Effects of humic acid and lipid on the sorption of phenanthrene on char

Bei Wen^{a,*}, Ri-xiang Huang^a, Rui-juan Li^a, Ping Gong^a, Shuzhen Zhang^a, Zhi-guo Pei^a, Jing Fang^a, Xiao-quan Shan^{a,*}, Shahamat U. Khan^b

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b Department of Chemistry and Biochemistry, MSN 3E2, Science and Technology, Building I, Room 358, George Mason University, 4400 University Drive, Fairfax, Virginia 22030-4444, USA

ARTICLE INFO

Article history:

Received 14 May 2008

Received in revised form 5 February 2009

Accepted 12 February 2009

Available online 5 March 2009

Keywords:

Phenanthrene

Sorption

Char

Lipid

Humic acid

Coating

ABSTRACT

The impact of two types of natural organic matters (NOM), humic acid (HA) and lipid, on char properties and sorption affinities for phenanthrene was studied. Char was coated with HA and lipid at a concentration of 0.060, 0.250 and 0.500 g/g char. HA, lipid, char and coated char were characterized and their sorption behaviors for phenanthrene were compared. Coating with NOM increased the polarity and aliphaticity, and reduced the specific surface area (SSA) of char, depending on the coated amount and the type of NOM. At the lower HA and lipid loading there was a strong attenuation of N₂-assessable SSA. The SSA attenuation was less pronounced at larger HA and lipid loadings, which was most likely due to the preferential sorption at reactive sites and formation of clusters. The sorption isotherms of phenanthrene on char and coated char fitted Freundlich equation well, suggesting that all sorption isotherms were nonlinear, with *N* values in the range of 0.495–0.873. Coated char with HA and lipid decreased the organic carbon-normalized sorption coefficients *K*_{FOC} and increased the *N* values. Lipid was more effective than HA in decreasing SSA, phenanthrene sorption capacity and sorption isotherm nonlinearity. The *N* values were correlated positively with the aliphaticity and negatively with pore volume of sorbents. The results of this investigation demonstrated that different NOM plays a different role in attenuating the SSA and sorption affinity of char for phenanthrene.

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1. Introduction

Black carbon (BC), a general term used for incomplete combustion products of fuel or biomass burning, is ubiquitous in the environment. It has been widely found in soils, lakes and deep-sea sediments (Cornelissen et al., 2005), atmospheric aerosols (Mittra and Sharma, 2002) and ice (Hansen and Nazarenko, 2004). Sorption of hydrophobic organic compounds (HOCs) on BC is up to 10–1000 times greater than that of soil organic matter (Cornelissen et al., 2005). BC has been reported to limit the availability of HOCs (Thorsen et al., 2004; Moermond et al., 2005; Brown et al., 2006). Therefore, it is considered as a cost-effective material for controlling the fate and remediation of anthropogenic contaminants (Koelmans et al., 2006). Thus the adsorbent properties of such BC in the field have been the subject of considerable interest.

It has been observed that sorption ability of BC in the field in the presence of organic matter is not as strong as “intrinsic” BC (Cornelissen and Gustafsson, 2004; Jonker et al., 2004). One of the possible mechanisms is the sorption of natural organic matter (NOM) on BC, leading to the sorption site competition and pore blockage. Direct evidence for surface activity attenuation of BC by NOM in soil was reported by Kwon and Pignatello (2005), who found that “aging” of

prepared wood char suspended in soil–water solution led to the benzene solids–water distribution coefficient reduction and the N₂ multipoint Brunauer–Emmett–Teller specific surface area (SSA) attenuation. In another experiment, they showed that the effect of HA on the surface area of char was dependent on the coating method. Compared with sorption of dissolved HA from water and co-flocculation with Al³⁺, coevaporation of char with HA was the most exertive method that dramatically reduced the SSA of the char. Sorption of phenanthrene on char was suppressed obviously by coating methods of both sorption of HA and co-flocculation HA with Al³⁺. However, Cornelissen and Gustafsson (2006) found that precipitation of HA coating on environmental BC did not reduce the sorption of phenanthrene, whereas PAH additions did.

