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The equilibria of bisolute sorption on soil

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ABSTRACT

The goal of this study was to investigate the effects of both concentration levels and loading sequence or contamination history of each pollutant on the equilibrium sorption of mixed organic pollutants on soils. We measured binary sorption equilibria for a soil using ten concentration levels for both phenanthrene and naphthalene. Both solutes were either simultaneously loaded or sequentially loaded (i.e., the second sorbate was loaded after the sorption of the first sorbate had attained equilibrium) on soil. The results showed different competitive sorption equilibria between phenanthrene and naphthalene. In the presence of phenanthrene and regardless of loading sequence, naphthalene exhibited consistently lower sorption capacities and the ideal adsorbed solution theory (IAST) slightly underestimates the naphthalene sorption equilibria. Conversely, the sorption equilibria of phenanthrene in the presence of naphthalene depended upon the loading sequence of the two sorbates on the soil. Little competition from naphthalene on the sorption equilibria of phenanthrene was observed when phenanthrene was loaded either simultaneously with or sequentially after naphthalene, but appreciable competition from naphthalene was observed when the soil had been pre-contaminated with phenanthrene. IAST slightly underestimates the phenanthrene sorption equilibria observed in the latter system, but it cannot estimate the phenanthrene sorption equilibria in the former two systems. We proposed that adsorption on internal surfaces of ink-bottle shaped pores within relatively flexible sorbent matrix may have caused the competitive sorption phenomena observed in this study. The study suggests that contamination history may have strong influence on the equilibrium sorption of organic pollutant mixtures.

1. Introduction

Mixtures of different hazardous organic chemicals are commonly found in contaminated sites and surface aquatic and groundwater systems (NRC, 1994; Ritter et al., 1996). These chemicals may be of the same class, such as chlorinated benzenes, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, or in combination of different classes (NRC, 1994; Ritter et al., 1996). Physical, chemical and biological processes that control the fate, transport and bioavailability of individual pollutants may vary in the presence of other solutes (Rao et al., 1990; Pignatello, 1991; McGinley et al., 1993; Li and Werth, 2001) and change as a function of contamination history at a given site. A complete understanding of this competitive effect is essential for accurately predicting the extent and the influence of contamination by mixed chemicals on environmental systems, for estimating their transport and chemical and biological reactivity, and for assessing water quality and environmental risks.

This study investigated in general the competitive effects on sorption of organic pollutant mixtures by soils and sediments. Sorption is a phase distribution process retarding transport and reducing chemical and biological activities for relatively hydrophobic organic contaminants (HOCs) in heterogeneous environmental systems. Despite the fact that HOCs are commonly occurring as mixtures in the environment, prior studies of sorption phenomena mainly focused on single-solute systems, and investigations of sorption behaviors for hazardous organic chemical mixtures are relatively limited. Some studies showed no competitive effect for bisolute systems (Chiou et al., 1985; Chiou and Kile, 1998). Other studies found that a solute sorbed on soils can be displaced partially by a second solute and that the sorption capacity, isotherm nonlinearity and desorption rate of a given HOC solute are all affected variously by the co-existing HOC solute (e.g., McGinley et al., 1993; Xing and Pignatello, 1998; White and Pignatello, 1999; Xia and Ball, 2000; Sander and Pignatello, 2005). Such competitive effects may be depended upon both the similarity of physicochemical properties of the cosolutes and the characteristics of the natural sorbents (McGinley et al., 1993, 1996; Xing et al., 1996; Pignatello, 1998; Huang et al., 2003; Pignatello et al., 2006; Zhang et al., 2010).

Several conceptual models and theories were found insufficient to predict competitive phenomena in many cases. The Ideal

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Adsorption Solution Theory (IAST) widely used for bisolute sorption on activated carbon materials, for example, can successfully predict competitive sorption behavior for some bisolute systems (McGinley et al., 1993; Sorial et al., 1993; Lu and Sorial, 2004; Lu and Pignatello, 2004), but fail in other systems (Xing and Pignatello, 1998; Yu and Huang, 2005; Zhang et al., 2010). Both dual mode sorption and pore-filling model have been found capable of mechanistically explaining the competitive effects (Xing et al., 1996; Xia and Ball, 1999; Allen-King et al., 2002), but they could not be used for quantifying the sorption equilibria of HOC mixtures. It appears that information on multi-solute sorption and desorption equilibria is still insufficient. Studies aimed at answering how HOC mixtures interact with different types of SOM over broad ranges of concentrations and how sorption isotherm and rate parameters of a given HOC solute are affected in the presence of other HOC solutes are needed.

We initiated this study to systematically examine the impact of different solute loading sequences on sorption equilibria for a phenanthrene–naphthalene bisolute system over broad aqueous concentration ranges. Unlike prior studies that used either a fixed initial concentration of the primary solute and multiple concentration levels of the competitor (Xing et al., 1996) or vice versa (Sander and Pignatello, 2005; Zhang et al., 2010), we used multiple concentration levels for both primary and competing solutes. In addition to the conventional method of loading both solutes simultaneously on soils, an experimental procedure was used here for loading the second solute after the sorption of the first solute had attained equilibrium. One of the advantages using this sequential loading procedure is that the displacement of phenanthrene presorbed on a soil by newly introduced naphthalene molecules, and vice versa, can be delineated over broad concentration ranges of both solutes. The extent of such displacement provides insight information on sorption mechanisms as well as desorbability of HOCs associated with a soil.

2. Materials and methods

2.1. Materials

Chelsea soil, a topsoil collected from Chelsea, MI, was selected as the sorbent since it had been well characterized and used extensively in our prior studies and literature studies (Huang, 1997). It has 5.45 wt.% of total organic carbon (TOC) content and 3.92 $m^2\ g^{-1}$ of N_2-BET specific surface area (Huang, 1997). Phenanthrene (98%) and naphthalene (99 +% spectrophotometric grade) obtained from Aldrich Chemical Company, Inc., were used as received. The two sorbates were chosen because they are among PAHs commonly found in contaminated aquatic systems and have been used extensively in previous sorption studies (Huang, 1997). The molecular weight (MW), octanol–water partitioning coefficient ($\log K_{OW}$), and aqueous solubility (S_W) are respectively 178.2, 4.57, and 6.28 μM for phenanthrene and 128.2, 3.30, and 247.27 μM for naphthalene.

