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Role of extractable and residual organic matter fractions on sorption of phenanthrene in sediments

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HIGHLIGHTS

- ▶ Riverine sediments were fractionated into five fractions using new methods.
- ▶ A dioxane extraction procedure was applied to the separation of lignin in sediments.
- ▶ Free lipid and lignin were much higher than previously reported values.
- ▶ The Phen sorption for the lipid and lignin fractions was linear, whereas that for the residual fractions was nonlinear.
- ▶ The residual fraction without lignin controlled the overall sorption, demonstrating the importance of condensed SOM.

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ABSTRACT

Two sediments were demineralized and sequentially fractionated into extracted fractions [free lipid (FL), bound lipid (BL) and lignin (LG)] and residual fractions [free lipid free (FLF), bound lipid free (BLF) and lignin free (LGF)]. The sorption isotherms of phenanthrene (Phen) were examined to evaluate the importance of various fractions on sorption. A lignin extraction procedure was for the first time applied to separate the lignin or degraded lignin fraction from sediment organic matter (SOM). The extracted LG was similar to model lignin in terms of elemental ratios and sorption behavior. FL and LG fractions were quite important, as their contents were much higher than reported values. Phen sorption for the extracted fractions was almost linear, whereas that for the residual fractions was nonlinear, especially for LGF with n 0.56–0.63. As the different organic fractions were removed sequentially, sorption energy distribution on the residual sediment organic matter (SOM) became more heterogeneous. In addition, increasing sorption capacity for the residual fractions, except for BLF with its high polarity, suggested that more sorption sites on the SOM matrix became accessible to Phen. The sorption capacity for LGF was comparable to that of condensed SOM. The residual fraction LGF generally controlled the overall sorption at low Phen concentration, but the extractable fraction FL surpassed the former fraction at high Phen concentration, demonstrating the importance of condensed SOM in the sorption of hydrophobic organic compounds (HOCs) in sediments.

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1. Introduction

The distribution, transport and fate of hydrophobic organic compounds (HOCs) are significantly controlled by their sorption on sediment organic matter (SOM). SOM often contains a range of physically and chemically different organic materials consisting of biopolymers such as lignin, polysaccharides, lipids and proteins, humic substances derived from biopolymers, and diagenetically matured kerogen and black carbon (BC) (e.g., Kohl and Rice, 1999; Ran et al., 2009). SOM can be conceptually divided into

two domains: a rubbery, soft, or amorphous domain and a glassy, hard, or condensed domain (e.g., Xing and Pignatello, 1997). Sorption on the former domain is linear, whereas that on the latter domain exhibits nonlinear sorption. Recent advances indicate that hard or condensed organic materials, such as nonhydrolyzable organic carbon (NHC), kerogen carbon, and BC, play an important role in the sorption of HOCs due to their high sorption capacity (Cornelissen and Gustafsson, 2004; Cornelissen et al., 2005; Ran et al., 2007; Sun et al., 2008). Compared with the insoluble and hard SOM, the expanded and soft SOM exhibits lower sorption capacity and a more linear isotherm for HOCs (e.g., Xing and Pignatello, 1997). New methods are being developed to distinguish the contribution of different SOM fractions to the total sorption of HOCs in soil and sediments.

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Chemical separation and characterization methods have been developed to differentiate various fractions of SOM. Some types of natural biomolecules, such as free lipids and bound lipids, can be separated from soil and sediments via chemical treatment, and their chemical and physical characteristics as well as sorption behavior for HOCs were investigated (e.g., Kohl and Rice, 1999). Comparison between the sorption characteristics of Phen before and after removal of free and bound lipids could help in understanding their role in the total sorption. For example, Wen et al. (2007) reported that Phen sorption by a solvent-extracted lipid exhibited a linear isotherm, and the removal of lipid increased the sorption nonlinearity and capacity of Phen by humin. This is similar to findings by Kohl and Rice (1999) who used lipid free soil as sorbent. Another frequently investigated biopolymer is lignin because of its relatively high aromaticity and high abundance among natural biopolymers (Chefetz et al., 2000). Wang et al. (2007a) found that the sorption isotherms of Phen and pyrene on a commercial lignin were almost linear, with the n value of 0.96 and 0.94, respectively. In contrast, pyrene displayed a strong non-linear sorption isotherm on a degraded lignin (Chefetz et al., 2000). Gunasekara et al. (2003) observed that Phen sorption isotherms were more linear on bleached humic acids that had lignin removed structurally than on the corresponding untreated humic acids. Hence the sorption mechanism of HOCs on lignin is still under discussion.

