contribute to the distinct sorption reactivity with NOCs (Karickhoff 1984, Liljestrand and Shimizu 1991, Rebhun et al. 1992, Shen and Jaffé 2000, Hur and Schlautman 2004, Wang and Xing 2005, Feng et al. 2006). Thus, overall sorption of NOCs by natural geosorbents is represented by the sum of the contributions of several active components in heterogeneously combined geosorbents.

Although the focus of these studies has been on characterizing the interactions of NOCs with the various types of geosorbents, most of the studies have involved single-sorbate systems to reveal sorption mechanisms for each component and to reconcile models for heterogeneous geosorbents. However, environmental contamination usually results in the presence of mixtures of compounds (e.g., gasoline, fuel hydrocarbon/chlorinated solvents, pesticides, and landfill leachates) in

the subsurface. Whereas the fate and transport of individual NOCs in the subsurface have been studied extensively in both saturated and unsaturated porous media (Zheng 1990), much less is known about the fate and transport of mixtures of NOCs. Additionally, models describing the simultaneous fate and transport of NOCs in complex mixtures routinely ignore mixture effects, such as competitive or synergistic sorption (Clement 1997, Clement et al. 1998). However, when such mixture effects are significant, the determination of pair-wise interaction parameters among NOCs is required to accurately predict the migration of mixtures of NOCs. Although the entire system of differential equations with interaction parameters that describe the migration of NOCs in mixtures can be solved simultaneously in space and time, this detailed approach can become increasingly more complicated and less computationally efficient as the number of compounds in mixtures increases, limiting the practical utility of the overall approach.

An alternative to this detailed approach (i.e., one equation per NOC with interaction parameters) is the so-called "lumped approach". The lumped approach has been used by (1) grouping the list of species, (2) grouping the list of reactions, or (3) dividing the kinetics into fast and slow parts (Maria 2005). Such a lumped approach has been widely applied in the oil-refining industry to provide tractable approximations to the stoichiometry, thermodynamics, and kinetics of complex hydrocarbon mixtures (Coxson and Bischoff 1987, Quann and Jaffe 1992, Jaffe et al. 2005). Also, the lumped approach has been applied in describing multicomponent adsorption to granular activated carbon (Calligaris and Tien 1982, Mehrotra and Tien 1984, Ramaswami and Tien 1986, Moon et al. 1991), sorption of heavy metals

to humic substances (Yu et al. 1996), wastewater treatment (Li et al. 1996), biodegradation rates of compound mixtures (Brown 1998), partitioning of secondary organic aerosol mixtures (Bian and Bowman 2002, 2005), toxicology of compound mixtures (Dennison et al. 2004), and reactive transport of compound mixtures in the unsaturated zone (Karapanagioti et al. 2004).

Based on the successful applications of the lumped approach to various complex systems, the use of a lumped approach to describe the sorption of NOCs in mixtures in terms of the sorption of a fewer number of pseudocompounds or groups of NOCs with similar sorption affinities was evaluated in this study. In grouping NOCs, all NOCs in mixtures can be grouped into a single pseudocompound (or parameter), such as dissolved organic carbon (TOC), or biological oxygen demand (BOD). Whereas this single-pseudocompound approach is simple and convenient, this approach can be prone to inaccuracy, especially when the NOCs in mixtures are dissimilar in terms of their sorption behavior. Additionally, if knowledge of individual priority NOCs in mixtures is required, then this simple approach may not be appropriate. Consequently, a more feasible approach is to consider grouping the various NOCs into several pseudocompounds.

However, the following questions must be resolved to implement the lumped approach to the sorption of NOC mixtures in subsurface systems: (1) what are the main grouping criteria, which determines the pseudocompounds?, (2) how are the number of pseudocompounds and their components determined?, (3) how are the number of pseudocompounds and their components affected by mixture compositions and heterogeneous subsurface environments?, (4) how are the relevant

sorption parameters of pseudocompound assigned?, and (5) can the sorption parameters of pseudocompounds be estimated from single-sorbate sorption parameters of their components? Thus, these questions were examined in this study.

Although the feasibility of the lumped approach in multicomponent adsorption has been studied using high-surface-area granular activated carbon as the sorbent (Calligaris and Tien 1982, Mehrotra and Tien 1984, Ramaswami and Tien 1986, Moon et al. 1991), both feasibility and accuracy of grouping NOCs for sorption of NOC mixtures has not yet been evaluated using mixtures containing NOCs with a wide range of hydrophobicities (i.e., $-0.24 \leq \log K_{ow} \leq 4.23$) or various types of low-surface-area aquifer sorbents. Furthermore, grouping criteria were suggested that single-sorbate sorption parameters of components belonging to pseudocompounds are within the same order of magnitude (Calligaris and Tien 1982), or within a factor of two (Mehrotra and Tien 1984) over the desired concentration ranges. Since these grouping criteria are situation-specific, a more general as well as more precise grouping criteria guided by statistical analyses is obviously needed.

Therefore, the specific objectives of this study were: (1) to describe the lumping procedure to determine pseudocompounds from experimental data using cluster analysis, (2) to evaluate the effectiveness of the lumped approach using both base case and random mixtures of NOCs in terms of different type of mineral surfaces and HA-mineral complexes with different organic carbon content (f_{oc}), and (3) to develop the lumping schemes which convert mixtures of NOCs into a fewer pseudocompounds in various type of simulated aquifer sorbents. To achieve these

objectives, the sorption behaviors of 12 NOCs with a variety of properties were evaluated using batch equilibrium sorption tests (BESTs) with a variety of simulated aquifer sorbents under abiotic conditions.

6.2 MATERIALS AND METHODS

6.2.1 Simulated Aquifer Sorbents

Both the detail preparation procedures and characterization of HA-coated sands and metal (hydr)oxide-coated sands were described in Chapters 2 and 3, respectively. Overall, four different types of simulated aquifer sorbents were used in this study, viz., (1) uncoated sand, (2) FeOOH-coated sand (FES), (3) Al₂O₃-coated sand (ALS), and (4) HA-coated sand with different f_{oc} (HAS). The physical and chemical properties of the simulated aquifer sorbents are summarized in Table 5.1.

6.2.2 Mixtures of Neutral Organic Compounds

Neutral organic compounds (NOCs) used in this study were selected based on priority hazardous compounds as listed by the Agency for Toxic Substances and Disease Registry (ATSDR 2005). Mixtures of neutral organic compounds are comprised of 12 NOCs, six of which are considered to be polar (hydrophilic) with polar functional groups (i.e., oxygen atom), and six of which are considered to be nonpolar (hydrophobic) without any polar functional groups. The six polar compounds include acetone (ACE), 2-butanone (2-BUT), 2-hexanone (2-HEX), phenol (PHE), *p*-cresol (*p*-CRE), and 2,4-dimethyl phenol (2,4-DMP). The six nonpolar compounds include benzene (BZ), toluene (TOL), *m*-xylene (*m*-XYL),

chlorobenzene (CB), 1,4-dichlorobenzene (1,4-DCB), and 1,2,4-trichlorobenzene (1,2,4-TCB). All NOCs were obtained from Sigma-Aldrich Co. (St. Louis, MO) and Fisher Scientific Co. (Pittsburgh, PA), and were of the highest available purity. Selected properties of all NOCs are summarized in Table 5.2.

Detailed procedures in preparing the solutions are described in Chapter 2. Based on Table 6.1, the stock solutions of NOC mixtures were prepared by adding the exact amount of neat compound to nanopure water (Barnstead/Thermolyne, Dubuque, IA) and by mixing the contents with a magnetic stirrer for 24 hrs before use.

6.2.3 Analytical Method

The concentration of each sorbate in mixtures was measured using gas chromatography (GC) (HP 5890 II, Hewlett-Packard Co., Inc) with a mass selective detector (MSD) and a flame ionization detector (FID). Both the qualitative identifications and quantitative determination of each sorbate were previously described in Chapter 5.

6.2.4 Batch Sorption Methodology

Detailed batch equilibrium sorption tests (BESTs) procedures are described in Chapter 2. The stock solutions of NOC mixtures with different initial concentrations (see Table 6.1) were diluted as the same mole fraction for eight bottle point sorption isotherm. The diluted solutions were added to sorbents and sealed immediately with a Teflon[®]-lined Mininert[®] valve (Valco Instruments Co. Inc.,

Houston, TX) without headspace. The bottle then was initially vortex mixed using a vortexer (VWR, West Chester, PA) for 20 s, and subsequently mixed end-over-end at 10 rpm and 20 °C during the entire experimental period to minimize the abrasion of sorbents. After the equilibrium time was pre-determined for each sorbate-sorbent system, the bottle was centrifuged at 450 g for 20 min, and 2-mL aliquots of the supernatant were transferred to 2-mL auto-sampler glass vial with gas-tight glass syringe (5 mL Purge and Trap Syringe, Hamilton Co., Reno, NV). The collected samples were stored at 4 °C in a refrigerator and analyzed within one week after sampling. All BESTs for each sorbent were performed at least three times in both single-sorbate systems and mixtures. The concentration of any HA in the supernatant resulting from the desorption of HA from HA-coated sand during the BESTs was measured at 254 nm with the spectrophotometer (DU[®] 640, Beckman Instruments, Inc., Fullerton, CA) after sampling.

6.2.5 Sorption Model

The Freundlich sorption model was used to describe and interpret all sorption isotherm data in this study. The Freundlich isotherm model has the form

$$q = K_f C^n \quad (6.1)$$

where q ($\mu\text{mol/kg}$) and C ($\mu\text{mol/L}$) represent the equilibrium solid-phase and aqueous-phase concentrations, respectively. The parameter K_f [$(\mu\text{mol/kg})/(\mu\text{mol/L})^n$] is the Freundlich unit sorption capacity, and n (dimensionless) is the joint

measure of the relative magnitude and diversity of energies (Weber et al. 1992). Although Freundlich model is often considered empirical, this model has been widely applied to describe the overall sorption for heterogeneous sorbents since the Freundlich model results from the summation of several Langmuir-type sorption phenomena representing different interaction energies and sorption capacities (Weber et al. 1992). Based on Eq. 6.1, two different sorption parameters (i.e., K_f and n) were used as the criteria for grouping NOCs in mixtures into pseudocompounds.

6.3 Lumped Approach

Although the lumped approach might be possible by inspecting the data, a more precise lumped approach guided by statistical analyses is obviously needed. Therefore, cluster analysis from statistics was adopted in this study. A schematic diagram illustrating the procedure of lumped approach for sorption of neutral organic compounds in mixtures to simulated aquifer sorbents was shown in Fig. 6.1.

6.3.1 Cluster Analysis

Cluster analysis is a technique for grouping individual or multiple objects into clusters such that objects in a same cluster tend to be more similar to each other than to those in different clusters (Anderberg 1973, Hair et al. 1998, Jain et al. 1999). Thus, the resulting clusters should have high internal (i.e., within-cluster) homogeneity and high external (i.e., between-cluster) heterogeneity. Since the main purpose for cluster analysis is to group objects based on the characteristics of objects,

each NOC can be grouped into pseudocompounds based on sorption behaviors (i.e., K_f and n) of each NOC in mixtures by using cluster analysis.

6.3.2 Distance or Similarity Measurement

The fundamental stage before applying cluster analysis is to establish a numerical distance or similarity measurement to characterize the relationships among the data. In order to assess the similarity among NOCs in terms of sorption behavior, sorption parameters for each NOC were plotted based on two clustering variables (i.e., K_f and n). For example, the sorption parameters for 12 NOCs to uncoated sand were plotted based on two clustering variables as shown in Fig. 6.2a. Also, to have equal weight in distance measurement, the sorption parameters for 12 NOCs were standardized by subtracting the mean and dividing by the standard deviation for each parameter, as shown in Fig. 6.2b. Then, the similarity among NOCs was measured according to the Euclidean distance between each pair of NOCs. Since Euclidean distance between the objects is the length of the hypotenuse of a right triangle, the Euclidean distance between NOCs (d_{12}) can be written, as shown in Fig. 6.2b.

$$d_{12} = \sqrt{(K_{f,2} - K_{f,1})^2 + (n_2 - n_1)^2} \quad (6.2)$$

where $K_{f,1}$ and $K_{f,2}$ are the standardized Freundlich sorption capacity for 1 and 2 NOCs, respectively (dimensionless), and n_1 and n_2 are the standardized Freundlich exponent for 1 and 2 NOCs, respectively (dimensionless). In this study, the

standardization of each sorption parameter was performed with the STANDARD (STD) option in PROC CLUSTER (SAS® 9.1, SAS Institute Inc. Cary, NC) prior to cluster analysis (see Appendix F).

Also, a preliminary screening for outliers, which were defined as the observations that were more than 2.5 times greater than the standard deviation from the mean, was performed since distance measurement is particularly sensitive to outliers. In this study, a preliminary screening was performed with the TRIM option in PROC CLUSTER (SAS® 9.1, SAS Institute Inc. Cary, NC) only for a high number of observations.

6.3.3 Clustering Algorithms

After the distance between NOCs was determined, the most appropriate clustering algorithm to maximize the differences between clusters relative to the variation within the clusters must be determined. In this regard, hierarchical cluster procedures sequentially define the arrangement of the set of NOCs in disjointed groups, and involve the construction of a hierarchy or tree-like structure (referred to as dendrogram) (Hair et al. 1998, Jain et al. 1999). The cluster procedure has several algorithms for determining the strategy of merging clusters. The clustering algorithms that are commonly used in cluster procedures include the (1) single linkage method, (2) complete linkage method, (3) average linkage method, (4) centroid method, (5) median method, and (6) Ward's method (Hair et al. 1998). In this study, preliminary results suggested that Ward's method (Ward 1963) provided the most accurate solutions among the cluster procedures, consistent with other

studies (Anderberg 1973, Blashfield 1976, DeGaetano 1996, Unal et al 2003). In this study, Ward's method was performed by specifying METHOD=WARD in PROC CLUSTER (SAS® 9.1, SAS Institute Inc. Cary, NC) (see Appendix F).

Ward's method (Ward 1963) was designed to generate clusters in such a way that the within-cluster sum of squares is minimized when merging two clusters at each step. Therefore, at each step, two of the previous clusters are merged based on the minimization of the increment of the total within-cluster error sum of squares caused by merging. This increment in the total within-cluster error sum of squares (ΔE_{KL}) due to the merging of K and L clusters can be computed from the following equations:

$$\Delta E_{KL} = \frac{N_K N_L}{N_K + N_L} d_{KL}^2 \quad (6.3)$$

where N_K and N_L are the number of objects in K and L clusters, respectively, and d_{KL} is the Euclidean distance between the means of K and L clusters

$$d_{KL}^2 = \sum_{i=1}^N (\bar{x}_{iK} - \bar{x}_{iL})^2 \quad (6.4)$$

where $\bar{x}_{iK}$ and $\bar{x}_{iL}$ are the mean vectors for K and L clusters, respectively. Compared to other cluster procedures, Ward's method can be versatile and tend to merge clusters with a small number of observations (Anderberg 1973, Blashfield 1976, Hair et al. 1998).

6.3.4 Number of Clusters

The agglomerative hierarchical cluster procedures do not provide a single cluster solution. Instead, cluster procedures provide a sequence of cluster solutions starting with n clusters (i.e., number of objects) and ending with one cluster. Therefore, the determination of an appropriate number of clusters is a significant issue. Although several criteria and guidelines have been suggested to solve this problem (Coxon and Bischoff 1987, Hair et al. 1998, Jain et al. 1999), no standard or objective selection procedure exists (Hartigan 1985). Generally, the distances between clusters (i.e., error variability measures or semi-partial R^2) at successive steps may be used as a guideline. When the distances between clusters exceed a specific threshold value or make a sudden jump, the cluster procedure should be terminated.

Other methods for the determination of an appropriate number of clusters are to investigate the values of R^2 (RS), cubic clustering criterion (CCC), pseudo F (PSF), and pseudo t^2 (PST2) statistics. Milligan and Cooper (1985) investigated the procedures for determining the number of clusters using four clustering algorithms, and found that PSF, PST2, and CCC performed the best in the studies with a high degree of error in the data. In this study, consensus between the two statistics (i.e., local peaks of the PSF combined with a small value of PST2 and a larger PST2 for the next cluster merging) was used as the indicator of the proper number of clusters. The PSF and PST2 statistics were readily obtained by PSEUDO option in PROC CLUSTER (SAS® 9.1, SAS Institute Inc. Cary, NC) (see Appendix F). After

evaluating all of possible clusters, the best number of clusters and cluster components were determined based on both statistics criteria and theoretical backgrounds.

6.4 RESULTS AND DISCUSSION

The feasibility of lumped approach (i.e., species grouping) for sorption of NOC mixtures was evaluated with simulated aquifer sorbents. Both sorption isotherms and Freundlich sorption parameters for a given NOC in mixtures were determined according to Table 6.1. All of the sorption isotherms and Freundlich sorption parameters for a given NOC in mixtures were presented in Chapter 5. The statistical analyses using cluster procedures were performed to determine the pseudocompounds in mixtures.

6.4.1 Sorption to Hydrophilic Mineral Surfaces

6.4.1.1 Hierarchical Cluster Analysis

In order to group individual or multiple NOCs into pseudocompounds in a meaning way, Ward's clustering algorithm was applied to 12 NOCs in mixtures sorbed to three hydrophilic mineral surfaces. As shown in Figs. 6.3a, 6.4a, and 6.5a for uncoated, FeOOH-coated, and Al₂O₃-coated sands, respectively, dendrograms showed a history of cluster analysis versus semi-partial R^2 values. In the first step, each NOC started as its own cluster. In subsequent steps, the two closest NOCs (or clusters) were combined into a new cluster until all 12 NOCs were lumped into one large cluster. Whereas semi-partial R^2 values increased slightly until four clusters for

both uncoated and FeOOH-coated sands, a relatively large increase in semi-partial R^2 values occurred from four to three clusters. On the contrary, a relatively large increase in semi-partial R^2 values occurred from five to four clusters for Al₂O₃-coated sand. These results indicate that 12 NOCs can be lumped into four pseudocompounds for both uncoated and FeOOH-coated sands, and five pseudocompounds for Al₂O₃-coated sand, as shown in Figs. 6.3b, 6.4b, and 6.5b for uncoated, FeOOH-coated, and Al₂O₃-coated sands, respectively.

The behavior of the PSF and PST2 in terms of number of clusters was illustrated in Figs. 6.6, 6.7, and 6.8 for uncoated, FeOOH-coated, and Al₂O₃-coated sands, respectively. A clear consensus between the two statistics (i.e., local peaks of PSF combined with a small value of PST2 and a larger PST2 for the next cluster merging) as to an appropriate number of clusters indicated that four or five pseudocompounds were appropriate for hydrophilic mineral surfaces, consistent with the determination based on semi-partial R^2 values. Although five pseudocompounds was appropriate for Al₂O₃-coated sand based on semi-partial R^2 values, the sorption behavior of *p*-CRE was similar to the sorption behavior of 2,4-DMP and 2-HEX (see Figs. 5.15 and 6.5b). Additionally, four pseudocompounds were still appropriate based on consensus between the two statistics as shown in Fig. 6.8. In this way, four pseudocompounds were determined to approximate the sorption behavior of 12 NOCs in mixtures to the hydrophilic mineral surfaces evaluated in this study.

6.4.1.2 Effects of Mixture Compositions and Type of Mineral Surfaces

Based on the cluster analysis, both base case and random mixtures were lumped into 4 pseudocompounds as summarized in Tables 6.2, 6.3, and 6.4 for uncoated, FeOOH-coated, and Al₂O₃-coated sands, respectively. The letters A, B, C, and D denote each pseudocompound to which NOCs in mixtures are assigned based on cluster analysis. For nonpolar NOCs in mixtures, 1,2,4-TCB and 1,4-DCB were assigned in pseudocompound A whereas CB, *m*-XYL, TOL, and BZ were assigned in pseudocompound B. These consistent lumping schemes indicate that effects of mixture compositions and type of mineral surfaces on the sorption of nonpolar NOCs to hydrophilic mineral surfaces are not significant. Although none of nonpolar NOCs in mixtures were assigned with polar NOCs in the same pseudocompound, some polar NOCs in mixtures were not assigned in the same pseudocompound in terms of mixture compositions and type of mineral surfaces. For example, PHE and 2-HEX were lumped together into pseudocompound C in test #1 and 3, whereas those were lumped together or separately into pseudocompound C or D in other tests, depending on mixture compositions and type of mineral surfaces. These inconsistent lumping schemes indicate that effects of mixture compositions and type of mineral surfaces on the sorption of polar NOCs to hydrophilic mineral surfaces are significant.

Compared to sorption of nonpolar NOCs in mixtures to hydrophilic mineral surfaces showing no mixture effects, the complex mixture effects for sorption of polar NOCs in mixtures to hydrophilic mineral surfaces can be attributed to the mutual competition for hydrophilic specific sorption sites, such as H-bonding (see Chapter 5 for detail information). Under this scenario, the suppression of nonlinear

sorption for a given polar NOC was likely due to the existence of other polar NOCs versus other nonpolar NOCs in mixtures. Also, the presence and magnitude of mutual competition among polar NOCs was subject to variation, depending on the mixture compositions (i.e., concentration and polarity of polar NOCs) and the type of mineral surfaces (i.e., specific volume of vicinal water region and availability of hydrophilic specific sorption sites). Thus, these inconsistent lumping schemes for polar NOCs are expected such that complex mutual competitions make the lumped approach for sorption of polar NOCs in mixtures to hydrophilic mineral surfaces more difficult.

Although the sorption of NOCs to hydrophilic mineral surfaces can be affected by factors other than the hydrophobicity of the NOCs in aqueous solution, the free energy of sorption of NOCs to hydrophilic mineral surfaces has been shown to be inversely related to the free energy of aqueous dissolution of NOCs (Schwarzenbach et al. 1993, Mader et al. 1997). Accordingly, components for pseudocompounds in terms of type of mineral surfaces were plotted versus $\log \gamma_w^{sat}$ (summarized in Table 5.2) for the NOCs in Fig. 6.9, where γ_w^{sat} is the aqueous activity coefficient at saturation. As shown in Fig. 6.9, the sorption behavior of 12 NOCs in mixtures to hydrophilic mineral surfaces can be lumped based on $\log \gamma_w^{sat}$. This result indicate that γ_w^{sat} can be used as the possible grouping criteria for sorption of NOC mixtures to hydrophilic mineral surfaces although the relative contributions of different forces (i.e., hydrophobic vs. hydrophilic) to the overall sorption may differ for different mixture compositions and types of mineral surfaces.

6.4.1.3 Evaluation of Effectiveness of Pseudocompounds to Hydrophilic Mineral Surfaces

The effectiveness of pseudocompounds was evaluated based on the comparison of sorption between each pseudocompound and components belonging to each pseudocompound. After the lumping schemes were determined, each pseudocompound was prepared by dissolving only components belonging to each pseudocompound in various compositions. In this study, the aqueous- and solid-phase concentrations of pseudocompounds were calculated by summation of the aqueous- and solid- phase concentration of components at equilibrium in each batch bottle, respectively. Then, the sorption of components in each pseudocompound were compared to the 95 % confidence intervals for the associated best-fit Freundlich sorption model based on sorption of pseudocompound, as shown in Figs. 6.10, 6.11, and 6.12 for uncoated, FeOOH-coated, and Al₂O₃-coated sands, respectively. For all hydrophilic mineral surfaces, the sorption isotherms of both pseudocompounds A and B (i.e., nonpolar NOCs) described the sorption behaviors of components better than those of both pseudocompounds C and D (i.e., polar NOCs) did. Also, each pseudocompound showed substantially different sorption behavior in terms of both sorption capacity and nonlinearity. For example, pseudocompound A showed greater sorption capacity and more linearity (i.e., $0.981 \leq n \leq 1.02$) whereas pseudocompound D showed lower sorption capacity and more nonlinearity (i.e., $0.627 \leq n \leq 0.708$). Although the maximum difference of the amount sorbed (q) for a given aqueous equilibrium concentration (C) between component and pseudocompound was nearly 20% (see Fig. 6.12d), the values of K_f

and n for pseudocompounds were within the ranges of those for components. This result indicates that each pseudocompound contains components of relatively similar sorption capacities and nonlinearity.

6.4.1.4 Estimation of sorption parameters for pseudocompounds from single-sorbate sorption parameters for components

In this study, the Freundlich sorption parameters for pseudocompounds were assigned based on the summation of the aqueous- and solid- phase concentration of components at equilibrium. However, a commonly used approach was to assign the Freundlich sorption parameters of pseudocompounds equal to the mole fraction-weighted averages of single-sorbate Freundlich sorption parameters of components belonging to pseudocompounds (Calligaris and Tien 1982). Thus, the feasibility for this approach was evaluated by comparison of Freundlich sorption parameters between pseudocompounds and estimation from mole fraction-weighted averages of single-sorbate individual components. All examples were based on the same initial mole concentrations (i.e., 50 $\mu\text{mol/L}$ and dilution) among individual components in both single-sorbate systems and pseudocompounds, and the comparison of Freundlich sorption parameters were summarized in Tables 6.5, 6.6, and 6.7 for uncoated, FeOOH-coated, and Al_2O_3 -coated sands, respectively.

Whereas the Freundlich sorption parameters for pseudocompounds A and B to mineral surfaces were estimated from mole fraction-weighted averages of single-sorbate Freundlich sorption parameters of individual components with less than 8% error, those for pseudocompounds C and D were estimated with error ranged from

1.3 to 47%. This result indicate that Freundlich sorption parameters of pseudocompounds consisting of polar NOCs are not perfectly represented by using the mole fraction-weighted averages of single-sorbate Freundlich sorption parameters of components. Since the significant mixture effects for sorption of polar NOCs to hydrophilic mineral surfaces were expected due to the mutual competition for hydrophilic specific sorption sites, both sorption capacity and nonlinearity for polar NOCs in single-sorbate systems to the hydrophilic mineral surfaces were altered by the presence and the quantity of other polar NOCs within pseudocompounds. Therefore, the assignment of the Freundlich sorption parameters of pseudocompounds using mole fraction-weighted averages of single-sorbate Freundlich sorption parameters of components leads to inaccuracy of sorption prediction.

6.4.2 Sorption to Humic Acid-Mineral Complexes

6.4.2.1 Hierarchical Cluster Analysis

In the same manner applied in sorption to mineral surfaces, Ward's clustering algorithm was applied to 12 NOCs in mixtures sorbed to three HA-coated sands (HAS) with different f_{oc} . As shown in Figs. 6.13a, 6.14a, and 6.15a for HAS1 ($f_{oc} = 0.051\%$), HAS2 ($f_{oc} = 0.119\%$), and HAS3 ($f_{oc} = 0.221\%$), respectively, dendrograms showed a history of cluster analysis versus semi-partial R^2 values. Whereas semi-partial R^2 values increased slightly until four, five, and six clusters for HAS1, HAS2, and HAS3, respectively, a relatively large increase in semi-partial R^2 values occurred at next clusters. These results indicate that 12 NOCs can be lumped

into four, five, and six pseudocompounds for HAS1, HAS2, and HAS3, respectively, as shown in Figs. 6.13b, 6.14b, and 6.15b for HAS1, HAS2, and HAS3, respectively.

The behavior of the PSF and PST2 in terms of number of clusters was illustrated in Figs. 6.16, 6.17, and 6.18 for HAS1, HAS2, and HAS3, respectively. A clear consensus between the two statistics (i.e., local peaks of PSF combined with a small value of PST2 and a larger PST2 for the next cluster merging) as to an appropriate number of clusters indicated that four, five, or six pseudocompounds were appropriate for HAS with different f_{oc} , consistent with the determination based on semi-partial R^2 values. Although higher numbers of pseudocompounds can describe the sorption behavior of 12 NOCs in mixtures accurately, fewer numbers of pseudocompounds were desired for simplicity. Thus, four, five, and six pseudocompounds were selected for HAS1, HAS2, and HAS3, respectively, to approximate the sorption behavior of 12 NOCs in mixtures to HAS with different f_{oc} .

6.4.2.2 Effects of Mixture Compositions and Fraction of Organic Carbon (f_{oc})

Based on the cluster analysis, both base case and random mixtures were lumped into various numbers of pseudocompounds as summarized in Tables 6.8, 6.9, and 6.10 for HAS1, HAS2, and HAS3, respectively. The letters A, B, C, D, E and F denote each pseudocompound to which NOCs in mixtures were assigned based on cluster analysis. For a given HAS, identical number of pseudocompounds can approximate the sorption behavior of 12 NOC mixtures in both base case and random mixtures, and the nonpolar NOCs in mixtures were assigned in the same pseudocompound, regardless of mixture compositions. These consistent lumping

schemes indicate that effect of mixture compositions on the sorption of nonpolar NOCs to HAS is not significant.

In contrast, for HAS1, polar NOCs in mixtures were not assigned in the same pseudocompound in terms of mixture compositions. For example, PHE in HAS1 was lumped into C pseudocompound in test #1, 3 and 5 whereas PHE was lumped into D pseudocompound in other tests, depending on mixture compositions. These inconsistent lumping schemes indicate that effect of mixture compositions on the sorption of polar NOCs to HAS1 is significant. However, for HAS2 and HAS3, polar NOCs in mixtures were assigned in the same pseudocompound, regardless of mixture compositions. The complex mixture effect for sorption of PHE to HA-coated sand with lower f_{oc} values (i.e., 0.051%) can be attributed to mutual competition for hydrophilic specific sites of both mineral surfaces and HA (see Chapter 5 for detail information). Thus, the presence and magnitude of competitive effect among various polar NOCs may be dependent on the composition of mixtures (i.e., concentration and polarity of NOCs) and the type of sorbents (i.e., availability of hydrophilic specific sites). Therefore, sorption of polar NOCs in mixtures to HAS1 was more subject to variation with concentrations and compositions in mixtures, compared to sorption of nonpolar NOCs.

Although the sorption of NOCs to HAS can be promoted by the several mechanisms, including both absorption (partitioning) and adsorption to HA domains and adsorption onto hydrophilic mineral surfaces, partitioning of NOCs in mixtures to HAS is an increasingly dominating contribution to overall sorption if a sufficient amount of competing NOCs is present (McGinley et al. 1993, Xing et al. 1996, Xia

and Ball 2000). Additionally, linear partitioning of NOCs to HA, whereby the distribution coefficient (K_d) is equal to the product of the fraction of organic carbon (f_{oc}) and the organic carbon partitioning coefficient (K_{oc}) (i.e., $K_d = f_{oc}K_{oc}$), has been shown to be a major component of sorption for sorbents with $f_{oc} > 0.1$ % (Karickhoff et al. 1984, Allen-King et al. 2002, Nguyen et al. 2005). Accordingly, components for pseudocompounds in terms of HAS with different f_{oc} values were plotted versus $\log K_{oc}$ (summarized in Table 5.2) for the NOCs in Fig. 6.19. As shown in Fig. 6.19, the sorption behavior of 12 NOC mixtures to HAS with different f_{oc} can be lumped based on $\log K_{oc}$. As the f_{oc} of HAS increases, the NOCs with higher K_{oc} (i.e., 1,2,4-TCB and 1,4-DCB) were separated from nonpolar pseudocompounds due to the greater dependency of sorption on f_{oc} . In contrast, the NOCs with lower K_{oc} were not separated from polar pseudocompounds substantially due to the lower dependency of sorption on f_{oc} . These results indicate that K_{oc} can be used as the possible grouping criteria for sorption of NOC mixtures to HAS with different f_{oc} although the relative contributions of different forces (i.e., absorption vs. adsorption to HA domains, and adsorption onto hydrophilic mineral surfaces) to the overall sorption may differ for different mixture compositions and f_{oc} values.

6.4.2.3 Evaluation of Effectiveness of Pseudocompounds to Humic Acid-Mineral Complexes

The effectiveness of pseudocompounds was evaluated based on the comparison of sorption between each pseudocompound and components belonging to each pseudocompound. The sorption of components in each pseudocompound

were compared to the 95 % confidence intervals for the associated best-fit Freundlich sorption model based on sorption of pseudocompound, as shown in Figs. 6.20, 6.21, and 6.22 for HAS1, HAS2, and HAS3, respectively. For all HASs, the sorption isotherms of pseudocompounds consisting of nonpolar NOCs described the sorption behaviors of components better than those of pseudocompounds consisting of polar NOCs did. Also, each pseudocompound showed clearly different sorption behavior in terms of both sorption capacity and nonlinearity. For example, pseudocompound consisting of nonpolar NOCs showed greater sorption capacity and more linearity (i.e., $0.928 \leq n \leq 1.03$) whereas pseudocompound consisting of polar NOCs showed lower sorption capacity and more nonlinearity (i.e., $0.661 \leq n \leq 0.898$). Although the maximum difference of the amount sorbed (q) for a given aqueous equilibrium concentration (C) between component and pseudocompound was nearly 50% (see Fig. 6.22e), the values of K_f and n for pseudocompounds were within the ranges of those for components. This result indicates that each pseudocompound contained components with relatively similar sorption capacities and nonlinearity.

6.4.2.4 Estimation of sorption parameters for pseudocompounds from single-sorbate sorption parameters for components

In this study, the Freundlich sorption parameters for pseudocompounds were assigned based on the summation of the aqueous- and solid- phase concentration of components at equilibrium. However, a commonly used approach was to assign the Freundlich sorption parameters of pseudocompounds equal to the mole fraction-

weighted averages of single-sorbate Freundlich sorption parameters of components belonging to pseudocompounds (Calligaris and Tien 1982). Thus, the feasibility for this approach was evaluated by comparison of Freundlich sorption parameters between pseudocompounds and estimation from mole fraction-weighted averages of single-sorbate individual components. All examples were based on the same initial mole concentrations (i.e., 50 $\mu\text{mol/L}$ and dilution) among individual components in both single-sorbate systems and pseudocompounds, and the comparison of Freundlich sorption parameters were summarized in Tables 6.11, 6.12, and 6.13 for HAS1, HAS2, and HAS3, respectively.

Whereas the Freundlich sorption parameters for pseudocompounds consisting of nonpolar NOCs were estimated from mole fraction-weighted averages of single-sorbate Freundlich sorption parameters of individual components with less than 12% error, those for pseudocompounds consisting of polar NOCs were estimated with error ranged from 2.4 to 51%. This result also indicate that Freundlich sorption parameters of pseudocompounds consisting of polar NOCs were not perfectly represented by using the mole fraction-weighted averages of single-sorbate Freundlich sorption parameters of components. Since the significant mixture effects for sorption of polar NOCs to HAS were expected due to the mutual competition for hydrophilic specific sorption sites, both sorption capacity and nonlinearity for polar NOCs in single-sorbate systems to HAS were altered by the presence and the quantity of other polar NOCs within pseudocompounds. Thus, sorption of polar NOCs in mixtures to HAS was more subject to variation with concentrations and compositions in mixtures, compared to sorption of nonpolar

NOCs to HAS. Therefore, the assignment of the Freundlich sorption parameters of pseudocompounds using mole fraction-weighted averages of single-sorbate Freundlich sorption parameters of components leads to inaccuracy of sorption prediction.

6.5 SUMMARY AND CONCLUSIONS

The feasibility of a lumped approach to describe the sorption of neutral organic compounds in mixtures in terms of the sorption of a fewer number of pseudocompounds (i.e., groups of NOCs with similar sorption affinities) was evaluated. The lumped approach for sorption to simulated aquifer sorbents was guided by cluster analysis from statistics. Then, the effectiveness of the lumped approach using both base case and random mixtures of neutral organic compounds in terms of different type of mineral surfaces and HA-mineral complexes with different organic carbon content (f_{oc}) was evaluated.