2.2. Solutions

The aqueous solution used in the sorption tests contained 0.005 M $CaCl_2$ as the major mineral constituent, 100 mg L^{-1} NaN_3 as an inhibitor of microorganisms, and 5 mg L^{-1} $NaHCO_3$ for buffering solution pH around 7. Primary stock solutions were prepared by dissolving an appropriate amount of each chemical in methanol (high performance liquid chromatography (HPLC) grade) and sequentially diluted to make a series of stock solutions of various concentrations. Initial aqueous solutions were prepared by spiking the aqueous solutions with appropriate volumes of the stock solutions; the spiked volumes of methanol stock solutions were controlled to be less than 0.1% of those of aqueous solutions.

2.3. Sorption experiments

Sorption equilibrium experiments were conducted at temperature of 22 ± 0.5 °C using flame-sealed glass ampules (20 mL, Kimble) as the completely-mixed batch reactors (CMBRs). The dosage of the sorbent was set to achieve 40–60% reduction of the initial aqueous phase concentrations (C_o) of naphthalene, the less sorbing solute. Sorption competition between phenanthrene and naphthalene was measured using three different loading sequences, simultaneously loading both sorbates on the soil, loading the strongly sorbing phenanthrene after the sorption of the weakly sorbing naphthalene had attained equilibrium, and vice versa. Each sequence was tested with an experimental matrix consisting of 100 CMBRs, which could be divided into ten subsets. Each subset had a fixed initial concentration of the first solute and ten different C_o levels of the second solute. This experimental matrix made it possible to compute ten sorption isotherms for each of the solute under ten different equilibrium concentrations of the second solute as the competing background solute. The experimental procedures for the three different loading sequences are detailed as below.

2.3.1. Method I

This procedure was used to load phenanthrene to the soil after the sorption of naphthalene had attained apparent equilibrium. In brief, a predetermined amount of the soil was introduced to each of the 100 CMBRs; ten different naphthalene C_o levels (approximately 0.3, 0.6, 1.2, 2.3, 4.7, 10.1, 19.5, 39.0, 78.0 and 156.0 μM) were prepared, and each was transferred into 10 ampules, yielding 10 replicate CMBRs at each naphthalene C_o level. The ampules were mixed horizontally in a shaker at 125 rpm for 21 d. Our preliminary study showed that both naphthalene and phenanthrene sorption isotherms measured at equilibration time of 14, 28, 42, and 56 d on the tested soil were nearly identical, indicating that a time period of 21 d was sufficient for attainment of apparent sorption equilibrium for both solutes. After mixing, the ampules were set upright overnight to allow suspended soil particles to settle. They were opened in propane flame, approximately 1.5 mL of the supernatant was withdrawn from each ampule, and the supernatant was mixed with a known amount of methanol (about 2 mL) in a 5 mL vial capped with Teflon lined cap. The exact amounts of the supernatant withdrawn and the methanol introduced were determined by weight. A dilution factor was calculated for each supernatant-methanol mixture following the method described in reference (Huang, 1997). Here methanol was used for preventing the potential solute loss due to volatilization and sorption to the compartments of glass vials (Huang, 1997). The mixture was then measured on an HPLC for quantifying the equilibrium concentration of naphthalene in aqueous phase.

After sampling of the supernatants, the CMBRs were immediately spiked with predetermined volume of concentrated phenanthrene stock solutions to achieve ten different phenanthrene C_o levels. The amounts of phenanthrene spiked were designed to achieve equilibrium aqueous phase concentrations (C_e) of phenanthrene ranging from a few hundredths to about 6.2 μM. Each spiked phenanthrene concentration level had 10 replicate CMBRs corresponding to the ten different naphthalene C_o levels. After spiking of phenanthrene, the CMBRs were flame sealed immediately, placed on the shaker, and mixed for 21 d. After completion of mixing, the CMBRs were set upright for 1 d, and then opened in propane flame again. An aliquot of supernatant was withdrawn from each ampule and mixed with methanol in a 5 mL vial. The mixtures were analyzed for C_e of both phenanthrene and naphthalene with HPLC.

2.3.2. Method II

This procedure was developed to load both naphthalene and phenanthrene simultaneously to the soil. Each ampule contained a predetermined amount of soil was carefully filled with background solution having a known initial concentration of naphthalene, and then spiked with a predetermined amount of high concentration phenanthrene stock solution immediately. A time interval between the loadings of the two solutes to the system was approximately 1–3 min. The CMBRs were flame sealed and mixed on a shaker for 21 d. After equilibration, the CMBRs were set upright for 1 d, and then opened for sampling of supernatants. The supernatant sample was mixed with methanol in a 5 mL vial, and the mixtures were analyzed for C_e of both phenanthrene and naphthalene with HPLC.

2.3.3. Method III

This method was used to load naphthalene on the soil after phenanthrene sorption had attained equilibrium. In brief, each ampule was filled with a predetermined amount of the sorbent and a known volume of background solution free of sorbates, and then spiked with a known volume of concentrated phenanthrene stock solution. It was flame sealed and placed on a shaker for 21 d to allow phenanthrene to attain sorption equilibrium. After equilibration, the ampules were set upright for 1 d and then flame opened. An aliquot was withdrawn from each reactor in a manner similar to Method I for analysis of phenanthrene concentration in the supernatant. The ampules were then spiked with a predetermined amount of concentrated naphthalene stock solution, flame sealed, shaken, and were set upright after mixing for 21 d. They were flame opened again for supernatant sampling and analysis of aqueous phase concentrations of both solutes.