In contrast to free lipids and bound lipids, efficient separation of lignin from soil and sediments has not been reported, although CuO oxidation has been extensively used for the semi-quantitative analysis of lignin phenols in soil, sediment and water (Hedges and Ertel, 1982; Kaiser and Benner, 2012). In the paper industry, some chemical treatments have been widely applied to isolate lignin from pulp (Gellerstedt et al., 1994). It has been reported that isolation with dioxane was considered as a relatively “soft” method because of less alteration to the extracted lignin (Gellerstedt et al., 1994; Evtuguin et al., 2001). Therefore, a dioxane-acid hydrolysis method was applied to the lignin isolation in this study. Considering that SOM is much more heterogeneous than pulp, it is expected that the lignin isolation would be significantly influenced by SOM matrix. Thus, we employed a series of measurements to verify the extracted lignin fraction.

Free lipid (FL), bound lipid (BL), and lignin (LG) were sequentially isolated from demineralized sediment (DM). Both the extractable fractions and the residual SOM fractions (DM, FLF, BLF and LGF) were investigated with respect to the Phen sorption isotherms. The investigation was conducted to further understand the sorption characteristics of HOCs on these organic fractions and the contribution of the different SOM constituents to the total sorption of HOCs in sediments.

2. Materials and methods

2.1. Sorbent isolation

Two sediments, Xialu (XL) and He'an (HA), were collected by using a boxing sampler from the Dongjiang River, a main tributary of the Pearl River. The samples were freeze-dried and finely ground to pass a 180 μm sieve. The total organic carbon (TOC) content of XL and HA (D12 and D16) was 3.31% and 1.62%, respectively (Gong et al., 2009). A given amount of each sediment was used to sequentially extract the various SOM fractions. The flow chart in Fig. S1 in the Supporting information summarizes the major steps for isolating the SOM fractions. The detailed procedures are described as follows.

Each sediment was decarbonated with 1 M HCl and demineralized (5 times) with 1 M HCl/10% HF (Gélinas et al., 2001). Inorganic

minerals and a small fraction of organic matter (OM) were dissolved in the acid solution and discarded along with the supernatants after centrifugation (4500 r min^{-1} , 30 min). The solid residue (DM) was rinsed with milli-Q water and dried in an oven at 50 °C.

The free lipids and bound lipids were respectively isolated on the basis of traditional treatment via solvent extraction and saponification (Hu et al., 2006). Briefly, free lipids were extracted repeatedly from an aliquot of DM with a dichloromethane (DCM)/MeOH (2:1, v/v) using ultrasonic cleaner. The combined extracts (FL) were concentrated with a rotary evaporator and the residual solvent removed under a gentle stream of N_2 . After removal of the free lipids, the solid residue (FLF) was dried at 45 °C. A subsample was saponified (1 M KOH containing 90:10 MeOH/water, 80 °C, 12 h). The reaction vessel was centrifuged (4000 r min^{-1} , 30 min) and the supernatant removed. The bound lipids were repeatedly extracted with DCM from the supernatant before and after adjusting the pH to 1. The DCM extracts were combined and rotary-evaporated to dryness. The residue (BLF) was freeze dried. The extracts (BL) were operationally defined as bound lipid. Only tens of mg of each BL were obtained, so the isotherms for the BL fraction were not investigated.

The acid hydrolysis method for lignin isolation is detailed elsewhere (Evtuguin et al., 2001). A subsample of the BLF fraction was refluxed in 0.1 M HCl solution containing 82:18 dioxane/water for 2 h under N_2 , and the mixture then separated by centrifugation. The residue (LGF) was washed (3 times) with 82:18 dioxane/water and freeze dried. The supernatants combined with the washing solution were evaporated at 40 °C until all the dioxane was removed. During this step, pure water was added to avoid over-concentrated acid being present. The residual solid (LG) was collected via centrifugation. The extracted lignin was washed with pure water till neutral and freeze-dried.

Each of the SOM fractions was ground prior to characterization and the sorption experiments. FL, BL, and LG were referred to as extracted fractions, whereas DM, FLF, BLF, and LGF were called residual fractions.