NOM is a complicated mixture originating from a variety of plant, animal and microorganism residues at varying stages of decomposition, which has different chemical composition and plays a different role in HOC sorption (Huang et al., 2003). NOM other than humic macromolecules such as lipid may also affect the surface properties of BC. Results obtained by Kohl and Rice (1999), and Tremblay et al. (2005) showed that after extraction of lipid from sediment and humin, the sorption capacity of phenanthrene increased drastically, and the nonlinearity of the sorption isotherms was much more pronounced, thereby revealing the important role of lipid in the HOC sorption. However, Drori et al. (2006, 2008) found that phenanthrene sorption was not significantly affected by lipid removal. Lipids were better competitors for sorbates capable of polar interactions than for

* Corresponding authors. Tel.: +86 10 62923560; fax: +86 10 62923563.

E-mail addresses: bwen@rcees.ac.cn (B. Wen), xiaoquan@rcees.ac.cn (X. Shan).

phenanthrene. They suggested that the composition of lipid might be a key consideration in unraveling the sorption of organic molecules in soils. Kwon and Pignatello (2005) found that vegetable oil could strongly reduce SSA determined by N₂-BET method of wood char. It should be pointed out that in the above-mentioned studies, sorption attenuation caused by HA and lipid have been studied separately, which makes it difficult to compare the roles of HA and lipid in affecting the sorption of HOCs. Xiao et al. (2004) expected that compared with hydrophilic fulvic and humic acids, hydrophobic lipid may play a more important role in blocking surfaces and pores of organic particles, hence lowering the overall sorption capacity.

Kaal et al. (2008) found that aged charcoal in soils afforded benzenes, PAHs, carbohydrates, N-compounds and lipids. Similar results were obtained by Laird et al. (2008). They hypothesized that as the BC particles, which were charcoal formed originally during prairie fires, aged in soil anomeric and aliphatic C may accumulate in the BC particles either by adsorption of dissolved biogenic compounds from the soil solution or by direct deposition. In order to better understand the role of BC in the environment on the fate and bioavailability of HOCs, and to evaluate the efficiency of added BC for soil/sediment remediation, it is essential to elucidate the interactions between different kinds of NOM and BC. In this study, a synthetic char was employed because it is difficult to isolate char from soil or sediment without destroying its original properties. The aims of the present study were (1) to compare the properties of HA and lipid-coated char; (2) to examine the sorption of phenanthrene, a model HOC compound, on these coated chars; and (3) to explore the relationship between properties of these sorbents and their sorption features for phenanthrene.

2. Materials and methods

2.1. Reagents and materials

Reference standard of phenanthrene (HPLC grade, 99.9%) and internal standard of naphthalene were obtained from Aldrich Chemical Co., Inc. The compounds were used without further purification. The aqueous solubility of phenanthrene is 1.29 mg/L, and the octanol–water partition coefficient, log K_{ow}, is 4.57.

All the organic solvents used were commercially available. Methanol (Mallinckrodt, USA) and dichloromethane (Merck, USA) were of pesticide grade.

Char was prepared by atmospheric pyrolysis according to the method of Braida et al. (2003). Willow-wood shavings were placed in a 15-cm watch-glass-covered crucible and heated at 400 °C for 2 h. The material was then pulverized gently in a mortar to pass through a sieve No. 65 (0.25 mm), and stored in a glass vial at room temperature.

2.2. Extraction of HA and lipid from peat soil

HA and lipid were extracted from a commercially available peat soil purchased from Jilin Changbai Mountain Peat Moss Development Co., Ltd. (Changchun, Jilin, China). Its organic matter content, determined by the Walkley–Black procedure (Nelson and Sommers, 1982), was 46.5%. pH value measured at a solid to 0.01 mol/L CaCl₂ solution ratio of 1:1 (w/v) was 6.6.

HA was isolated from peat soil according to the International Humic Substances Society (Swift, 1996) with 0.1 mol/L NaOH solution (a soil:solvent ratio of 1:10), and precipitated with 6 mol/L HCl added to the extract until a pH of 2.0 was reached. The precipitated HA were separated by centrifugation and purified by successive redissolution-precipitation of the extracts, then dialyzed by Spectrapor membrane (size exclusion limit 6000–8000 D) and finally freeze dried.

Lipid materials were extracted from the peat soil by Soxhlet extraction with benzene:methanol (3:1, v/v) for 72 h (Tremblay et al., 2005). The extracted lipids were recovered by rotary evaporation.