In sorption to hydrophilic mineral surfaces, the following conclusions can be drawn:

- Four pseudocompounds were determined to approximate the sorption behavior of 12 neutral organic compounds in mixtures to hydrophilic mineral surfaces, and each pseudocompound contained components of relatively similar sorption capacities and nonlinearity. Whereas nonpolar neutral organic compounds in mixtures showed the consistent lumping schemes, polar neutral organic compounds in mixtures showed inconsistent lumping

schemes due to the mutual competition for hydrophilic specific sorption sites among polar neutral organic compounds.

- The sorption of 12 neutral organic compounds in mixtures to hydrophilic mineral surfaces can be lumped based on aqueous activity coefficient at saturation (γ_w^{sat}) although the relative contributions of different forces (i.e., hydrophobic vs. hydrophilic) to the overall sorption may differ for different mixture compositions and types of mineral surfaces.
- Since both sorption capacity and nonlinearity for polar neutral organic compounds in single-sorbate systems to hydrophilic mineral surfaces were altered by the presence and the quantity of other polar neutral organic compounds in mixtures, the assignment of the Freundlich sorption parameters of pseudocompounds using single-sorbate Freundlich sorption parameters of components led to inaccuracy of sorption prediction.

In sorption to humic acid-mineral complexes with different f_{oc} , the following conclusions can be drawn:

- Different numbers of pseudocompounds were determined to approximate the sorption behavior of 12 neutral organic compounds in mixtures to humic acid-coated sands with different f_{oc} , and each pseudocompound contained components of relatively similar sorption capacities and nonlinearity. Whereas nonpolar neutral organic compounds in mixtures showed the consistent lumping schemes, polar neutral organic compounds in mixtures showed inconsistent lumping schemes due to the mutual competition for

hydrophilic specific sorption sites of both mineral surfaces and humic acid among polar neutral organic compounds.

- The sorption behavior of 12 neutral organic compounds in mixtures to humic acid-coated sands with different f_{oc} can be lumped based on the organic carbon partitioning coefficient (K_{oc}) although the relative contributions of different forces (i.e., absorption vs. adsorption to HA domains, and adsorption onto hydrophilic mineral surfaces) to the overall sorption may differ for different mixture compositions and f_{oc} values.
- Since both sorption capacity and nonlinearity for polar neutral organic compounds in single-sorbate systems to humic acid-coated sands with low f_{oc} (i.e., 0.051%) were altered by the presence and the quantity of other polar neutral organic compounds in mixtures, the assignment of the Freundlich sorption parameters of pseudocompounds using single-sorbate Freundlich sorption parameters of components led to inaccuracy of sorption prediction.

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Table 6.1 Summary of experimental conditions for sorption of neutral organic compounds in mixtures to all simulated aquifer sorbents.

Experimental Conditions					
Sorbates	Concentration of Each Stock Solution ($\mu\text{mol/L}$) ^a				
	Test Number				
	1	2	3	4	5
1,2,4-trichlorobenzene	50	100	50	68	60
1,4-dichlorobenzene	50	50	50	21	56
chlorobenzene	50	50	50	28	35
<i>m</i>-xylene	50	50	50	35	62
Toluene	50	50	50	89	34
Benzene	50	50	50	28	71
2,4-dimethyl phenol	50	50	50	50	52
<i>p</i>-cresol	50	50	50	16	36
phenol	50	50	50	82	54
2-hexanone	50	50	50	44	24
2-butanone	50	50	50	30	89
acetone	50	50	100	71	64
SUM	600	650	650	562	637

^a Stock solutions were diluted as the same mole fraction for eight bottle point sorption isotherm

Table 6.2 Summary of lumped cluster assignments for sorption of neutral organic compounds in mixtures to uncoated sands.

Sorbates	Test Number ^a				
	1	2	3	4	5
1,2,4-trichlorobenzene	A	A	A	A	A
1,4-dichlorobenzene	A	A	A	A	A
chlorobenzene	B	B	B	B	B
<i>m</i>-xylene	B	B	B	B	B
Toluene	B	B	B	B	B
Benzene	B	B	B	B	B
2,4-dimethyl phenol	C	C	C	C	C
<i>p</i>-cresol	C	C	C	C	C
phenol	C	C	C	D	C
2-hexanone	C	C	C	C	D
2-butanone	D	D	D	D	D
acetone	D	D	D	D	D

^aA, B, C, and D represent each pseudocompound to which NOCs in mixtures are assigned based on cluster analysis.

Table 6.3 Summary of lumped cluster assignments for sorption of neutral organic compounds in mixtures to FeOOH-coated sands.

Sorbates	Test Number ^a				
	1	2	3	4	5
1,2,4-trichlorobenzene	A	A	A	A	A
1,4-dichlorobenzene	A	A	A	A	A
chlorobenzene	B	B	B	B	B
<i>m</i>-xylene	B	B	B	B	B
Toluene	B	B	B	B	B
Benzene	B	B	B	B	B
2,4-dimethyl phenol	C	C	C	C	C
<i>p</i>-cresol	C	C	C	C	C
phenol	C	D	C	D	C
2-hexanone	C	C	C	C	C
2-butanone	D	D	D	D	D
acetone	D	D	D	D	D

^aA, B, C, and D represent each pseudocompound to which NOCs in mixtures are assigned based on cluster analysis.

Table 6.4 Summary of lumped cluster assignments for sorption of neutral organic compounds in mixtures to Al₂O₃-coated sands.

Sorbates	Test Number ^a				
	1	2	3	4	5
1,2,4-trichlorobenzene	A	A	A	A	A
1,4-dichlorobenzene	A	A	A	A	A
chlorobenzene	B	B	B	B	B
<i>m</i>-xylene	B	B	B	B	B
Toluene	B	B	B	B	B
Benzene	B	B	B	B	B
2,4-dimethyl phenol	C	C	C	C	C
<i>p</i>-cresol	C	C	C	C	C
phenol	C	D	C	D	C
2-hexanone	C	D	C	C	D
2-butanone	D	D	D	D	D
acetone	D	D	D	D	D

^aA, B, C, and D represent each pseudocompound to which NOCs in mixtures are assigned based on cluster analysis.

Table 6.5 Comparison of Freundlich sorption parameters between pseudocompounds and estimation from single-sorbate individual components for uncoated sands (initial mole concentrations for all sorbates is 50 $\mu\text{mol/L}$).

Pseudocompound	Components	Single-Sorbate		Pseudocompound		Comparison of Average	
		$K_{f, \text{single}}$	N_{single}	$K_{f, \text{PS}}$	N_{PS}	$K_{f, \text{single}} / K_{f, \text{PS}}$	$N_{\text{single}} / N_{\text{PS}}$
A	1,2,4-TCB	0.263	0.979	0.246	1.00	1.04	0.973
	1,4-DCB	0.248	0.967				
	AVE.	0.256	0.973				
B	CB	0.222	0.951	0.243	0.956	1.08	0.992
	<i>m</i> -XYL	0.325	0.935				
	TOL	0.262	0.968				
	BZ	0.241	0.939				
	AVE.	0.263	0.948				
C	2,4-DMP	0.102	0.830	0.081	0.851	1.17	0.923
	<i>p</i> -CRE	0.095	0.763				
	PHE	0.089	0.739				
	2-HEX	0.092	0.810				
	AVE.	0.095	0.786				
D	2-BUT	0.077	0.714	0.086	0.708	1.20	0.972
	ACE	0.129	0.662				
	AVE.	0.103	0.688				

Table 6.6 Comparison of Freundlich sorption parameters between pseudocompounds and estimation from single-sorbate individual components for FeOOH-coated sands (initial mole concentrations for all sorbates is 50 $\mu\text{mol/L}$).

Pseudocompound	Components	Single-Sorbate		Pseudocompound		Comparison of Average	
		$K_{f, \text{single}}$	N_{single}	$K_{f, \text{PS}}$	N_{PS}	$K_{f, \text{single}} / K_{f, \text{PS}}$	$N_{\text{single}} / N_{\text{PS}}$
A	1,2,4-TCB	0.184	1.05	0.194	1.02	0.928	1.00
	1,4-DCB	0.175	0.998				
	AVE.	0.180	1.02				
B	CB	0.147	0.949	0.182	0.944	0.923	1.01
	<i>m</i> -XYL	0.227	0.927				
	TOL	0.145	0.985				
	BZ	0.152	0.933				
	AVE.	0.168	0.949				
C	2,4-DMP	0.142	0.825	0.103	0.898	1.47	0.863
	<i>p</i> -CRE	0.248	0.724				
	PHE	0.131	0.715				
	2-HEX	0.088	0.837				
	AVE.	0.152	0.775				
D	2-BUT	0.208	0.647	0.173	0.689	1.31	0.914
	ACE	0.247	0.613				
	AVE.	0.227	0.630				

Table 6.7 Comparison of Freundlich sorption parameters between pseudocompounds and estimation from single-sorbate individual components for Al₂O₃-coated sands (initial mole concentrations for all sorbates is 50 µmol/L).

Pseudocompound	Components	Single-Sorbate		Pseudocompound		Comparison of Average	
		$K_{f,single}$	N_{single}	$K_{f,PS}$	N_{PS}	$K_{f,single} / K_{f,PS}$	N_{single} / N_{PS}
A	1,2,4-TCB	0.223	0.978	0.208	0.981	0.929	1.02
	1,4-DCB	0.162	1.02				
	AVE.	0.193	0.999				
B	CB	0.156	0.956	0.171	0.960	0.971	0.996
	<i>m</i> -XYL	0.160	1.01				
	TOL	0.218	0.911				
	BZ	0.131	0.946				
	AVE.	0.166	0.956				
C	2,4-DMP	0.098	0.781	0.094	0.863	1.44	0.888
	<i>p</i> -CRE	0.221	0.722				
	PHE	0.132	0.692				
	2-HEX	0.088	0.869				
	AVE.	0.135	0.766				
D	2-BUT	0.286	0.611	0.191	0.627	1.32	0.987
	ACE	0.219	0.626				
	AVE.	0.253	0.619				

Table 6.8 Summary of lumped cluster assignments for sorption of neutral organic compounds in mixtures to HA-coated sands ($f_{oc} = 0.051\%$).

Sorbates	Test Number				
	1	2	3	4	5
1,2,4-trichlorobenzene	A	A	A	A	A
1,4-dichlorobenzene	B	B	B	B	B
chlorobenzene	B	B	B	B	B
<i>m</i> -xylene	B	B	B	B	B
Toluene	B	B	B	B	B
Benzene	B	B	B	B	B
2,4-dimethyl phenol	C	C	C	C	C
<i>p</i> -cresol	C	C	C	C	C
phenol	C	D	C	D	C
2-hexanone	C	C	C	C	C
2-butanone	D	D	D	D	D
acetone	D	D	D	D	D

^aA, B, C, and D represent each pseudocompound to which NOCs in mixtures are assigned based on cluster analysis.

Table 6.9 Summary of lumped cluster assignments for sorption of neutral organic compounds in mixtures to HA-coated sands ($f_{oc} = 0.119\%$).

Sorbates	Test Number				
	1	2	3	4	5
1,2,4-trichlorobenzene	A	A	A	A	A
1,4-dichlorobenzene	B	B	B	B	B
chlorobenzene	C	C	C	C	C
<i>m</i>-xylene	B	B	B	B	B
Toluene	C	C	C	C	C
Benzene	C	C	C	C	C
2,4-dimethyl phenol	D	D	D	D	D
<i>p</i>-cresol	D	D	D	D	D
phenol	D	D	D	D	D
2-hexanone	D	D	D	D	D
2-butanone	E	E	E	E	E
acetone	E	E	E	E	E

^aA, B, C, D, and E represent each pseudocompound to which NOCs in mixtures are assigned based on cluster analysis.

Table 6.10 Summary of lumped cluster assignments for sorption of neutral organic compounds in mixtures to HA-coated sands ($f_{oc} = 0.221\%$).

Sorbates	Test Number				
	1	2	3	4	5
1,2,4-trichlorobenzene	A	A	A	A	A
1,4-dichlorobenzene	B	B	B	B	B
chlorobenzene	C	C	C	C	C
<i>m</i>-xylene	C	C	C	C	C
Toluene	D	D	D	D	D
Benzene	D	D	D	D	D
2,4-dimethyl phenol	E	E	E	E	E
<i>p</i>-cresol	E	E	E	E	E
phenol	E	E	E	E	E
2-hexanone	E	E	E	E	E
2-butanone	F	F	F	F	F
acetone	F	F	F	F	F

^aA, B, C, D, E, and F represent each pseudocompound to which NOCs in mixtures are assigned based on cluster analysis.

Table 6.11 Comparison of Freundlich sorption parameters between pseudocompounds and estimation from single-sorbate individual components for HA-coated sands ($f_{oc}=0.051\%$) (initial mole concentrations for all sorbates is $50\text{ }\mu\text{mol/L}$).

Pseudocompound	Components	Single-Sorbate		Pseudocompound		Comparison of Average	
		$K_{f,single}$	N_{single}	$K_{f,PS}$	N_{PS}	$K_{f,single} / K_{f,PS}$	N_{single} / N_{PS}
A	1,2,4-TCB	0.958	1.01	0.932	0.997	1.03	1.01
	AVE.	0.958	1.01				
B	DCB	0.363	1.06	0.330	0.964	0.882	1.03
	CB	0.266	0.979				
	<i>m</i> -XYL	0.295	1.01				
	TOL	0.264	0.981				
	BZ	0.268	0.948				
	AVE.	0.291	0.996				
C	2,4-DMP	0.174	0.797	0.069	0.872	1.46	0.914
	<i>p</i> -CRE	0.075	0.813				
	PHE	0.093	0.766				
	2-HEX	0.061	0.812				
	AVE.	0.101	0.797				
D	2-BUT	0.138	0.578	0.142	0.661	1.07	0.898
	ACE	0.165	0.610				
	AVE.	0.152	0.594				

Table 6.12 Comparison of Freundlich sorption parameters between pseudocompounds and estimation from single-sorbate individual components for HA-coated sands ($f_{oc}=0.119\%$) (initial mole concentrations for all sorbates is $50\text{ }\mu\text{mol/L}$).

Pseudocompound	Components	Single-Sorbate		Pseudocompound		Comparison of Average	
		$K_{f,single}$	N_{single}	$K_{f,PS}$	N_{PS}	$K_{f,single} / K_{f,PS}$	N_{single} / N_{PS}
A	1,2,4-TCB	2.31	0.952	2.21	0.975	1.04	0.976
	AVE.	2.31	0.952				
B	1,4-DCB	0.802	1.01	0.663	1.03	1.10	0.956
	<i>m</i> -XYL	0.655	0.959				
	AVE.	0.729	0.985				
C	CB	0.420	1.01	0.456	0.957	0.887	1.01
	TOL	0.529	0.908				
	BZ	0.265	0.973				
	AVE.	0.405	0.964				
D	2,4-DMP	0.297	0.821	0.151	0.898	1.51	0.883
	<i>p</i> -CRE	0.224	0.783				
	PHE	0.242	0.735				
	2-HEX	0.148	0.832				
	AVE.	0.223	0.793				
E	2-BUT	0.070	0.728	0.132	0.701	0.807	0.984
	ACE	0.143	0.652				
	AVE.	0.107	0.690				

Table 6.13 Comparison of Freundlich sorption parameters between pseudocompounds and estimation from single-sorbate individual components for HA-coated sands ($f_{oc}=0.221\%$) (initial mole concentrations for all sorbates is $50\text{ }\mu\text{mol/L}$).

Pseudocompound	Components	Single-Sorbate		Pseudocompound		Comparison of Average	
		$K_{f,single}$	N_{single}	$K_{f,PS}$	N_{PS}	$K_{f,single} / K_{f,PS}$	N_{single} / N_{PS}
A	1,2,4-TCB	3.90	0.937	3.96	0.929	0.985	1.01
	AVE.	3.90	0.937				
B	1,4-DCB	1.50	0.977	1.53	0.957	0.980	1.02
	AVE.	1.50	0.977				
C	<i>m</i> -XYL	0.882	0.963	0.899	0.928	0.952	1.01
	CB	0.830	0.920				
	AVE.	0.856	0.942				
D	TOL	0.427	0.957	0.346	0.978	1.12	0.983
	BZ	0.349	0.966				
	AVE.	0.388	0.962				
E	2,4-DMP	0.699	0.821	0.368	0.857	1.14	0.945
	<i>p</i> -CRE	0.484	0.810				
	PHE	0.203	0.806				
	2-HEX	0.285	0.805				
	AVE.	0.418	0.810				
F	2-BUT	0.225	0.740	0.208	0.749	0.976	0.950
	ACE	0.181	0.684				
	AVE.	0.203	0.712				

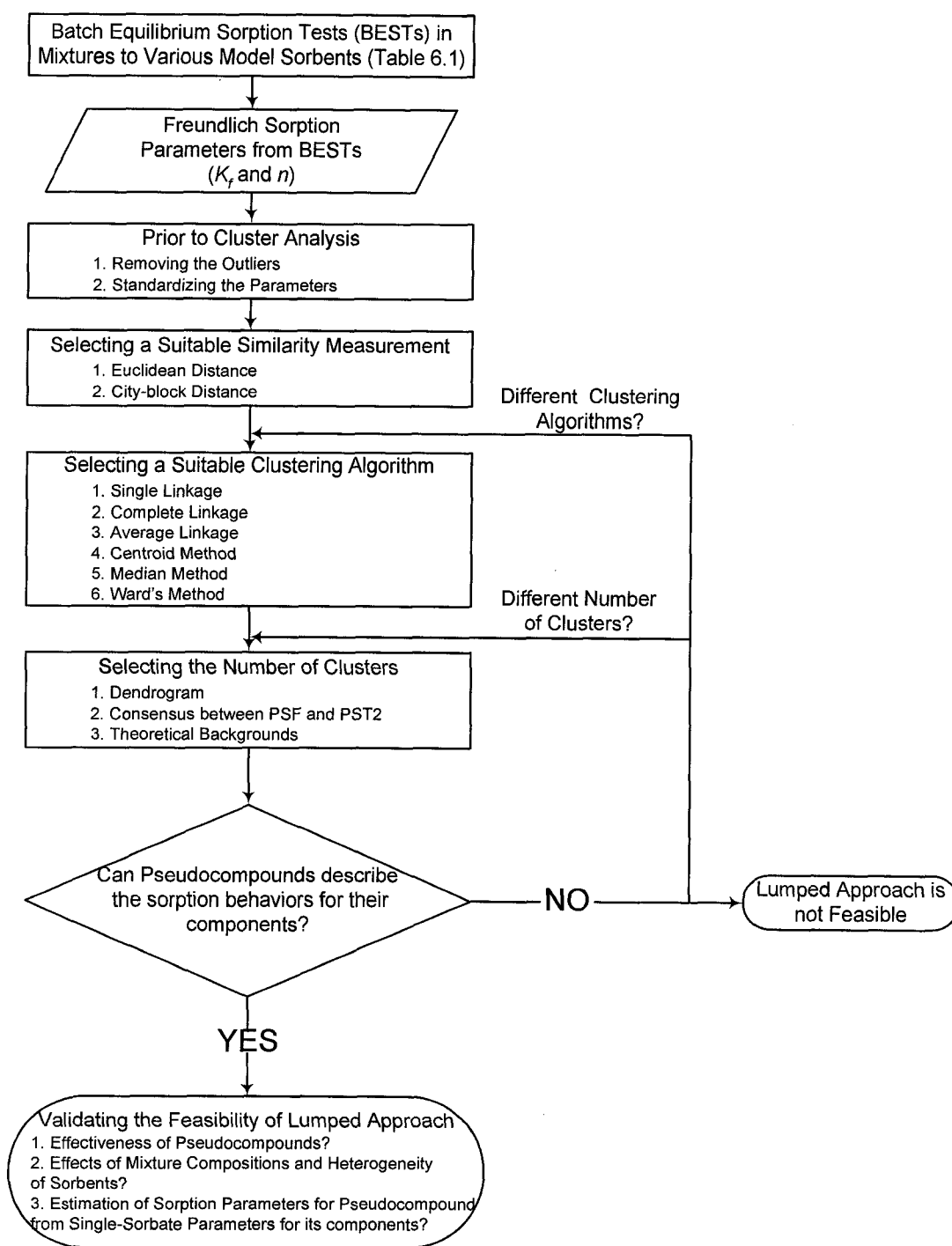


Fig. 6.1 A schematic diagram illustrating the procedure of lumped approach for sorption of neutral organic compounds in mixtures to simulated aquifer sorbents.

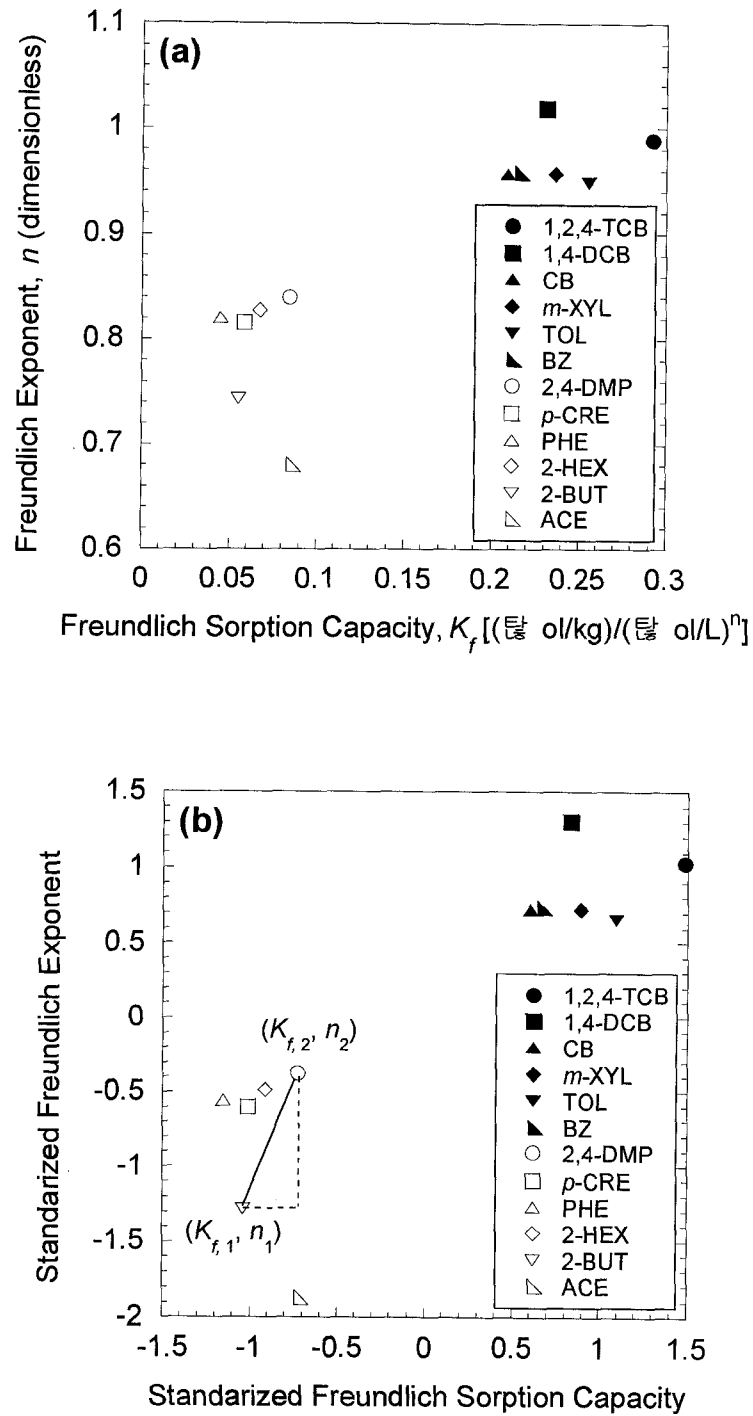


Fig. 6.2 Two-dimensional configuration of Freundlich sorption parameters of 12 NOCs in mixture to uncoated sand ($f_{oc} = 0.006\%$). (a) Before standardization, and (b) after standardization.

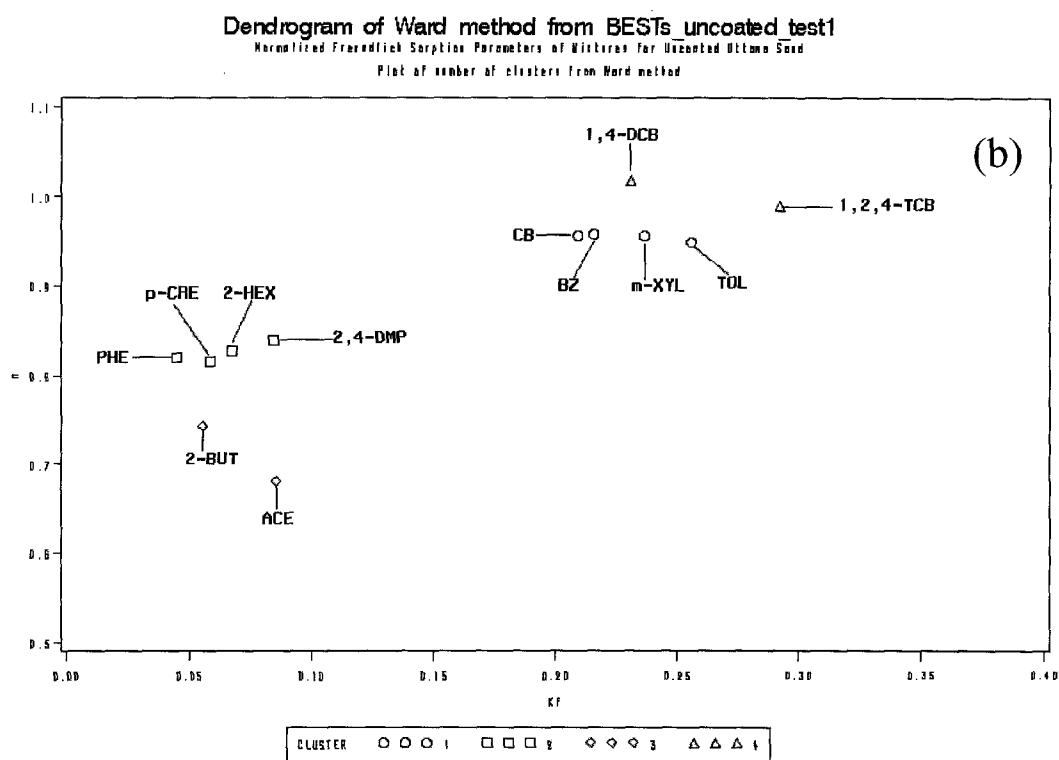
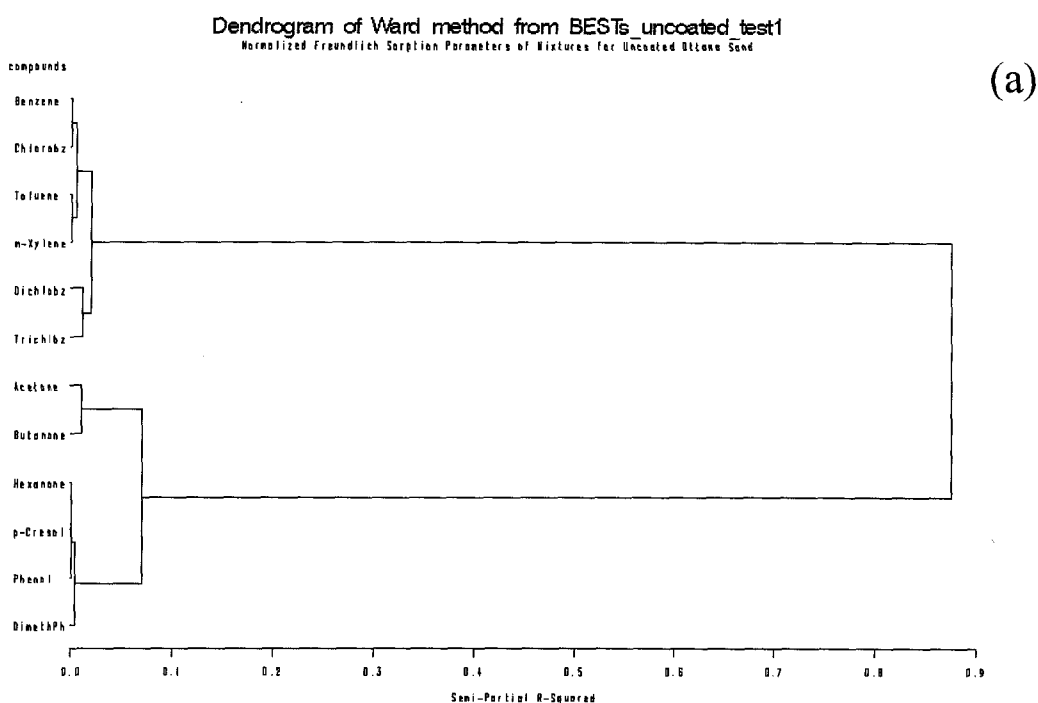


Fig. 6.3 A dendrogram (a) and clusters (b) for sorption of 12 NOCs in mixtures (Test #1 in **Table 6.1**) to uncoated sands.

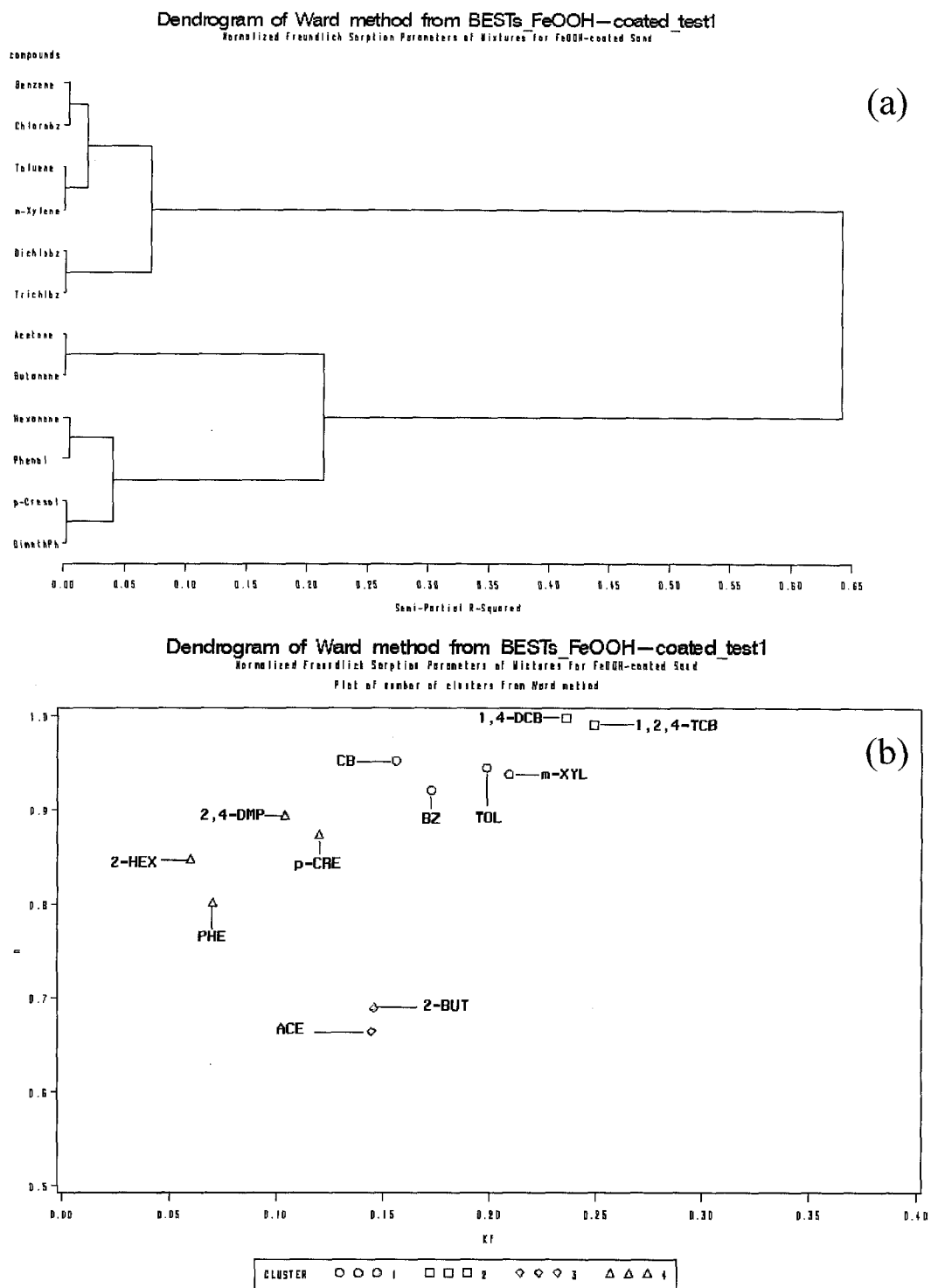


Fig. 6.4 A dendrogram (a) and clusters (b) for sorption of 12 NOCs in mixtures (Test #1 in **Table 6.1**) to FeOOH-coated sands.

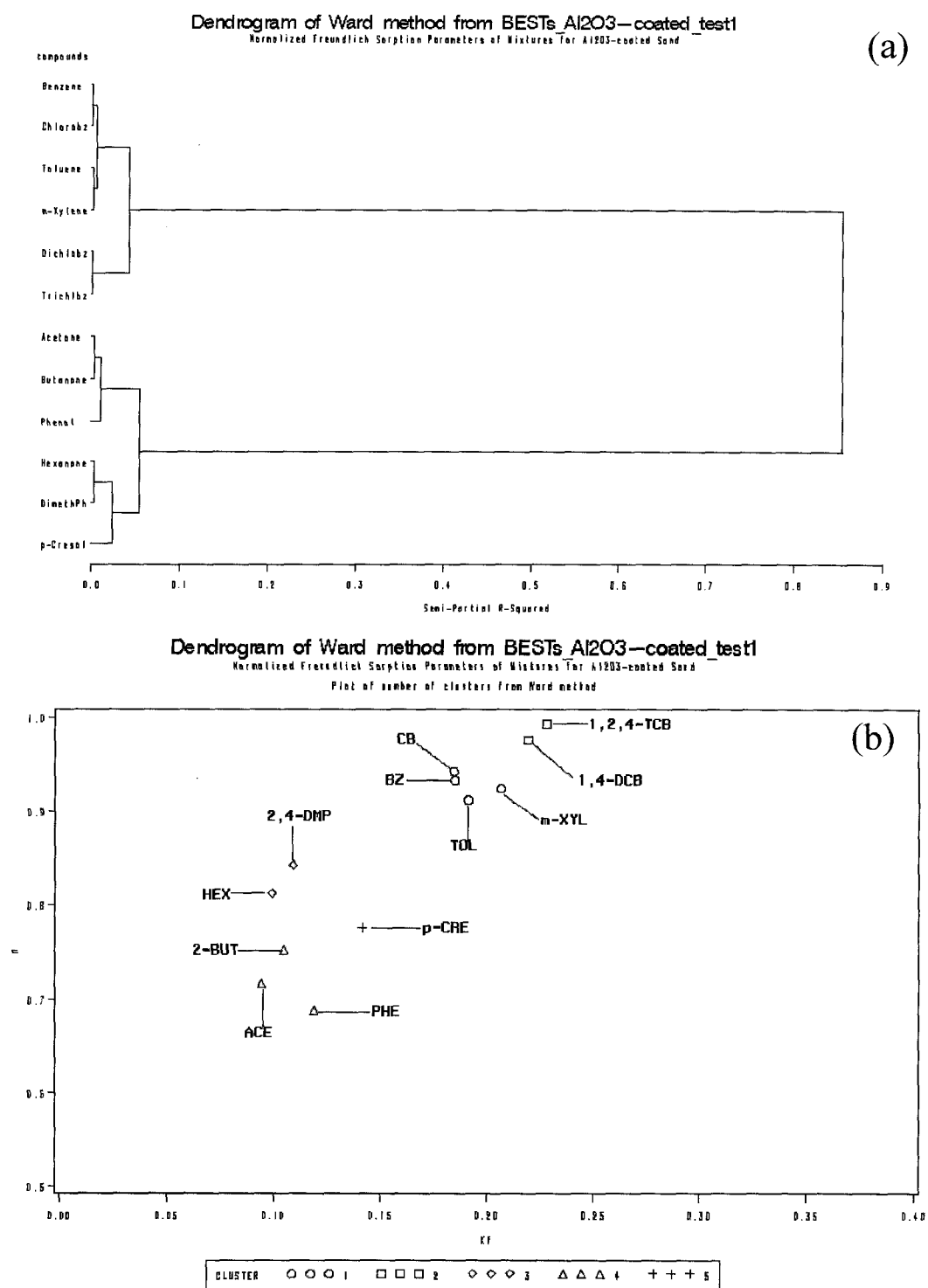


Fig. 6.5 A dendrogram (a) and clusters (b) for sorption of 12 NOCs in mixtures (Test #1 in **Table 6.1**) to Al₂O₃-coated sands.