2.2. Characterization of each fraction

The samples were analyzed in duplicate for C, H, N, and O contents using an Elementar Vario EL III. The standard used for the calibration was acetanilide. The relative standard deviation for the duplicate analyses was ca. $\pm 0.3\%$. A Bruker VERTEX-70 infrared spectrophotometer was used to generate the Fourier transformed infrared (FTIR) spectra. The cross-polarization/magic-angle spinning (CP/MAS) ^{13}C NMR spectra were determined with a Bruker DSX400 spectrometer. The elemental composition and carbon distribution are shown in Table S1.

2.3. Batch sorption experiments

A batch technique using a given amount of sorbent (2–40 mg) and 20/50 mL ampoules was utilized for building sorption isotherms. The background solution was a mixture of 0.01 M CaCl_2 , 200 mg L^{-1} NaN_3 and 5 mg L^{-1} NaHCO_3 . Each isotherm was obtained using 10 levels of Phen concentrations. All the samples, along with the blanks, were run in duplicate, with 14 d mixing time on a shaker required to reach apparent sorption equilibrium. Preliminary tests showed that the apparent sorption equilibrium was reached at 7 d and 14 d for the original samples and organic fractions. The reactors were then placed in the dark (3 d) to allow the suspended sorbent particles to settle completely. An aliquot of any supernatant was mixed with 1 mL of MeOH and analyzed for the aqueous Phen concentration using a reverse phase high pressure liquid chromatography (HPLC, Shimadzu LC-20A) and a C_{18}

Table 1
Sorption parameters of the Phen isotherms and single point K_{oc} .

Sample	n	Log K_F ($\mu\text{g g}^{-1}$)/($\mu\text{g L}^{-1}$) ⁿ	N^a	R^2	Log K_{Foc}^b ($\mu\text{g g}^{-1}$ OC)/($\mu\text{g L}^{-1}$) ⁿ	K_{oc} (mL g^{-1})		
						$C_e = 0.005S_w^c$	$C_e = 0.05S_w^c$	$C_e = 0.5S_w^c$
<i>Xialu</i>								
OS	0.883 ± 0.011 ^d	0.210 ± 0.028 ^d	19	0.997	1.682	39 347	30 061	22 967
DM	0.890 ± 0.013	1.392 ± 0.024	20	0.997	1.774	49 166	38 200	29 680
FLF	0.708 ± 0.003	1.731 ± 0.003	19	0.994	2.162	87 806	44 846	22 905
BLF	0.686 ± 0.007	1.572 ± 0.016	18	0.997	2.099	73 194	35 528	17 245
LGF	0.559 ± 0.015	2.120 ± 0.036	17	0.993	2.613	191 768	69 467	25 164
FL	1.012 ± 0.014	1.618 ± 0.019	20	0.997	1.756	58 197	59 800	61 447
LG	0.985 ± 0.003	1.197 ± 0.028	20	0.996	1.419	25 557	24 661	23 797
<i>He'an</i>								
OS	0.796 ± 0.011	0.025 ± 0.007	19	0.994	1.753	39 859	24 919	15 579
DM	0.804 ± 0.011	1.480 ± 0.027	20	0.997	1.989	69 610	44 338	28 241
FLF	0.691 ± 0.004	1.706 ± 0.013	20	0.995	2.228	99 151	48 629	23 851
BLF	0.650 ± 0.009	1.575 ± 0.022	20	0.996	2.194	85 609	38 240	17 081
LGF	0.627 ± 0.008	1.968 ± 0.028	17	0.991	2.596	207 224	87 789	37 191
FL	1.101 ± 0.017	1.346 ± 0.021	20	0.997	1.507	38 234	48 233	60 848
LG	0.916 ± 0.001	1.335 ± 0.004	20	0.997	1.577	32 678	26 925	22 185

^a The number of the observation.

^b $K_{Foc} = K_F/OC\%$.

^c The unit of C_e is $\mu\text{g L}^{-1}$.

^d Standard deviation.

column (4.6 mm × 15 cm) with a UV detector. The instrumental detection limit for Phen was 0.07 $\mu\text{g L}^{-1}$, which was estimated at a signal to noise ratio of three. The Phen sorbed concentration was obtained using mass balance calculation. The detailed procedure can be found in Ran et al. (2007) and Sun et al. (2008).

The sorption data were fitted to the Freundlich isotherm model:

$$\log Q_e = \log K_F + n \log C_e \quad (1)$$

where Q_e is the solid phase concentration ($\mu\text{g g}^{-1}$), and C_e the liquid phase equilibrium concentration ($\mu\text{g L}^{-1}$). K_F is the sorption capacity-related parameter [$(\mu\text{g g}^{-1})/(\mu\text{g L}^{-1})^n$], and n the isotherm non-linearity index. The modeling results and fitting parameters are listed in Table 1.