2.3. Coated char with HA and lipid

HA (0.060 g for char–HA-low, 0.250 g for char–HA-medium, and 0.500 g for char–HA-high) was dissolved in 40 mL 0.01 mol/L KOH (pH 12). One gram of char was added to each HA solution. After shaking for 30 min, HA and char were allowed to settle down for 24 h. Water was removed in a rotary evaporator at 40 °C under vacuum established by water aspiration. Char–HA was pulverized gently in a mortar to pass through a sieve No. 65 (0.25 mm), and stored in a glass vial at room temperature. The char–HA-low, char–HA-medium and char–HA-high samples are referred as CHL, CHM and CHH, respectively.

Lipid (0.060 g for char–lipid-low, 0.250 g for char–lipid-medium, and 0.500 g for char–lipid-high) was dissolved in 40 mL benzene and methanol (3:1, v/v). One gram of char was added to each lipid solution. After shaking for 30 min, the char was allowed to settle down for 24 h. Benzene and methanol were evaporated by rotary evaporator. The char coatings were freeze dried for 24 h, pulverized gently in a mortar to pass through a sieve No. 65 (0.25 mm), and stored in a glass vial at room temperature. The char–lipid-low, char–lipid-medium and char–lipid-high samples are referred as CLL, CLM and CLH, respectively.

2.4. Characterization of the HA, lipid, char and coated char

The elemental composition (C, H, N) was analyzed with a high-temperature combustion method (PE 2400 SERIES II analyzer, PE, Inc.). Oxygen content was calculated by the mass difference. Ash content was determined by combustion at 800 °C for 4 h.

The char and char coating morphologies were observed by using scanning electron microscopy (SEM, JSM-6700F, JEOL Co., Japan).

Fourier transform infrared (FTIR) spectra were obtained on a NEXUS 670 spectroscopy (Thermo Nicolet Company, Madison, Wisconsin, USA) equipped with deuterated triglycine (DTGS) and mercury–cadmium–telluride (MCT) detectors (Thermo Nicolet Company, Madison, Wisconsin, USA), a KBr beam splitter (Thermo Nicolet Company, Madison, Wisconsin, USA) and a sample bench purged with dry air. The resolution of FTIR spectroscopy was 2.0 cm^{−1}, and a total of 64 scans were collected for each spectrum. For FTIR analyses a mixture of 5.0 mg of lipid or HA, or 1.0 mg of char and coated char, and 100 mg of dried KBr was pressed to pellet under reduced pressure.

The ¹³C NMR spectra of the lipid, HA, char and coated char were obtained by using a cross-polarization and magic angle-spinning (CPMAS) and on a 300-MHz NMR spectrometer (Varian, San Francisco, USA). Spectra were acquired at a frequency of 75 MHz for ¹³C MAS spinning rate of 13 kHz, contact time of 5 ms, 4 s recycle delay. The number of scans was from 5000 to 10,000 per sample.

2.5. Surface area measurement

Char and coated char were dried to constant weight at room temperature in a vacuum desiccator prior to surface area analysis. Samples were heated at 80 °C and degassed at this temperature under a vacuum of 10^{−5} Torr to constant pressure. The weight of the sample cell containing char remained unchanged after degassing, confirming negligible loss of material during this step. Nitrogen specific surface area (SSA) of char and coated char was estimated by using an ASAP 2010 surface area analyzer (Micromeritics Instrument Corp., Norcross, Georgia, USA). Nitrogen sorption–desorption isotherms were measured at 77 K. The isotherms were used to calculate the SSA, micropore volume (V_{mic}), and mesopore volume (V_{mes}). All the above parameters were calculated using the Density Functional Theory (DFT) (Olivier, 1998). Precision of replicated samples averaged 5%.

2.6. Sorption experiments

A batch technique with fixed sorbent amount was utilized for all sorption experiments. Background solutions of 0.01 mol/L CaCl₂ and

200 mg/L NaN_3 were used in all sorption experiments in order to prevent any potential dissolution of HA in solution and biological degradation of phenanthrene. pH was adjusted to 4.0. In brief, 40-mL glass tubes with Teflon-lined cap were used as batch reactors. The tubes were filled to a minimal headspace with phenanthrene solution (42.4 mL) and sealed. According to our preliminary sorption rate and equilibrium studies, an equilibration time of 15 days was found to be adequate. Our preliminary tests indicated that apparent equilibrium was reached before 3 days for HA and lipid and 15 days for char and coated char. The initial aqueous-phase phenanthrene concentrations (0.05–1.0 mg/L) were selected to yield a set of isotherm data for each sample that distributed evenly on a log–log scale plot to span approximately 2 orders of magnitude in aqueous-phase solute equilibrium concentrations (C_e in mg/L). The amount of sample (10–20 mg) in each tube corresponded to a sample-to-solution ratio that would result in 15–99% uptake of phenanthrene. Reactors filled with sorbent and initial aqueous solution were mixed completely by shaking at 125 rpm at room temperature ($20 \pm 1^\circ\text{C}$) for 15 days. After centrifugation at 1667 g for 20 min, phenanthrene in the supernatant was determined by high performance liquid chromatography (HPLC).