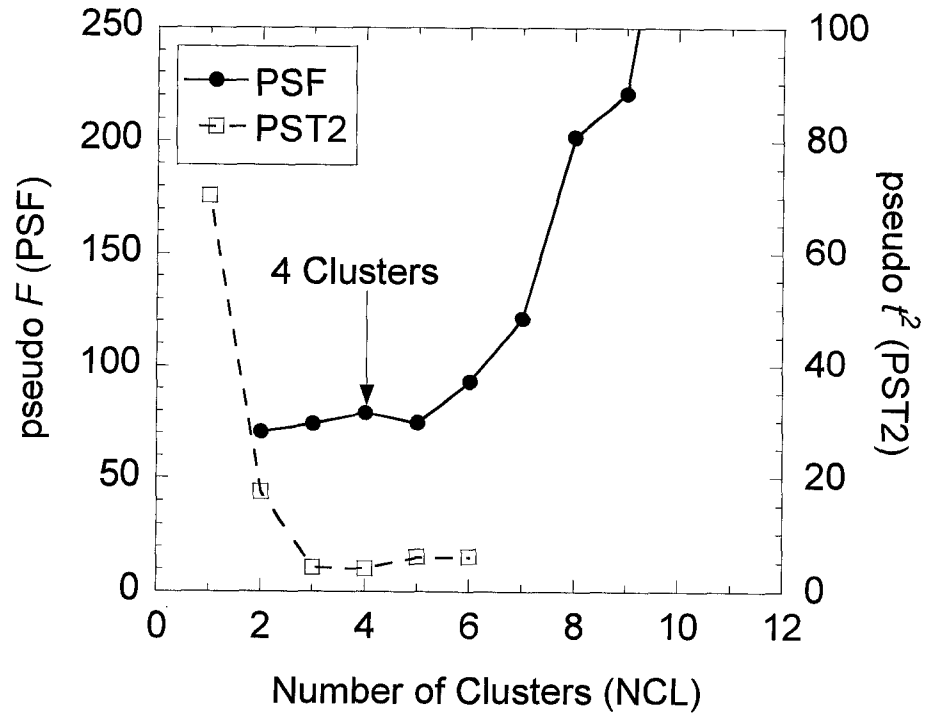


Fig. 6.6 The changes in pseudo F statistic (PSF) and pseudo t^2 statistic (PST2) between cluster steps for sorption of 12 NOCs in base case mixtures (Test #1 in **Table 6.1**) to uncoated sands.

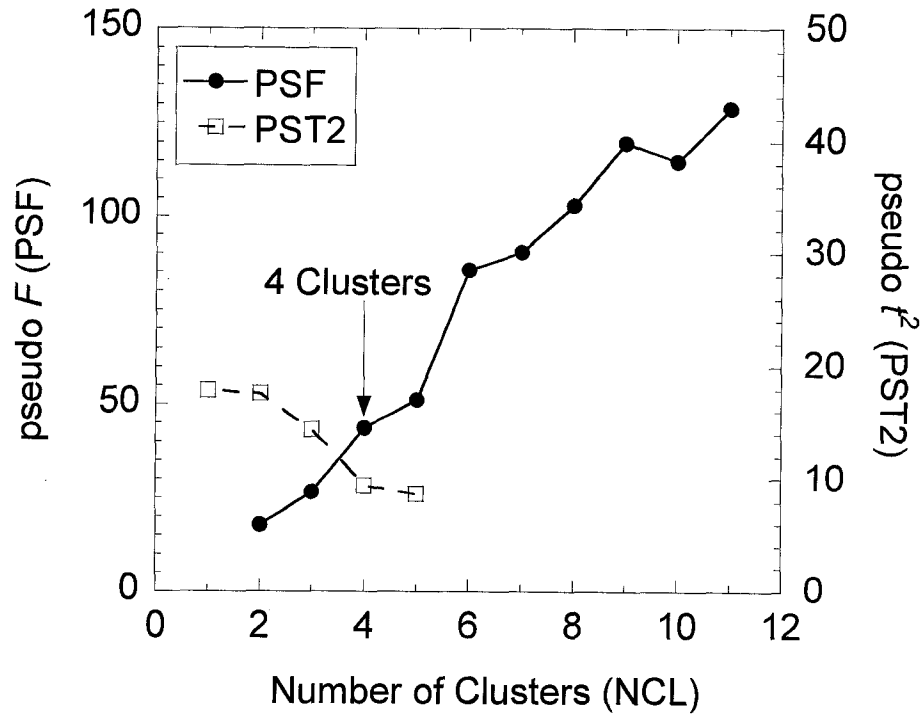


Fig. 6.7 The changes in pseudo F statistic (PSF) and pseudo t^2 statistic (PST2) between cluster steps for sorption of 12 NOCs in base case mixtures (Test #1 in **Table 6.1**) to FeOOH-coated sands.

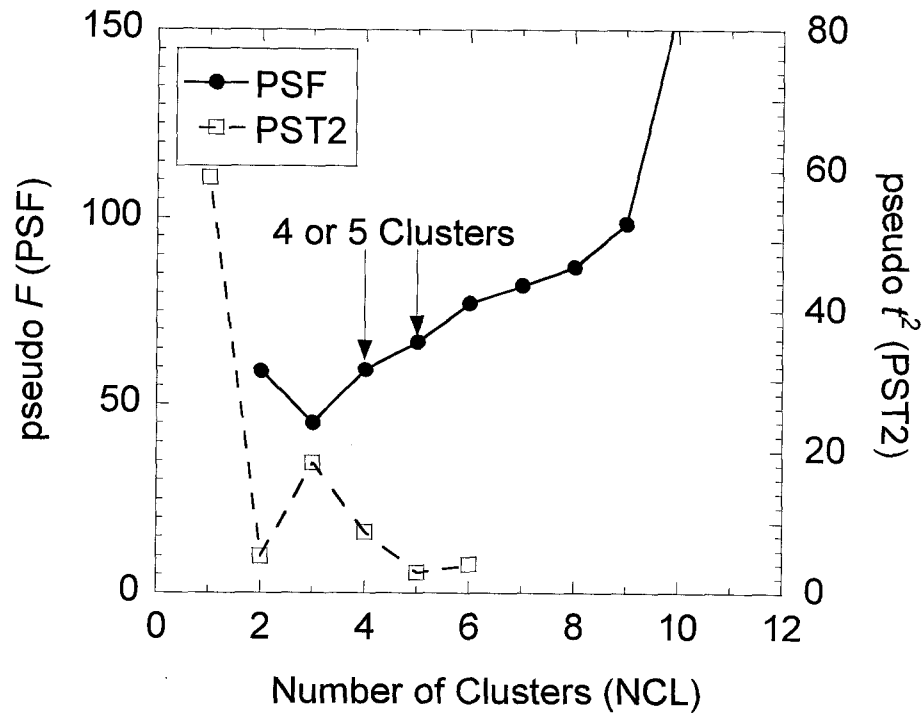


Fig. 6.8 The changes in pseudo F statistic (PSF) and pseudo t^2 statistic (PST2) between cluster steps for sorption of 12 NOCs in base case mixtures (Test #1 in **Table 6.1**) to Al_2O_3 -coated sands.

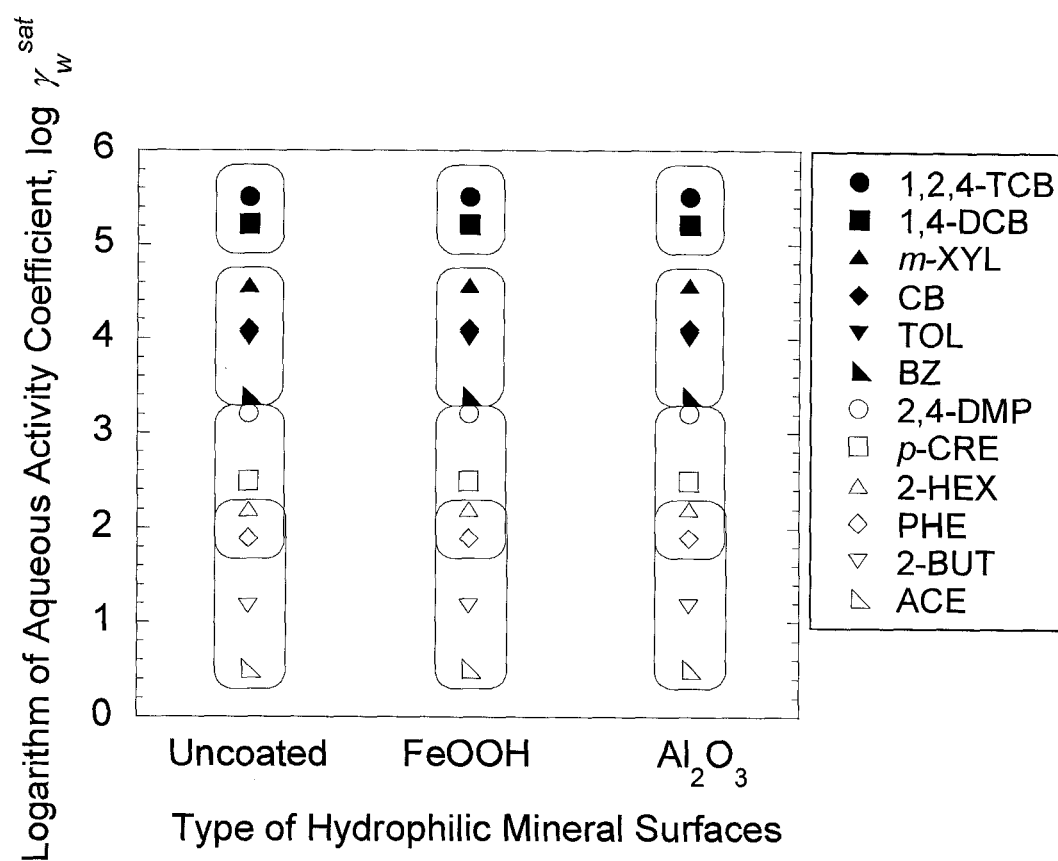


Fig. 6.9 Effect of type of hydrophilic mineral surfaces on pseudocompounds and their components (aqueous solubility of ACE is assumed to be 10^6 mg/L)

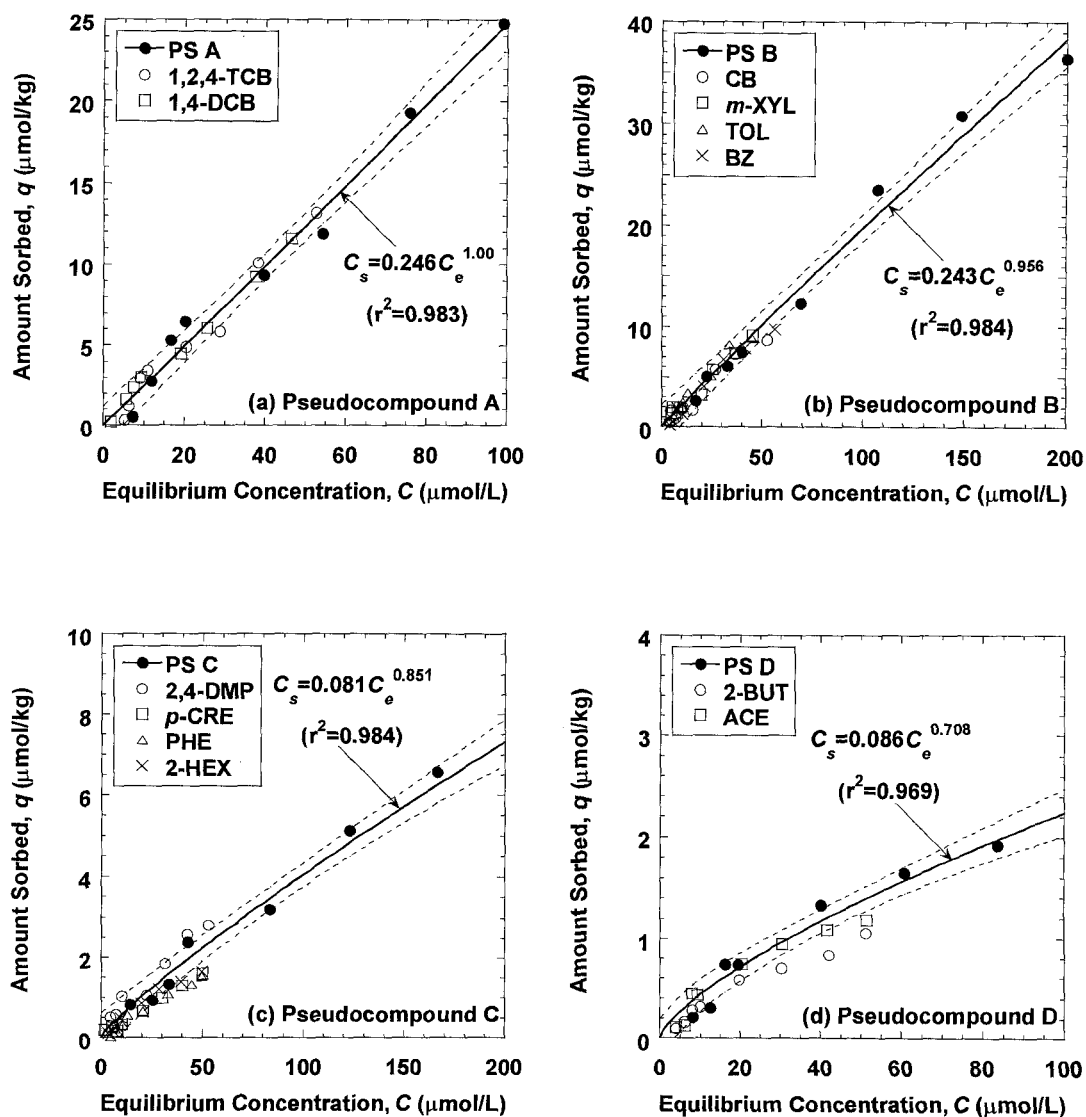


Fig. 6.10 Sorption isotherms of individual pseudocompounds to uncoated sand. The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for pseudocompounds.

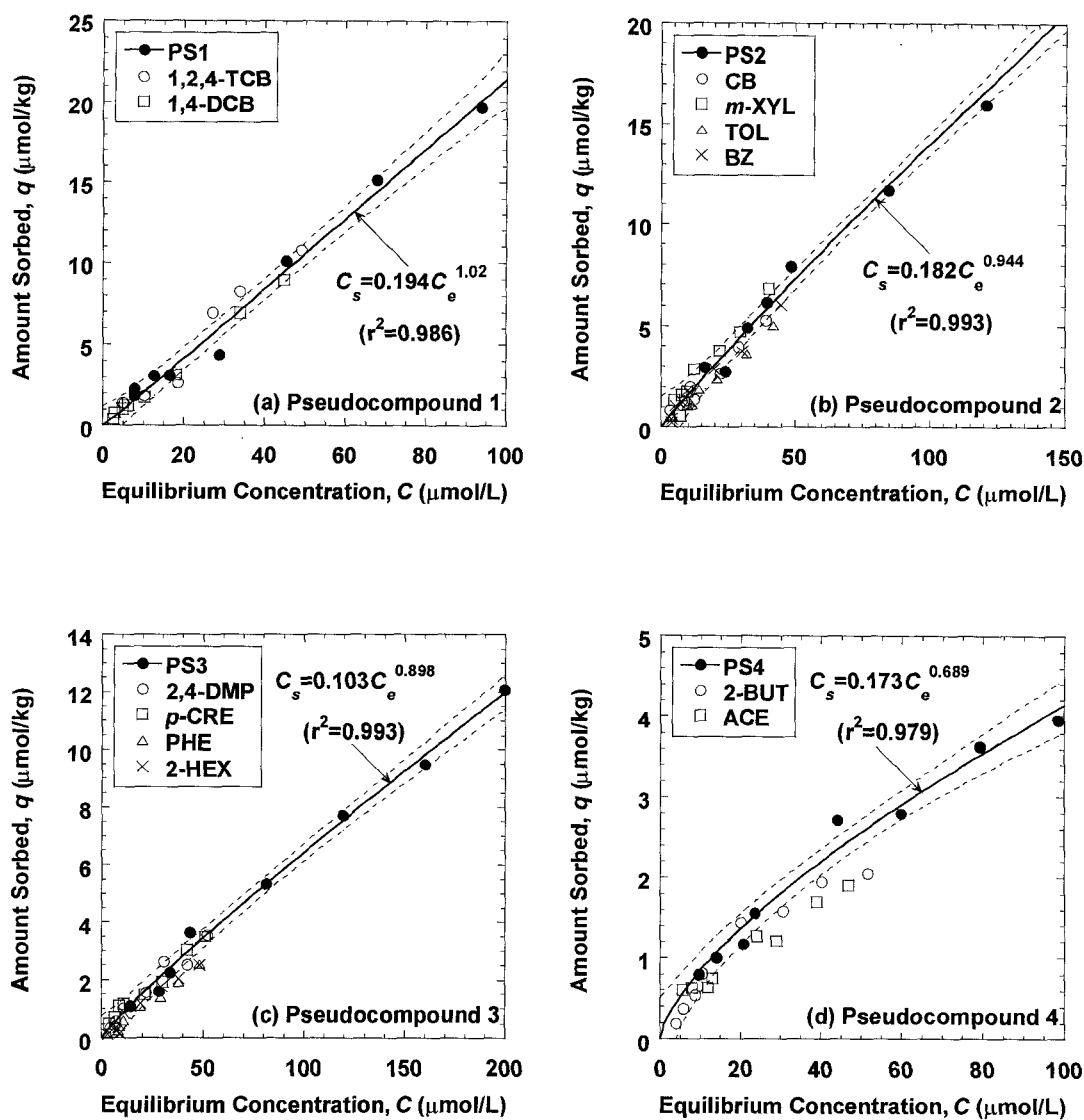


Fig. 6.11 Sorption isotherms of individual pseudocompounds to FeOOH-coated sand. The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for pseudocompounds.

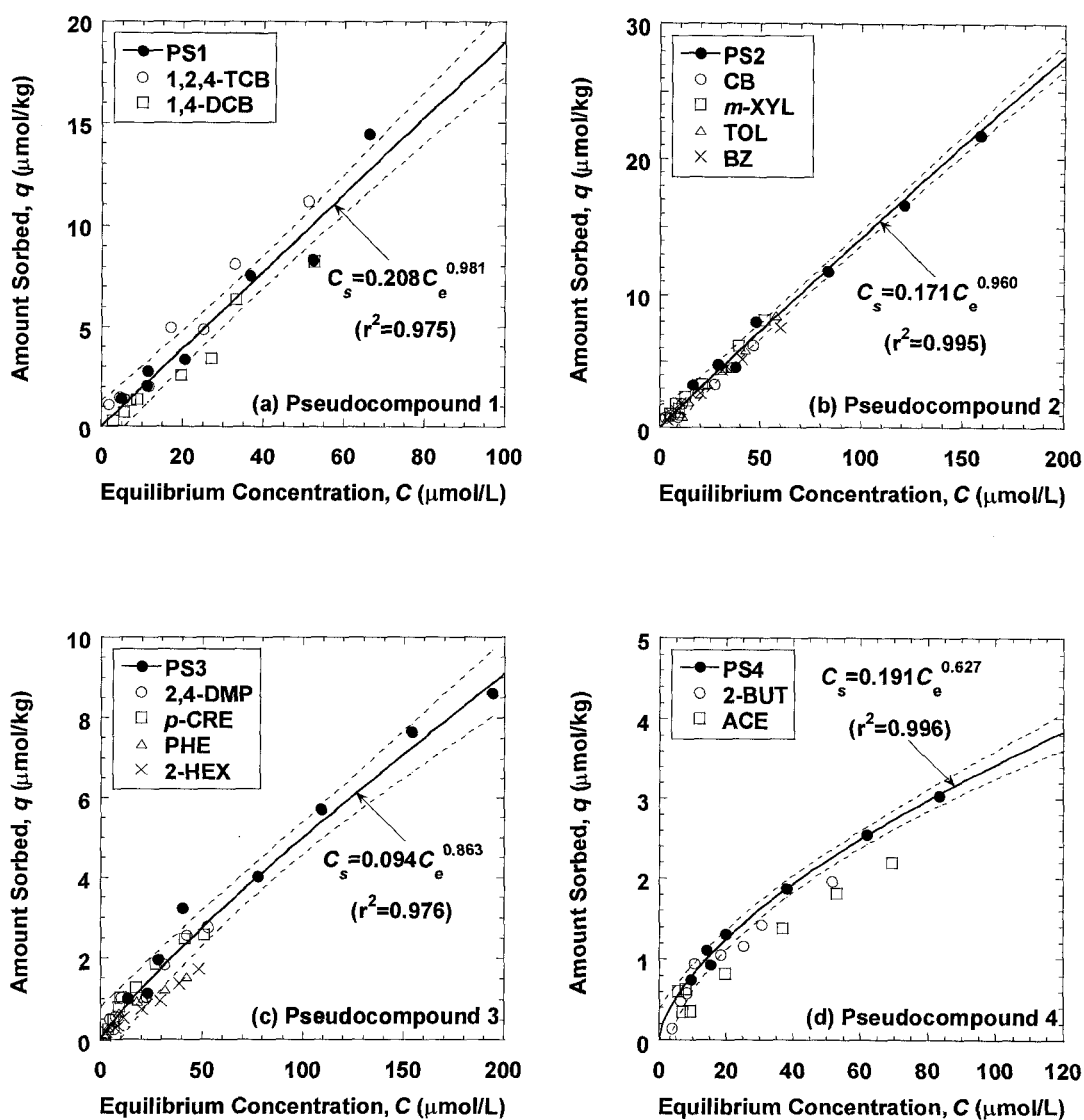


Fig. 6.12 Sorption isotherms of individual pseudocompounds to Al_2O_3 -coated sand. The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for pseudocompounds.

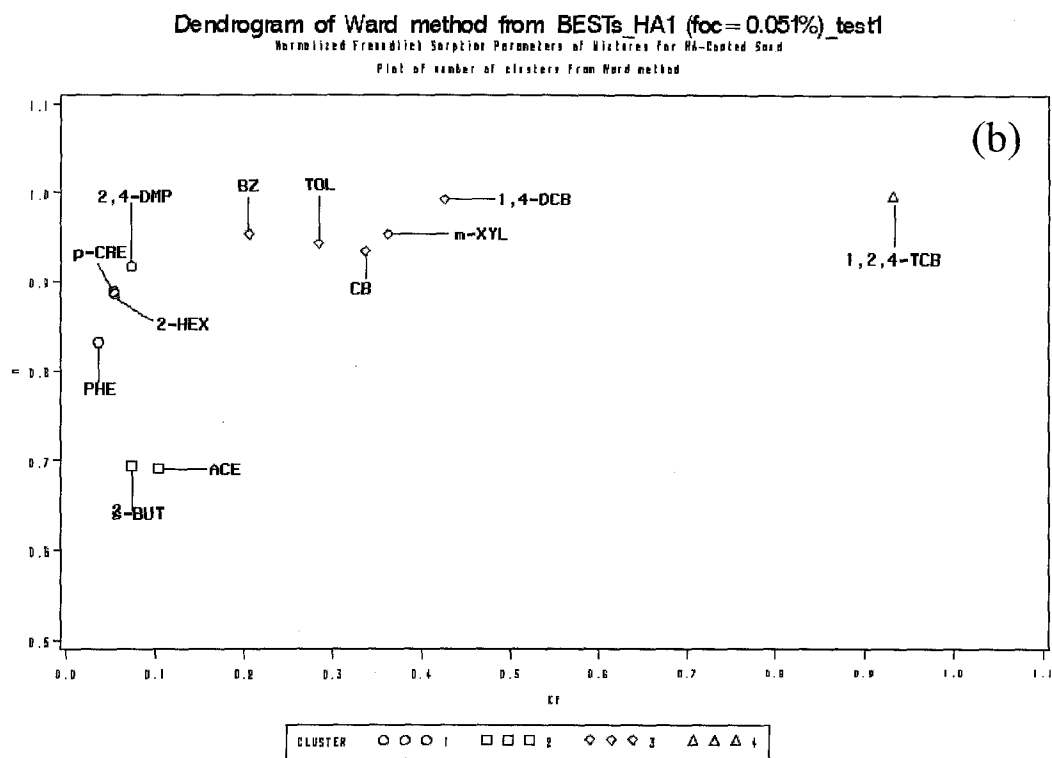
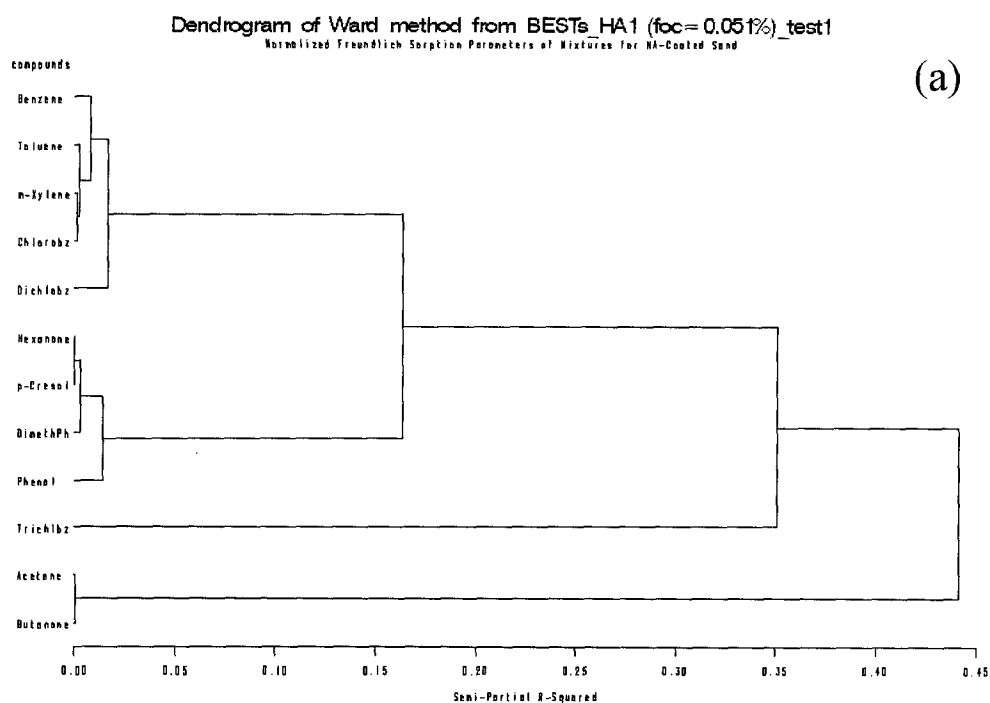


Fig. 6.13 A dendrogram (a) and clusters (b) for sorption of 12 NOCs in mixtures (Test #1 in **Table 6.1**) to HA-coated sands ($f_{oc} = 0.051\%$).

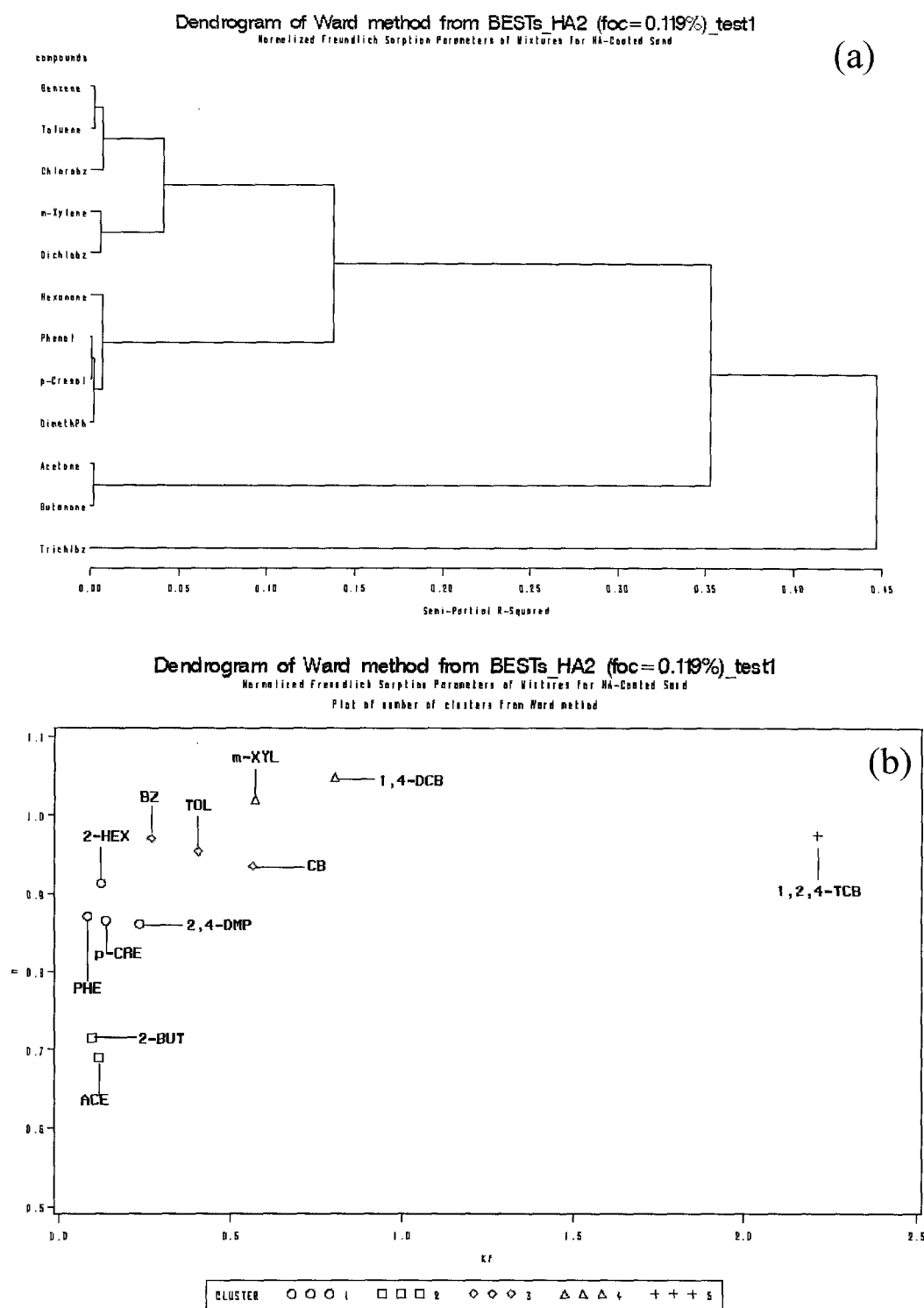


Fig. 6.14 A dendrogram (a) and clusters (b) for sorption of 12 NOCs in mixtures (Test #1 in **Table 6.1**) to HA-coated sands ($f_{oc} = 0.119\%$).

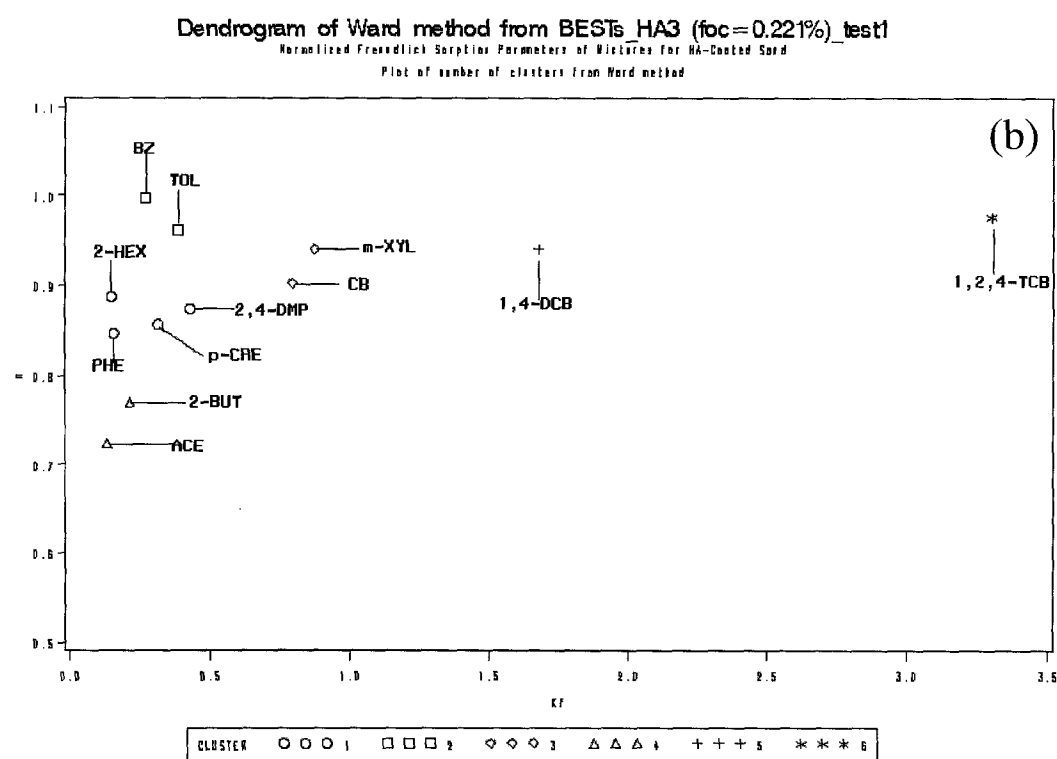
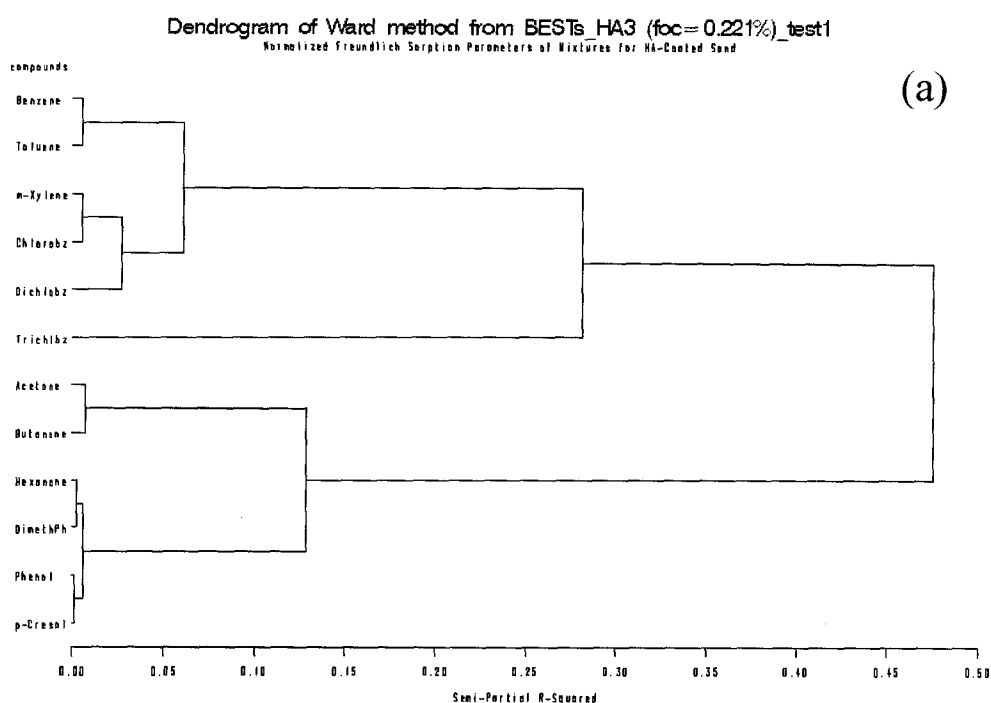


Fig. 6.15 A dendrogram (a) and clusters (b) for sorption of 12 NOCs in mixtures (Test #1 in **Table 6.1**) to HA-coated sands ($f_{oc} = 0.221\%$).