3. Results and discussion

3.1. Content and properties of SOM fractions

The organic carbon (OC) remaining in DM accounted for 74% and 67% of TOC in XL and HA and was still representative of the bulk SOM (Table S1). On average, 30% of the OC in the original sediment was lost in the demineralization step. The unrecovered OM contained mainly carbohydrate-like materials (Gélinas et al., 2001). Compared with an average 20% of OC lost in the study by Gélinas et al. (2001), the slightly higher OC loss in this study could result from the revised method for demineralization with a longer interval and more times. However, the organic matter (OM) lost seemed to have a limited impact on the Phen sorption on SOM, as suggested by the similar nonlinearity and sorption capacity for the original sediments (OS) and DM fractions (Table 1). Besides, loss of OM (<13%) occurred during the BL and LG isolation steps (Table S1). During the treatment, the non-target treatment solutions were retained and analyzed for their TOC concentration. If these solutions are included, OC recovery was close to 100%.

The relative yields of the organic fractions were calculated on the basis of TOC in DM and shown in Table S1. The average yields of the residual fractions were 84% for FLF, 68% for BLF and 50% for LGF, respectively. FL accounted respectively for 18% and 11% of TOC of the two sediments. It is noted that each of these values was much higher than that of the free lipid (<5%) extracted directly from bulk soil and sediments (Tremblay et al., 2005). Additionally, the yield of LG in each of the two sediments (0.44% and 0.21%) was two orders of magnitude higher than that reported in the previous

investigations, in which lignin in sediments and soil was quantified via CuO oxidation under alkaline conditions (Hedges and Ertel, 1982). The above phenomena are likely related to demineralization because it increases the exposure of OM initially entrapped in minerals (Gélinas et al., 2001). Another possibility for the high extraction yield of lignin was the different extraction method, and other acid-hydrolyzable material besides lignin being extracted in the isolation. The latter possibility seems to be supported by the occurrence of N-containing compounds (average N ~ 3.2%) in the LG isolates, which were supposed to contain no N. However, for the degraded lignin, amid functional groups can be added to the aromatic carbon in lignin during humification (Schmidt-Rohr et al., 2004). Moreover, the contents of C and O in the LG isolates were much close to the values for the reported lignin in the other studies, while H contents were slightly higher than their values (Xing et al., 1994; Chefetz et al., 2000; Wang et al., 2007b; Yang et al., 2010). Furthermore, a van Krevelen diagram (Fig. 1) showed that the elemental ratios of the LG isolates almost fell in the range of lignin.

In addition to elemental composition, the FTIR and ¹³C NMR spectra (Fig. 2, Fig. S3) of LG isolate displayed a series of bands of lignin. From the FTIR spectra, the band of aromatic skeletal vibration was present at 1630 cm^{-1} , 1510 cm^{-1} and 1450 cm^{-1} . The two strong signal of C—O—C asymmetric stretching vibration of aryl ether occurred between 1230 cm^{-1} and 1250 cm^{-1} . The other main peaks were assigned as follows: O—H stretching vibration of carboxylic C (3420 cm^{-1}), C—H stretching vibration of aliphatic C (2925 cm^{-1} , 2850 cm^{-1}), and C=O stretching vibration of carboxylic C (1710 cm^{-1}). From the ¹³C NMR spectra, the peak of methoxyl C (49–65 ppm) has been considered to be a characteristic of lignin. The evident peaks at 49–65 ppm, combined with the aryl and O-aryl peaks at 109–161 ppm, suggested the presence of lignin in the LG fractions. However, much stronger signals occurred at 0–49 ppm. This indicated that the LG fractions isolated from the complex SOM also contained a fraction of aliphatic compounds such as bound lipid.