2.4. Solute analysis

The aqueous phase concentrations of phenanthrene and naphthalene were measured with an HPLC (Agilent 1100) equipped with Hypersil ODS C18 column (5 μm, 2.1 × 250 mm), diode array detector (DAD), and fluorescence detector (FLD). phenanthrene and naphthalene were analyzed simultaneously using DAD with multiple wavelengths of 250 nm (phenanthrene) and 205 nm (naphthalene) for high concentrations and using FLD with excitation/emission wavelengths of 250/364 nm and 250/333 nm for low concentrations. External methanol solution standards of phenanthrene and naphthalene were 0.028–5.6 μM and 0.05–156 μM, respectively. The mobile phase was a mixture of acetonitrile and water at a volume ratio of 65:35 and flow-rate was set at 0.30 mL min^{-1}. The solute concentrations in the initial and equilibrated aqueous phases were calculated from the measured solute concentration in the mixtures and dilution factors. The solid phase concentrations of both solutes were computed based on the mass balance of the solutes between the solid and aqueous phases. Control reactors without sorbent were set up similarly and run simultaneously to assess loss of solute due to sorption to reactor components and volatilization during experimental procedures. Average system losses were shown to be consistently less than one percent of initial solute concentrations, and therefore no corrections were made in both mass balance calculation and model prediction.

2.5. Model prediction

The equilibrium phenanthrene and naphthalene sorption isotherm data measured for both single- and bi-solute systems were fit to the Freundlich sorption model having the following logarithmically transferred form

$$\log q_e = \log K_F + n \log C_e \tag{1}$$

where q_e and C_e are the equilibrium concentrations of the sorbate in the sorbent and in the solution phases and expressed in units of μmol kg^{-1} and μM, respectively; K_F (μmol kg^{-1}) (μM^n)$^{-1}$ and n are the pre-exponent constant and the nonlinearity parameter of the model, respectively.

The competitive sorption tested in this study was modeled using the ideal adsorbed solution theory (IAST). IAST is a thermodynamically based model and had been successfully used in previous studies of HOC sorption on granular activated carbon (Crittenden et al., 1985; Sorial et al., 1993; Lu and Sorial, 2004) and soils (McGinley et al., 1993, 1996; Ju and Young, 2004). The underlying assumptions are that the sorption process is primarily entropy-driven, the activities of coexisting solutes in both aqueous and adsorbed phases are proportional to their concentrations; and that the quantity of sorption in a multi-solute system having N number of sorbates can be related to the sorption in each of the single-solute systems at the same spreading pressure by

$$\frac{1}{q^{M}_{e,T}} = \sum_{i=1}^{N} \frac{z_i}{q^{S}_{e,i}} \tag{2}$$

where $q^{M}_{e,T}$, the sum of the sorbent-phase concentrations of all sorbates in a multi-solute system, and $q^{S}_{e,i}$, the sorbent-phase concentration of the ith sorbate in its single-solute system, are measured at the same spreading pressure condition. Z_i is the mole fraction of the ith solute in the sorbent-phase.

For the given bisolute (phenanthrene and naphthalene) sorption system, the sorption equilibria can be quantified using the following equations.

$$C^{B}_{e,Naph} = \frac{q^{B}_{e,Naph}}{q^{B}_{e,Naph} + q^{B}_{e,Phen}} \left(\frac{n^{S}_{Phen} q^{B}_{e,Naph} + n^{S}_{Naph} q^{B}_{e,Phen}}{n^{S}_{Phen} K^{S}_{F,Naph}} \right)^{\frac{1}{n^{S}_{Naph}}} \tag{3}$$

$$C^{B}_{e,Phen} = \frac{q^{B}_{e,Phen}}{q^{B}_{e,Naph} + q^{B}_{e,Phen}} \left(\frac{n^{S}_{Phen} q^{B}_{e,Naph} + n^{S}_{Naph} q^{B}_{e,Phen}}{n^{S}_{Naph} K^{S}_{F,Phen}} \right)^{\frac{1}{n^{S}_{Phen}}} \tag{4}$$

The mass balance of each batch system is given by the following two equations:

$$q^{B}_{e,Naph} = \frac{V_{Reactor}}{M_{Sorbent}} \left(C^{B}_{0,Naph} - C^{B}_{e,Naph} \right) \tag{5}$$

$$q^{B}_{e,Phen} = \frac{V_{Reactor}}{M_{Sorbent}} \left(C^{B}_{0,Phen} - C^{B}_{e,Phen} \right) \tag{6}$$

where superscripts B and S denote to bisolute and single solute, respectively, and V and M are the aqueous solution volume (L) and the mass (g) of the sorbent, respectively. $q^{B}_{e,Naph}$, $q^{B}_{e,Phen}$, $C^{B}_{e,Naph}$ and $C^{B}_{e,Phen}$ of each CMBR were computed simultaneously using the f_{solve} function of Matlab 7.0 (Matlab Corp., Natick, MA).