Control reactors prepared similarly but contained no sorbent were run simultaneously for assessing loss of solutes to reactor during sorption test. Blank reactors were conducted similarly but no sorbate. No detectable phenanthrene was found in blank. The dissolved organic carbon (DOC) in blank was qualified at the end of the experiments with a fully automated total organic carbon analyzer (Phoenix 8000, Tekmar-Dohrmann Company, Cincinnati, OH, USA). The DOC concentrations in solutions were 0.068, 0.248, 0.406 mg/L for CHL, CHM, CHH, and 0.049, 0.197, and 0.355 $\mu\text{g/L}$ for CLL, CLM, CLH, respectively, showing that the desorption amount of HA and/or lipid was less than 1% of those coated on the char. Results of triplicate sorption at each C_0 level showed that the average solution phase concentrations of each solute were consistently within 98–103% of the respective initial concentration of the same solution, indicating that microbial degradation and volatilization during the sorption, and the uptake to the glass walls were negligible. Hence, no correction was made during sorption experiments.

Freundlich model was applied to sorption data fitting in this work due mainly to its advantages in isotherm nonlinearity investigation. The model has the following form:

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

where Q_e is the solid-phase solute concentration (mg/kg) and C_e is the liquid-phase equilibrium concentration (mg/L). The parameter K_F is a Freundlich unit sorption capacity coefficient [(mg/kg)/(mg/L)^N] and N (dimensionless) is the index of isotherm nonlinearity. The estimated model parameters and their standard errors were calculated by linear for Freundlich model regression of data using the Origin version 7.0 at 95% confidence. Correlation coefficients (R^2) were used to evaluate the goodness of fitting.

2.7. Determination of phenanthrene

The concentrations of phenanthrene were determined using HPLC (reversed-phase C18 column, 4.6 mm $\times$ 25 cm, Agilent Technologies, Wilmington, USA) with a diode array detector (DAD) for concentrations ranging from 50 to 1000 $\mu\text{g/L}$ and a fluorescence detector for concentrations from approximately 0.3 to 50 $\mu\text{g/L}$. Isocratic elution was performed at a flow rate of 0.9 mL/min using the mobile phase of methanol:water (90%:10%). Naphthalene was used as internal standard. Under the HPLC conditions described phenanthrene showed a single peak at the retention time of 7.9 min. The solid-phase sorbate phenanthrene concentration (Q_e in mg/kg) was calculated for each reactor from a solute mass balance between the two phases.

3. Results and discussion

3.1. Characteristics of HA, lipid, char and coated char

Scanning electron microscopy results (Fig. 1) revealed that char and coated char retain the external physical morphology of the original wood structure.

The elemental compositions of char, lipid, HA and coated char, and their atomic ratios are presented in Table 1. Ash contents were very

Fig. 1. Scanning electron micrographs of char (a, b), CHH (c), and CLH (d).

Table 1
Morphological and chemical features of char, HA, lipid, and coated char

Sorbents	Mass fraction composition		SSA ^a (m ² /g)	Ash (%)	Elemental composition (wt.%)			Atomic ratio				Pore volume (cm ³ /kg)	
	<i>f</i> _{NOM}	<i>f</i> _{char}			C	H	N	O/C	H/C	C/N	(O+N)/C	<i>V</i> _{mic}	<i>V</i> _{mes}
Char	0	1	290.3	3.53	72.9	3.17	0.550	0.204	0.522	154.6	0.211	141	35.2
HA	1	0	0.78	1.61	53.2	5.29	3.56	0.512	1.1932	17.4	0.570	ND	ND
Lipid	1	0	ND ^b	0.75	55.4	7.64	2.51	0.456	1.655	25.8	0.495	ND	ND
CHL	0.057	0.943	192.4	3.24	71.8	3.30	0.955	0.216	0.552	87.7	0.228	132	17.0
CHM	0.200	0.800	31.2	3.16	69.1	3.49	1.03	0.252	0.606	78.1	0.265	91.0	8.04
CHH	0.333	0.667	29.2	3.37	66.3	3.87	1.27	0.285	0.700	60.98	0.301	68.3	5.89
CLL	0.057	0.943	177.1	3.27	72.3	3.41	0.588	0.212	0.566	143.5	0.219	116	10.6
CLM	0.200	0.800	24.5	3.11	69.3	4.18	0.752	0.245	0.724	107.5	0.255	61.5	5.08
CLH	0.333	0.667	22.9	3.18	67.1	5.18	0.901	0.264	0.926	87.0	0.276	57.3	4.07