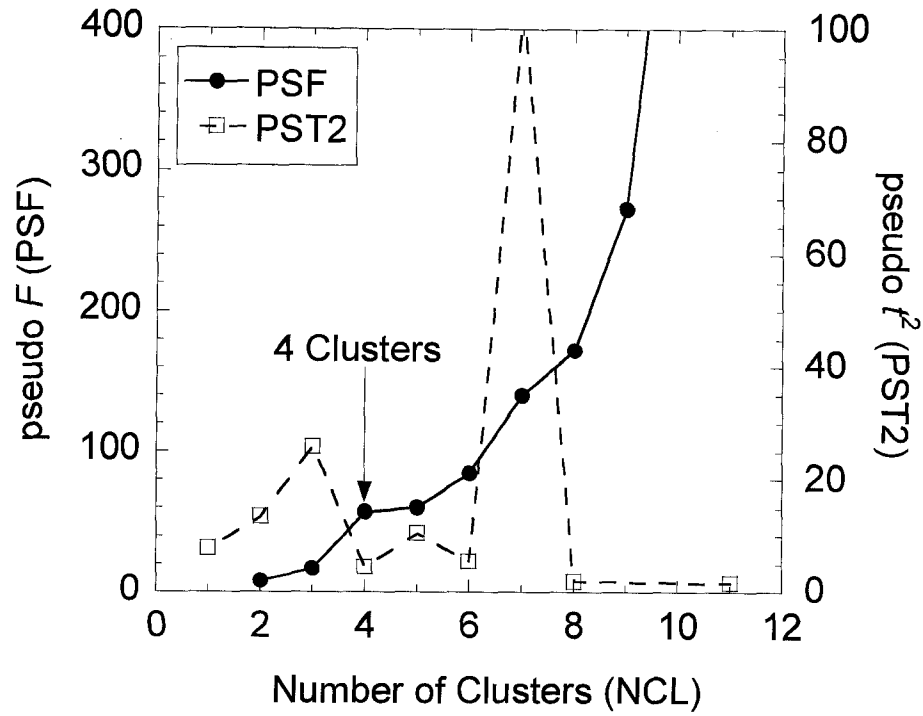


Fig. 6.16 The changes in pseudo F statistic (PSF) and pseudo t^2 statistic (PST2) between cluster steps for sorption of 12 NOCs in base case mixtures (Test #1 in **Table 6.1**) to HA-coated sands ($f_{oc} = 0.051\%$).

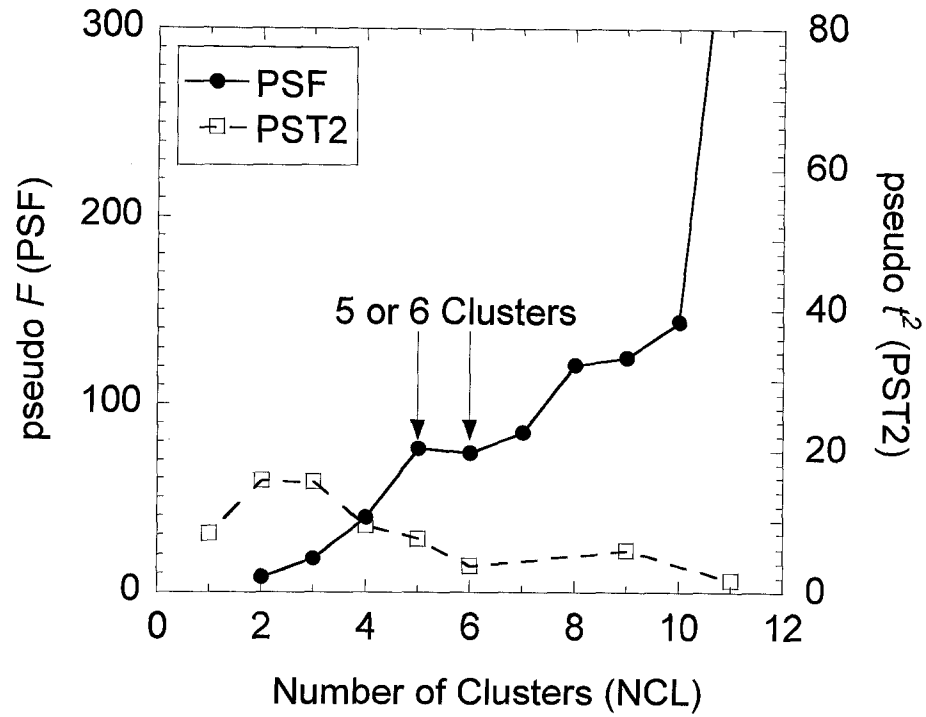


Fig. 6.17 The changes in pseudo F statistic (PSF) and pseudo t^2 statistic (PST2) between cluster steps for sorption of 12 NOCs in base case mixtures (Test #1 in **Table 6.1**) to HA-coated sands ($f_{oc} = 0.119\%$).

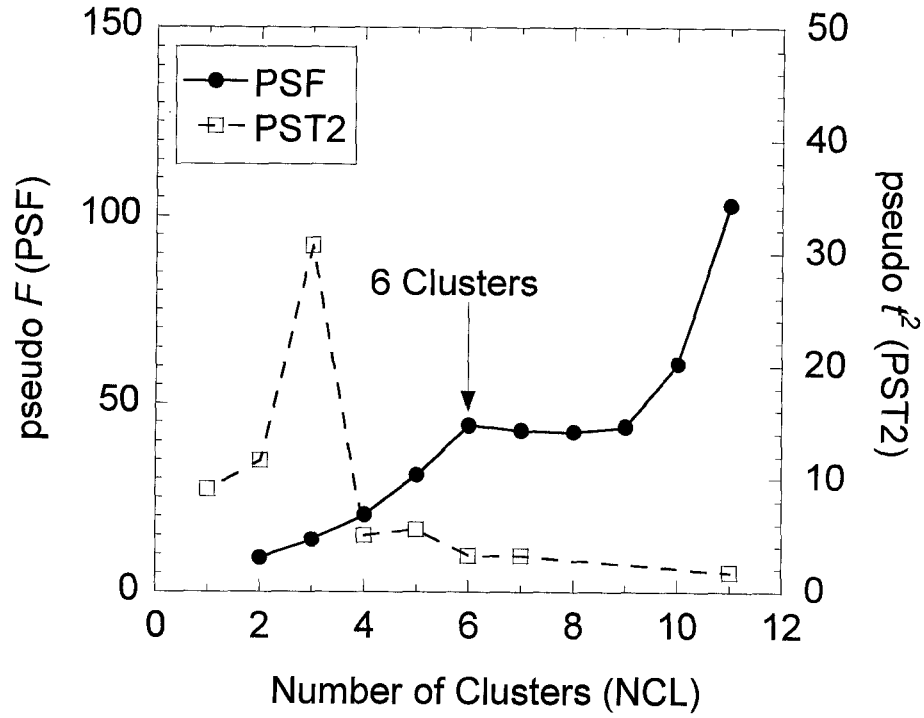


Fig. 6.18 The changes in pseudo F statistic (PSF) and pseudo t^2 statistic (PST2) between cluster steps for sorption of 12 NOCs in base case mixtures (Test #1 in **Table 6.1**) to HA-coated sands ($f_{oc} = 0.221\%$).

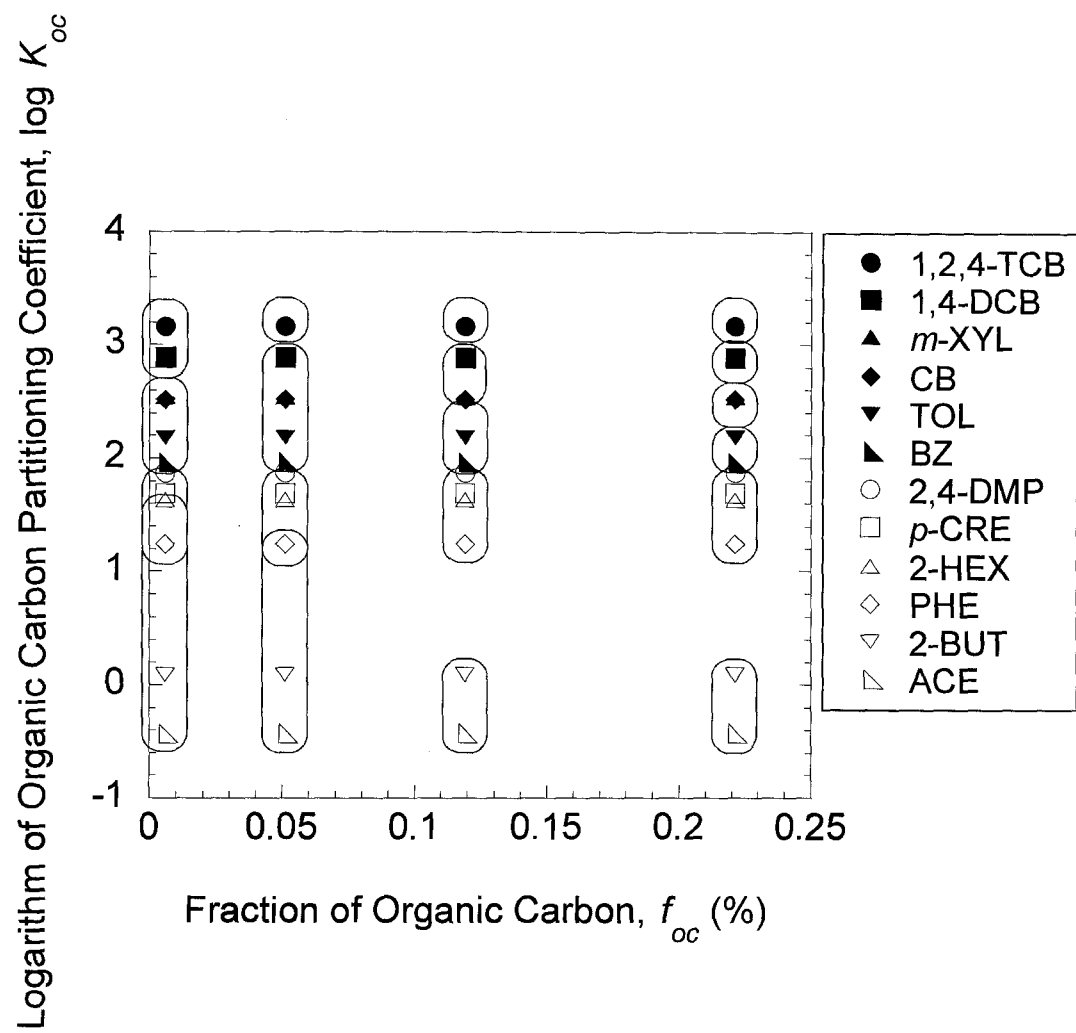


Fig. 6.19 Effect of the fraction of organic carbon on pseudocompounds and their components.

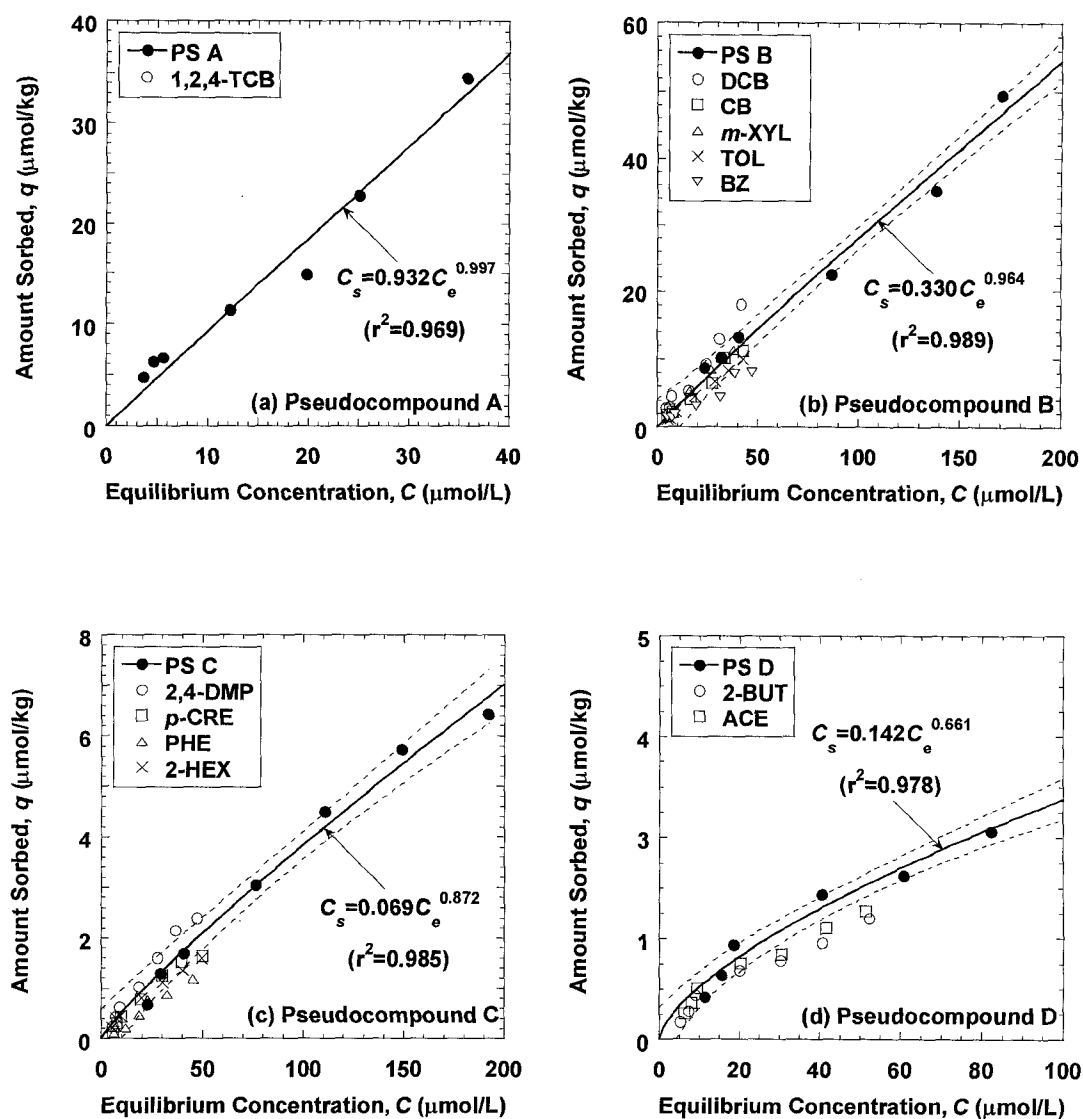


Fig. 6.20 Sorption isotherms of individual pseudocompounds to HA-coated sands ($f_{oc} = 0.051\%$). The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for pseudocompounds.

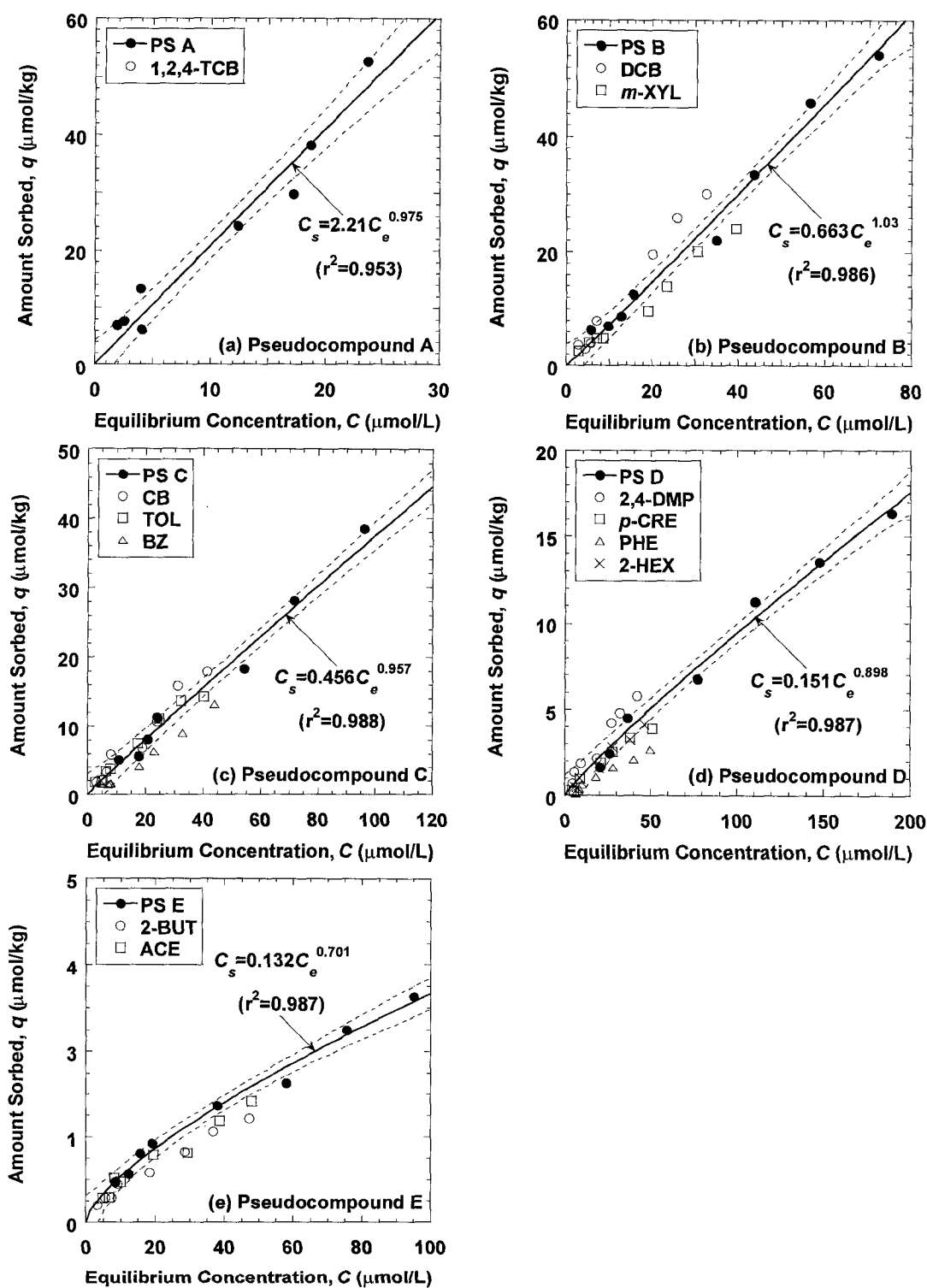


Fig. 6.21 Sorption isotherms of individual pseudocompounds to HA-coated sands ($f_{oc} = 0.119\%$). The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for pseudocompounds.

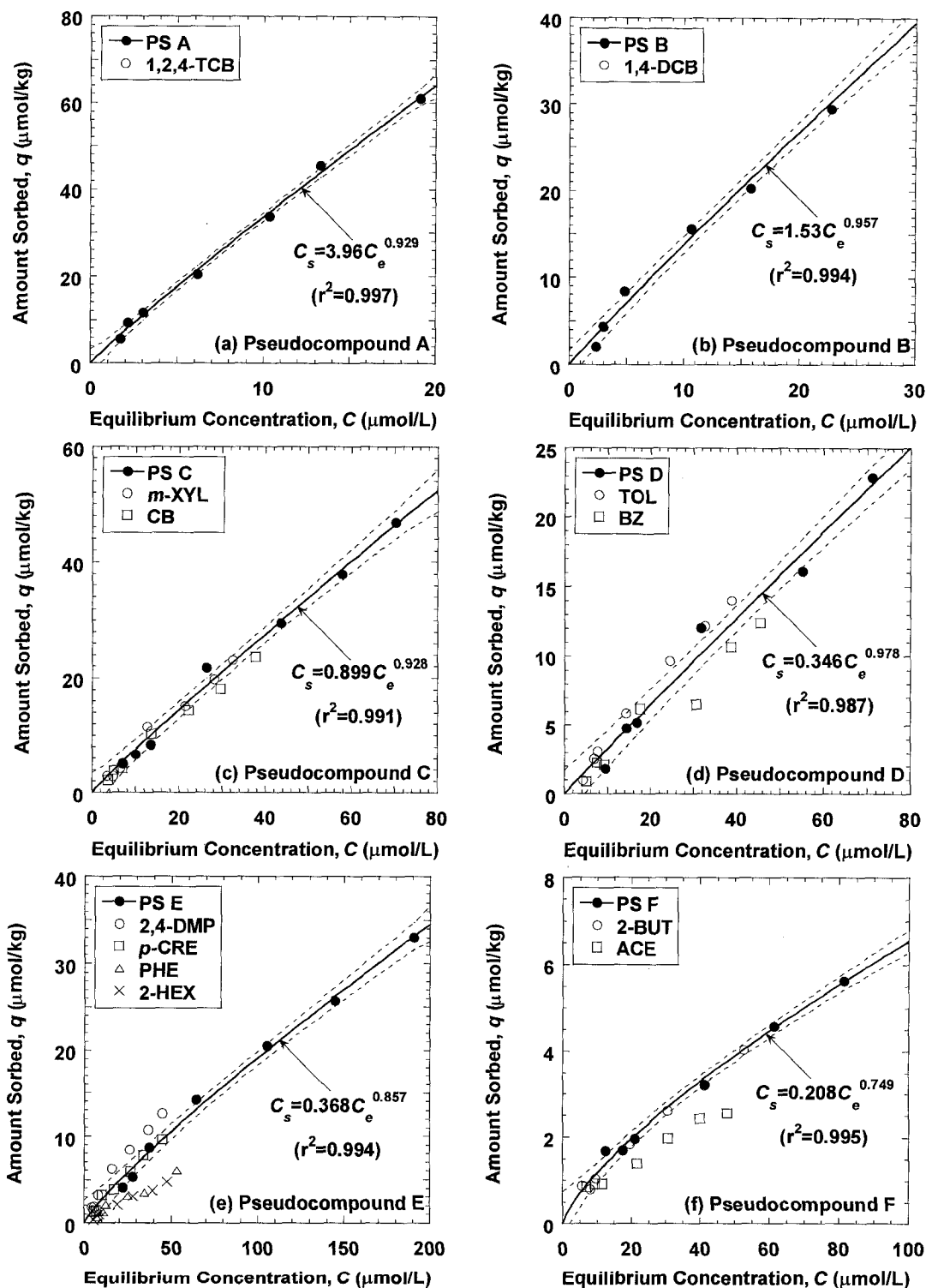


Fig. 6.22 Sorption isotherms of individual pseudocompounds to HA-coated sands ($f_{oc} = 0.221\%$). The dashed lines denote the corresponding 95 % confidence intervals for the associated best-fit Freundlich sorption model for pseudocompounds.

CHAPTER 7

MODELING SORPTION OF NEUTRAL ORGANIC COMPOUND MIXTURES TO SIMULATED AQUIFER SORBENTS WITH PSEUDOCOMPOUNDS

Abstract: Both the feasibility and the accuracy of the ideal adsorbed solution theory (IAST) with Pseudocompounds (groups of compounds) to reduce difficulty and effort in computation in predictions of sorption of 12 neutral organic compounds (NOCs) with a wide range of hydrophobicities (i.e., $-0.24 \leq \log K_{ow} \leq 4.23$) in full mixtures to simulated aquifer sorbents were investigated. All sorption isotherms from both individual- and multi- Pseudocompound systems were fitted reasonably well by the Freundlich sorption model over the aqueous concentration ranges tested (i.e., $\leq 200 \mu\text{mol/L}$). Also, each Pseudocompound showed substantially different sorption behavior in terms of both sorption capacity and nonlinearity. The presence and magnitude of mutual competition among Pseudocompounds was subject to variation, depending on both the composition of full mixtures (i.e., concentration and polarity of Pseudocompounds) and the properties of mineral surface (i.e., f_{oc} values and availability of hydrophilic specific sorption sites). Finally, the comparisons of IAST predictions with Pseudocompounds and experimentally measured data revealed that the incorporating Pseudocompounds into IAST to predict sorption of NOCs in full mixtures was feasible unless the deviations from ideality increased to an extent to IAST cannot predict. Thus, further study is warranted to facilitate model improvement by adding terms or empirical correlations to account for the differential availability of sorption sites and the unequal and nonideal competition.

Key Words: ideal adsorbed solution theory, neutral organic compounds, mixtures, mutual competition, Pseudocompound, sorption

7.1 INTRODUCTION

Environmental contamination usually results in the presence of mixtures of compounds (e.g., gasoline, fuel hydrocarbon/chlorinated solvents, pesticides, and landfill lactates) in the subsurface. Whereas the fate and transport of individual neutral organic compounds (NOCs) in the subsurface have been studied extensively in both saturated and unsaturated porous media (Zheng 1990), much less is known about the fate and transport of mixtures of NOCs. Additionally, models describing the simultaneous fate and transport of NOCs in complex mixtures routinely ignore mixture effects, such as competitive or synergistic sorption (Clement 1997, Clement et al. 1998). However, when such mixture effects are significant, the determination of pair-wise interaction parameters among NOCs is required to accurately predict the fate and transport of mixtures of NOCs. Although the entire system of differential equations with interaction parameters that describe the fate and transport of NOCs in mixtures can be solved simultaneously in space and time, this detailed approach can become increasingly more complicated and less computationally efficient as the number of NOCs in mixtures increases, limiting the practical utility of the overall approach.

An alternative to this detailed and comprehensive approach (i.e., one equation per NOC with interaction parameters) is the lumped approach which describes the fate and transport of NOCs in complex mixtures in terms of the fate

and transport of a fewer number of Pseudocompounds or groups of NOCs with similar behaviors. As a part of study of the feasibility of lumped approach for the fate and transport of NOCs in complex mixtures, both feasibility and accuracy of lumped approach to group 12 NOCs in mixtures into a fewer number of Pseudocompounds in sorption processes were evaluated using mixtures containing NOCs with a wide range of hydrophobicities (i.e., $-0.24 \leq \log K_{ow} \leq 4.23$) and various types of low-surface-area simulated aquifer sorbents in Chapter 6. As confirmed by the relatively consistent lumping schemes for each sorbent and the acceptable approximation of sorption behavior of NOC mixtures using Pseudocompounds, the lumped approach using Pseudocompounds was found to be feasible to simplify the complex sorption behaviors of NOC mixtures.

Since the Pseudocompounds are groups of NOCs that behave as an individual compound during sorption processes, using Pseudocompounds in multicomponent sorption models can reduce the computational requirements to render sorption models more amenable to full mixtures. Thus, evaluating multicomponent sorption models using parameters from individual-Pseudocompound sorption isotherm is paramount to predict the sorption of NOCs in full mixtures (i.e., multi-Pseudocompounds). Although a variety of empirical and thermodynamic multicomponent sorption models, such as the multicomponent Langmuir model (Do 1998) or the ideal adsorbed solution theory (IAST) (Radke and Prausnitz 1972), have been developed to model mixture effects using only individual-sorbate sorption isotherm parameters, the IAST was chosen in this study since the IAST has been effectively used to predict multicomponent sorption for

numerous sorbents with a variety of sorbates (McGinley et al. 1993, 1996, Xing et al. 1996, Li and Werth 2001, 2002).

In this chapter, the capability of the IAST using parameters from individual-Pseudocompound sorption isotherm to predict the sorption of NOCs in full mixtures was investigated. The specific objectives of this study are (1) to investigate the complex interactions in full mixtures (i.e., competitive or synergistic effect) among Pseudocompounds in terms of sorption to simulated aquifer sorbents with low f_{oc} (≤ 0.221 %), and (2) to evaluate both the feasibility and accuracy of using the IAST with Pseudocompounds to predict the sorption of NOCs in full mixtures. This is critical because both accurate and simple modeling of multicomponent sorption is important to predict the fate and transport of NOCs in mixtures and the risk to potential receptors.

7.2 MATERIALS AND METHODS

The materials and methods used in this study were described in detail in the previous Chapters 2, 3, 4, 5, and 6. The description includes (1) the extraction and characterization of HA, (2) the preparation procedures and characterization of model sorbents [i.e., uncoated sand, FeOOH-coated sand (FES), Al₂O₃-coated sand (ALS), HA-coated sand with different f_{oc} (HAS)], (3) the physicochemical properties of the 12 NOCs [i.e., six polar compounds include acetone (ACE), 2-butanone (2-BUT), 2-hexanone (2-HEX), phenol (PHE), *p*-cresol (*p*-CRE), and 2,4-dimethyl phenol (2,4-DMP) whereas six nonpolar compounds include benzene (BZ), toluene (TOL), *m*-xylene (*m*-XYL), chlorobenzene (CB), 1,4-dichlorobenzene (1,4-DCB), and 1,2,4-

trichlorobenzene (1,2,4-TCB)], (4) the preparation procedures for the solutions of each Pseudocompound and 12 NOC mixtures, (5) the analytical methods using gas chromatography with a flame ionization detector and a mass selective detector, (6) the methodology for the batch equilibrium sorption tests (BESTs), (7) the procedures for analyzing the results of BESTs, (8) the evaluation of the potential effect on the observed sorption coefficients due to desorption of HA from HA-coated sand, (9) the determination of the equilibration time of 48 h for the BESTs, and (10) the procedure of lumped approach for sorption of neutral organic compounds in full mixtures to simulated aquifer sorbents.

7.3 MODELING SORPTION OF ORGANIC COMPOUND MIXTURES

7.3.1 Ideal Adsorbed Solution Theory (IAST)

The ideal adsorbed solution theory (IAST) has been successfully applied to the prediction of sorption equilibrium of NOC mixtures in dilute solutions to activated carbon (Calligaris and Tien 1982, Crittenden et al. 1985, Jayaraj and Tien 1985, Smith and Weber 1987, Li et al. 2002, Wigton and Kilduff 2004) and to soils and sediments (McGinley et al. 1993, 1996, Xing et al. 1996, Li and Werth 2001, 2002). The IAST was originally developed for vapor-phase adsorption and later applied to liquid sorbate systems by Radke and Prausnitz (1972), and is thermodynamic model derived from the Gibbs equation. The underlying assumptions of the IAST are (1) that sorbates in mixtures have access to the same sorption sites, (2) that sorbed phase forms an ideal two-dimensional solution in dilute systems, analogous to three-dimensional Raoult's law, and (3) that total

spreading pressure is equivalent for both individual-sorbate and mixture systems under conditions of equal activity in solution at any given temperature (Xing et al. 1996, Haws et al. 2006). Regardless of the potential weakness of the ideality assumption in the sorbed phase, the IAST has been widely used since the IAST has a solid theoretical foundation and requires only individual-sorbate sorption isotherms in predicting mixture sorption.

The IAST relates the concentration of sorbate i (C_i) in mixtures to a corresponding concentration of sorbate i in individual-sorbate systems (C_i^0) (Radke and Prausnitz 1972):

$$C_i = (\pi, T, z_i) = z_i C_i^0(\pi, T) \quad (7.1)$$

where z_i is the mole fraction of sorbate i in the sorbed phase, π is the spreading pressure on the sorbent surface, and T is the absolute temperature. In Eq. (7.1), the spreading pressure is the difference in interfacial tension between pure solvent (i.e., water)-solid interface (σ^0) and the solution (i.e., water + sorbates)-solid interface (σ) at the same temperature. Thus, the spreading pressure (π) can be written as follows:

$$\pi = \sigma^0 - \sigma \quad (7.2)$$

Eq. (7.1) holds only when π and T in mixtures are the same as those in the respective individual-sorbate systems.

Individual-sorbate sorption data are required to compute the spreading pressure of each sorbates, i , according to the following equations (Radke and Prausnitz 1972):

$$\pi_i(C_i) = \frac{RT}{A} \int_0^{C_i^0} \frac{q_i^0}{C_i^0} dC_i^0 \quad (7.3)$$

$$\pi_i(q_i) = \frac{RT}{A} \int_0^{q_i^0} \frac{d \ln C_i^0}{d \ln q_i^0} dq_i^0 \quad (7.4)$$

where R is ideal gas constant, A is the specific surface area of the sorbent, C_i^0 and q_i^0 are the aqueous- and solid- phase concentration of sorbate i in individual-sorbate systems, respectively. By changing the independent variable from C_i^0 to q_i^0 , Eq. (7.3) was converted into Eq. (7.4), and the spreading pressure becomes a function of the total amount sorbed (q_i^0). Other basic equations for the IAST to predict the sorption behaviors in mixtures from individual-sorbate sorption data are as follows (Radke and Prausnitz 1972, Crittenden et al. 1985, Weber and Smith 1987):

$$q_T = \sum_{i=1}^N q_i \quad (7.5)$$

$$z_i = \frac{q_i}{q_T} \quad i = 1 \text{ to } N \quad (7.6)$$

$$C_i = z_i C_i^0 \quad i = 1 \text{ to } N \quad (7.7)$$

$$\frac{1}{q_T} = \sum_{i=1}^N \frac{z_i}{q_i^0} \quad (7.8)$$

$$\pi_i = \pi \quad i = 1 \text{ to } N \quad (7.9)$$

where C_i and q_i are the aqueous- and solid- phase concentration of sorbate i in mixtures, respectively, q_T defines the total surface loading from the mixtures, z_i defines the mole fraction of sorbate i in the sorbed phase, and N is the total number of sorbates in mixtures. Eq. (7.7) is analogous to Raoult's law, and Eq. (7.8) is the expression for no area change per mole on mixing in mixtures from the individual-sorbate sorption at the spreading pressure of mixtures. Finally, Eq. (7.9) indicates that total spreading pressure is equivalent for both individual-sorbate and mixture systems. In this study, Freundlich sorption model has been consistently applied for both individual- and multi- Pseudocompound systems. Thus, the aqueous- and solid-phase concentration of sorbate i in mixtures can be calculated by substitution of the Freundlich sorption model into the IAST.