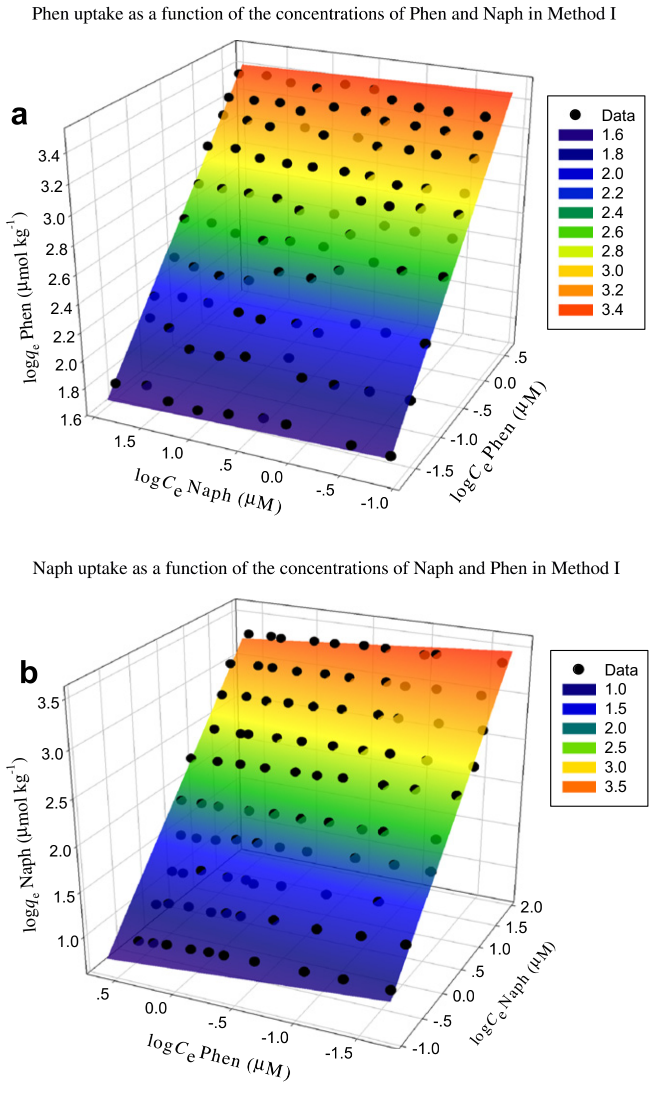
3. Results and discussion

3.1. Bisolute sorption equilibria

Fig. 1 presents two 3D plots of the solid phase concentration of phenanthrene (a) and naphthalene (b) as a function of aqueous phase phenanthrene and naphthalene concentrations using the data collected with Method I. The following two equations represent the best fit of the data using a 3D Plane regression approach of SigmaPlot 10.0 (Systat Software, Inc.):

$$\log q_{e,Phen} = 2.982 + 0.740 \times \log C_{e,Phen} - 0.017 \times \log C_{e,Naph} \quad R^2 = 0.996 \tag{7}$$

$$\log q_{e,Naph} = 1.587 + 0.885 \times \log C_{e,Naph} - 0.107 \times \log C_{e,Phen} \quad R^2 = 0.995 \tag{8}$$


Phen uptake as a function of the concentrations of Phen and Naph in Method I

Naph uptake as a function of the concentrations of Naph and Phen in Method I

Fig. 1. 3-D plots of the binary sorption equilibria measured with Method I.

The 3D plots of the binary sorption equilibria using the other two experimental methods are included in the Supporting information (Fig. SI-1). Eqs. (7) and (8) indicate that the solid phase concentration of a given sorbate can be quantitatively correlated with the aqueous phase concentrations of the both solutes. The negative coefficients for C_e of the background solute indicate the competitive effect that reduces the sorbent-phase concentration of the primary sorbate in the binary solute system. The goodness of fit ($R^2 > 0.99$) suggests that sorption equilibria in a binary solute system can be described quantitatively with a modified Freundlich-like equation that includes the aqueous concentrations of both solutes. However, the mechanistic significance of the pre-logarithmic coefficients requires further elucidation with additional studies.

To better understand competitive sorption behavior differences of phenanthrene and naphthalene in the three experimental systems, 10 pairs of solid phase and aqueous-phase solute concentration data at a relatively constant concentration of the competing solute were regrouped and a total of 60 isotherms were generated and fit to Eq. (1) using a regression procedure built in SYSTAT software (Version 11, SYSTAT Inc.). The isotherm parameters, log K_F and n, along with their standard deviations (σ), number of observations, and R^2 values of naphthalene and phenanthrene are listed in Table 1. To graphically present the competitive sorption phenomena observed for the bisolute system, traditional isotherms plots of the sorption data are also presented in Fig. 2.

Fig. 2 shows that both phenanthrene and naphthalene isotherms in the binary systems fall below their respective single-solute sorption isotherms, indicating various competitive effects in the presence of a cosolute. Detailed analysis indicated that the effect of the cosolute on the equilibrium sorption of the primary solute is highly depended upon the concentrations of both solutes, the sorption affinity of each individual solute, and the loading sequence of two solutes on the soil. The major findings are summarized in Table 2 and detailed in the latter sections.

3.2. Naphthalene sorption equilibria in the bisolute systems

As summarized in Table 2, naphthalene sorption equilibria measured with all three methods were strongly affected by the presence of the cosolute phenanthrene regardless of the loading sequence. Fig. 2(a, c and e) clearly demonstrate strong competitive effect of phenanthrene on the sorption of naphthalene. Due to greater competitive effect at lower naphthalene concentrations, the naphthalene sorption isotherm became increasingly linear and the naphthalene sorption capacity decreased as the C_e of phenanthrene increased. As shown in Table 1 and Fig. SI-2(a and b), the n values of naphthalene sorption isotherms increased from 0.758 for the single solute system to 0.815, 0.850, and 0.858 as the C_e of phenanthrene was at 0.02, 0.01, and 0.03 μM (i.e., the minimal C_e) in Methods I–III, respectively; and the n values increased to 0.933, 0.969, and 0.971 as the C_e of phenanthrene was at 3.37, 3.12 and 4.14 μM (i.e., the maximal C_e) in Methods I–III, respectively. Meanwhile, the log K_F values decreased from 1.879 for the single solute system to 1.790, 1.803, and 1.732 at the respective minimal C_e of phenanthrene of 0.02, 0.01, and 0.03 μM in Methods I–III. The log K_F value decreased further to 1.487, 1.562, and 1.482 at the respective maximal phenanthrene C_e of 3.37, 3.12 and 4.14 μM in Methods I–III.

The strong competitive effect of phenanthrene on naphthalene sorption was also demonstrated by the decrease of the single-point naphthalene K_{OC}. In the absence of phenanthrene and at the equilibrium aqueous phase naphthalene concentration equating 0.5% of its water solubility (1.24 μM or 158.5 μg L^{-1}), the naphthalene K_{OC} was approximately 1318. In all three testing methods, the naphthalene K_{OC} values decreased to 960.1–1129 at phenanthrene $C_e = 0.01$–0.03 μM and to 553–665 at phenanthrene $C_e = 3.12$–4.14 μM. At the latter phenanthrene C_e level, the average naphthalene K_{OC} decreased as much as 55%.