The H/C and O/C ratios in the SOM fractions were presented in the van Krevelen plot, and compared with those of several types of biopolymers and condensed organic matter previously reported (Kim et al., 2003; Ran et al., 2007, 2009) (Fig. 1). The residual fractions (DM, FLF, and LGF) were different from NHC fraction (NHC) reported before (Ran et al., 2007, 2009; Sun et al., 2008). H/C and O/C ratios in the last residual fraction LGF were higher than in

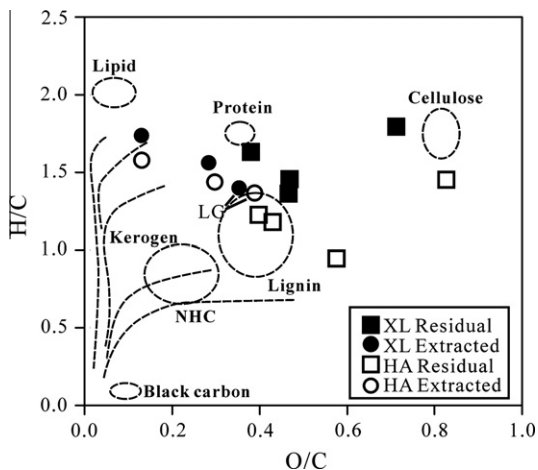


Fig. 1. The van Krevelen diagram for the different organic fractions in the sediments. The ranges (dashed circles and lines) of some natural and condensed organic matter are also showed in the diagram. NHC represents nonhydrolyzable organic carbon.

any of the extracted fraction and NHC (Table S1, Fig. 1), implying that it still contained some amount of biopolymer. Due to the lowest ratios of O/C, the FL fractions had the lowest polarity among the SOM fractions, consistent with previous investigations (Kohl and Rice, 1999; Wen et al., 2007). The polarity was highest for the BLF fraction because the saponification-derived hydroxyl and carboxyl bonds were linked to the organic matrix. This pattern also occurred in the BL fraction which yielded depleted carbon and enriched oxygen.

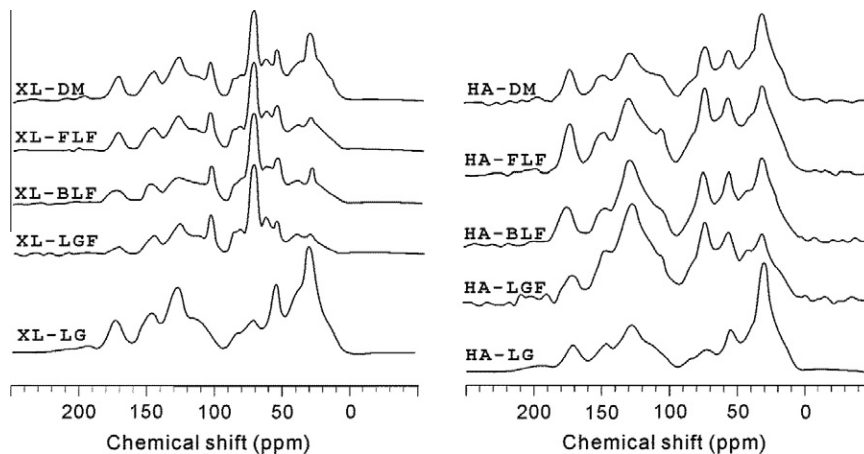


Fig. 2. CP/MAS ^{13}C NMR spectra of the residual and LG fractions.

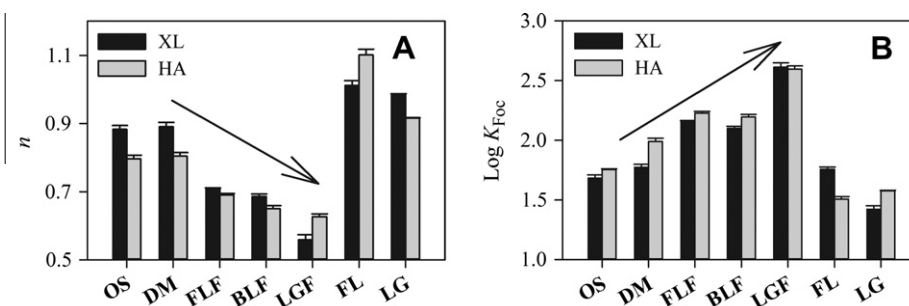


Fig. 3. The nonlinearity (A) expressed by n and the sorption capacity (B) expressed by $\log K_{\text{Foc}}$ for the Phén sorption isotherm on the original sample as well as the extracted and residual fractions. The unit of K_{Foc} is $(\mu\text{g g}^{-1} \text{OC})/(\mu\text{g L}^{-1})^n$.

The ^{13}C NMR spectra were similar for the XL and HA residual fractions (Table S1, Fig. 2), except for the peaks of alkyl C (0–49 ppm) and aryl C (109–141 ppm). The integrated area of the alkyl C decreased as the extractable components were removed, while the aryl C increased. The alkyl C peak in FLF was considerably lower than in DM, indicating the FL isolates were riched in nonpolar aliphatic C. Additionally, carboxyl C (161–188 ppm) was noticeably removed from the LGF fractions.