7.3.2 Ideal Adsorbed Solution Theory (IAST) Using the Freundlich Sorption Model

The Freundlich sorption model was used to describe and interpret all sorption isotherm data in this study. The Freundlich isotherm model has the form

$$q = K_f C^n \quad (7.10)$$

The parameter K_f [$(\mu\text{mol/kg})/(\mu\text{mol/L})^n$] is the Freundlich unit sorption capacity, and n (dimensionless) is the joint measure of the relative magnitude and diversity of

energies (Weber et al. 1992). Recognizing that for natural log-linearized Freundlich isotherms, $d \ln C_i^0 = d \ln q_i^0/n_i$, Eq. (7.4) can be given as follows:

$$\pi_i(q_i) = \frac{RT}{A} \int_0^{q_i^0} \frac{d \ln C_i^0}{d \ln q_i^0} dq_i^0 = \frac{RT}{A} \int_0^{q_i^0} \left(\frac{dq_i^0}{n_i} \right) = \frac{RTq_i^0}{An_i} \quad (7.11)$$

Since sorption of each individual sorbates exerts the same spreading pressure as the mixture, Eq. (7.11) will simplify to the following expression.

$$\frac{q_1^0}{n_1} = \frac{q_2^0}{n_2} = \dots = \frac{q_N^0}{n_N} \quad (7.12)$$

After the further algebraic manipulations of Eqs. (7.7), (7.8), and (7.12), a useful relationship between the aqueous- and solid- phase concentration of any sorbate, i , can be calculated as follows:

$$C_i = \frac{q_i}{\sum_{j=1}^N q_j} \left[\frac{\sum_{j=1}^N \frac{q_j}{n_j}}{\frac{K_{f,i}}{n_i}} \right]^{1/n_i} \quad \text{for } i = 1 \text{ to } N \quad (7.13)$$

Eq. (7.13) may be considered as a simplification of the IAST equations, and can be combined with the mass balance in each batch bottle given in Eq. (7.14) to eliminate aqueous-phase concentration in IAST predictions.

$$q_i = (C_{i,int} - C_i)V / M_s \quad (7.14)$$

where $C_{i,int}$ is the initial concentration of sorbate i in mixtures, V is the volume of the solution and M_s is the mass of sorbent in each batch bottle. Finally, the q_i can be determined by setting F_i equal to zero based on Eq. (7.15).

$$F_i(q_1, q_2, \dots, q_N) = C_{i,int} - \frac{M_s}{V} q_i - \frac{q_i}{\sum_{j=1}^N q_j} \left[\frac{\sum_{j=1}^N \frac{q_j}{n_j}}{\frac{K_{f,i}}{n_i}} \right]^{1/n_i} = 0 \quad \text{for } i = 1 \text{ to } N \quad (7.15)$$

In Eq. (7.15), all that is needed to define the equilibrium are the individual-sorbate Freundlich sorption parameters for each sorbate, the initial concentration of each sorbate, the volume of the solution and the mass of sorbent in each batch bottle.

This set of N nonlinear simultaneous equations with N unknown q_i values must be solved to estimate the final equilibrium in each batch bottle. This set of equations was solved by using a Newton-Raphson algorithm in the similar manner described in other studies (Crittenden et al. 1985, McGinley et al. 1993, Xing et al. 1996). Once the q_i values are known, the corresponding values of C_i in mixtures can be obtained from Eq. (7.14). A computer program MATLAB (R2007a, The Mathworks, Inc.) employing a Newton-Raphson algorithm were used for solving the nonlinear equations (see Appendix G). Similar to the results from Xing et al. (1996),

sensitivity analysis for the Freundlich sorption parameters indicated that uncertainty in sorption exponent (n) was more sensitive than that in sorption capacity (K_f).

7.3.3 Comparison of Sorption Results between Measured and Predicted Data

The agreement of the experimentally measured data to the predicted data using the IAST was evaluated in terms of the average percent error (APE) defined in the Eq. (7.16).

$$APE = \frac{100\%}{P} \sum_{i=1}^P \frac{|X_{i,mes} - X_{i,pred}|}{X_{i,mes}} \quad (7.16)$$

where $X_{i,mes}$ and $X_{i,pred}$ are the measured and predicted data, respectively, for C or q . This error function attempts to minimize the fractional error distribution across the entire concentration range from the comparison of measured sorption data with the corresponding predicted data for both C and q , respectively (Porter et al. 1999).

7.4 RESULTS AND DISCUSSION

7.4.1 Sorption to Hydrophilic Mineral Surfaces

7.4.1.1 Sorption in Individual-Pseudocompound Systems

After the lumping schemes were determined guided by cluster analysis (see Chapter 6 for detail information), the resulting four Pseudocompounds were determined to approximate the sorption behavior of 12 NOCs in full mixtures to hydrophilic mineral surfaces. For example, Pseudocompound A consisted of 1,2,4-TCB and 1,4-DCB, Pseudocompound B consisted of CB, *m*-XYL, TOL, and BZ,

Pseudocompound C consisted of 2,4-DMP, *p*-CRE, PHE, and 2-HEX, and Pseudocompound D consisted of 2-BUT and ACE. Each Pseudocompound was prepared by dissolving only components belonging to each Pseudocompound. After the equilibrium was reached in each batch bottle, the aqueous- and solid- phase concentrations of each Pseudocompound were calculated by summation of the aqueous- and solid- phase concentrations of components, respectively.

Results for the individual-Pseudocompound sorption to hydrophilic mineral surfaces were shown in Figs. 7.1, 7.2, and 7.3 for uncoated, FeOOH-coated, and Al₂O₃-coated sands, respectively. The sorption isotherms were fitted reasonably well by the Freundlich sorption model over the aqueous concentration ranges tested (i.e., $C \leq 200 \text{ } \mu\text{mol/L}$). Also, each Pseudocompound showed substantially different sorption behavior in terms of both sorption capacity and nonlinearity. For example, Pseudocompound A showed greater sorption capacity and more linearity (i.e., $0.981 \leq n \leq 1.02$) whereas Pseudocompound D showed lower sorption capacity and more nonlinearity (i.e., $0.627 \leq n \leq 0.708$). However, none showed evidence of a saturation plateau within the C ranges tested. Finally, the Freundlich sorption parameters of Pseudocompounds were reasonably represented by using the mole fraction-weighted averages of individual-sorbate Freundlich sorption parameters of components (see Chapter 6 for detail information).

The near linear (i.e., $0.944 \leq n \leq 1.02$) sorption of both Pseudocompounds A and B can be attributed to preferential adsorption of chemically adsorbed water molecules onto hydrophilic mineral surfaces, since nonpolar NOC molecules belonging to both Pseudocompounds A and B cannot effectively compete with

strongly chemisorbed water molecules (Drost-Hansen 1969, Schwarzenbach et al. 1993, Goss and Eisenreich 1996, Huang et al. 1996, Xing et al. 1996, Huang and Weber 1997, Mader et al. 1997, Su et al. 2006). Thus, strongly chemisorbed water molecules over hydrophilic mineral surfaces may reduce the heterogeneous adsorption potential caused by surface irregularity, resulting in the practically linear sorption of both Pseudocompounds A and B to energetically homogeneous vicinal water region (Schwarzenbach et al. 1993, Huang et al. 1996, Xing et al. 1996, Mader et al. 1997, Su et al. 2006).

On the contrary, the nonlinear sorption (i.e., $0.627 \leq n \leq 0.898$) of both Pseudocompounds C and D is due to the greater contribution from hydrophilic specific interactions, presumably H-bonding of polar NOC molecules belonging to both Pseudocompounds C and D with surface hydroxyls or with strongly chemisorbed water molecules, than that from hydrophobic nonspecific interactions (Karickhoff 1984, Southworth and Keller 1986, Xing et al. 1996). Also, Pseudocompound D with greater polarity (i.e., 2-BUT and ACE) showed more nonlinear sorption than Pseudocompound C with less polarity (i.e., 2,4-DMP, *p*-CRE, PHE, and 2-HEX), suggesting that the nonlinear sorption of Pseudocompounds C and D was related to the polarity of NOC molecules belonging to both Pseudocompounds C and D. Although the sorption of Pseudocompounds to hydrophilic mineral surfaces can be affected by factors other than the hydrophobic nonspecific interactions, more hydrophobic Pseudocompounds A and B were sorbed to a greater extent than less hydrophobic Pseudocompounds C and D by all hydrophilic mineral surfaces tested.

7.4.1.2 Sorption in Multi-Pseudocompound Systems

Both the complex interactions and the collective effects of multiple classes of Pseudocompounds on the sorption of individual Pseudocompound were evaluated by investigating the sorption behavior of 12 NOCs in full mixtures. Based on the comparison of sorption isotherms between individual- and multi- Pseudocompounds systems presented in Figs. 7.1, 7.2, and 7.3 for uncoated, FeOOH-coated, and Al₂O₃-coated sands, respectively, the sorption of both Pseudocompounds A and B was not affected by the presence of other Pseudocompounds with various structure and physicochemical properties. This result indicates that there appear to be little, if any, mixture effects for sorption of both Pseudocompounds A and B to hydrophilic mineral surfaces within the *C* ranges tested. Also, the effect of changes in full mixture composition on sorption of both Pseudocompounds A and B to hydrophilic mineral surfaces was found to be insignificant (see Chapters 5 and 6 for detail information).

This noncompetitive sorption of both Pseudocompounds A and B within full mixtures can be attributed to the accumulation of nonpolar NOCs in the vicinal water region without competition for the specific sorption sites with other nonpolar NOCs. Additionally, nonpolar NOCs cannot compete with polar NOCs and water for the specific sorption sites on these hydrophilic mineral surfaces and, therefore, sorb further away from the surface due to an incapability of H-bonding (Huang et al. 1996, Xing et al. 1996). Thus, near-linear and noncompetitive sorption of both Pseudocompounds A and B in full mixtures to hydrophilic mineral surfaces was

expected at low surface coverage, where the molecules of NOCs were at a discrete molecular state (Su et al. 2006).

On the contrary, the sorption of both Pseudocompounds C and D was affected by the presence of other Pseudocompounds with various structure and physicochemical properties. As shown in Figs. 7.1, 7.2, and 7.3 for uncoated, FeOOH-coated, and Al₂O₃-coated sands, respectively, the sorption of both Pseudocompounds C and D decreased and became more linear in the presence of the other Pseudocompounds relative to sorption in individual-Pseudocompound systems. However, both sorption capacity and nonlinearity to hydrophilic mineral surfaces were affected to different extents not only between Pseudocompounds C and D but also among the hydrophilic mineral surfaces, indicating that sorption of the polar NOCs in full mixtures to hydrophilic mineral surfaces is more complex than that of nonpolar NOCs.

This complex mixture effects for both Pseudocompounds C and D to hydrophilic mineral surfaces can be attributed to the mutual competition for hydrophilic specific sorption sites. Also, Pseudocompounds D with greater polarity (i.e., 2-BUT and ACE) can be more powerful competitors than Pseudocompounds C with less polarity (i.e., 2,4-DMP, *p*-CRE, PHE, and 2-HEX) for hydrophilic specific sorption sites. As a result, Pseudocompounds D may suppress the nonlinear interactions of Pseudocompounds C with hydrophilic specific sites such that both sorption capacity and nonlinearity for Pseudocompounds C decreased significantly. Thus, the presence and magnitude of mutual competition was subject to variation and depended on both the composition of full mixtures (i.e., concentration and

polarity of Pseudocompounds) and the type of mineral surface (i.e., specific volume of vicinal water region and availability of hydrophilic specific sorption sites).

7.4.1.3 Ideal Adsorbed Solution Theory (IAST) Predictions

The IAST predictions for C_i and q_i based on Eqs. (7.14) and (7.15) were performed using combinations of soil mass (M_s), solution volume (V), and initial concentration of Pseudocompounds ($C_{i,int}$) in each batch bottle, and individual-Pseudocompound Freundlich sorption parameters ($K_{f,i}$ and n_i). In all cases, soil mass (M_s) and solution volume (V) were held constant whereas initial concentrations of Pseudocompounds ($C_{i,int}$) were varied in each batch bottle. Predicted sorption data by the IAST were compared to corresponding experimentally measured data in Figs. 7.1, 7.2, and 7.3 for uncoated, FeOOH-coated, and Al₂O₃-coated sands, respectively. Also, the comparisons between the IAST predictions and corresponding experimentally measured data in full mixtures based on Eq. (7.16) were summarized in Table 7.1.

As shown in Figs. 7.1, 7.2, and 7.3 for uncoated, FeOOH-coated, and Al₂O₃-coated sands, respectively, the IAST predictions closely simulated the sorption behavior for Pseudocompounds A, B, and C in full mixtures. However, the IAST significantly overpredicted the competition against Pseudocompounds D in full mixtures. As is evident by Table 7.1, the APE values in predicting q for Pseudocompound D by the IAST was greater than those for Pseudocompounds A, B, and C, indicating that less precision in predicting q for Pseudocompound D was expected. Also, these results indicate that the accuracy of the IAST predictions with

Pseudocompounds in full mixtures to hydrophilic mineral surfaces depended on the physicochemical properties of Pseudocompounds.

Aforementioned in sorption of multi-Pseudocompound systems, the different sorption behavior between polar and nonpolar Pseudocompounds is due to the differentiated sorption domains from the hydrophilic mineral surfaces. Thus, both Pseudocompounds A and B cannot effectively compete with both Pseudocompounds C and D. The presence of this differentiated sorption domains among Pseudocompounds is the violation of the assumption of same sorption sites to all sorbates in the IAST. Also, Pseudocompound D can be more powerful competitor than Pseudocompound C for hydrophilic specific sorption sites. This unequal and nonideal competition between polar Pseudocompounds is the violation of the assumption of equal and ideal competition in the IAST. As a result, the violation of these assumptions results in the failure of the IAST prediction, especially Pseudocompound D.

However, the IAST does not overpredict the competition against Pseudocompounds A and B despite of the violation of the assumptions in the IAST. Since sorption capacities of hydrophilic mineral surfaces for polar Pseudocompounds were lower than those for nonpolar Pseudocompounds by a factor ranging from three to eight, there is negligible competition between polar and nonpolar Pseudocompounds. Also, since the individual-Pseudocompound sorption for both Pseudocompounds A and B is near linear, competitive sorption between nonpolar Pseudocompounds does not occur. Therefore, the IAST closely predicts the sorption behaviors of both Pseudocompounds A and B. Interestingly, the IAST

closely predicts the sorption behavior of Pseudocompound C although both sorption capacity and nonlinearity for Pseudocompound C was significantly suppressed by Pseudocompound D. This result may be due to the combinative competition against Pseudocompounds C with both polar and nonpolar Pseudocompounds in the IAST.

Since the IAST becomes increasingly difficult to use for increasing numbers of sorbates in full mixtures, both difficulty and effort in computation to implement the IAST can be reduced by using Pseudocompounds. Considering that lumped approach is a tradeoff between accuracy and simplicity, the Freundlich sorption parameters of Pseudocompounds estimated from individual-sorbate sorption parameters of their components can reduce the computational requirements of the IAST to render the IAST more amenable to full mixtures in predictions of multicomponent sorption equilibria. In spite of the attractions of the IAST with Pseudocompounds for the acceptable and simple predictions, the IAST is rigorously appropriate only for entropy-driven sorption reactions (Weber and DiGiano 1996). Also, the deviations from ideality increases as the dissimilarities between sorbates increase, and these deviations from ideality cannot be predicted by the IAST (Yonge and Keinath 1986, Yonge et al. 1988, Xing et al. 1996, Lordgooei and Kim 2004). Thus, the modifications of the IAST with Pseudocompounds should be employed by adding terms or empirical correlations to account for the differential availability of sorption sites and the unequal and nonideal competition.

7.4.2 Sorption to Humic Acid-Mineral Complexes with Different f_{oc}

7.4.2.1 Sorption in Individual-Pseudocompound Systems

In the same manner applied in sorption to hydrophilic mineral surfaces, the resulting Pseudocompounds were determined to approximate the sorption behavior of 12 NOCs in full mixtures to HA-coated sands (HAS) with different f_{oc} (see Chapter 6 for detail information). For example, 12 NOCs can be lumped into four, five, and six Pseudocompounds for HAS1 ($f_{oc} = 0.051\%$), HAS2 ($f_{oc} = 0.119\%$), and HAS3 ($f_{oc} = 0.221\%$), respectively, as shown in Figs. 7.4, 7.5, and 7.6 for HAS1, HAS2, and HAS3, respectively. As the f_{oc} of HAS increases, the NOCs with higher K_{oc} (i.e., 1,2,4-TCB and 1,4-DCB) were separated from nonpolar Pseudocompounds due to the greater dependency of sorption on f_{oc} . Thus, higher numbers of Pseudocompounds were needed to describe the sorption behavior of 12 NOCs in full mixtures to HAS with different f_{oc} , compared to sorption to hydrophilic mineral surfaces.

Results for the individual-Pseudocompound sorption to HAS with different f_{oc} were shown in Figs. 7.4, 7.5, and 7.6 for HAS1, HAS2, and HAS3, respectively. The sorption isotherms were fitted reasonably well by the Freundlich sorption model over the C ranges tested (i.e., $\leq 200 \mu\text{mol/L}$). Also, each Pseudocompound showed substantially different sorption behavior in terms of both sorption capacity and nonlinearity. For example, Pseudocompounds consisting of nonpolar NOCs (i.e., Pseudocompounds A and B in HAS1; Pseudocompounds A, B, and C in HAS2; Pseudocompounds A, B, C and D in HAS3) showed greater sorption capacity and more linearity (i.e., $0.928 \leq n \leq 1.03$) whereas Pseudocompounds consisting of polar NOCs (i.e., Pseudocompounds C and D in HAS1; Pseudocompounds D and E in HAS2; Pseudocompounds E and F in HAS3) showed lower sorption capacity and

more nonlinearity (i.e., $0.661 \leq n \leq 0.898$). However, none showed evidence of a saturation plateau within C ranges tested. Finally, the Freundlich sorption parameters of Pseudocompounds were reasonably represented by using the mole fraction-weighted averages of individual-sorbate Freundlich sorption parameters of components (see Chapter 6 for detail information).

The near linear sorption of nonpolar Pseudocompounds can be attributed to both absorptive partitioning into HA and the suppression of adsorption onto mineral surface by vicinal water region, and is thermodynamically expected for partitioning into highly amorphous, gel-like SOM as well as for sorption to the energetically homogeneous vicinal water region on the hydrophilic mineral surfaces. For the HA used in this study, substantial condensed domains of HA or HASCM, such as charcoal and soot, likely do not exist based on the high oxygen/carbon ratio (see Table 2.1) for the HA and the low surface areas of the HAS (see Table 5.1). Thus, molecules of nonpolar NOCs primarily partition into loosely knit macromolecules of HA, relegating the role of adsorption or hole filling onto tightly knit macromolecules of HA or HSACM as insignificant even at low concentration ranges (i.e., $C \leq 20$ $\mu\text{mol/L}$). As a result, strong sorbate adsorption was not likely, such that linear sorption behavior in individual-sorbate systems with low f_{oc} sorbents was expected.

On the contrary, the nonlinear sorption of Pseudocompounds consisting of polar NOCs can be attributed to the energetic and site-specific hydrophilic specific interactions, such as H-bonding with the functional groups of HA and surface hydroxyls of mineral surfaces (Isaacson and Frink 1984, Spurlock and Biggar 1994). Similar to sorption to hydrophilic mineral surfaces, sorption of Pseudocompounds

consisting of polar NOCs to HAS became progressively nonlinear with increasing polarity of NOCs, implying that the sorption nonlinearity of Pseudocompounds consisting of polar NOCs is a complex function of both the polarity and the H-bonding ability of the polar NOCs with HA and mineral surfaces. As expected, the sorption of both nonpolar and polar Pseudocompounds to HAS increased with increasing f_{oc} . However, more hydrophobic Pseudocompounds were sorbed to a great extent than less hydrophobic Pseudocompounds due to the different dependency of sorption on f_{oc} .

7.4.2.2 Sorption in Multi-Pseudocompound Systems

Both the complex interactions and the collective effect of multiple classes of Pseudocompounds on the sorption of individual Pseudocompound were evaluated by investigating the sorption behavior of 12 NOCs in full mixtures. Based on the comparison of sorption isotherms between individual- and multi- Pseudocompounds systems presented in Figs. 7.4, 7.5, and 7.6 for HAS1, HAS2, and HAS3, respectively, the sorption of nonpolar Pseudocompounds was not affected by the presence of other Pseudocompounds with various structure and physicochemical properties. This result indicates that there appear to be little, if any, mixture effects for sorption of nonpolar Pseudocompounds to HAS with different f_{oc} within C ranges tested. Also, the effect of changes in mixture composition on sorption of nonpolar Pseudocompounds to HAS with different f_{oc} was found to be insignificant (see Chapters 5 and 6 for detail information).

As indicated by the near linear and noncompetitive sorption isotherms of nonpolar Pseudocompounds to all HASs in both individual- and multi-Pseudocompound systems, the absence of mixture effects can be attributed to the dominance of partitioning of nonpolar NOCs into loosely knit macromolecules of HA, relative to the adsorption or hole-filling of nonpolar NOCs onto tightly knit macromolecules of HA. Additionally, nonpolar NOCs cannot compete effectively with polar NOCs and water for the oxygen- and hydroxyl-containing functional groups of the HA (Karickhoff 1984, Spurlock and Biggar 1994, Xing et al. 1996, Chiou and Kile 1998). Thus, the individual-Pseudocompound sorption to the HAS were not significantly altered by the presence and quantity of other Pseudocompounds evaluated in this study. However, the collective effects of multiple classes of Pseudocompounds on the sorption of a given Pseudocompound to HA-mineral complexes may not be ignored if the competitive adsorption of NOCs onto condensed domains of HA is significant.

On the contrary, the sorption of a given polar Pseudocompound was affected by the presence of other Pseudocompounds with similar structure and physicochemical properties. These results indicate that there appears to be mixture effects for sorption of polar Pseudocompounds to HAS in the *C* ranges tested. Compared to sorption in individual-Pseudocompound systems, the sorption of polar Pseudocompounds decreased and became more linear in the presence of the other Pseudocompounds. However, both sorption capacity and nonlinearity were affected to a different extent not only between polar Pseudocompounds but also among the

HASs, indicating that sorption of the polar NOCs in full mixtures to HAS is more complex than that of nonpolar NOCs.

The complex mixture effect for sorption of polar Pseudocompounds to HAS can be attributed to mutual competition for hydrophilic specific sites of both mineral surfaces and HA. Also, Pseudocompounds with greater polarity (i.e., 2-BUT and ACE) can be more powerful competitors than Pseudocompounds with less polarity (i.e., 2,4-DMP, *p*-CRE, PHE, and 2-HEX) for hydrophilic specific sorption sites. As a result, Pseudocompounds with greater polarity may suppress the nonlinear interactions of Pseudocompounds with less polarity with hydrophilic specific sites. However, the effect of these mixture factors on the sorption of the polar Pseudocompounds to HAS decreased with increasing f_{oc} . Thus, the presence and magnitude of mutual competition was subject to variation and depended on both the composition of full mixtures (i.e., concentration and polarity of Pseudocompounds) and the type of mineral surface (i.e., f_{oc} values and availability of hydrophilic specific sorption sites).

7.4.2.3 Ideal Adsorbed Solution Theory (IAST) Prediction

The IAST predictions for C_i and q_i to HAS with different f_{oc} were performed in the same manner applied in sorption to hydrophilic mineral surfaces. Predicted sorption data by the IAST were compared to corresponding experimentally measured data in Figs. 7.4, 7.5, and 7.6 for HAS1, HAS2, and HAS3, respectively. Also, the comparisons between the IAST predictions and corresponding

experimentally measured data in full mixtures based on Eq. (7.16) were summarized in Table 7.2.

As shown in Figs. 7.4, 7.5, and 7.6 for HAS1, HAS2, and HAS3, respectively, the IAST predictions closely simulated the sorption behavior for nonpolar Pseudocompounds in full mixtures. However, the IAST overpredicted the competition against polar Pseudocompounds, especially polar Pseudocompound with greater polarity (i.e., 2-BUT and ACE). As is evident by Table 7.2, the APE values in predicting q for polar Pseudocompound with greater polarity (i.e., Pseudocompound D in HAS1; Pseudocompound E in HAS2; Pseudocompound F in HAS3) by the IAST was much greater than those for other Pseudocompounds, indicating that less precision in predicting q for polar Pseudocompound with greater polarity was expected. Also, these results indicate that the accuracy of the IAST predictions using Pseudocompounds in full mixtures to HAS with different f_{oc} depended on the physicochemical properties of Pseudocompounds.

Aforementioned in sorption of multi-Pseudocompound systems, sorption of polar Pseudocompounds may not be strongly influenced by nonpolar Pseudocompounds due to the differentiated sorption domains and lack of competition between polar and nonpolar Pseudocompounds for specific sites of both mineral surface and HA (Karickhoff 1984, Xing et al. 1996, Chiou and Kile 1998). Instead, substantial mutual competition of polar Pseudocompounds occurs only if other polar Pseudocompounds compete for specific sites of both mineral surfaces and HA. Additionally, the suppression in the sorption of a given polar Pseudocompound by other polar Pseudocompounds may be a complex function of

polarity and hydrophilic specific interactions (Isaacson and Frink 1984, Spurlock and Biggar 1994, Xing et al. 1996, Chiou and Kile 1998).

The presence of this differentiated sorption domains for specific sites of both mineral surface and HA among Pseudocompounds is the violation of the assumption of same sorption sites to all sorbates in the IAST. Also, the unequal and complex competition among polar Pseudocompounds as a function of polarity and hydrophilic specific interactions is the violation of the assumption of equal and ideal competition in the IAST. As a result, the violation of these assumptions results in the failure of the IAST prediction, especially polar Pseudocompound with greater polarity (i.e., 2-BUT and ACE).

However, the IAST does not overpredict the competition against nonpolar Pseudocompounds despite of the violation of these assumptions in the IAST. Since sorption capacities of HAS for polar Pseudocompounds are substantially lower than those for nonpolar Pseudocompounds, depending on the f_{oc} of HAS, there is negligible competition between polar and nonpolar Pseudocompounds. Also, since the individual-Pseudocompound sorption for nonpolar Pseudocompounds is near linear, competitive sorption among nonpolar Pseudocompounds does not occur significantly. Therefore, the IAST closely predicts the sorption behaviors of nonpolar Pseudocompounds in all cases. Interestingly, the IAST closely predicts the sorption behavior of polar Pseudocompound with less polarity although both sorption capacity and nonlinearity for polar Pseudocompound with less polarity was significantly suppressed by polar Pseudocompound with greater polarity. This result

may be due to the combinative competition against polar Pseudocompound with less polarity with both polar and nonpolar Pseudocompounds in the IAST.

Since the IAST becomes increasingly difficult to use for increasing numbers of sorbates in full mixtures, both difficulty and effort in computation to implement the IAST can be reduced by using Pseudocompounds. In this study, the competitive reductions in the sorption of Pseudocompounds in full mixtures by nonlinearly sorbing components were found to modeled reasonably well with IAST, except for Pseudocompounds with greater polarity (i.e., 2-BUT and ACE). Also, the comparisons of IAST predictions with Pseudocompounds and experimentally measured data reveal that the incorporating Pseudocompounds into IAST to predict sorption of NOCs in full mixtures is feasible unless the deviations from ideality increases to a extent to IAST cannot predict. Thus, the modifications of the IAST with Pseudocompounds should be employed by adding terms or empirical correlations to account for the differential availability of sorption sites and the effect of nonideal competition. Considering that lumped approach is a tradeoff between accuracy and simplicity, the IAST with Pseudocompounds can reduce the computational requirements of the IAST to render the IAST more amenable to full mixtures in predictions of multicomponent sorption equilibria.

7.5 SUMMARY AND CONCLUSIONS

Both the feasibility and the accuracy of the ideal adsorbed solution theory (IAST) with Pseudocompounds (groups of compounds) to reduce difficulty and effort in computation in predictions of sorption of 12 neutral organic compounds

(NOCs) with a wide range of hydrophobicities (i.e., $-0.24 \leq \log K_{ow} \leq 4.23$) in full mixtures to simulated aquifer sorbents were investigated.

In sorption to hydrophilic mineral surfaces, the following conclusions can be drawn:

- The near linear (i.e., $0.944 \leq n \leq 1.02$) sorption of nonpolar Pseudocompounds can be attributed to preferential adsorption of chemically adsorbed water molecules onto hydrophilic mineral surfaces whereas the nonlinear (i.e., $0.627 \leq n \leq 0.898$) sorption of polar Pseudocompounds is due to the greater contribution from hydrophilic specific interactions than that from hydrophobic nonspecific interactions
- The noncompetitive sorption of nonpolar Pseudocompounds within full mixtures can be attributed to the accumulation of nonpolar NOCs in the vicinal water region without competition for the specific sorption sites whereas the competitive sorption of polar Pseudocompounds within full mixtures can be attributed to the mutual competition for hydrophilic specific sorption sites.
- The presence and magnitude of mutual competition was subject to variation and depended on both the composition of full mixtures (i.e., concentration and polarity of Pseudocompounds) and the type of mineral surface (i.e., specific volume of vicinal water region and availability of hydrophilic specific sorption sites).
- The comparisons of IAST predictions with Pseudocompounds and experimentally measured data revealed that the incorporating

Pseudocompounds into IAST to predict sorption of NOCs in full mixtures was feasible unless the deviations from ideality increased to an extent to IAST cannot predict.

In sorption to humic acid-mineral complexes with different f_{oc} , the following conclusions can be drawn:

- The near linear (i.e., $0.928 \leq n \leq 1.03$) sorption of nonpolar Pseudocompounds can be attributed to both absorptive partitioning into HA and the suppression of adsorption onto mineral surface by vicinal water region whereas the nonlinear sorption (i.e., $0.661 \leq n \leq 0.898$) of polar Pseudocompounds can be attributed to the energetic and site-specific hydrophilic specific interactions, such as H-bonding with the functional groups of HA and surface hydroxyls of mineral surfaces.
- The noncompetitive sorption of nonpolar Pseudocompounds can be attributed to the dominance of partitioning of nonpolar NOCs into loosely knit macromolecules of HA, relative to the adsorption or hole-filling of nonpolar NOCs onto tightly knit macromolecules of HA whereas the competitive sorption of polar Pseudocompounds can be attributed to mutual competition for hydrophilic specific sites of both mineral surfaces and HA.
- The presence and magnitude of mutual competition was subject to variation and depended on both the composition of full mixtures (i.e., concentration and polarity of Pseudocompounds) and the type of mineral surface (i.e., f_{oc} values and availability of hydrophilic specific sorption sites).

- The competitive reductions in the sorption of Pseudocompounds in full mixtures by nonlinearly sorbing components were found to modeled reasonably well with IAST, except for Pseudocompounds with greater polarity (i.e., 2-BUT and ACE). Thus, the modifications of the IAST with Pseudocompounds should be employed by adding terms or empirical correlations to account for the differential availability of sorption sites and the effect of nonideal competition.
- Considering that lumped approach is a tradeoff between accuracy and simplicity, the IAST with Pseudocompounds can reduce the computational requirements of the IAST to render the IAST more amenable to full mixtures in predictions of multicomponent sorption equilibria.

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Table 7.1 Comparison between Ideal Adsorbed Solution Theory predictions and experimentally-measured data in 12 neutral organic compounds in full mixtures and hydrophilic mineral surfaces

Sorbents	Pseudocompounds	Average % Error ^a Using IAST		No. of Data	C range, μmol/L	q range, μmol/kg
		C	q			
Uncoated sand	A	11.4	5.91	8	7.17-90.7	1.39-20.1
	B	9.31	12.6	8	14.5-198	2.75-34.4
	C	6.39	14.6	8	15.6-197	0.42-5.72
	D	7.81	45.8	8	7.91-100	0.18-2.02
FeOOH-coated sand	A	13.8	14.9	8	6.40-99.7	1.19-20.2
	B	10.5	13.3	8	13.0-189	1.56-24.4
	C	6.01	8.05	8	13.5-199	0.93-10.6
	D	14.5	38.6	8	6.79-99.0	0.29-3.68
Al ₂ O ₃ -coated sand	A	7.65	16.5	8	6.11-94.1	1.29-16.2
	B	9.08	14.1	8	13.9-200	1.89-29.6
	C	4.92	12.6	8	15.3-201	0.99-7.57
	D	5.58	42.5	8	7.81-103	0.38-3.02

^aAverage Percent Error was calculated based on Eq. (7.16)

Table 7.2 Comparison between Ideal Adsorbed Solution Theory predictions and experimentally-measured data in 12 neutral organic compounds in full mixtures and HA-mineral complexes with different f_{oc}

Sorbents	Pseudocompounds	Average % Error ^a Using IAST		No. of Data	C range, $\mu\text{mol/L}$	q range, $\mu\text{mol/kg}$
		C	q			
HA-coated sand 1 ($f_{oc} = 0.051\%$)	A	7.63	13.5	7	3.66-37.5	4.69-34.6
	B	4.12	7.89	7	23.4-221	7.83-58.3
	C	1.70	17.9	7	22.6-195	0.51-6.43
	D	4.39	63.1	7	11.4-104	0.52-3.08
HA-coated sand 2 ($f_{oc} = 0.119\%$)	A	7.83	14.1	8	1.92-24.5	6.25-52.8
	B	10.4	15.7	8	5.98-76.0	4.03-55.3
	C	4.82	6.12	8	9.99-128	4.01-46.4
	D	8.82	14.8	8	13.2-192	1.36-15.6
	E	4.72	62.6	8	7.87-98.7	0.26-3.54
HA-coated sand 3 ($f_{oc} = 0.221\%$)	A	9.87	11.5	7	1.82-20.1	4.62-61.5
	B	9.34	16.5	7	2.42-31.3	2.01-37.5
	C	10.7	6.96	7	7.17-76.6	5.56-46.9
	D	5.93	10.3	7	9.67-87.6	2.43-24.8
	E	2.94	7.58	7	21.5-186	4.50-28.6
	F	4.58	46.0	7	10.9-100	0.75-6.84

^aAverage Percent Error was calculated based on Eq. (7.16)

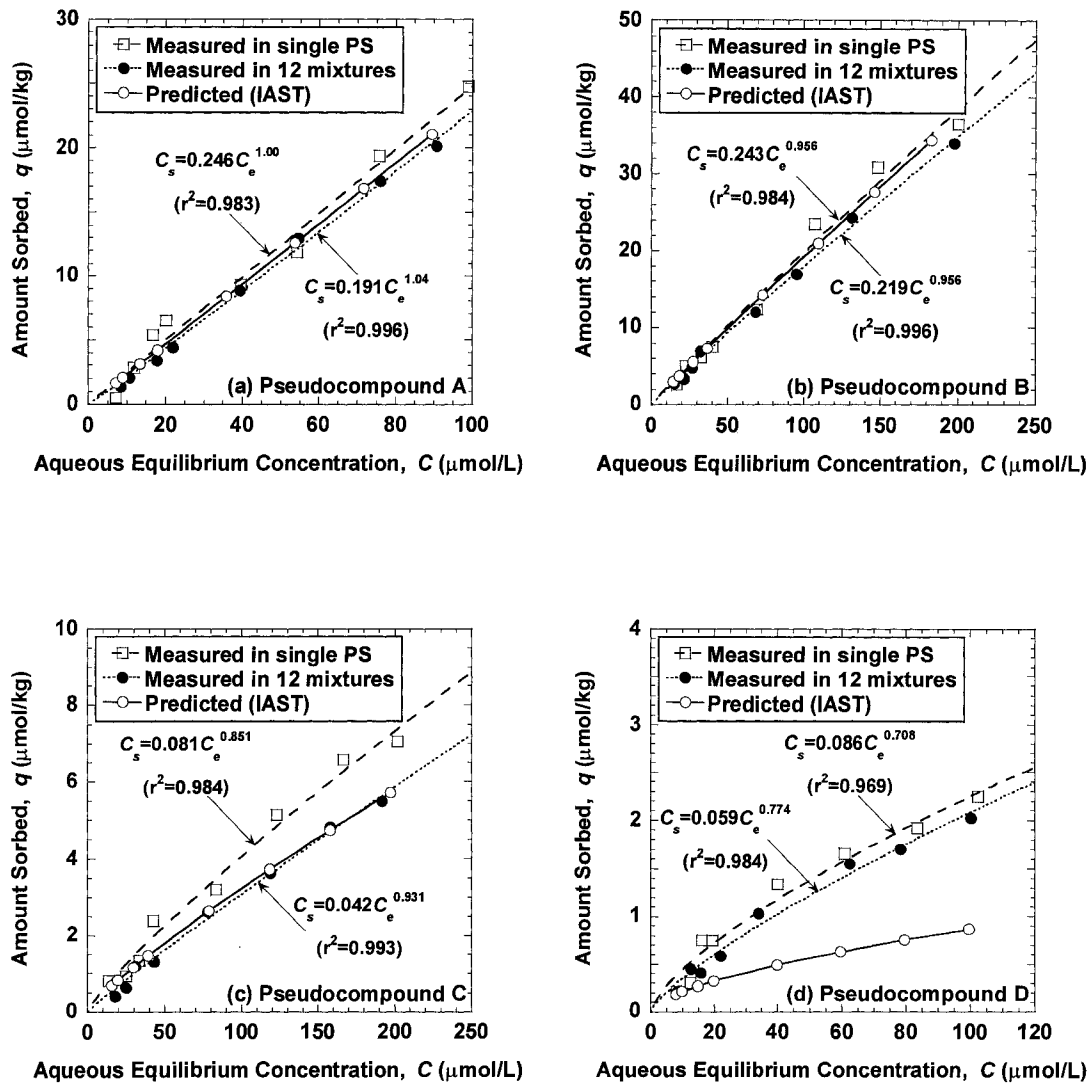


Fig. 7.1 Sorption isotherms of pseudocompounds to uncoated sand in both individual- and multi- pseudocompound systems (i.e., full mixtures). The dashed lines denote the associated best-fit Freundlich sorption model for pseudocompounds. The solid lines denote the IAST predicted isotherms in 12-sorbate full mixtures.