3.3. Phenanthrene sorption equilibria in the bisolute systems

As shown in Table 2, phenanthrene exhibited very different competitive sorption equilibria than naphthalene in the binary sorption systems. Fig. 2(b,d and f) and Fig. SI-2(c and d) and Table 1 show strong competitive effect of naphthalene on the sorption of phenanthrene in the binary system of Method III, but little effect in other two binary systems observed in Methods I and II. According to the Method III data listed in Table 1, the n and log K_F values of the phenanthrene sorption isotherm at naphthalene $C_e = 0$ were 0.730 and 2.990, respectively, and had little or no changes when naphthalene C_e at the minimum of 0.19 μM. However, the values of n and log K_F changed to 0.905 and 2.878 at the maximal background naphthalene C_e of 85.82 μM. The data listed in Table 1 for Methods I and II indicate that, regardless of the naphthalene C_e levels, both n and log K_F values of phenanthrene isotherm fall into narrow ranges which are close to the values of the single phenanthrene sorption isotherm (i.e., naphthalene $C_e = 0$). For example, the measured single-point phenanthrene K_{OC} (at phenanthrene $C_e = 0.005S_w$) values were approximately 46 215 at naphthalene $C_e = 0$ μM, 44 160–45 089 at naphthalene $C_e = 0.12$–0.16 μM, and 39 345–41 267 at naphthalene $C_e = 80.82$–88.22 μM. The

Table 1
Sorption isotherm parameters for naphthalene and phenanthrene.

Naphthalene								Phenanthrene							
Cosolute Phen C_e (μM)	n	log KF (μmol kg^{-1}) (μM^n)$^{-1}$	N	R^2	KOC				n	log KF (μmol kg^{-1}) (μM^n)$^{-1}$	N	R^2	KOC		
					0.005Sw 158.5 μg L^{-1}	0.05S$_w$ 1585 μg L^{-1}	0.5S$_w$ 15850 μg L^{-1}	Cosolute Naph C_e (μM)					0.005S$_w$ 5.6 μg L^{-1}	0.05S$_w$ 56 μg L^{-1}	0.5S$_w$ 560 μg L^{-1}
Single solute															
0	0.758±0.003	1.879±0.004	100	0.998	1318	756	433	0	0.730±0.003	2.990±0.003	99	0.998	46215	24600	13165
Method I															
0.02	0.815±0.015	1.790±0.016	9	0.998	1087	710	464	0.16	0.739±0.010	2.993±0.008	10	0.999	45089	24511	13394
0.05	0.828±0.015	1.761±0.016	10	0.997	1020	687	462	0.37	0.746±0.009	2.989±0.007	10	0.999	43593	24088	13378
0.10	0.844±0.020	1.715±0.020	10	0.996	920	643	449	0.75	0.772±0.018	2.992±0.011	9	0.996	40070	23527	13877
0.20	0.881±0.018	1.675±0.018	10	0.997	846	644	489	1.49	0.734±0.009	2.981±0.007	10	0.999	44636	23983	12954
0.37	0.911±0.018	1.619±0.018	10	0.997	749	610	497	2.57	0.747±0.011	2.960±0.009	10	0.998	40634	22506	12528
0.57	0.898±0.012	1.616±0.013	10	0.998	741	586	464	5.6	0.715±0.013	2.968±0.011	10	0.997	46305	23799	12302
0.91	0.906±0.011	1.580±0.011	10	0.999	684	551	444	10.28	0.735±0.024	2.983±0.020	10	0.992	44686	24065	13029
1.58	0.903±0.016	1.557±0.016	10	0.998	648	518	415	21.53	0.732±0.015	2.960±0.012	10	0.997	42829	22904	12315
2.16	0.935±0.017	1.516±0.018	10	0.997	594	511	440	42.57	0.746±0.016	2.942±0.012	10	0.996	39121	21617	12006
3.37	0.933±0.018	1.487±0.019	10	0.997	555	476	408	80.82	0.747±0.024	2.946±0.018	10	0.992	39345	21792	12130
Method II															
0.01	0.850±0.010	1.803±0.011	10	0.999	1129	800	566	0.12	0.741±0.014	2.987±0.014	10	0.997	44160	24118	13240
0.03	0.873±0.015	1.774±0.016	10	0.998	1061	792	591	0.19	0.754±0.012	2.997±0.013	10	0.998	43175	24307	13752
0.06	0.893±0.012	1.764±0.013	10	0.998	1041	814	636	0.48	0.733±0.011	2.993±0.012	10	0.998	46048	24684	13302
0.10	0.909±0.013	1.744±0.013	10	0.998	998	810	656	0.88	0.727±0.006	2.996±0.006	10	1.000	47353	25030	13303
0.20	0.934±0.012	1.719±0.012	10	0.999	947	814	699	2.11	0.728±0.006	2.997±0.007	10	0.999	47296	25058	13349
0.35	0.945±0.014	1.695±0.014	10	0.998	898	792	698	4.59	0.730±0.006	2.967±0.007	10	0.999	43831	23331	12486
0.55	0.923±0.017	1.647±0.018	10	0.997	801	671	562	8.66	0.731±0.010	2.949±0.011	10	0.998	41904	22358	11993
0.95	0.935±0.015	1.629±0.016	10	0.998	770	663	571	17.57	0.775±0.008	2.983±0.008	10	0.999	38838	22964	13639
1.77	0.957±0.015	1.588±0.016	10	0.998	704	638	578	45.50	0.743±0.018	2.976±0.018	10	0.995	42755	23460	12939
3.12	0.969±0.012	1.562±0.013	10	0.999	665	619	576	88.22	0.738±0.020	2.953±0.020	10	0.994	41266	22380	12201
Method III															
0.03	0.858±0.008	1.732±0.008	10	0.999	960	693	500	0.19	0.736±0.011	2.997±0.010	10	0.998	45988	24825	13471
0.05	0.865±0.008	1.722±0.008	10	0.999	940	689	505	0.37	0.730±0.009	2.991±0.008	10	0.999	46321	24657	13196
0.10	0.886±0.010	1.683±0.010	10	0.999	863	664	511	0.67	0.764±0.007	2.998±0.006	10	0.999	41783	24079	13942
0.16	0.899±0.010	1.664±0.010	10	0.999	828	657	520	1.35	0.763±0.012	2.979±0.011	9	0.998	40135	23076	13330
0.28	0.908±0.012	1.637±0.012	10	0.999	780	631	511	2.32	0.771±0.007	2.987±0.006	10	0.999	39750	23285	13703
0.49	0.917±0.010	1.613±0.010	10	0.999	739	611	505	5.45	0.787±0.008	2.976±0.006	10	0.999	36642	22282	13607
0.84	0.935±0.012	1.581±0.012	10	0.999	689	594	511	10.36	0.812±0.008	2.962±0.006	10	0.999	32502	20952	13558
1.31	0.942±0.010	1.563±0.011	10	0.999	662	580	507	21.25	0.844±0.011	2.955±0.009	10	0.999	28587	19859	13838
2.37	0.966±0.010	1.512±0.011	10	0.999	592	548	506	40.56	0.868±0.009	2.923±0.007	10	0.999	24413	17937	13213
4.14	0.971±0.013	1.482±0.014	9	0.999	553	518	484	85.82	0.905±0.007	2.878±0.005	10	1.000	19332	15486	12428