3.2. Sorption parameters on the SOM fractions

Table 1 and Fig. S3 show that the sorption isotherms of Phén by all the sorbents were fitted well by the Freundlich model, as indicated by the correlation coefficients (>0.99). The value of K_{Foc} was calculated by dividing K_{F} by TOC content, which represented the sorption capacity on SOM.

The K_{Foc} values in the OS sediments were 48.12 and 56.64 $(\mu\text{g g}^{-1} \text{OC})/(\mu\text{g L}^{-1})^n$, respectively, which were similar to the previously reported values (Ran et al., 2007). At a given C_e , the two demineralized (DM) sediments samples have a similar K_{OC} value to that of their respective bulk sediment sample, suggesting that NOM properties were not greatly affected by the dilute acid treatment. Moreover, the nonlinearity of the OS samples ($n = 0.88, 0.80$) was close to that of the corresponding DM fraction. Similar pattern was also observed in other sediments, humic acid, humin, and their demineralized fractions (Ran et al., 2007). This fact implies that the nonlinear sorption of Phén is closely associated to the organic phase, rather than the inorganic mineral.

The removal of the free lipid components greatly increased the sorption capacity as well as the nonlinearity (Table 1, Fig. 3). Free

lipids mainly consisting of n-alkanes, saturated and unsaturated fatty acids, diols, as well as n-alkyl monoesters, may occupy a set of sorption sites with different sorption energies on SOM. The removal of these compounds led to exposure of these heterogeneous sorption sites (Kohl and Rice, 1999). In turn, the presence of free lipids in SOM should block the accessibility of sorption sites for Phen. And a strong competition between lipids and Phen had been observed (Wang et al., 2007b). The single K_{oc} for the FLF fractions increased mainly at lower aqueous concentrations, while it decreased at higher concentrations. This phenomenon is related to the nonlinear sorption of Phen on FLF. It also suggests that the sites occupied by the FL component are partially associated with high energy sorption. The sorption of Phen by the FL fractions was almost linear, consistent with the previous investigations (Wen et al., 2007). It supports the hypothesis that free lipid compounds exhibit a partitioning domain in SOM. The n values for FL were slightly >1 , probably due to self-adsorption in higher concentrations (Henrichs and Sugai, 1993; Kohl and Rice, 1999). Saponification had a relatively insignificant effect on the sorption nonlinearity of Phen on the residual SOM, as indicated by the small decrease in $\log K_{Foc}$ value from 2.19 for FLF to 2.15 for BLF and n value from 0.70 to 0.67. The highly elevated ratios of O/C after saponification suggested an obvious increase in the polarity for the BLF samples, which was responsible for the slightly decreasing sorption capacity compared to the FLF fraction. More specific mechanism could be explained as follows. After saponification, the increase of hydrophilic groups (e.g., carboxyl and hydroxyl) may block the access of hydrophobic Phen to adsorption sites and partitioning domains in the SOM matrix (Chefetz and Xing, 2009). However, the release should not largely influence the sorption behavior of Phen because of the extremely low contents of bound lipids in the investigated sediments.

A striking change in the sorption occurred when the third distinct bio-component was removed from SOM. The highest nonlinearity ($n = 0.56, 0.63$) was present in LGF among the fractions. In addition, the single K_{oc} values for Phen on LGF, especially at low Phen concentration, were much higher than those of the other residual fractions. These sorption parameters of LGF were similar to those of glass, hard, or condensed SOM. For instance, the n values of the Phen for NHC ranged from 0.65 to 0.77, and those for BC ranged from 0.51 to 0.55 (Ran et al., 2007; Sun et al., 2008). The signal K_{oc} values ($C_e = 5.6 \mu\text{g L}^{-1}$) were comparable to those of NHC ranging from 90000 to 278000 mL g^{-1} (Ran et al., 2007; Sun et al., 2008). It has been reported that K_{oc} and n are positively associated with aromatic content of SOM (Cornelissen et al., 2005). The increase in sorption capacity and nonlinearity for LGF is consistent with the significantly elevated aromaticity (Table S1). The depletion in carboxyl carbon could also contribute to the elevated sorption in SOM matrix. It could be expected that the removed lignin component in SOM may produce a strong sorption competition with Phen, just like the FL fraction mentioned above. This competition was further supported by a fact that both phenanthrene and lignin contain aromatic carbon groups.