^a SSA is the specific surface area.

^b ND: not determined.

low for all adsorbents. Char had lower N, H and O contents, and higher C content compared with HA and lipid. Thus, the polarity [(N+O)/C] was found to be the lowest for char. The H/C ratio of char is the lowest thereby suggesting its lower degree of aliphaticity. With the increasing amount of HA and lipid loading on char, the H/C and the polarity [(N+O)/C] increased.

The N₂-BET method has been the standard method for pore and surface characterization of porous materials and is an important tool for characterizing the preservation and locations of NOM in soil (Kaiser and Guggenberger, 2003), although it was thought to be not a reliable assessment of total surface area for microporous materials (Pignatello et al., 2006). SSA of char was 290.3 m²/g (Table 1). This value was lower than that of maple char (400 m²/g) (Kwon and Pignatello, 2005) but equivalent to red gum char (273 m²/g) (Yu et al., 2006) synthesized at the same temperature (400 °C).

The SSA of char reduced with increasing loading of HA and/or lipid (Table 1). The reduction was greater at small NOM loadings than at larger ones. For HA coated char, the reduction of the SSA, normalized to the amount of HA sorbed were 1718 m²/g HA at a loading of 0.060 g HA/g char, and 1296 and 784 m²/g HA at loadings of 0.250 and 0.500 g HA/g char, respectively. Similar or much obvious SSA attenuations were observed for char coated with lipid. The reduction of the SSA were 1986 m²/g lipid at loadings of 0.060 g lipid/g char, and 1329 and 803 m²/g lipid at loadings of 0.250 and 0.500 g lipid/g char, respectively. This indicates that HA or lipid sorbed on uncovered surfaces or surfaces with a small surface loading occupied a large portion of the available surface area. Similar phenomenon was observed in the sorption of NOM on mineral surface (Kaiser and Guggenberger, 2003), and on char surface (Pignatello et al., 2006). One possible explanation is that at small surface loadings, NOM molecules sorb in an uncoiled and spread-out conformation that allows a maximum sorption of NOM to attach to the adsorbent surface. At larger surface loadings the available surface is reduced, resulting in fewer NOM sorption and thus leaving part of the NOM molecules which do not attach to the adsorbent surface. Consequently, the surface area covered is smaller than at small surface loadings on a unit molecule basis. A second explanation is that with increasing surface loading an increasing portion of the NOM molecules does not attach to char surfaces but forms organic multilayers. Accumulation of HA and/or lipid on char surface is likely to occur in cluster rather than in the form of a continuous coating. A third explanation is that at small surface loadings sorption takes place primarily at sites such as pores where multiple attachment to the adsorbent surface at minimum stretching or unfolding of the sorbed molecules is possible. The molecular weight of HA varied considerably. Shinozuka et al. (2004) reported that the average molecular weight of peat-based and soil-based HA were 3700 and 10,500 D, respectively. Baigorri et al. (2007) analyzed the molecular size distribution of gray HA and brown HA by using ultrafiltration, and found that all the molecular weight of HA studied were higher than 5000 D. Lipid in different soils can differ considerably in chain length. Fatty acids are a major component of lipids in soils, originating from microorganisms (n-C_{4:0} to n-C_{26:0}) and waxes of plants and insects (n-C_{26:0} to

n-C_{38:0}) (Schnitzer et al., 1986). Burdon (2001) reported that lipid in the A horizon were dominant at C-25 and C-27. Wiesenberger et al. (2004) found that the lipid extracted from various agricultural soils distributed broadly, from C-13 to C-37. Accordingly, compared with HA, lipid is assumed to have small molecular weight, and thus smaller size, which may result in a more pronounced decrease of SSA of lipid-coated char and thus support the third explanation noted above. Pignatello et al. (2006) found that when co-evaporated with char, FA was slightly more effective than HA in suppressing surface area of the char, which may also come from the comparatively low molecular weight of FA.