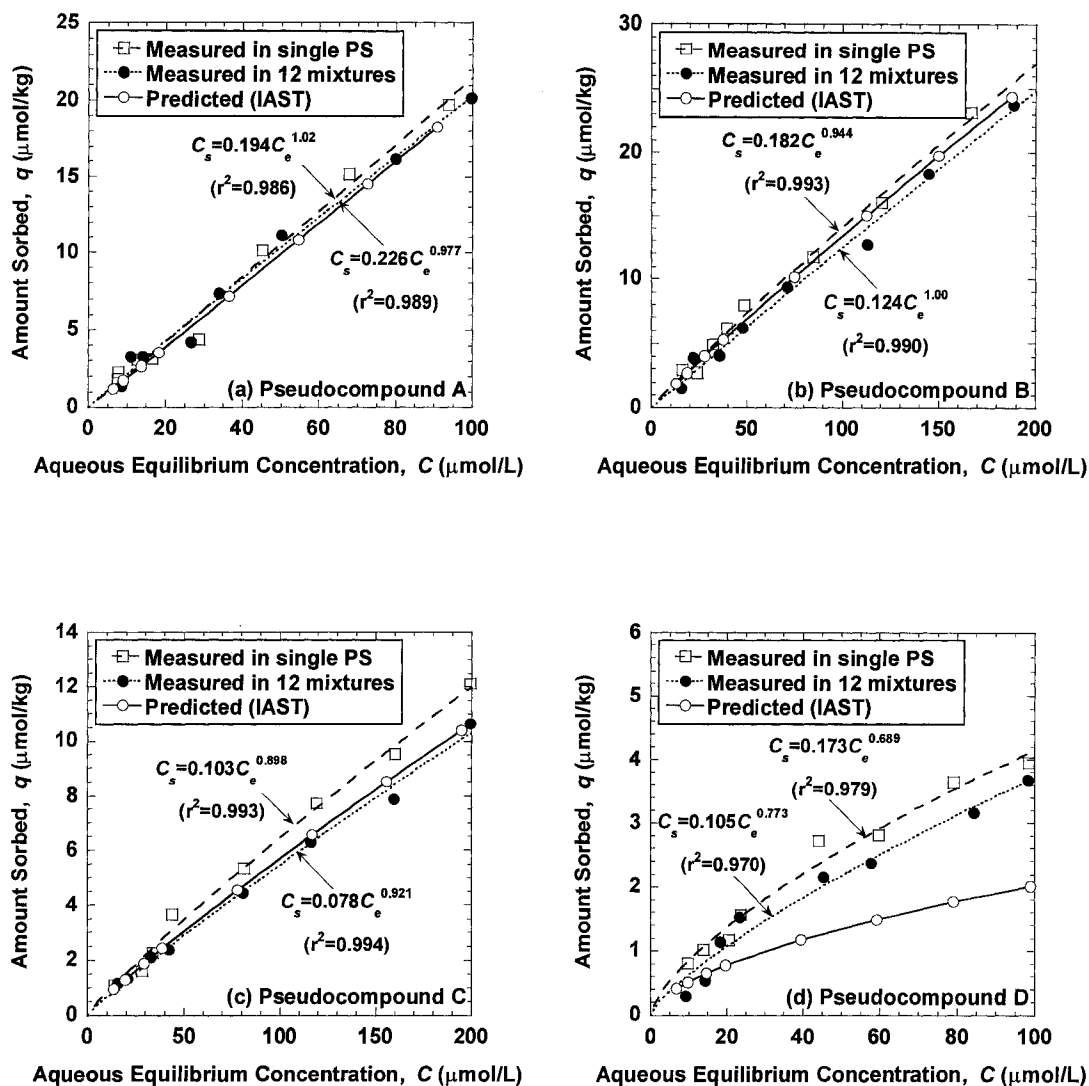


Fig. 7.2 Sorption isotherms of pseudocompounds to FeOOH-coated sand in both individual- and multi- pseudocompound systems (i.e., full mixtures). The dashed lines denote the associated best-fit Freundlich sorption model for pseudocompounds. The solid lines denote the IAST predicted isotherms in 12-sorbate full mixtures.

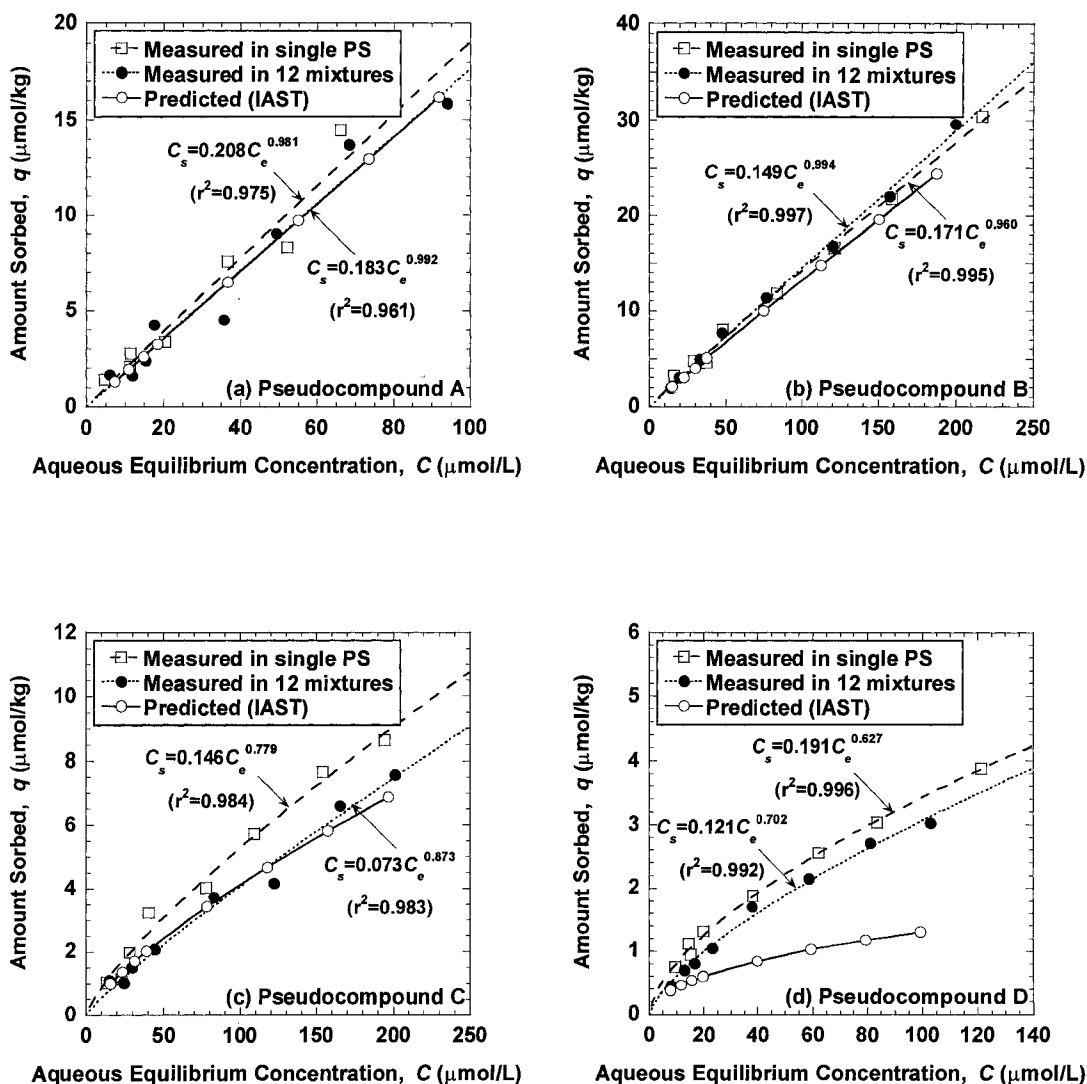


Fig. 7.3 Sorption isotherms of pseudocompounds to Al_2O_3 -coated sand in both individual- and multi- pseudocompound systems (i.e., full mixtures). The dashed lines denote the associated best-fit Freundlich sorption model for pseudocompounds. The solid lines denote the IAST predicted isotherms in 12-sorbate full mixtures.

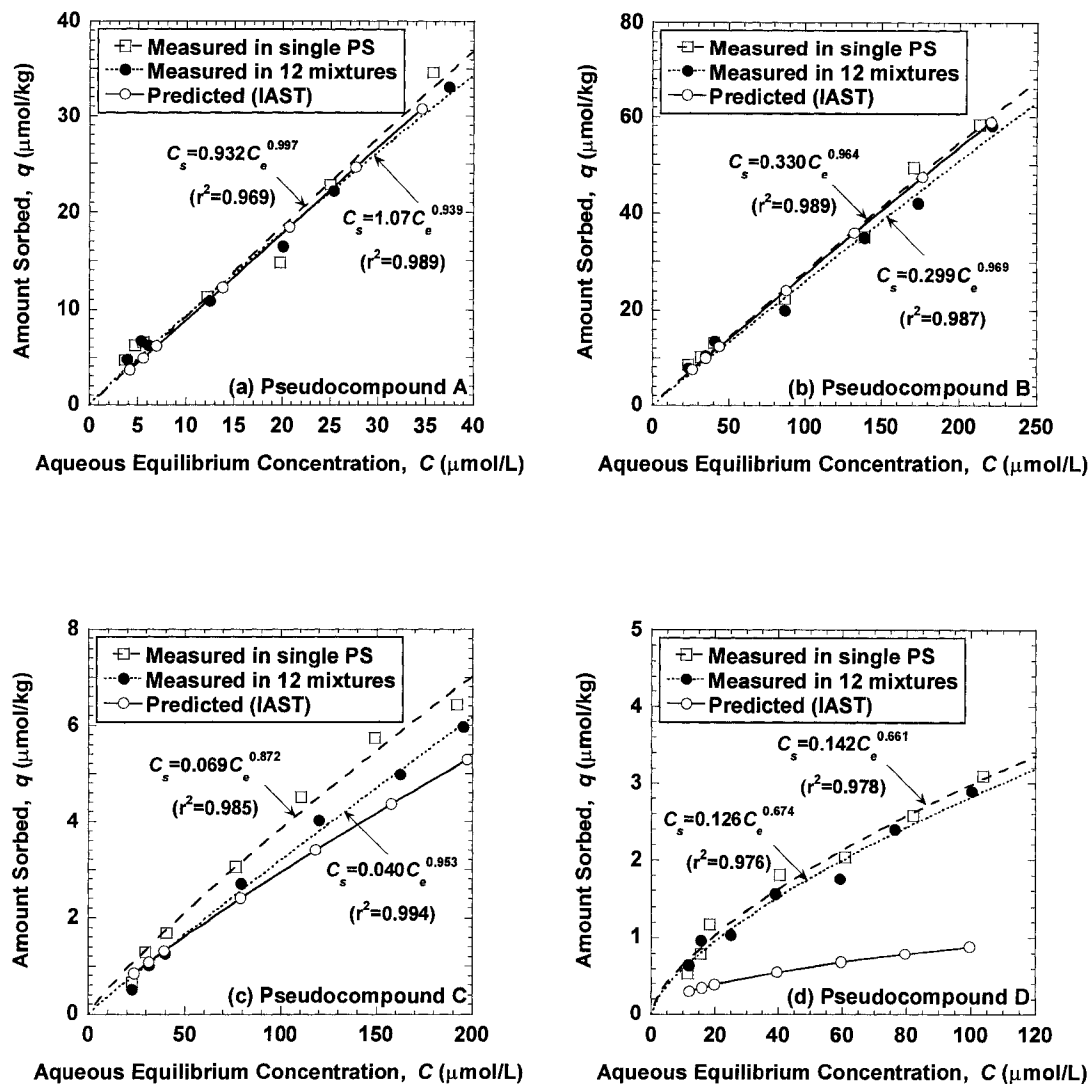


Fig. 7.4 Sorption isotherms of pseudocompounds to humic acid-coated sand ($f_{oc} = 0.051\%$) in both individual- and multi- pseudocompound systems (i.e., full mixtures). The dashed lines denote the associated best-fit Freundlich sorption model for pseudocompounds. The solid lines denote the IAST predicted isotherms in 12-sorbate full mixtures.

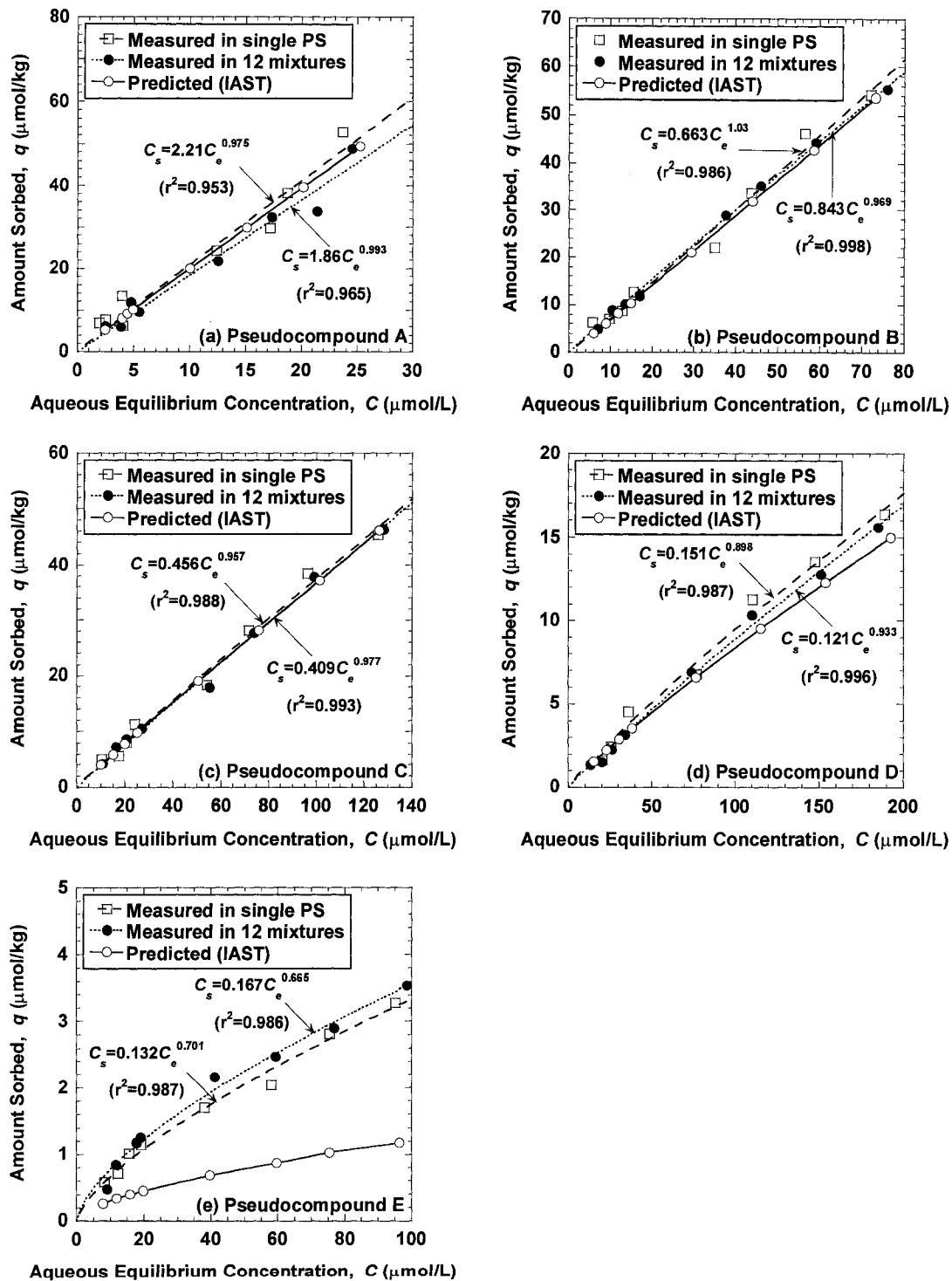


Fig. 7.5 Sorption isotherms of pseudocompounds to humic acid-coated sand ($f_{oc} = 0.119\%$) in both individual- and multi- pseudocompound systems (i.e., full mixtures). The dashed lines denote the associated best-fit Freundlich sorption model for pseudocompounds. The solid lines denote the IAST predicted isotherms in 12-sorbate full mixtures.

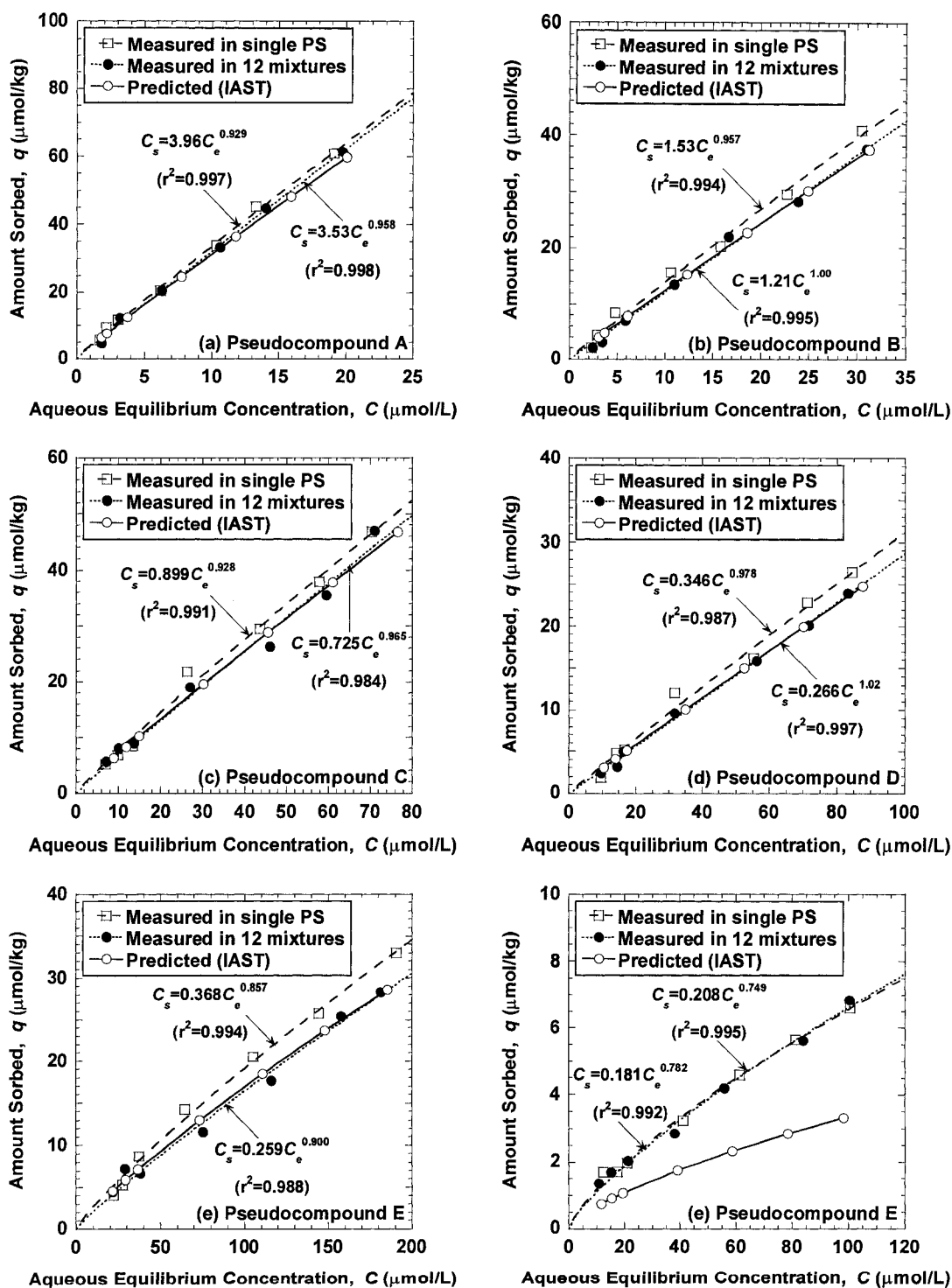


Fig. 7.6 Sorption isotherms of pseudocompounds to humic acid-coated sand ($f_{oc} = 0.221\%$) in both individual- and multi- pseudocompound systems (i.e., full mixtures). The dashed lines denote the associated best-fit Freundlich sorption model for pseudocompounds. The solid lines denote the IAST predicted isotherms in 12-sorbate full mixtures.

CHAPTER 8

SUMMARY AND CONCLUSIONS

8.1 SUMMARY

The feasibility and accuracy of using a lumped approach to describe the sorption of 12 neutral organic compounds (NOCs), 6 polar NOCs (acetone, 2-butanone, 2-hexanone, phenol, *p*-cresol, and 2,4-dimethyl phenol) and 6 nonpolar NOCs (1,2,4-trichlorobenzene, 1,4-dichlorobenzene, chlorobenzene, *m*-xylene, toluene, benzene), in mixtures to simulated aquifer sorbents with fractions of organic carbon (f_{oc}) ranging from 0.005 to 0.221 % were mainly evaluated. The lumped approach consisted of grouping one or more components in mixtures of NOCs into a fewer number of pseudocompounds that exhibit similar sorption behavior. Batch equilibrium sorption tests (BESTs) were performed to measure the sorption behaviors of the 12 NOCs existing as both single NOCs and in mixtures of NOCs in aqueous solution with each sorbent. The results of the BESTs were analyzed using the Freundlich sorption equation, and the lumped approach was evaluated on the basis of experimentally derived lumping criteria (i.e., Freundlich sorption parameters). Also, the use of the ideal adsorbed solution theory (IAST) with the determined pseudocompounds for predicting the sorption of the 12 NOCs within complex mixtures to simulated aquifer sorbents was investigated.

Besides, the contributions of mineral-bound humic acid (HA) and mineral surface to the overall sorption of individual nonpolar NOCs by low-surface-area simulated aquifer sorbents were evaluated on the basis of measured data and four different sorption

models. Moreover, the complex interactions in NOC mixtures (i.e., competitive or synergistic effect) among either the same or the different NOC classes within environmental concentration ranges, at aqueous equilibrium concentrations (C_e) that are low relative to the solubility (S_w) (i.e., $C_e/S_w \leq 0.3$), in terms of sorption to various simulated aquifer sorbents were investigated.

8.2 CONCLUSIONS

First, sorption of individual nonpolar NOCs to both uncoated and heated sands was nearly linear (i.e., $0.869 \leq n \leq 1.11$) due to the coverage of hydrophilic mineral surface with the ordered vicinal water region. Sorption of nonpolar NOCs to HA-coated sands was also essentially linear (i.e., $0.870 \leq n \leq 1.04$), and resulted from a combination of sorption to both mineral-bound HA and mineral surface, with the dominance of either contribution depending on the properties of the sorbents (e.g., f_{oc}) and the NOCs (e.g., K_{ow}). A proposed two-component model for sorption including blocking effect was appropriate for quantifying the contributions of mineral-bound HA and mineral surface to the overall sorption. However, conventional sorption models considering the contributions of both mineral-bound HA and mineral surface provided essentially as good agreement between predicted and measured distribution coefficients as the more complicated, two-component model for sorption that takes into account mineral surface blocking by HA.

Second, when associated with dissolved HA, strong hysteresis effects were observed for both metal (hydr)oxide- (i.e., FeO(OH)- or Al₂O₃-) coated sands whereas a weaker hysteresis effect was observed for uncoated sand, suggesting that adsorption-

desorption of HA to model sorbents is dependent on the affinity of chemical interactions between HA and surface composition of model sorbents. Also, adsorption of HA molecules onto metal (hydr)oxide-coated sands can be attributed to ligand exchange for lower molecular weight (MW) HA fractions and hydrophobic interaction for higher MW HA fractions, illustrating that both kinetic and fractional adsorption-desorption of HA subcomponents to metal (hydr)oxide-coated sands should be considered to understand the HA adsorption dynamics at solid-water interfaces and, therefore, the subsequent impact on binding reactivity of NOCs in the subsurface.

Third, sorption of nonpolar NOCs to metal (hydr)oxide-coated sands was nearly linear (i.e., $0.905 \leq n \leq 1.08$) and increased with increasing hydrophobicity of NOCs. Sorption of nonpolar NOCs to the HA-mineral complexes was also essentially linear (i.e., $0.898 \leq n \leq 1.06$), and resulted from a combination of sorption to both mineral-bound HA and mineral surface. The reactivity of mineral-bound HA to nonpolar NOCs (i.e., K_{oc}^*) were not significantly different between two metal (hydr)oxide-coated sands, indicating that the conformational and fractional (i.e., molecular weight and specific functional groups) changes of mineral-bound HA could be similar between two mineral surfaces. Finally, the amended contributions of mineral-bound HA and mineral surfaces should be considered to accurately predict the sorption of NOCs to HA-mineral complexes with low f_{oc} .

Fourth, mixture effects (e.g., sorption competition) were not statistically significant within a 95 % confidence level for sorption of the nonpolar NOCs to the hydrophilic mineral surfaces, whereas suppression in the sorption of some polar NOCs in mixtures was found to be statistically significant, but only in a complex and selective

manner. Similarly, mixture effects were not statistically significant for sorption of the nonpolar NOCs to the HA-mineral complexes, whereas mixture effects were statistically significant for some polar NOCs. Thus, sorption of polar NOCs in mixtures to the simulated aquifer sorbents was more subject to variation in the concentrations and compositions of the mixtures and, therefore, was more complex and difficult to predict, compared to sorption of the nonpolar NOCs to the simulated aquifer sorbents.

Fifth, each pseudocompound contained components of relatively similar sorption capacities and nonlinearity, and approximated the sorption behavior of the NOC mixtures to within a 95 % confidence level of the Freundlich sorption isotherms for the pseudocompounds. For a given sorbent, the lumping schemes for the nonpolar NOCs in the mixtures were consistent, i.e., independent of the compositions of the NOC mixtures, whereas those for the polar NOCs in the mixtures were inconsistent, due to the complex mutual competition for hydrophilic specific sorption sites among the polar NOCs. The lumping of the NOCs into pseudocompounds for sorption can be described according to the hydrophobicity (γ_w^{sat}) and the organic carbon partitioning coefficient (K_{oc}) of the NOCs in mixtures. Thus, the pseudocompounds could have been determined directly *a priori* (i.e., without the need for experimentation) simply from the properties of the individual NOCs in mixtures.

Finally, based on comparisons of predicted sorption behavior using IAST with pseudocompounds to the measured sorption behavior, incorporating pseudocompounds into IAST to predict sorption of NOCs in complex mixtures was found to be feasible except in the case where the underlying assumptions of IAST (i.e., same access to sorption sites and ideal sorbed phase) became invalid. Nonetheless, further study is

required to improve IAST predictions using pseudocompounds by incorporating terms to account for the differential availability of sorption sites and nonideal competition.

Appendix A. Definitions for the ratio of the uncoated (or exposed) fraction of mineral surface relative to the total mineral surface area (β_{min})

As shown in Figs. 2.2 and 2.3, the coating of humic acid (HA) onto heated sand is a linear process resulting in a coated monolayer of HA with an essentially uniform thickness. This result suggests that the thin layer of HA is physically distributed onto the surface of the heated sand in different coverages that are proportional to the fractional mass of organic matter (f_{om}). As f_{om} increases, the surface area of the coated organic matter increases, whereas the mineral surface area decreases. Thus, the overall total surface area at any f_{om} is a combination of these two opposing trends, and does not change significantly relative to total surface area of the pure mineral (i.e., $\leq \pm 5\%$), as indicated in Table 2.3. Since the overall total surface area is the sum of the uncoated mineral surface area and the surface area for the thin coating of HA, the fraction of the uncoated mineral surface area relative to the overall total surface area can be determined.

As illustrated schematically in Fig. A.1, the coating of HA onto the heated sand results in a relatively thin monolayer of HA. Measured values for the thickness of this coated monolayer of HA using the scanning electron microscopy (SEM) images shown in Fig. A.2 and the procedure outline in Fig. A.3 are summarized in Table A.1. Although the thicknesses of the coated monolayer of HA were approximately measured since the thickness is the distance perpendicular to SEM images, at higher resolution ($\times 12,000$), the thickness becomes the distance between two points.

As indicated by the results in Table A.1, the thicknesses of the coated monolayer of HA range from only $0.05\ \mu\text{m}$ to $0.10\ \mu\text{m}$, which suggest that the monolayer of coated HA is essentially uniform.

Since characterization of sorption coefficients (i.e., K_d and K_f) and the constituents of the solid phase (i.e., f_{om} and f_{min}) typically are based on mass instead of surface area, the total surface area that is attributed to the coated and the uncoated mineral surface can be expressed by the relative amounts by mass of organic matter and mineral in the binary solids. Thus, the surface area of organic matter can be written as follows:

$$SA_{om} = M_{om} \frac{1}{\rho_{om}} \frac{1}{t_{om}} \quad (A.1)$$

where SA_{om} is the surface area of organic matter (cm^2), M_{om} is the mass of organic matter (g of organic matter), ρ_{om} is the density of organic matter (g/cm^3), and t_{om} is the thickness of the organic matter coated onto the sand (cm). Since the mass of organic matter is equal to the product of the fractional mass of organic matter, f_{om} and the mass of solid, M_s (i.e., $M_{om} = f_{om}M_s$), Eq. A.1 can be written as follows:

$$SA_{om} = f_{om}M_s \frac{1}{\rho_{om}} \frac{1}{t_{om}} = af_{om} \quad (A.2)$$

where a is given by

$$a = M_s \frac{1}{\rho_{om}} \frac{1}{t_{om}} \quad (A.3)$$

Also, the surface area of the exposed (uncoated) mineral surface, $SA_{min,exposed}$ (cm²), can be calculated as follows:

$$SA_{min,exposed} = M_{min} \frac{SA_{min,total}}{M_{min}} b \quad (A.4)$$

where M_{min} is the mass of mineral (g of mineral), $SA_{min,total}$ is the total surface area of pure mineral surface before coating (cm²), and b is the function explaining how the fraction of the exposed mineral surface relative to the total surface area is altered due to the coating by organic matter (i.e., f_{om}).

Since the mass of mineral is equal to the product of the fractional mass of mineral, f_{min} , and M_s (i.e., $M_{min} = f_{min}M_s$), Eq. A.4 can be written as follows:

$$SA_{min,exposed} = f_{min}M_s \frac{SA_{min,total}}{M_{min}} b = cf_{min} \quad (A.5)$$

where c is given by

$$c = M_s \frac{SA_{min,total}}{M_{min}} b \quad (A.6)$$

Note that c is constant at a given f_{om} and independent of the sorbate. Thus, the exposed fraction of mineral surface relative to the total mineral surface area, β_{min} , can be written in terms of f_{om} and f_{min} through the use of Eqs. A.2 and A.5 as follows:

A.3

$$\beta_{\min} = \frac{SA_{\min, \text{exposed}}}{SA_{\min, \text{total}}} = \frac{SA_{\min, \text{exposed}}}{SA_{\min, \text{exposed}} + SA_{\min, \text{covered}}} = \frac{cf_{\min}}{cf_{\min} + af_{\text{om}}} \quad (\text{A.7})$$

where $SA_{\min, \text{covered}}$ is the area of the mineral surface that is blocked (or covered) due to coating by HA (cm^2), and is exactly equivalent to the surface area of organic matter resulting from coating with HA (i.e., $SA_{\min, \text{covered}} = SA_{\text{om}}$).

Finally, $\beta_{\min}$ can be defined using a physical blocking parameter describing the effectiveness of mineral blockage by organic matter, $\omega_{\text{om-min}}$, and the relative amounts by mass of organic matter and mineral in the binary solids as follows:

$$\beta_{\min} = \frac{cf_{\min}}{cf_{\min} + af_{\text{om}}} = \frac{1}{1 + \frac{af_{\text{om}}}{cf_{\min}}} = \frac{1}{1 + \omega_{\text{om-min}} \frac{f_{\text{om}}}{f_{\min}}} \quad (\text{A.8})$$

where

$$\omega_{\text{om-min}} = \frac{a}{c} = \frac{f_{\min}}{f_{\text{om}}} \cdot \frac{SA_{\text{om}}}{SA_{\min, \text{exposed}}} \quad (\text{A.9})$$

Additionally, if R is taken as the ratio of the fraction of organic matter to the fraction of organic carbon (i.e., $R = f_{\text{om}}/f_{\text{oc}}$), Eq. A.8 can be written in terms of f_{oc} as follows:

$$\beta_{min} = \frac{1}{1 + \omega_{om-min} \frac{Rf_{oc}}{f_{min}}} = \frac{1}{1 + \omega_{oc-min} \frac{f_{oc}}{f_{min}}} \quad (\text{A.10})$$

where

$$\omega_{oc-min} = R\omega_{om-min} \quad (\text{A.11})$$

Eq. A.10 is identical to the formula proposed by Karickhoff (1984) and Liljestrand and Shimizu (1991) to describe the blocking effect of mineral surface by amorphous metal oxide or humic substances.