[*] Phen = phenanthrene; Naph = naphthalene; K_{OC} = organic carbon normalized single-point distribution coefficient; factors for converting log K_F from μmol-based unit to μg-based unit are 128.2^{1-n} and 178.2^{1-n} for naphthalene and phenanthrene, respectively

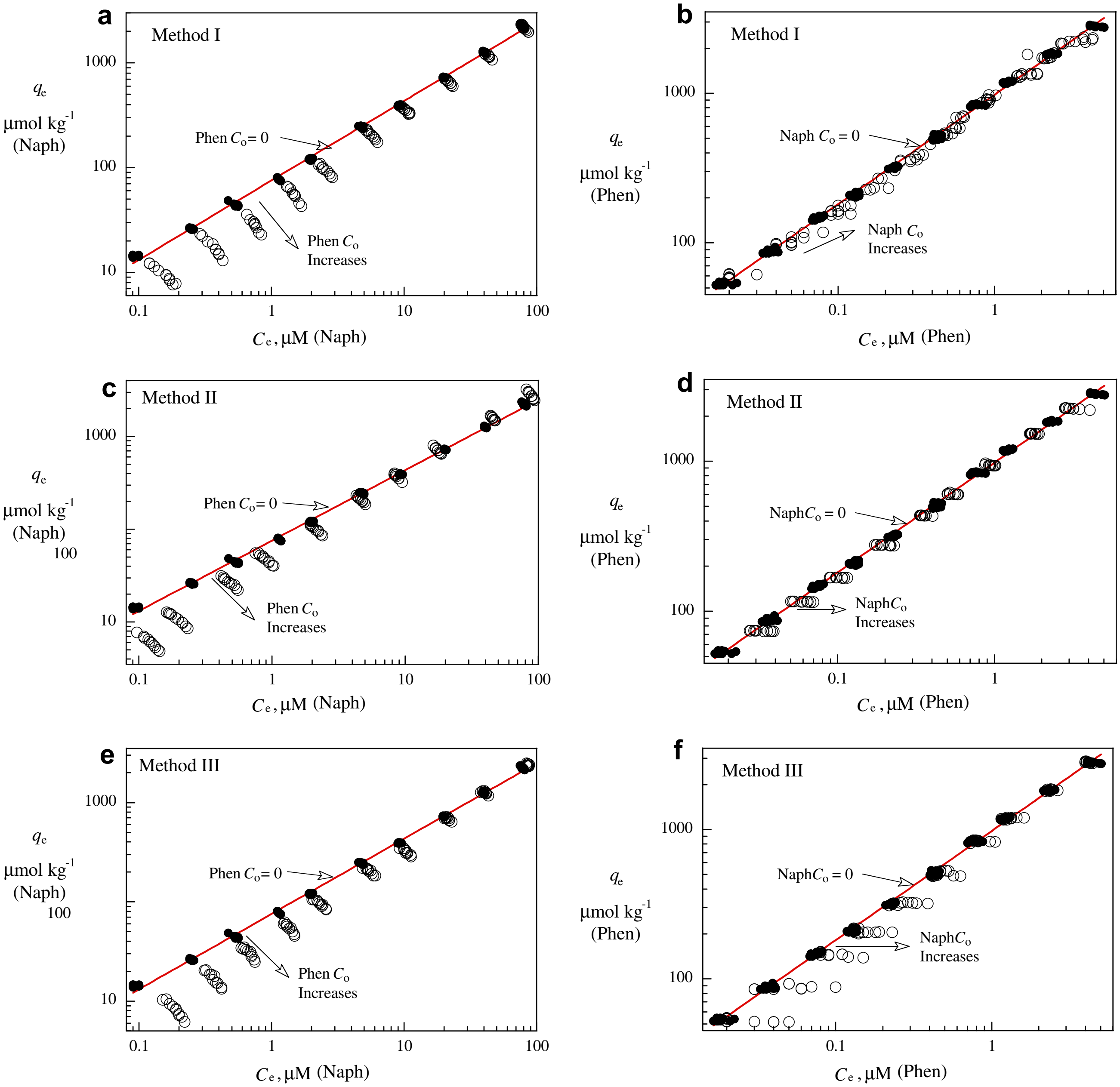


Fig. 2. Naphthalene (a, c and e) and phenanthrene (b, d and f) sorption data measured for the binary sorption systems with the three different loading methods.

maximum decrease of phenanthrene K_{OC} values measured with Methods I and II was about 15%, which is much lower when compared to the 55% decrease of naphthalene K_{OC}. This indicates that the phenanthrene sorption was far less affected by naphthalene. However, with Method III, the maximum decrease of phenanthrene K_{OC} values was about 58%, indicating that the phenanthrene sorption was strongly affected by the presence of naphthalene when phenanthrene was loaded prior to naphthalene to the solid.