A decrease trend of cumulative pore volume of both micro- and mesopore with increasing HA or lipid coating was evident (Table 1). It was suggested that most HA and lipid co-evaporated with char are present mainly on the external particles surface of char because they are too large to penetrate deeply into pore network (Kwon and Pignatello, 2005; Pignatello et al., 2006). Gun'ko et al. (2006) found that lipopolysaccharide, with molecular weight of 10 to 20 kD, mainly adsorbed on the meso- and macro-pore of carbon sieve. Kaiser and Guggenberger (2003) also proposed that penetration of NOM molecules through small size of micropores (<2 μm) seems unlikely.

The FTIR spectra of char, lipid, HA and coated char between 4000 and 800 cm⁻¹ are illustrated in Fig. 2. The broad band at 3440 cm⁻¹ is assigned to the stretching vibration of hydroxyl stretching. The bands of 1720 and 1658 cm⁻¹ are due to the C=O stretching. The absorbance at 2923 and 2850 cm⁻¹ results from aliphatic or alicyclic C–H stretching. The absorbance at 1276 and 1470 cm⁻¹ are attributed to C–O of phenolic, carboxylic and alcohol groups. The broad peak about 1210 is contributed to OH stretching of phenolic –OH. The prominent peak of 1610 cm⁻¹ represents the C=C aromatic moieties and the

Fig. 2. FTIR spectra of HA, lipid and coated chars.

Fig. 3. CPMAS ^{13}C NMR spectra of HA, lipid and coated chars.

asymmetric C=O stretching in $-\text{COOH}$ group. The peak of 1070 cm^{-1} is characteristic of C–O stretching of carbohydrate-like substances.

The differences in FTIR spectra among char, HA and lipid represent their different physicochemical and structural nature. Char has very low absorbance at 3440 cm^{-1} and high absorbance at 1610 cm^{-1} , revealing that it has small amount of hydroxyl groups and high amount of aromatic carbon. The absorbance at 2923 and 2854 cm^{-1} , 1410 – 1467 cm^{-1} , 1130 cm^{-1} in the lipid fraction are relatively large, thereby implying the aliphatic nature of the lipid fraction, which is consistent with its higher H/C value. The peak of 1399 cm^{-1} of lipid fraction was assigned to the stretching of carboxylate. HA has relatively higher absorbance at 3440 cm^{-1} , as well as 1720 , 1658 cm^{-1} , showing its higher polar contents. With increasing amount of lipid and HA loading, the absorbance at 2923 , 2850 , and 1720 cm^{-1} increased gradually in the coated char, which is consistent with their increase of H/C ratio and polarity. Compared with the IR spectra of individual HA, lipid and char alone, the stretching band of carboxylate COO^- of the HA- and lipid-coated char was shifted from 1720 to 1700 cm^{-1} , indicating that COO^- functional groups of HA and lipid may have a specific interaction of hydrogen bond with char surface. The peak intensity of 1070 cm^{-1} significantly diminished after HA sorption to char, which may imply high affinity for the C–O functional groups of HA.

The ^{13}C CP/MAS spectra and integrated data of char, HA, lipid and coated char are presented in Fig. 3 and Table 2, respectively. The spectra can be quantified by integrating the regions as follows: alkyl C

Fig. 4. Freundlich model data fitting for phenanthrene sorption by char (■), HA (●), lipid (▲) and char coatings, CHL (□), CHM (○), CHH (△), CLL (▼), CLM (×), CLH (*).

(0–50 ppm); O-alkyl C (predominantly carbohydrates, 50–110 ppm); aromatic C (110–165 ppm); carboxylic- and amide-C (165–190 ppm); and ketonic/aldehyde-C (190–220 ppm). The percentage of polar organic carbon (POC) was calculated as the combined fractions of the 50–110 and 165–220 ppm regions of the NMR spectra (Wen et al., 2007). The subordinate small and broad peaks near 230 ppm are due to spinning side bands originating from the dominant aryl peak.

A main resonance of char at 110–140 ppm, centered at approximately 130 ppm, is assigned to aromatic carbon. In addition to the main aromatic carbon resonance there is a slight shoulder at approximately 150 ppm, which is attributed to phenolic and aromatic ether carbons. The small peak from 0 to 110 ppm suggests that char has small amount of alkyl C. The carboxylic carbon at or about 167 ppm chemical shift is very small.