The Phen sorption by the extracted LG fraction had relatively linear isotherms, with n value close to 0.95. This observation was consistent with the linear sorption ($n = 0.96$) on an organic solvent-extracted wood lignin (Wang et al., 2007a). The lignin component was previously assumed to provide an explanation for the sorption nonlinearity of HOCs. The Phen sorption on the LG fractions did not exhibit strong nonlinearity, due in part to its aliphatic component. In contrast, nonlinear sorption ($n = 0.80, 0.63$) by an extracted lignin and a degraded lignin had been found in other studies (Chefetz et al., 2000; LeBoeuf and Weber, 2000). The variation in the nonlinearity of Phen sorption by lignin could be due in part to the different lignin sources, extraction methods, and sorption experiment approaches. However, the LG fraction in the pres-

ent investigation appeared to contribute to the absorption domain because of its extractability and approximately linear sorption isotherm for Phen.

3.3. Sorption trend for the SOM fractions

Obvious differences occurred in the sorption characteristics between the extracted and residual fractions (Fig. 3). The Freundlich isotherms of Phen on the extracted fractions (FL and LG) were relatively linear with n values ranging from 0.92 to 1.10, whereas those on the residual fractions were nonlinear with n varying from 0.56 to 0.89. In addition, the sorption capacity of the residual fractions was generally higher than that of the extracted fractions. The above result indicated that the extracted fractions belonged to the rubbery domain characterized by linear sorption and low sorption capacity (absorption), and the residual fractions contained glassy, hard SOM characterized by nonlinear sorption and high capacity (adsorption) (Xing and Pignatello, 1997).

The sorption capacity $\log K_{Foc}$ of each residual fraction increased as each of three bio-components were sequentially removed (Fig. 3). A remarkable increase in the Phen sorption on each of the LGF samples occurred over the whole concentrations of Phen (Table 1). As demonstrated above, the LGF fraction was similar to the condensed SOM such as NHC. However, BLF was an exception to this trend, which showed lower sorption coefficient K_{oc} over the entire concentrations of Phen (Table 1). This phenomenon was associated with its high O/C ratio and polarity.

Fig. 3 shows that the n values in each of the residual fractions decreased from 0.85 to 0.59 as the different biopolymers were removed from the SOM matrix. In other words, the more the biopolymers were removed, the more nonlinear the Phen isotherms on the SOM fractions were. According to dual sorption model, the nonlinearity for the sorption isotherm was linked to energy distributions of sorption sites of SOM (Xing and Pignatello, 1997). Thus the increasing nonlinearity meant that the energy of adsorption sites is enhanced after removals of different extractable OM fractions (Kohl and Rice, 1999). The n value for LGF was comparable to that of condensed SOM, such as NHC and BC (Ran et al., 2007), indicating that amorphous SOM was efficiently removed using the three different treatments.

3.4. Importance of organic fractions to total sorption by SOM

The relative contribution to the total sorption, based on an assumption that the SOM fraction in DM was fractionated to three extractable components (FL, BL, and LG) and residual fraction (LGF), was evaluated using the following equations:

$$Q_e = \phi_{FL} K_{F,FL} C_e^{n_{FL}} + \phi_{BL} K_{F,BL} C_e^{n_{BL}} + \phi_{LG} K_{F,LG} C_e^{n_{LG}} + \phi_{LGF} K_{F,LGF} C_e^{n_{LGF}} \quad (2)$$

$$f_i = \left(\frac{\phi_i K_{F,i} C_e^{n_i}}{Q_e} \right) \times 100\% \quad (3)$$

where Q_e is the sum of concentrations of sorbed Phen in each fraction ($\mu\text{g g}^{-1}$), and ϕ_{FL} , ϕ_{BL} , ϕ_{LG} , ϕ_{LGF} the relative yields based on the TOC of DM (Table S1). f_i is the proportion of each fraction contributing to the total sorption. The Freundlich sorption parameters of Phen by BL (not shown) were cited from our another work in which the bound lipids were extracted from coal using the same treatment.