In summary, we observed different competitive sorption equilibria between phenanthrene and naphthalene in three different testing methods. In the presence of phenanthrene and regardless of loading sequence, naphthalene exhibits sorption capacities consistently lower than in the single solute systems. Conversely, the sorption equilibria of phenanthrene in the presence of naphthalene depend upon the loading sequence of the two sorbates on the soil. Little or no competition from naphthalene on the sorption equilibria of phenanthrene was observed with Methods I and II, but appreciable competition was observed in Method III.

3.4. IAST prediction

As summarized in Table 2, the isotherms computed based on IAST differ variously from the sorption isotherms measured experimentally with the three methods. Fig. SI-4 further illustrates the IAST predictions in comparison with the experimentally measured sorption isotherms of the binary solute systems. In the cases of naphthalene as the primary solute, IAST slightly underestimates the naphthalene sorption equilibria observed with all three methods at the high concentrations (3.2–4.2 µM) of phenanthrene, and slightly overestimates the naphthalene sorption equilibria observed with Methods II and III at the low concentrations (0.035–0.043 µM) of phenanthrene. In the cases of phenanthrene as the

Table 2
Summary of the bisolute sorption equilibria.

Method	Phenanthrene sorption equilibria		Naphthalene sorption equilibria	
Method I (Naph → Phen)	Week competition from naphthalene	IAST fails to predict phenanthrene sorption equilibria	Strong competition from phenanthrene	IAST slightly underestimates naphthalene sorption equilibria
Method II (simultaneous)	Week competition from naphthalene	IAST fails to predict phenanthrene sorption equilibria	Strong competition from phenanthrene	IAST slightly underestimates naphthalene sorption equilibria
Method III (Phen → Naph)	Strong competition from naphthalene	IAST slightly underestimates phenanthrene sorption equilibria	Strong competition from phenanthrene	IAST slightly underestimates naphthalene sorption equilibria

primary solute, IAST provides acceptable predictions for the phenanthrene sorption equilibria with the three methods at the low concentrations of naphthalene (0.02–0.04 μM). However, at the high concentrations of naphthalene (85–92 μM), IAST slightly underestimates the phenanthrene sorption equilibria measured with Method III, and dramatically under-predicts the phenanthrene sorption equilibria measured with Methods I and II as little or no competitive sorption was observed with the two methods.

To better illustrate the details of the IAST predictions, the IAST sorption data computed from Eqs. (3)–(6) for all the bisolute systems were regrouped into isotherm datasets, each isotherm of the primary solute has a roughly constant aqueous concentration of the background solute. The calculated IAST isotherm data were then fit to Eq. (1) for obtaining the Freundlich model parameters. Fig. SI-3 presents the n and log K_F parameters of the IAST predicted isotherms as a function of the aqueous phase concentration of the respective cosolute. It shows that the n values of the IAST-predicted sorption isotherms increase as a function of the C_e of the competing solute whereas their log K_F values decrease accordingly for both phenanthrene and naphthalene. A major feature shown in Fig. SI-3 is that the IAST-predicted sorption isotherm parameters have very little deviations among the three different methods. This is very different from the parameters of the experimentally measured sorption isotherms presented in Fig. SI-2 where the n values and log K_F values of the three methods are very scattered at a given C_e of the competing solute. A close comparison of the n values of the phenanthrene isotherms between Figs. SI-2c and -3c indicates that the IAST predictions are obviously inconsistent with the experimentally measured parameters with Methods I and II.

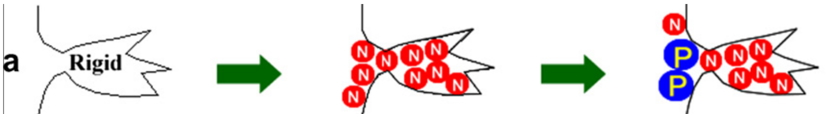
The similarity of the sorption phenomena observed with Methods I and II may result from the similar sequence of loading the two solutes on the soil. As mentioned above, in Method II phenanthrene was indeed loaded to the system 1–3 min after naphthalene. Such a minute difference in loading time may have caused preferential occupation of sorption sites (especially on the external surfaces) by naphthalene on the sorbent. Weber and Huang (1996) showed that the ratio of $q(t)/q_e$ for phenanthrene had achieved approximately 0.2 and 0.3 within 1 and 5 min of soil-solution contact times. Once naphthalene arrives at the external surfaces, it diffuses into the internal surfaces at faster speeds since naphthalene has greater diffusion coefficient than phenanthrene of larger molecular size. As a result of two sequential processes, the loading sequence for phenanthrene and naphthalene may be identical, and the sorption equilibria observed for both solutes are also identical in Methods I and II. In fact, even if the two sorbing molecules were loaded simultaneously to the soil, the faster diffusion rate of naphthalene may have resulted in similar sorption equilibria for the two chemicals.

3.5. Mechanistic interpretations

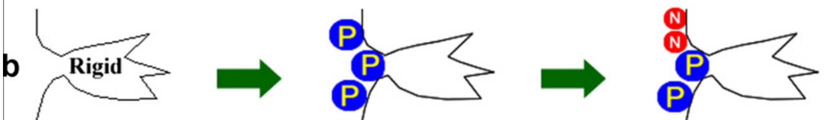
The mechanisms that cause loading sequence dependent competitive sorption for phenanthrene but loading sequence independent competitive sorption for naphthalene may be very complicated. The competitive sorption phenomenon observed for naphthalene is generally consistent with the observations reported in the literature (McGinley et al., 1996; Xing et al., 1996; Xing and Pignatello, 1998) and can be explained via sorption on condensed soil organic matter domains. It is known that soil organic matter (SOM) consists of both humic materials and charcoal/soot; the former may be in rigid glassy status under room temperature conditions (LeBoeuf and Weber, 1997) and both components may possess heterogeneous external and internal surfaces (Pignatello and Xing, 1996; Gustafsson et al., 1997; Pignatello, 1998). Competitive sorption has been observed for both glassy humic materials (Xing and Pignatello, 1997; Schaefer et al., 2000) and charcoal/soot materials (Sander and Pignatello, 2005; Wang et al., 2006; Yang et al., 2006) and has been explained via a surface adsorption mechanism due to capacity limitation in the binding of organic pollutants on rigid surfaces.