In contrast to the definition for β_{min} given by Eq. A.7, the ordered water immediately adjacent to HA-coating may be different from that of a pure mineral surface due to the disordered transition (see Fig. 2.5c), such that the surface-area-normalized distribution coefficient for the mineral component of the HA-coated sand, $K_{S,c}$, is different from that for the heated sand (i.e., $f_{oc} = 0$), K_S (i.e., $K_{S,c} \neq K_S$). In this case, β_{min} can be defined as follows:

$$\beta_{min} = \frac{SA_{min,exposed} K_{S,c}}{SA_{min,total} K_S} \quad (\text{A.12})$$

Unlike the definition of β_{min} given by Eq. A.7, which is independent of the sorbate, the definition of β_{min} given by Eq. A.12 is a function not only of the sorbent in terms of the ratio of surface areas, $SA_{min,exposed}/SA_{min,total}$, but also of the sorbate in terms of the ratio of surface-area-normalized distribution coefficients, $K_{S,c}/K_S$. In the case where $K_{S,c} = K_S$, the

definition of β_{min} given by Eq. A.12 reduces to that given by Eq. A.7 such that β_{min} is only a physical parameter that is independent of the sorbate, as proposed by Karickhoff (1984) and Liljestrand and Shimizu (1991).

Table A.1 Estimation of thickness of humic acid coating using SEM software (JSM-6500F)

Sorbent	Fraction of Organic Carbon, f_{oc} (%)	Location	Measured Thickness (μm)	Average (μm)
Humic acid-coated sand	0.152	1	0.10	0.08
		2	0.08	
		3	0.06	
	0.119	1	0.10	0.09
		2	0.08	
		3	0.08	
	0.072	1	0.10	0.07
		2	0.07	
		3	0.05	

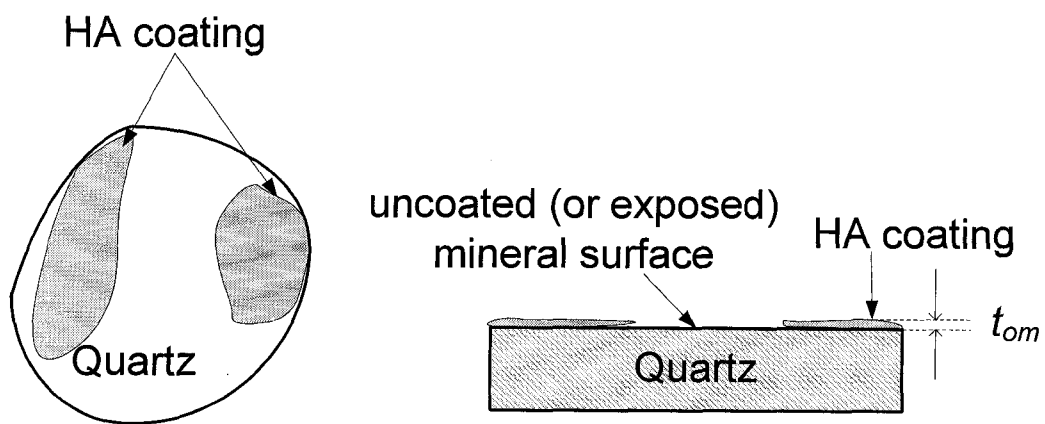


Fig. A.1 The schematic diagram of humic acid (HA)-coated sand

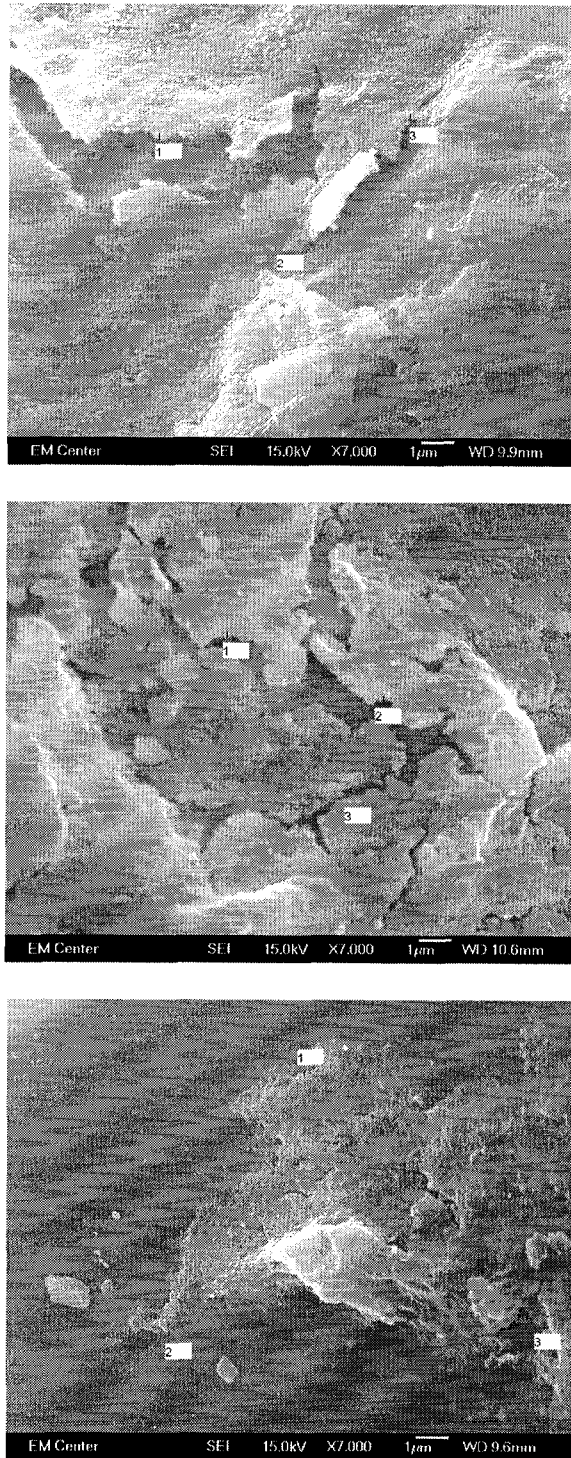
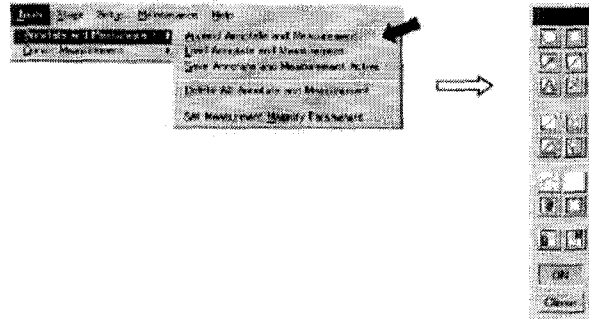


Fig. A.2 Scanning electron microscopic images of humic acid-coated sand indicating the locations at which the thickness of humic acid coating was estimated using SEM software (JSM-6500F): top: $f_{oc} = 0.152\%$; middle: $f_{oc} = 0.119\%$; bottom: $f_{oc} = 0.072\%$.

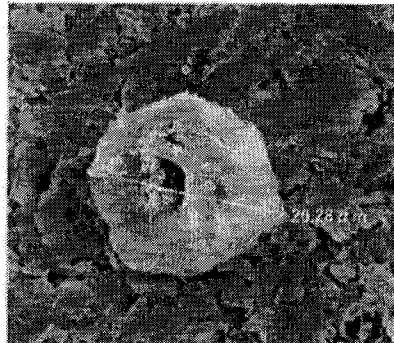
3.12 Measuring Size (Example: Measuring the Distance between Two Points)

1. Select Tools--Annotate and Measurement--Append Annotate and Measurement from the menu bar.

Button with equivalent function:  Append Annotate and Measurement button
The Append Annotate and Measurement tool bar opens.



2. Click the Magnifier Indication button .
The Magnifier Indication button changes to .
3. Click the Distance Measurement button .
4. Move the pointer  to one end of the feature to be measured, drag the pointer to the other end of it, and release the left button of the mouse.
The double-headed arrow cursor and measurement values are shown.



5. Move the pointer  to near one of the heads of the arrow.
The shape of the pointer changes to .
6. Press the left button of the mouse.
The image near the head of the arrow is magnified.
7. Drag the head of the arrow exactly to the end of the feature and release the left button.
The image near the head of the arrow returns to the previous size.
8. Perform the same operation at the other head of the arrow.

Fig. A.3 The procedure for measuring the distance between two points using SEM software (JSM-6500F)

Appendix B. Linear Regression and Correlation

Appendix B.1 The coefficient of determination (r^2)

The coefficient of determination (r^2) is the single most extensively used measure of goodness of fit for regression models (Kvalseth 1985). If the models are only linear with an intercept term (i.e., $y = \beta_0 + \beta_1 x + \varepsilon$), the analyst will not use an inappropriate r^2 statistics and will not end up with possibly misleading results (Montgomery and Peck 1982, Kvalseth 1985). However, if the models are linear with no-intercept term (i.e., $y = \beta_1 x + \varepsilon$), the various r^2 statistics yield different values (e.g., even negative r^2) due to the different definition of r^2 statistics. Additionally, these various r^2 statistics are generally not comparable and may produce misleading results if the analyst fails to realize these differences among r^2 statistics. Thus, care must be taken when various statistics program packages for linear regression are used.

The simple regression model; that is, a model with a single regressor x , and the relationship between the response y and x a straight line. This simple linear regression model is

$$y = \beta_0 + \beta_1 x + \varepsilon \quad (\text{B.1})$$

where the intercept β_0 and the slope β_1 are unknown constants and ε is a random error component. The errors are assumed to have mean zero and unknown variance σ^2 . Since the parameters β_0 and β_1 are unknown and must be estimated using the method of least squares or maximum likelihood (Montgomery and Peck 1982, Myung 2003). For least

square method making the sum of squares of differences between observed y_i and predicted $\hat{y}_i$ a minimum, the fitted or estimated regression line is as follows:

$$\hat{y} = \hat{\beta}_0 + \hat{\beta}_1 x \quad (\text{B.2})$$

where $\hat{\beta}_0$ and $\hat{\beta}_1$ are the least squares estimators of the intercept and the slope, respectively, and $\hat{y}$ is the fitted y value. Note that each pair of observations satisfies the relationship

$$\hat{y}_i = \hat{\beta}_0 + \hat{\beta}_1 x_i + \varepsilon_i, i = 1, 2, \dots, n \quad (\text{B.3})$$

where $\varepsilon_i = y_i - \hat{y}_i$ is called the residual. Residuals play an important role in investigating the adequacy of the fitted regression model and in detecting departures from the underlying assumptions.

A method called the analysis of variance can be used to test for significance of regression. The procedure partitions the total variability in the response variable into meaningful components as the basis for the test. The analysis of variance identity is as follows (Montgomery and Peck 1982, Montgomery and Runger 2003):

$$\sum_{i=1}^n (y_i - \bar{y})^2 = \sum_{i=1}^n (\hat{y}_i - \bar{y})^2 + \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (\text{B.4})$$

where $\bar{y} = (1/n) \sum_{i=1}^n y_i$.

Two components on the right-hand-side of Eq. B.4 measure the amount of variability in y_i accounted for by the regression line and the residual variation left unexplained by the regression line, respectively. Symbolically, Eq. B.4 can be written as

$$SS_{total,corrected} = SS_{regression} + SS_{residual} \quad (B.5)$$

where $SS_{total,corrected}$ is the total corrected sum of squares of y , $SS_{regression}$ is the regression sum of squares, and $SS_{residual}$ is the residual error sum of squares.

The quantity (in general)

$$r_1^2 = \frac{\sum_{i=1}^n (y_i - \bar{y})^2 - \sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} = \frac{SS_{total,corrected} - SS_{residual}}{SS_{total,corrected}} \quad (B.6)$$

is called the coefficient of determination (r^2). Since SS_{total} is a measure of the variability in y without considering the effect of the regressor variable x , and $SS_{residual}$ is a measure of the variability in y remaining after x has been considered, r^2 is often called the proportion of variation explained (PVE) by the regressor x (Montgomery and Peck 1982, Montgomery and Runger 2003).

Since the sum of squared residuals ($SS_{residual}$) is greater than total sum of square ($SS_{total,corrected}$) for TOL and BZ in Fig. 2.19a, r_1^2 is negative, indicating that simple linear

regression through the origin fits the data worse than a horizontal line at the mean K_d value (Kvalseth 1985). This finding suggests that simple linear regression through the origin is a totally inappropriate least squares regression model since y -intercept is fixed to an inappropriate constant value. Instead of using ambiguous and negative r^2 values, Montgomery and Peck (1982) proposed the alternative r^2 statistics that yield different positive r^2 values for linear no-intercept regression by using $SS_{total,uncorrected}$ (i.e., $\sum_{i=1}^n (y_i)^2$) about the origin as follows:

$$r_2^2 = \frac{\sum_{i=1}^n (y_i)^2 - \sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i)^2} = \frac{SS_{total,uncorrected} - SS_{residual}}{SS_{total,uncorrected}} \quad (B.7)$$

Although r_1^2 for linear model with an intercept is the proportion of variability, observed by the sum of squares about the mean $\bar{y}$, accounted for by regression, r_2^2 for linear model with no intercept measures the proportion of variability in the y 's about the origin explained by regression.

However, r_1^2 for linear model with an intercept is calculated differently from r_2^2 for linear model with no intercept such that two r^2 values should not be directly compared. Thus, in this study, only r_1^2 for linear regression with an intercept (i.e., $SS_{total,corrected}$ about the mean $\bar{y}$, $\sum_{i=1}^n (y_i - \bar{y})^2$) is utilized for comparison.

To exemplify the differences between r_1^2 and r_2^2 , one set of data (i.e., BZ sorption to HA-coated sand in Fig. 2.19a) was used. The observed and predicted values of y (i.e.,

K_d) at each value of x (i.e., f_{oc}), along with $SS_{total,corrected}$, $SS_{total,uncorrected}$ and $SS_{residual}$ are presented in Table B.1. Using the values of $SS_{total,corrected}$, $SS_{total,uncorrected}$ and $SS_{residual}$ given in Table B.1, the values of r_1^2 and r_2^2 can be calculated.

The value of r_1^2 for model with an intercept can be calculated as follows:

$$r_1^2 = \frac{\sum_{i=1}^n (y_i - \bar{y})^2 - \sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} = \frac{(0.02265 - 0.21067)}{0.02265} = -8.30 \quad (B.8)$$

This r_1^2 is identical to those from output of Microsoft Excel and Tablecurve 2-D software using linear model forcing through the origin. On the other hand, the value of r_2^2 for linear model forcing through the origin, using identical data set, can be calculated as follows:

$$r_2^2 = \frac{\sum_{i=1}^n (y_i)^2 - \sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i)^2} = \frac{(0.97274 - 0.21067)}{0.97274} = 0.783 \quad (B.9)$$

This r_2^2 is identical to that from output of SAS software using the REG procedure with noint option. Montgomery and Peck (1982) and Kvalseth (1985) has proposed that r_2^2 should be used for linear model with no intercept while r_1^2 should be used for linear model with an intercept. However, these two r^2 statistics are not generally comparable

and may, if the analyst fails to realize this difference, produce misleading results, as illustrated by a proceeding example. Thus, in this study, only r_1^2 for linear regression with intercepts (i.e., $SS_{total,corrected}$ about the mean $\bar{y}$, $\sum_{i=1}^n (y_i - \bar{y})^2$) is utilized for comparison. The SAS input source code and output results for linear model with no intercept are displayed in Appendices B.2 and B.3, respectively.

Table B.1 The observed and predicted values of K_d at each value of f_{oc} , along with $SS_{total,corrected}$, $SS_{residual}$, and $SS_{total,uncorrected}$

	x	y	$\hat{y}$	$\varepsilon_i = y_i - \hat{y}_i$	$(y_i - \bar{y})^2$	$(y_i - \hat{y}_i)^2$	$(y_i)^2$
1	0.00005	0.17500	0.01024	0.16476	0.00057	0.027147	0.03063
2	0.00005	0.15500	0.01024	0.14476	0.00193	0.020956	0.02403
3	0.00006	0.15700	0.01229	0.14471	0.00176	0.020942	0.02465
4	0.00006	0.18100	0.01229	0.16871	0.00032	0.028465	0.03276
5	0.00023	0.16913	0.04709	0.12204	0.00089	0.014893	0.02860
6	0.00023	0.16603	0.04709	0.11894	0.00108	0.014146	0.02757
7	0.00024	0.17407	0.04914	0.12493	0.00062	0.015607	0.03030
8	0.00026	0.17410	0.05324	0.12086	0.00062	0.014608	0.03031
9	0.00048	0.17774	0.09828	0.07946	0.00045	0.006313	0.03159
10	0.00051	0.18362	0.10443	0.07919	0.00024	0.006271	0.03372
11	0.00051	0.17932	0.10443	0.07489	0.00039	0.005609	0.03216
12	0.00053	0.18726	0.10852	0.07874	0.00014	0.006200	0.03507
13	0.00071	0.18686	0.14538	0.04148	0.00015	0.001721	0.03492
14	0.00071	0.18851	0.14538	0.04313	0.00011	0.001860	0.03554
15	0.00072	0.20548	0.14743	0.05805	0.00004	0.003370	0.04222
16	0.00072	0.20537	0.14743	0.05794	0.00004	0.003357	0.04218
17	0.00116	0.22635	0.23752	-0.01117	0.00075	0.000125	0.05123
18	0.00118	0.22452	0.24162	-0.01710	0.00065	0.000292	0.05041
19	0.00119	0.24237	0.24366	-0.00129	0.00188	0.000002	0.05874
20	0.00122	0.24744	0.24981	-0.00237	0.00235	0.000006	0.06123
21	0.00148	0.23395	0.30304	-0.06909	0.00122	0.004774	0.05473
22	0.00152	0.24053	0.31124	-0.07071	0.00173	0.004999	0.05785
23	0.00153	0.24285	0.31328	-0.07043	0.00193	0.004961	0.05898
24	0.00154	0.25168	0.31533	-0.06365	0.00278	0.004051	0.06334
Average	0.00070	0.19897	0.14410	0.05487	0.00094	0.00878	0.04053
$\sum_{i=1}^n ()$	0.01689	4.77518	3.45840	1.31678	0.02265	0.21067	0.97274

Appendix B.2 SAS input source code of the REG procedure for least square estimation of the parameters

```
option ls=74 ps=50 nodate;
goptions hpos=60 vpos=20;
data BZ;
    input x y;
cards;
0.00005      0.17500
0.00005      0.15500
0.00006      0.15700
0.00006      0.18100
0.00023      0.16913
0.00023      0.16603
0.00024      0.17407
0.00026      0.17410
0.00048      0.17774
0.00051      0.18362
0.00051      0.17932
0.00053      0.18726
0.00071      0.18686
0.00071      0.18851
0.00072      0.20548
0.00072      0.20537
0.00116      0.22635
0.00118      0.22452
0.00119      0.24237
0.00122      0.24744
0.00148      0.23395
0.00152      0.24053
0.00153      0.24285
0.00154      0.25168
;
proc means;
    var x y;
proc gplot;
    plot y*x;
proc reg;
    model: model y=x/noint;
    plot y*x;
    plot r.*p.;
run;
```

Appendix B.3 SAS output results from the REG procedure for least square estimation of the parameters

The SAS System						2
The REG Procedure						
Model: model						
Dependent Variable: y						
Number of Observations Read						24
Number of Observations Used						24
NOTE: No intercept in model. R-Square is redefined.						
Analysis of Variance						
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F	
Model	1	0.76207	0.76207	83.20	<.0001	
Error	23	0.21067	0.00916			
Uncorrected Total	24	0.97274				
Root MSE		0.09571	R-Square	0.7834		
Dependent Mean		0.19897	Adj R-Sq	0.7740		
Coeff Var		48.10192				
Parameter Estimates						
Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > t	
x	1	204.76425	22.44904	9.12	<.0001	

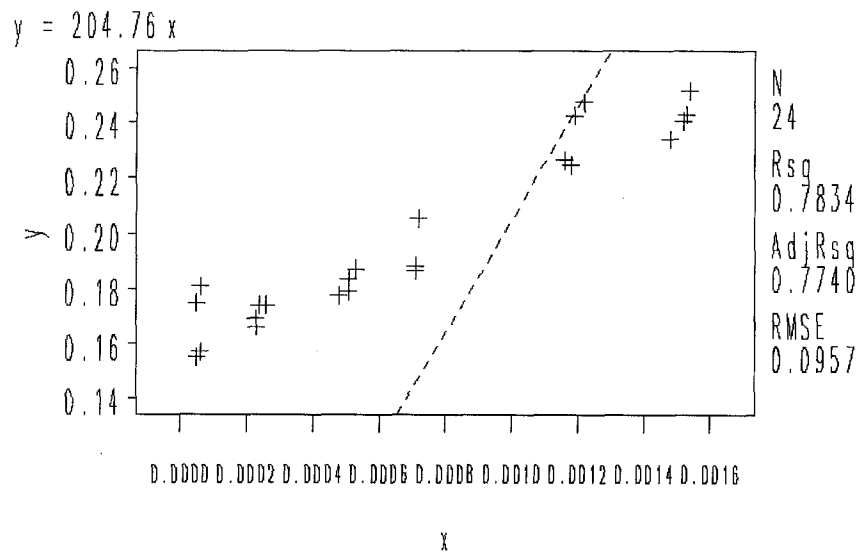


Fig. B.1 Scatter plot of K_d versus f_{oc} and regression model from SAS software

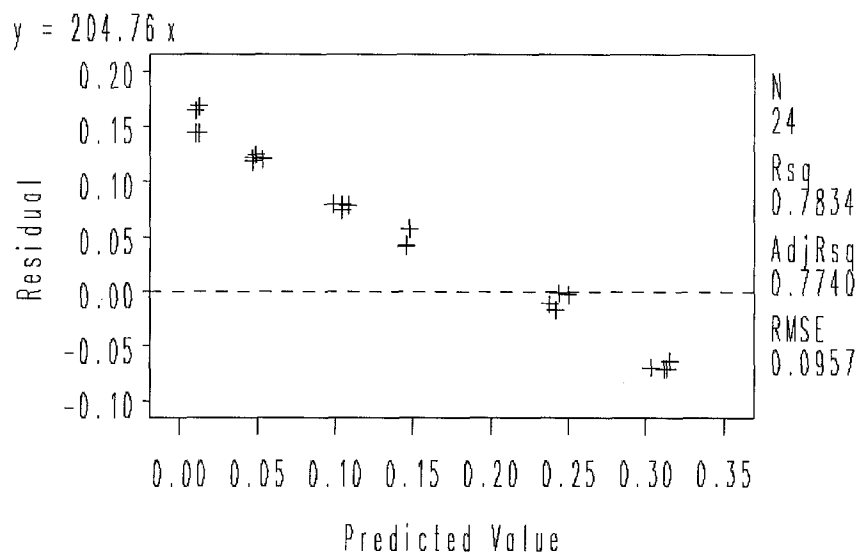


Fig. B.2 Plot of residuals versus predicted K_d from SAS software

Appendix B.4 Maximum likelihood estimation of the parameters

Since the method of least square used to estimate the parameters in a linear regression model produced the ambiguous and negative r_1^2 values for TOL and BZ in Fig. 2.16a, an alternative method of parameter estimation, the method of maximum likelihood, was used to discriminate between models. Unlike the least-square estimation which is a primarily a descriptive tool applying linear regression models, maximum likelihood estimation is a preferred method of parameter estimation for many statistical modeling technique due to the sufficiency, consistency, efficiency, and parameter invariance (Montgomery and Peck 1982, Myung 2003).

If the observations y_i in the data set are normally and independently distributed random variables with mean $\beta_0 + \beta_1 x_i$ and variance σ^2 , the likelihood function is found from the joint distribution of the observations. If we consider this joint distribution with the observations given and the parameters β_0 , β_1 , and σ^2 unknown constants, the likelihood function can be obtained. For the simple linear regression model with normal errors, the likelihood function is

$$\begin{aligned} L(y_i, x_i, \beta_0, \beta_1, \sigma^2) &= \prod_{i=1}^n (2\pi\sigma^2)^{-1/2} \exp\left[-\frac{1}{2\sigma^2}(y_i - \beta_0 - \beta_1 x_i)^2\right] \\ &= (2\pi\sigma^2)^{-n/2} \exp\left[-\frac{1}{2\sigma^2} \sum_{i=1}^n (y_i - \beta_0 - \beta_1 x_i)^2\right] \end{aligned} \quad (\text{B.10})$$

The maximum likelihood estimators are the parameters values that maximize L , or equivalently, $\ln L$. Thus,

$$\ln L(y_i, x_i, \beta_0, \beta_1, \sigma^2) = -\left(\frac{n}{2}\right) \ln(2\pi) - \left(\frac{n}{2}\right) \ln \sigma^2 - \left(\frac{1}{2\sigma^2}\right) \sum_{i=1}^n (y_i - \beta_0 - \beta_1 x_i)^2 \quad (\text{B.11})$$

Note that the maximum likelihood estimators of the intercept and slope are identical to the least squares estimators of these parameters. The SAS input source code and output results for the method of maximum likelihood are displayed in Appendices B.5 and B.6, respectively.

Appendix B.5 SAS input source code for the GENMODE procedure for maximum likelihood estimation of the parameters

```
option ls=74 ps=50 nodate;
goptions hpos=60 vpos=20;
data BZ;
    input x y;
datalines;
0.00024    0.17407
0.00023    0.16913
0.00023    0.16603
0.00026    0.1741
0.00048    0.17774
0.00051    0.18362
0.00051    0.17932
0.00053    0.18726
0.00071    0.18686
0.00072    0.20548
0.00072    0.20537
0.00071    0.18851
0.00122    0.24744
0.00119    0.24237
0.00116    0.22635
0.00118    0.22452
0.00154    0.25168
0.00153    0.24285
0.00152    0.24053
0.00148    0.23395
5.00E-05    0.175
5.00E-05    0.155
6.00E-05    0.157
6.00E-05    0.181
;
run;
proc gplot;
    plot y*x;
proc genmod data=BZ;
    model y=x/ dist = normal;
    output out      = Residuals
           pred     = Pred
           resraw   = Resraw
           reschi   = Reschi
           resdev   = Resdev
           stdreschi = Stdreschi
           stdresdev = Stdresdev
           reslik   = Reslik;
run;
```

Appendix B.6 SAS output results for the GENMODE procedure for maximum likelihood estimation of the parameters

The SAS System

3

The GENMOD Procedure

Model Information

Data Set	WORK.BZ
Distribution	Normal
Link Function	Identity
Dependent Variable	y

Number of Observations Read	24
Number of Observations Used	24

Criteria For Assessing Goodness Of Fit

Criterion	DF	Value	Value/DF
Deviance	22	0.0019	0.0001
Scaled Deviance	22	24.0000	1.0909
Pearson Chi-Square	22	0.0019	0.0001
Scaled Pearson X2	22	24.0000	1.0909
Log Likelihood		79.2386	

Algorithm converged.

Analysis Of Parameter Estimates

Parameter	DF	Estimate	Standard Error	Wald 95% Confidence Limits	Chi-Square	Pr > ChiSq
Intercept	1	0.1586	0.0031	0.1525 0.1646	2629.54	<.0001
x	1	57.4257	3.5530	50.4620 64.3895	261.23	<.0001
Scale	1	0.0089	0.0013	0.0067 0.0118		

NOTE: The scale parameter was estimated by maximum likelihood.

Appendix C. Multiple Comparison with Tukey-Cramer Method for Blocking Effect

Appendix C. 1 SAS input source code of the GLM procedure for multiple comparison with Tukey-Cramer method

```
options nodate ps=40 ls=73;
goptions hpos=80 vpos=30 cback=white colors=(black);
data NOCs;
input NOCs $ foc psi;
cards;
TCB 0.00024011      1.0678
TCB 0.00023010      1.0635
TCB 0.00023010      1.1100
TCB 0.00026013      1.1623
TCB 0.00048044      1.1129
TCB 0.00051049      1.1035
TCB 0.00051049      1.0905
TCB 0.00053053      1.1807
TCB 0.00071096      1.1179
TCB 0.00072098      1.1540
TCB 0.00072098      1.1476
TCB 0.00071096      1.1352
TCB 0.0012228       1.2892
TCB 0.0011927       1.1758
TCB 0.0011626       1.1459
TCB 0.0011826       1.2223
TCB 0.0015445       1.2739
TCB 0.0015344       1.2329
TCB 0.0015244       1.2528
TCB 0.0014842       1.2689
DCB 0.00024011      1.0345
DCB 0.0002301       1.0541
DCB 0.0002301       1.0724
DCB 0.00026013      1.0885
DCB 0.00048044      1.1172
DCB 0.00051049      1.0895
DCB 0.00051049      1.1125
DCB 0.00053053      1.0719
DCB 0.00071096      1.1155
DCB 0.00072098      1.1164
DCB 0.00072098      1.1162
DCB 0.00071096      1.0722
DCB 0.0012228       1.1546
DCB 0.0011927       1.2145
DCB 0.0011626       1.1493
DCB 0.0011826       1.1778
DCB 0.0015445       1.2387
DCB 0.0015344       1.2326
DCB 0.0015244       1.2052
DCB 0.0014842       1.1618
CB 0.00048044       1.0606
CB 0.00051049       1.0518
CB 0.00051049       1.051
CB 0.00053053       1.0568
```

CB 0.00071096	1.0763
CB 0.00072098	1.0309
CB 0.00072098	1.0579
CB 0.00071096	1.0758
CB 0.0012228	1.137
CB 0.0011927	1.1254
CB 0.0011626	1.1139
CB 0.0011826	1.0971
CB 0.0015445	1.1343
CB 0.0015344	1.1158
CB 0.0015244	1.1212
CB 0.0014842	1.1209
CB 5.00E-05	1.0125
CB 5.00E-05	0.96084
CB 6.00E-05	1.0052
CB 6.00E-05	1.0084
XYL 0.00048044	1.0632
XYL 0.00051049	1.0611
XYL 0.00051049	1.0389
XYL 0.00053053	1.0295
XYL 0.00071096	1.1001
XYL 0.00072098	1.0721
XYL 0.00072098	1.0424
XYL 0.00071096	1.0566
XYL 0.0012228	1.1241
XYL 0.0011927	1.1064
XYL 0.0011626	1.1054
XYL 0.0011826	1.1187
XYL 0.0015445	1.1583
XYL 0.0015344	1.1717
XYL 0.0015244	1.1279
XYL 0.0014842	1.1572
XYL 5.0005e-05	1.0053
XYL 5.0005e-05	1.0080
XYL 6.0007e-05	1.0061
XYL 6.0007e-05	1.0084
TOL 0.00048044	1.0514
TOL 0.00051049	1.0693
TOL 0.00051049	1.053
TOL 0.00053053	1.0397
TOL 0.00071096	1.082
TOL 0.00072098	1.0705
TOL 0.00072098	1.0677
TOL 0.00071096	1.0745
TOL 0.0012228	1.0851
TOL 0.0011927	1.1235
TOL 0.0011626	1.1246
TOL 0.0011826	1.1052
TOL 0.0015445	1.1376
TOL 0.0015344	1.1371
TOL 0.0015244	1.1647
TOL 0.0014842	1.1685
TOL 5.00E-05	1.0087
TOL 5.00E-05	1.0075
TOL 6.00E-05	1.0132
TOL 6.00E-05	1.0163
BZ 0.00024011	1.0355

```

BZ 0.0002301      1.0645
BZ 0.0002301      1.0261
BZ 0.00026013     1.0428
BZ 0.00048044     1.052
BZ 0.00051049     1.0754
BZ 0.00051049     1.0624
BZ 0.00053053     1.0583
BZ 0.00071096     1.0814
BZ 0.00072098     1.0415
BZ 0.00072098     1.0422
BZ 0.00071096     1.072
BZ 0.0012228      1.1003
BZ 0.0011927      1.1024
BZ 0.0011626      1.1139
BZ 0.0011826      1.135
BZ 0.0015445      1.1582
BZ 0.0015344      1.1468
BZ 0.0015244      1.1574
BZ 0.0014842      1.194
;
proc means mean std;
                                var foc psi;
                                class NOCs;

proc gplot;
                                plot psi*foc=NOCs;
                                symbol1 v='A' i=rl l=1;
                                symbol2 v='B' i=rl l=2;
                                symbol3 v='C' i=rl l=3;
                                symbol4 v='D' i=rl l=4;
                                symbol5 v='E' i=rl l=5;
                                symbol6 v='F' i=rl l=6;

proc glm;
                                class NOCs;
                                model psi=foc;

proc glm;
                                class NOCs;
                                model psi=foc NOCs NOCs*foc;

proc glm;
                                class NOCs;
                                model psi=foc NOCs / solution clm;
                                lsmeans NOCs/ pdiff cl;
                                lsmeans NOCs/ pdiff cl adj=tukey;
                                output out=out1 predicted=predpsi;

proc gplot data=put1;
                                plot predpsi*foc=NOCs;
                                symbol1 v='A' i=rl l=1;
                                symbol2 v='B' i=rl l=2;
                                symbol3 v='C' i=rl l=3;
                                symbol4 v='D' i=rl l=4;
                                symbol5 v='E' i=rl l=5;
                                symbol6 v='F' i=rl l=6;

run;

```

Appendix C.2 SAS output results of the GLM procedure for multiple comparison with Tukey-Cramer method

```

The SAS System
3

The GLM Procedure

Dependent Variable: psi

Source              DF          Sum of
                    Squares    Mean Square  F Value  Pr > F
Model                1      0.30825173      0.30825173   191.11  <.0001
Error              118      0.19032528      0.00161293
Corrected Total    119      0.49857701

R-Square      Coeff Var      Root MSE      psi Mean
0.618263      3.644390      0.040161      1.102002

Source              DF      Type I SS    Mean Square  F Value  Pr > F
foc                 1      0.30825173      0.30825173   191.11  <.0001

Source              DF      Type III SS   Mean Square  F Value  Pr > F
foc                 1      0.30825173      0.30825173   191.11  <.0001

```


The GLM Procedure
Least Squares Means
Adjustment for Multiple Comparisons: Tukey-Kramer

NOCs	psi LSMEAN	LSMEAN Number
BZ	1.08622398	1
CB	1.07256306	2
DCB	1.12788898	3
TCB	1.16349898	4
TOL	1.08188606	5
XYL	1.07995093	6

Least Squares Means for effect NOCs
Pr > |t| for H0: LSMean(i)=LSMean(j)

Dependent Variable: psi

i/j	1	2	3	4	5	6
1		0.4352	<.0001	<.0001	0.9916	0.9569
2	0.4352		<.0001	<.0001	0.8026	0.9159
3	<.0001	<.0001		<.0001	<.0001	<.0001
4	<.0001	<.0001	<.0001		<.0001	<.0001
5	0.9916	0.8026	<.0001	<.0001		0.9998
6	0.9569	0.9159	<.0001	<.0001	0.9998	