As shown in Fig. 4, each fraction differed greatly in its contribution to the total sorption on SOM. Because of extremely low yield, the BL fractions had a negligible contribution to total sorption. The LG fraction reached a maximum sorption contribution of 9% when

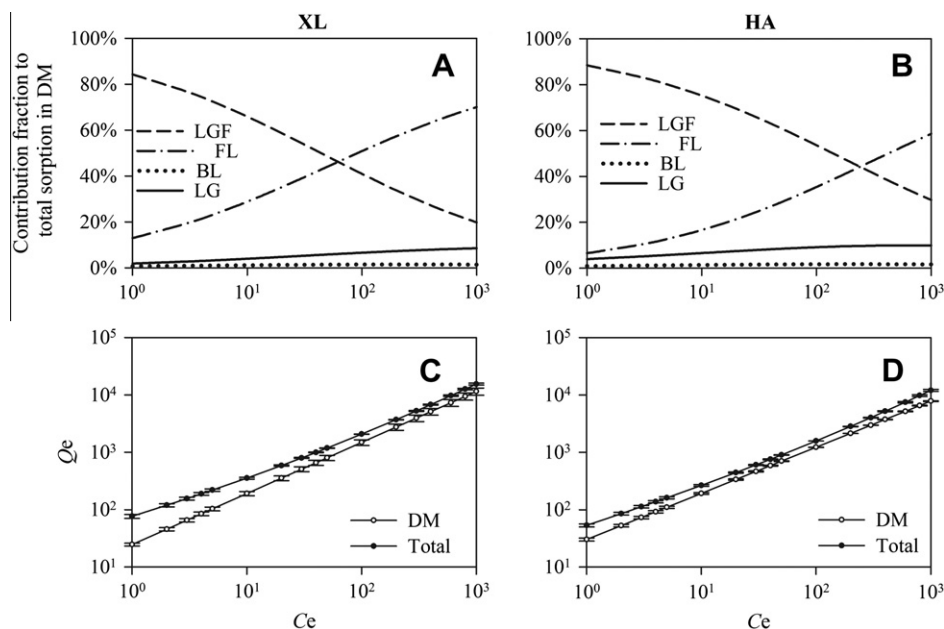


Fig. 4. (A and B) The calculated percentages for the contributions of the extractable FL, BL, and LG as well as the residual LGF to the total sorbed Phen in DM. (C and D) Comparison between the total sorption of Phen by four SOM fractions (FL, BL, LG, and LGF) and that by DM. The units of C_e and Q_e are $\mu\text{g L}^{-1}$ and $\mu\text{g g}^{-1}$, respectively.

the aqueous Phen concentration was at $1000 \mu\text{g L}^{-1}$, indicating the extractable lignin fraction accounted for a small portion of the Phen sorption. The contribution of LGF was most important at the low concentrations of Phen and decreased as the aqueous concentration increased, which was opposite to the trends of FLs. The contribution of FL in the XL sediment to total sorption even exceeded that of LGF, accounting for 64% of the total sorption at low Phen. The contribution of the FL fraction in the HA sediment was also significant when the Phen concentration is higher than 200 ng mL^{-1} . The above observations suggested that the sorption of Phen by FL became important at high concentrations of Phen, while the residual LGF fraction dominated the majority of the Phen sorption at the low aqueous concentrations.

The sum of sorbed Phen in the four organic fractions exceeded that in their parent DM, especially at the relatively low concentration of Phen (Fig. 4). This can be explained by competition of Phen with the extracted fractions and partition of Phen on the extracted fractions. Prior to removal, the extracted components occupied active sorption sites on organic matrix. Thus these sites were not available for Phen. However, the extracted fractions still formed a partition phase to sorb Phen. Therefore, the Phen sorption only occurred on the partitioning domain, whereas no adsorption on the occupied sorption sites occurred. Removal of the extractable components released these occupied sorption sites, which enhance adsorption capacity of organic matrix. Such enhancement should account for the difference between the sum of sorbed Phen on four separated fractions and that of SOM in DM.

4. Conclusion

In the present study, we investigated the role of different organic fractions in the sorption of Phen on SOM. The extracted lignin showed comparable properties with other model or degraded lignin in term of elemental ratios and sorption behaviors, demonstrating that the dioxane extraction procedure was suitable for the separation of lignin in the field sediments. It was found that FL and LG were quite important, as their contents were higher than previously reported values. When any of the extractable fractions was removed, the heterogeneity of sorption energy distribution

and sorption capacity of SOM increased. The extracted fractions basically exhibited linear isotherms and low sorption capacity for Phen. But the residual fractions showed nonlinear isotherms and high sorption capacities for Phen. The high sorption capacity and nonlinearity for LGF were similar to those of reported condensed SOM, suggesting that the residual and condensed SOM dominated the sorption. However, FL was an important partitioning domain for the sorption at high aqueous concentrations of Phen.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2012.10.064>.

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