However, the very different observations on the equilibrium sorption of phenanthrene in the same bisolute systems of the three experimental methods cannot be explained simply using the adsorption mechanism delineated above for naphthalene. Sorption equilibria are thermodynamic states that should be identical at constant temperature for a fixed sorbate–sorbent system regardless of pathways or histories of the process. For example, adsorption on flat surfaces may create competition between two different sorbates if the sorption follows similar mechanisms. In the case of sorption driven by non-specific hydrophobic interactions, the sorption at external surfaces is expected to be completely reversible and the competition between two sorbates is expected to be identical, regardless of the adsorption sequence of the two sorbates. This can explain the situation for naphthalene, but not for phenanthrene which demonstrated loading sequence-dependent competition by naphthalene. As a result, it is highly unlikely that the observed competitive sorption is caused solely by adsorption at the external surfaces of SOM matrix.

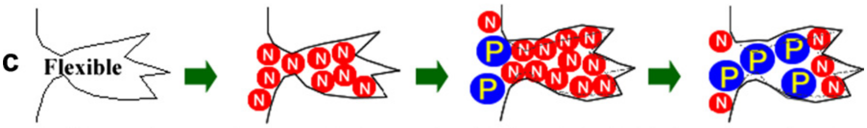
Adsorption into porous matrix having pore diameters of the sizes of sorbates may generate competition between two sorbates of different sizes due to a size-exclusion or pore-blocking mechanism. This mechanism is especially important when the pores are irregular and tortuous, and even have ink-bottle shapes. Fig. 3 schematically shows the bisolute adsorption into such a pore with opening being smaller than the size of the larger molecule but greater than the smaller one. Depending upon the rigidity of the sorbent matrix, the competition between the two sorbates may differ dramatically, resulting in different adsorption phenomena that may be described conceptually hereafter. If the sorbent matrix is rigid, pore sizes remain constant before and after loading of the first sorbate. Fig. 3a depicts the situation when the smaller sorbate (naphthalene) is loaded prior to the larger (phenanthrene) to the sorbent (Methods 1 and II) where no competition occurs within the pore into which the larger sorbate cannot enter. Fig. 3b depicts the situation when the larger sorbate is loaded prior to the smaller to the sorbent (Method III). The pore is not accessible by the



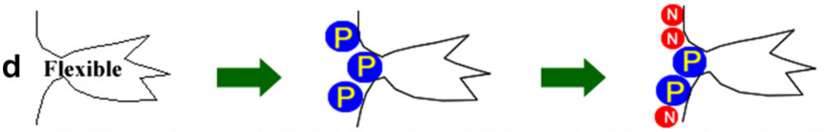
Rigid matrix scenario for Method I & II (naphthalene is loaded before phenanthrene)



Rigid matrix scenario for Method III (naphthalene is loaded after phenanthrene)



Flexible matrix scenario for Method I & II (naphthalene is loaded before phenanthrene)



Flexible matrix scenario for Method III (naphthalene is loaded after phenanthrene)

Fig. 3. A conceptual diagram for illustrating the competitive sorption of phenanthrene (P) and naphthalene (N) within a micropore of rigid (a and b) and expandable (c and d) SOM matrix.

smaller sorbate since the pre-occupied larger one blocks the opening. As a result, the K_D value for the smaller sorbate in Fig. 3b is presumably smaller than the situation depicted in Fig. 3a, whereas the K_D value for the larger sorbate remains the same in both situations depicted in Fig. 3a and b. Apparently, the situations described in Fig. 3a and b are inconsistent with our observations that the K_D value for the smaller sorbate (naphthalene) remains the same whereas the K_D value for the larger sorbate (phenanthrene) is different in different loading methods.

If the sorbent matrix is less rigid, pore sizes may increase after loading of the first sorbate, especially when the first sorbate reaches a relative high concentration inside the space of the pores (LeBoeuf and Weber, 2000). Fig. 3c depicts the situation when the smaller sorbate is loaded prior to the larger to the sorbent (Methods 1 and II). After the sorbent matrix is relaxed and the pore opening increases, the pore that was not accessible before can now be accessed by the larger sorbate. It is possible that the sorption sites in the deformed or expanded pores created by the smaller molecules are high energy sites that are preferentially occupied by the stronger and larger sorbate. Consequently, competition by the larger and strongly sorptive sorbate expels the smaller and less sorptive sorbate from the pore. On the other hand, when the larger sorbate is loaded prior to the smaller to the sorbent (Method III) as depicted in Fig. 3d, the pore is blocked by the pre-occupied larger sorbate and is not accessible by the smaller sorbate. As a result, the K_D value for the larger sorbate in Method III (Fig. 3d) is smaller than in Methods I and II (Fig. 3c), whereas the K_D value for the smaller sorbate remains relatively unchanged in both situations.

As delineated above, among various adsorption mechanisms, adsorption on internal surfaces of ink-bottle shaped pores within relatively flexible sorbent matrix can better explain the competitive sorption phenomena observed in this study. We believe that the different abilities of phenanthrene and naphthalene to modify, and to be sorbed by, the micropores of the soil result in significant differences of their competitive sorption equilibria shown in this study. The creation of tenant pores by naphthalene for accommodating phenanthrene violates the basis of IAST, causing the failure of IAST prediction on phenanthrene sorption in these two experimental systems. Pore deformation mechanism was proposed in the literature (Huang and Weber, 1997; Lu and Pignatello, 2002) for interpreting desorption hysteresis phenomena. Our study further demonstrated that deformation and blocking of micropores may play an important role in the competitive sorption of pollutant mixtures on soils. The results indicated that contamination sequence or history may have various effects on sorption of mixed organic pollutants by soils.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.02.009.

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