NOCs	psi LSMEAN	95% Confidence Limits		
BZ	1.086224	1.075909	1.096539	
CB	1.072563	1.062248	1.082878	
DCB	1.127889	1.117574	1.138204	
TCB	1.163499	1.153184	1.173814	
TOL	1.081886	1.071571	1.092201	
XYL		1.079951	1.069636	1.090266

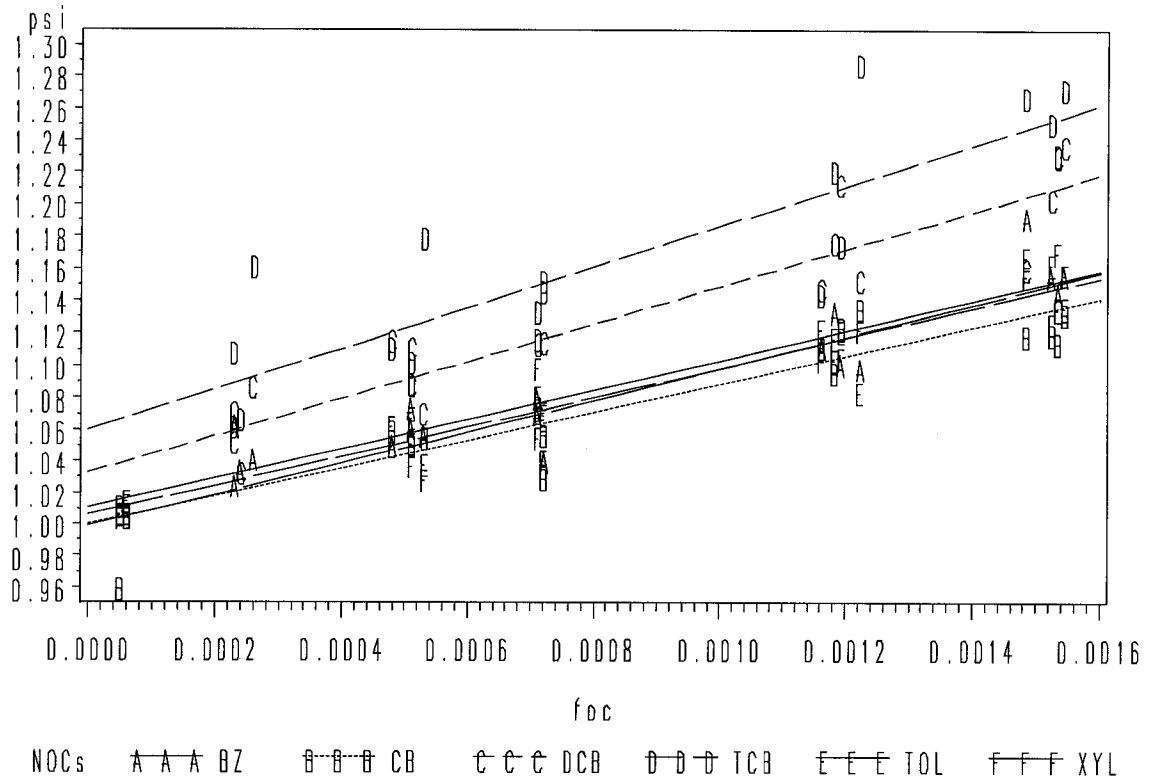


Fig. C.1 Scatter plot of f_{oc}/f_{min} versus ψ and least-square linear regression model from SAS software

Appendix D. Multiple Comparison with Tukey-Cramer Method for Mineral Surfaces

Appendix D. 1 SAS input source code of the GLM procedure for multiple comparison with Tukey-Cramer method

```
options nodate ps=40 ls=73;
goptions hpos=80 vpos=30 cback=white colors=(black);
data sorbents;
input sorbents $ rw Kd;
cards;
untreated 5.5079 -3.9959
untreated 5.2218 -4.0677
untreated 4.5615 -4.0325
untreated 4.0971 -4.0645
untreated 3.9974 -4.0779
untreated 3.387 -4.0761
heated 5.5079 -3.9953
heated 5.2218 -4.0349
heated 4.5615 -4.0356
heated 4.0971 -4.0838
heated 3.9974 -4.0687
heated 3.387 -4.0779
Fe(OH)3 5.5079 -3.829
Fe(OH)3 5.2218 -3.9217
Fe(OH)3 4.5615 -4.0015
Fe(OH)3 4.0971 -4.0558
Fe(OH)3 3.9974 -4.0902
Fe(OH)3 3.387 -4.1085
Al(OH)3 5.5079 -3.8049
Al(OH)3 5.2218 -3.8981
Al(OH)3 4.5615 -3.9265
Al(OH)3 4.0971 -3.964
Al(OH)3 3.9974 -3.9897
Al(OH)3 3.387 -4.0333
;
proc means mean std;
var rw Kd;
class sorbents;

proc gplot;
plot Kd*rw=sorbents;
symbol1 v='A' i=rl l=1;
symbol2 v='B' i=rl l=2;
symbol3 v='C' i=rl l=3;
symbol4 v='D' i=rl l=4;

proc glm;
class sorbents;
model Kd=rw;

proc glm;
class sorbents;
model Kd=rw sorbents sorbents*rw;

proc glm;
class sorbents;
```

```

model Kd=rw sorbents / solution clm;
lsmeans sorbents/ pdiff cl;
lsmeans sorbents/ pdiff cl adj=tukey;
output out=out1 predicted=pred_Kd;

proc gplot data=put1;

plot pred_Kd*rw=sorbents;
symbol1 v='A' i=rl l=1;
symbol2 v='B' i=rl l=2;
symbol3 v='C' i=rl l=3;
symbol4 v='D' i=rl l=4;

run;

```

Appendix D.2 SAS output results of the GLM procedure for multiple comparison with Tukey-Cramer method

The SAS System

3

The GLM Procedure

Dependent Variable: Kd

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.06875745	0.06875745	17.65	0.0004
Error	22	0.08571219	0.00389601		
Corrected Total	23	0.15446964			

R-Square	Coeff Var	Root MSE	Kd Mean
0.445119	-1.556656	0.062418	-4.009750

Source	DF	Type I SS	Mean Square	F Value	Pr > F
rw	1	0.06875745	0.06875745	17.65	0.0004

Source	DF	Type III SS	Mean Square	F Value	Pr > F
rw	1	0.06875745	0.06875745	17.65	0.0004

D.3

The GLM Procedure
Least Squares Means
Adjustment for Multiple Comparisons: Tukey

sorbents	Kd LSMEAN	LSMEAN Number
Al(OH)3	-3.93608333	1
Fe(OH)3	-4.00111667	2
heated	-4.04936667	3
untreate	-4.05243333	4

Least Squares Means for effect sorbents
Pr > |t| for H0: LSMean(i)=LSMean(j)

Dependent Variable: Kd

i/j	1	2	3	4
1		0.0590	0.0007	0.0006
2	0.0590		0.2139	0.1723
3	0.0007	0.2139		0.9992
4	0.0006	0.1723	0.9992	

sorbents	Kd LSMEAN	95% Confidence Limits	
Al(OH)3	-3.936083	-3.971345	-3.900822
Fe(OH)3	-4.001117	-4.036378	-3.965855
heated	-4.049367	-4.084628	-4.014105
untreate	-4.052433	-4.087695	-4.017172

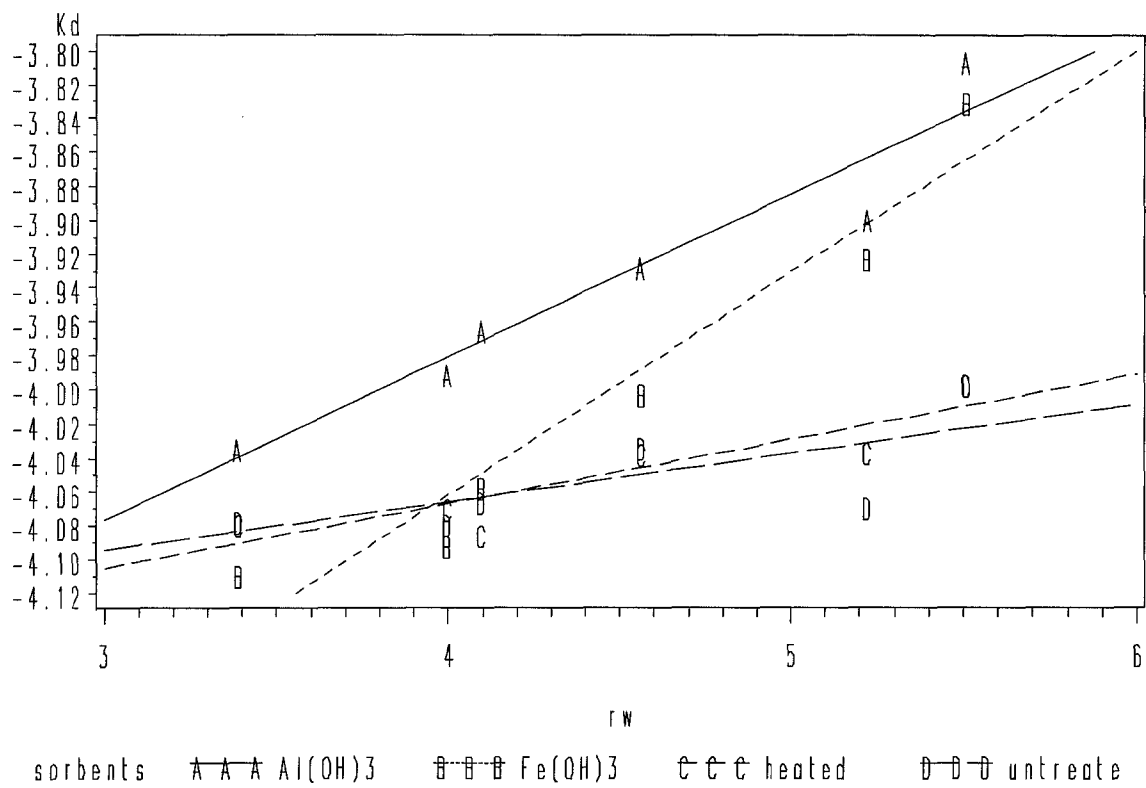


Fig. D.1 Scatter plot of γ_w^{sat} versus K_S and least-square linear regression model from SAS software

Appendix E. Multiple Comparison with Dunnett's procedure

Appendix E. 1 SAS input source code of the GLM procedure for multiple comparison of K_f values with Dunnett's procedure

```
data test;
    input trt $ kf;
    cards;
s      0.361
s      0.265
s      0.271
s      0.323
t1     0.221
t1     0.265
t1     0.178
t5     0.202
t5     0.242
t5     0.162
t6     0.305
t6     0.366
t6     0.254
t7     0.293
t7     0.352
t7     0.234
t8     0.263
t8     0.315
t8     0.227
t9     0.255
t9     0.301
t9     0.209
;
run;

proc glm data=test;
    class trt;
    model kf=trt;
    lsmeans trt/ adjust=dunnett cl pdiff=control('s'); * defines control
level as 's' level ;
run;
```


Appendix E.2 SAS output results of the GLM procedure for multiple comparison of K_f values with Dunnett's procedure

2007 3

The SAS System

11:52 Thursday, August 2,

The GLM Procedure
Least Squares Means
Adjustment for Multiple Comparisons: Dunnett

trt	kf LSMEAN	H0:LSMean=Control Pr > t
s	0.30500000	
t1	0.22133333	0.1599
t5	0.20200000	0.0614
t6	0.30833333	1.0000
t7	0.29300000	0.9992
t8	0.26833333	0.8382
t9	0.25500000	0.6087

trt	kf LSMEAN	95% Confidence Limits	
s	0.305000	0.253817	0.356183
t1	0.221333	0.162232	0.280434
t5	0.202000	0.142899	0.261101
t6	0.308333	0.249232	0.367434
t7	0.293000	0.233899	0.352101
t8	0.268333	0.209232	0.327434
t9	0.255000	0.195899	0.314101

Least Squares Means for Effect trt

i	j	Difference Between Means	Simultaneous 95% Confidence Limits for LSMean(i)-LSMean(j)	
2	1	-0.083667	-0.190645	0.023312
3	1	-0.103000	-0.209978	0.003978
4	1	0.003333	-0.103645	0.110312
5	1	-0.012000	-0.118978	0.094978
6	1	-0.036667	-0.143645	0.070312
7	1	-0.050000	-0.156978	0.056978

Appendix E. 3 SAS input source code of the GLM procedure for multiple comparison of n values with Dunnett's procedure

```
data test;
  input trt $ n;
  cards;
s      0.869
s      0.953
s      0.947
s      0.904
t1     0.983
t1     1.08
t1     0.895
t5     0.996
t5     0.896
t5     0.915
t6     0.945
t6     0.895
t6     0.915
t7     0.939
t7     0.953
t7     0.895
t8     0.971
t8     0.890
t8     0.957
t9     0.915
t9     0.965
t9     0.993
;
run;

proc glm data=test;
  class trt;
  model n=trt;
  lsmeans trt/ adjust=dunnett cl pdiff=control('s'); * defines control
level as 'a' level ;
run;
```

Appendix E.4 SAS output results of the GLM procedure for multiple comparison of n values with Dunnett's procedure

2007 6

The SAS System

11:52 Thursday, August 2,

The GLM Procedure
Least Squares Means
Adjustment for Multiple Comparisons: Dunnett

trt	n LSMEAN	H0:LSMean=Control Pr > t
s	0.91825000	
t1	0.98600000	0.3583
t5	0.93566667	0.9949
t6	0.91833333	1.0000
t7	0.92900000	0.9996
t8	0.93933333	0.9866
t9	0.95766667	0.8192

trt	n LSMEAN	95% Confidence Limits	
s	0.918250	0.865035	0.971465
t1	0.986000	0.924553	1.047447
t5	0.935667	0.874220	0.997114
t6	0.918333	0.856886	0.979780
t7	0.929000	0.867553	0.990447
t8	0.939333	0.877886	1.000780
t9	0.957667	0.896220	1.019114

Least Squares Means for Effect trt

i	j	Difference Between Means	Simultaneous 95% Confidence Limits for LSMean(i)-LSMean(j)	
2	1	0.067750	-0.043475	0.178975
3	1	0.017417	-0.093808	0.128642
4	1	0.000083333	-0.111142	0.111308
5	1	0.010750	-0.100475	0.121975
6	1	0.021083	-0.090142	0.132308
7	1	0.039417	-0.071808	0.150642

Appendix F. Cluster Analysis

Appendix F.1 SAS input source code of the Cluster procedure

```
Title1'Dendrogram of Ward method from BESTs_HA1 (foc=0.051%)_test1';
Title2'Normalized Freundlich Sorption Parameters of Mixtures for HA-
Coated Sand';

options ps=60 nodate;
data lumps;
input compounds $ Kf      n @@;
datalines;
Benzene      0.20581      0.95387
Toluene      0.28432      0.94328
m-Xylene     0.36182      0.95346
Chlorobz     0.33646      0.93439
Dichlobz     0.42597      0.99256
Trichlbz     0.93175      0.99716
Acetone      0.10478      0.69164
Butanone     0.073942     0.69472
Hexanone     0.053814     0.8891
Phenol       0.036604     0.83207
p-Cresol     0.055043     0.88621
DimethPh     0.073275     0.91702
;
proc cluster data=lumps method=ward std ccc pseudo simple
    outtree=lumptree;
    var kf n;
    id compounds;
run;
    goptions vsize=10 in htext=1.5pct htitle=3.0pct;
proc tree data=lumptree out=new nclusters=2;
    copy kf n;
    id compounds;
run;
proc tree data=lumptree out=new nclusters=4 horizontal spaces=4;
    copy kf n;
    id compounds;
run;
legend1 frame cframe=white cborder=black
    position=center value=(justify=center);
axis1 label=(angle=90 rotate=0) minor=none order=(0.5 to 1.1 by 0.1);
axis2 minor=none order=(0 to 1.1 by 0.1);
proc gplot data=new;
    plot n*kf=cluster/frame cframe=white
        legend=legend1 vaxis=axis1 haxis=axis2;
        symbol1 c=black v=circle l=2;
        symbol2 c=black v=square l=2;
        symbol3 c=black v=diamond l=2;
        symbol4 c=black v=triangle l=2;
        title4 "Plot of number of clusters from Ward
method";
run;
```

Appendix F.2 SAS output results of the Cluster procedure

Dendrogram of Ward method from BESTs_HA1 (foc=0.051%)_test1
Normalized Freundlich Sorption Parameters of Mixtures for HA-Coated Sand

1

The CLUSTER Procedure Ward's Minimum Variance Cluster Analysis

Variable	Mean	Std Dev	Skewness	Kurtosis	Bimodality
Kf	0.2453	0.2565	1.9113	4.3358	0.5560
n	0.8905	0.1029	-1.2534	0.6368	0.5505

Eigenvalues of the Correlation Matrix

	Eigenvalue	Difference	Proportion	Cumulative
1	1.59487971	1.18975942	0.7974	0.7974
2	0.40512029		0.2026	1.0000

The data have been standardized to mean 0 and variance 1
Root-Mean-Square Total-Sample Standard Deviation = 1
Root-Mean-Square Distance Between Observations = 2

Cluster History

NCL	Clusters	Joined--	FREQ	SPRSQ	RSQ	ERSQ	CCC	PSF	PST2	T i e
11	Hexanone	p-Cresol	2	0.0000	1.00	.	.	5421	.	.
10	Acetone	Butanone	2	0.0003	1.00	.	.	605	.	.
9	m-Xylene	Chlorobz	2	0.0010	.999	.	.	273	.	.
8	Toluene	CL9	3	0.0019	.997	.	.	172	1.9	.
7	CL11	DimethPh	3	0.0026	.994	.	.	140	143	.
6	Benzene	CL8	4	0.0080	.986	.	.	84.9	5.5	.
5	CL7	Phenol	4	0.0141	.972	.	.	60.7	10.6	.
4	CL6	Dichlobz	5	0.0165	.955	.	.	57.2	4.5	.
3	CL4	CL5	9	0.1632	.792	.	.	17.2	25.9	.
2	CL3	Trichlbz	10	0.3511	.441	.669	-2.1	7.9	13.5	.
1	CL2	CL10	12	0.4412	.000	.000	0.00	.	7.9	.

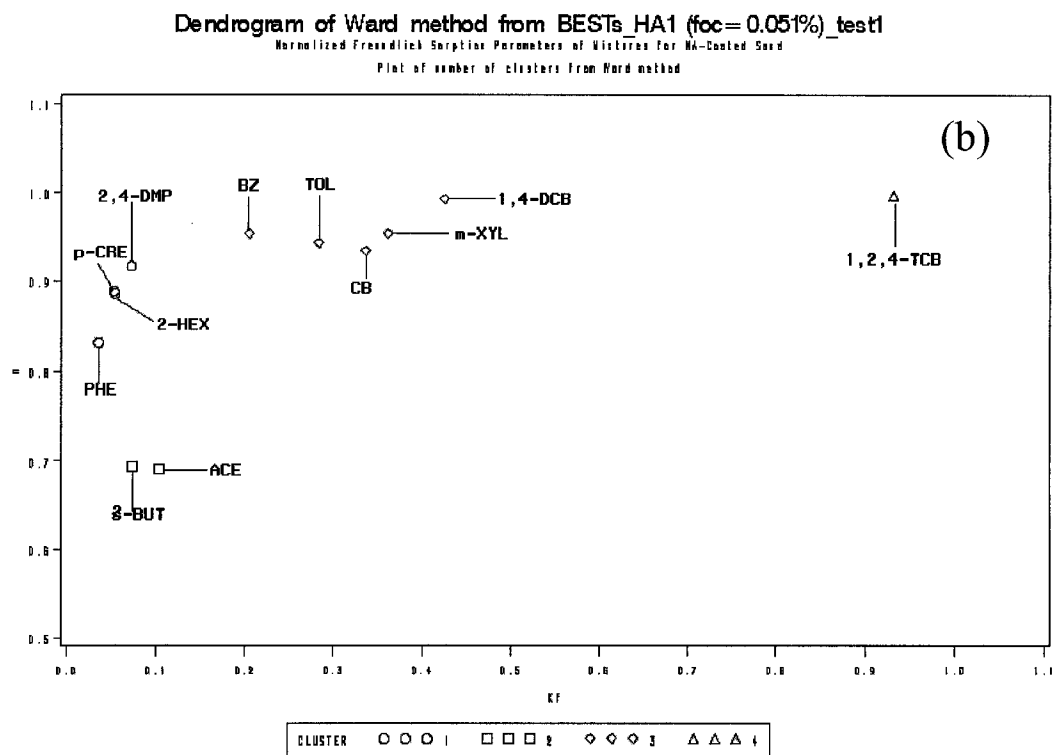
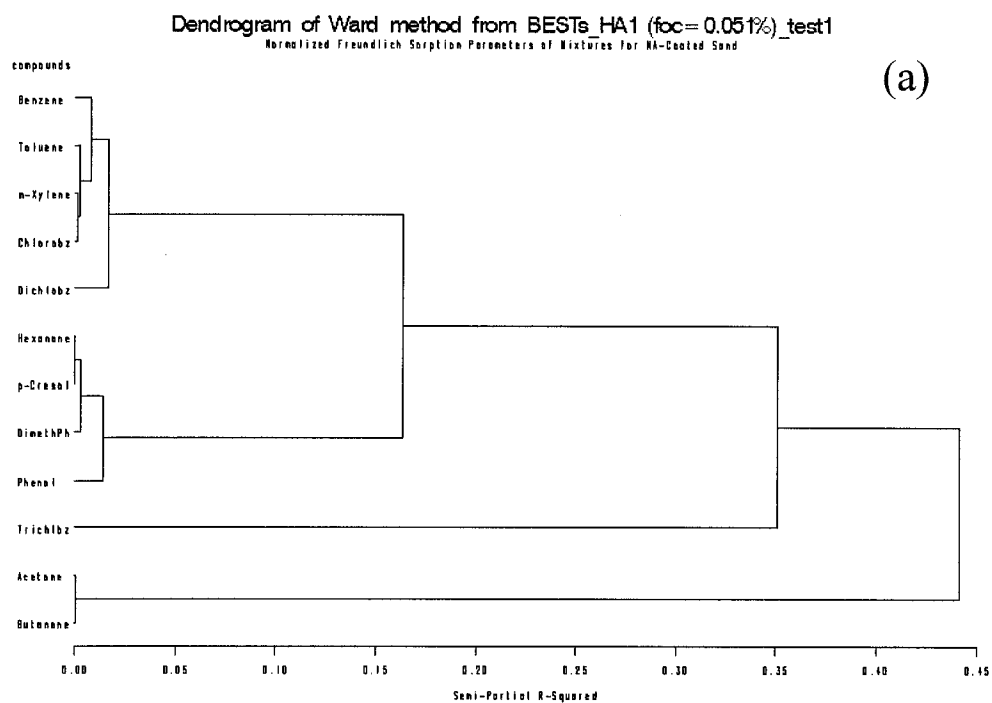


Fig. F.1 A dendrogram (a) and clusters (b) for sorption of 12 NOCs in mixtures (Test #1 in Table 6.1) to HA-coated sands ($f_{oc} = 0.051\%$).

Appendix G. Ideal Adsorbed Solution Theory (IAST) Using the Freundlich Sorption

Model

Appendix G.1 Matlab input source code for Newton-Raphson algorithm

```
function [r, niter] = NR(f, J, x0, tol, rerror, maxiter, varargin)

% Zero r of the nonlinear system of equations f(x) = 0.
% Here J is the Jacobian matrix of f and x0 is the initial
% approximation of the zero r.
% Computations are interrupted either if the norm of
% f at current approximation is less (in magnitude)
% than the number tol, or if the relative error of two
% consecutive approximations is smaller than the prescribed
% accuracy error, or if the number of allowed iterations
% maxiter is attained.
% The second output parameter niter stands for the number
% of performed iterations.

if isempty(tol)
    tol = 100*eps;
end
if isempty(rerror)
    rerror = 100*eps;
end
x0 = x0(:);
Jc = feval(J,x0,varargin{:});
if rcond(Jc) < 1e-10
    error('Try a new initial approximation x0.')
end
xold = x0;
xnew = xold - Jc\feval(f,xold,varargin{:});
for k=1:maxiter
    xold = xnew;
    niter = k+1;
    Jc = feval(J,xold,varargin{:});
    if rcond(Jc) < 1e-10
        error('Try a new initial approximation x0.')
    end
    xnew = xold - Jc\feval(f,xold,varargin{:});
    if (norm(feval(f,xnew,varargin{:}))) < tol) |...
        norm(xold - xnew, 'inf')/norm(xnew, 'inf') < rerror|...
        (niter == maxiter)
        break
    end
end
r = xnew(:);
```

Appendix G.2 Matlab input source code for the systems of nonlinear equations

```
function z = fun_1(x)

v = 34.5; %34.5 mL of volume of solution
m = 17.25; %17.25 g of sorbent
C0_1 = 100; %50 umol/L of PS1
C0_2 = 200; %50 umol/L of PS2
C0_3 = 200; %50 umol/L of PS3
C0_4 = 100; %50 umol/L of PS4

k1 = 0.246; %individual Freundlich sorption parameters for PS1
n1 = 1.00; %individual Freundlich sorption parameters for PS1
k2 = 0.243; %individual Freundlich sorption parameters for PS2
n2 = 0.956; %individual Freundlich sorption parameters for PS2
k3 = 0.081; %individual Freundlich sorption parameters for PS3
n3 = 0.851; %individual Freundlich sorption parameters for PS3
k4 = 0.086; %individual Freundlich sorption parameters for PS4
n4 = 0.708; %individual Freundlich sorption parameters for PS4

z = zeros(8,1);
z(1) = x(1) -
(x(5)/(x(5)+x(6)+x(7)+x(8))) * (((x(5)/n1)+(x(6)/n2)+(x(7)/n3)+(x(8)/n4)) /
(k1/n1))^(1/n1));
z(2) = x(2) -
(x(6)/(x(5)+x(6)+x(7)+x(8))) * (((x(5)/n1)+(x(6)/n2)+(x(7)/n3)+(x(8)/n4)) /
(k2/n2))^(1/n2));
z(3) = x(3) -
(x(7)/(x(5)+x(6)+x(7)+x(8))) * (((x(5)/n1)+(x(6)/n2)+(x(7)/n3)+(x(8)/n4)) /
(k3/n3))^(1/n3));
z(4) = x(4) -
(x(8)/(x(5)+x(6)+x(7)+x(8))) * (((x(5)/n1)+(x(6)/n2)+(x(7)/n3)+(x(8)/n4)) /
(k4/n4))^(1/n4));
z(5) = x(5) -
(v/m)*C0_1+(v/m)*(x(5)/(x(5)+x(6)+x(7)+x(8))) * (((x(5)/n1)+(x(6)/n2)+(x(7)
)/n3)+(x(8)/n4)) / (k1/n1))^(1/n1));
z(6) = x(6) -
(v/m)*C0_2+(v/m)*(x(6)/(x(5)+x(6)+x(7)+x(8))) * (((x(5)/n1)+(x(6)/n2)+(x(7)
)/n3)+(x(8)/n4)) / (k2/n2))^(1/n2));
z(7) = x(7) -
(v/m)*C0_3+(v/m)*(x(7)/(x(5)+x(6)+x(7)+x(8))) * (((x(5)/n1)+(x(6)/n2)+(x(7)
)/n3)+(x(8)/n4)) / (k3/n3))^(1/n3));
z(8) = x(8) -
(v/m)*C0_4+(v/m)*(x(8)/(x(5)+x(6)+x(7)+x(8))) * (((x(5)/n1)+(x(6)/n2)+(x(7)
)/n3)+(x(8)/n4)) / (k4/n4))^(1/n4));
```


Appendix G.3 Matlab input source code for the Jacobian matrix

```
function s = J_1(x)

v = 34.5; %34.5 mL of volume of solution
m = 17.25; %17.25 g of sorbent
C0_1 = 100; %50 umol/L of PS1
C0_2 = 200; %50 umol/L of PS2
C0_3 = 200; %50 umol/L of PS3
C0_4 = 100; %50 umol/L of PS4

k1 = 0.246; %individual Freundlich sorption parameters for PS1
n1 = 1.00; %individual Freundlich sorption parameters for PS1
k2 = 0.243; %individual Freundlich sorption parameters for PS2
n2 = 0.956; %individual Freundlich sorption parameters for PS2
k3 = 0.081; %individual Freundlich sorption parameters for PS3
n3 = 0.851; %individual Freundlich sorption parameters for PS3
k4 = 0.086; %individual Freundlich sorption parameters for PS4
n4 = 0.708; %individual Freundlich sorption parameters for PS4

s = [1 0 0 0 -
1/(x(5)+x(6)+x(7)+x(8))*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^(1/n1)
+x(5)/(x(5)+x(6)+x(7)+x(8))^2*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^(1/n1)-
x(5)/(x(5)+x(6)+x(7)+x(8))*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^(1/n1)/n1^2/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)
x(5)/(x(5)+x(6)+x(7)+x(8))^2*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^(1/n1)-
x(5)/(x(5)+x(6)+x(7)+x(8))*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^(1/n1)/n1/n2/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)
x(5)/(x(5)+x(6)+x(7)+x(8))^2*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^(1/n1)-
x(5)/(x(5)+x(6)+x(7)+x(8))*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^(1/n1)/n1/n3/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)
x(5)/(x(5)+x(6)+x(7)+x(8))^2*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^(1/n1)-
x(5)/(x(5)+x(6)+x(7)+x(8))*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^(1/n1)/n1/n4/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4);
0 1 0 0
x(6)/(x(5)+x(6)+x(7)+x(8))^2*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^(1/n2)-
x(6)/(x(5)+x(6)+x(7)+x(8))*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^(1/n2)/n1/n2/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) -
1/(x(5)+x(6)+x(7)+x(8))*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^(1/n2)
+x(6)/(x(5)+x(6)+x(7)+x(8))^2*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^(1/n2)-
x(6)/(x(5)+x(6)+x(7)+x(8))*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^(1/n2)/n2^2/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)
x(6)/(x(5)+x(6)+x(7)+x(8))^2*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^(1/n2)-
x(6)/(x(5)+x(6)+x(7)+x(8))*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^(1/n2)/n2/n3/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)
x(6)/(x(5)+x(6)+x(7)+x(8))^2*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^(1/n2)-
x(6)/(x(5)+x(6)+x(7)+x(8))*((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^(1/n2)/n2/n4/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4);
```

$$\begin{aligned}
& 0 \ 0 \ 1 \ 0 \\
& x(7)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k3*n3)^{(1/n3)} - \\
& x(7)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k3*n3)^{(1/n3)/n1/n3/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)} \\
& x(7)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k3*n3)^{(1/n3)} - \\
& x(7)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k3*n3)^{(1/n3)/n2/n3/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)} - \\
& 1/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k3*n3)^{(1/n3)} + x(7)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k3*n3)^{(1/n3)} - \\
& x(7)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k3*n3)^{(1/n3)/n3^2/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)} \\
& x(7)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k3*n3)^{(1/n3)} - \\
& x(7)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k3*n3)^{(1/n3)/n3/n4/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)}; \\
& 0 \ 0 \ 0 \ 1 \\
& x(8)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k4*n4)^{(1/n4)} - \\
& x(8)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k4*n4)^{(1/n4)/n1/n4/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)} \\
& x(8)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k4*n4)^{(1/n4)} - \\
& x(8)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k4*n4)^{(1/n4)/n2/n4/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)} \\
& x(8)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k4*n4)^{(1/n4)} - \\
& x(8)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k4*n4)^{(1/n4)/n3/n4/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)} - \\
& 1/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k4*n4)^{(1/n4)} + x(8)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k4*n4)^{(1/n4)} - \\
& x(8)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k4*n4)^{(1/n4)/n4^2/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)}; \\
& 0 \ 0 \ 0 \ 0 \\
& 1+v/m/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^{(1/n1)} - \\
& v/m*x(5)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^{(1/n1)} + v/m*x(5)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^{(1/n1)/n1^2/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)} - \\
& v/m*x(5)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^{(1/n1)} + v/m*x(5)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^{(1/n1)/n1/n2/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)} - \\
& v/m*x(5)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^{(1/n1)} + v/m*x(5)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^{(1/n1)/n1/n3/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)} - \\
& v/m*x(5)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^{(1/n1)} + v/m*x(5)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k1*n1)^{(1/n1)/n1/n4/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)}; \\
& 0 \ 0 \ 0 \ 0 \ - \\
& v/m*x(6)/(x(5)+x(6)+x(7)+x(8))^{*2}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^{(1/n2)} + v/m*x(6)/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^{(1/n2)/n1/n2/(x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)} \\
& 1+v/m/(x(5)+x(6)+x(7)+x(8))^{*}((x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)/k2*n2)^{(1/n2)} -
\end{aligned}$$

$$\begin{aligned}
& v/m \cdot x(6) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k2 \cdot \\
& n2^{(1/n2)} + v/m \cdot x(6) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k2 \cdot n2^{(1/n2)} / n2^{*2} / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) - \\
& v/m \cdot x(6) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k2 \cdot \\
& n2^{(1/n2)} + v/m \cdot x(6) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k2 \cdot n2^{(1/n2)} / n2 / n3 / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) - \\
& v/m \cdot x(6) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k2 \cdot \\
& n2^{(1/n2)} + v/m \cdot x(6) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k2 \cdot n2^{(1/n2)} / n2 / n4 / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4); \\
& \quad 0 \quad 0 \quad 0 \quad 0 \quad - \\
& v/m \cdot x(7) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k3 \cdot \\
& n3^{(1/n3)} + v/m \cdot x(7) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k3 \cdot n3^{(1/n3)} / n1 / n3 / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) - \\
& v/m \cdot x(7) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k3 \cdot \\
& n3^{(1/n3)} + v/m \cdot x(7) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k3 \cdot n3^{(1/n3)} / n2 / n3 / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) \\
& 1 + v/m / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k3 \cdot n3^{(1/n3)} - \\
& v/m \cdot x(7) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k3 \cdot \\
& n3^{(1/n3)} + v/m \cdot x(7) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k3 \cdot n3^{(1/n3)} / n3^{*2} / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) - \\
& v/m \cdot x(7) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k3 \cdot \\
& n3^{(1/n3)} + v/m \cdot x(7) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k3 \cdot n3^{(1/n3)} / n3 / n4 / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4); \\
& \quad 0 \quad 0 \quad 0 \quad 0 \quad - \\
& v/m \cdot x(8) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k4 \cdot \\
& n4^{(1/n4)} + v/m \cdot x(8) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k4 \cdot n4^{(1/n4)} / n1 / n4 / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) - \\
& v/m \cdot x(8) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k4 \cdot \\
& n4^{(1/n4)} + v/m \cdot x(8) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k4 \cdot n4^{(1/n4)} / n2 / n4 / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) - \\
& v/m \cdot x(8) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k4 \cdot \\
& n4^{(1/n4)} + v/m \cdot x(8) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k4 \cdot n4^{(1/n4)} / n3 / n4 / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) \\
& 1 + v/m / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k4 \cdot n4^{(1/n4)} - \\
& v/m \cdot x(8) / (x(5)+x(6)+x(7)+x(8))^{*2} \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4) / k4 \cdot \\
& n4^{(1/n4)} + v/m \cdot x(8) / (x(5)+x(6)+x(7)+x(8)) \cdot (x(5)/n1+x(6)/n2+x(7)/n3+x(8) \\
&) / n4 / k4 \cdot n4^{(1/n4)} / n4^{*2} / (x(5)/n1+x(6)/n2+x(7)/n3+x(8)/n4)] ;
\end{aligned}$$