Compared with HA, lipid had the highest alkyl carbon content (0–50 ppm). The contents of aromatic carbon (110–165 ppm) and the carboxylic carbon at about 167 ppm were extremely low. Overall, the aliphatic carbon content increased in the order char < HA < lipid, while the polarity was in the order HA > lipid > char. After being co-evaporated with HA and lipid, the aliphatic carbon contents and polarity of char increased.

3.2. Sorption isotherms

Phenanthrene sorption isotherms for the char, HA, lipid and coated char fit Eq. (1) well, with all the correlation coefficients higher than 0.99 (Fig. 4, Table 3). The sorption capacity coefficients (K_F) were

Table 2

Integration results of solid-state ^{13}C NMR spectra and ratios of the sum of aliphatic to aromatic peak area of char, HA, lipid, and coated char

Sample	Distribution of C chemical shift (ppm) (%)						Aliphatic C (%)	Aromatic C (%)	Aliphaticity	POC (%)
	Alkyl C (0–50)	O-alkyl C (50–110)	Aromatic C (110–140)	O-aryl C (140–165)	Carboxyl C (165–190)	Carbonyl C (190–220)				
Char	10.4	7.95	55.5	13.2	4.56	8.39	18.4	68.7	0.267	34.1
HA	22.1	13.2	23	17.5	13.9	10.3	35.3	40.5	0.872	54.9
Lipid	78.8	12.6	2.93	2.26	2.97	0.44	91.4	5.19	17.6	18.3
CHL	12.3	10.7	50.2	13.4	5.05	8.35	23.0	63.6	0.362	37.5
CHM	13.1	11.1	48.4	13.6	5.44	8.36	24.2	62.0	0.390	38.5
CHH	16.95	11.7	42.1	14.8	6.05	8.45	28.6	56.9	0.503	41.0
CLL	15.6	8.81	48.1	14.4	4.71	8.38	24.4	62.5	0.391	36.3
CLM	24.6	8.92	44.2	11.1	4.83	6.35	33.5	55.3	0.606	31.2
CLH	29.0	8.90	41.6	9.58	5.44	5.45	37.9	51.2	0.740	29.4

Aliphatic C: total aliphatic carbon region (1–110 ppm). Aromatic C: total aromatic carbon region (110–165).

POC: the polarity of organic carbon was calculated from the peak areas listed above with an equation: $\text{POC} = (\text{O-alkyl C} + \text{O-aryl C} + \text{carboxyl C} + \text{carbonyl C}) / (\text{alkyl C} + \text{O-alkyl C} + \text{aromatic C} + \text{O-aryl C} + \text{carboxyl C} + \text{carbonyl C}) \times 100$.

Aliphaticity = aliphatic C (0–110 ppm) / aromatic C (110–165 ppm).

Table 3

Freundlich isotherm parameters for phenanthrene sorption onto char, HA, lipid, and coated char

Sample	Freundlich isotherm parameters						Single-point log K_{OC}^a					
	K_F^b	F_{OC}^c	K_{FOC}^b	N	n^d	R^2	$C_e=0.001$ (mg/L)		$C_e=0.01$ (mg/L)		$C_e=0.1$ (mg/L)	
							Of sample	Of char calculated ^e	Of sample	Of char calculated	Of sample	Of char calculated
Char	66,088±80	72.9	90,655	0.495±0.013 ^f	16	0.995	6.47	na	5.97	na	5.46	na
HA	10,234±46	53.2	19,238	0.910±0.016	16	0.998	4.55	na	4.46	na	4.37	na
Lipid	19,058±12	55.4	34,401	0.992±0.019	16	0.997	4.56	na	4.55	na	4.54	na
CHL	27,299±55	71.8	38,021	0.601±0.007	16	0.999	5.78	5.80	5.38	5.39	4.98	4.99
CHM	18,472±85	69.1	26,733	0.787±0.022	16	0.995	5.07	5.12	4.85	4.90	4.64	4.68
CHH	16,642±27	66.3	24,101	0.792±0.019	16	0.996	5.02	5.12	4.80	4.90	4.61	4.67
CLL	21,869±24	72.3	30,247	0.678±0.012	16	0.998	5.45	5.47	5.12	5.14	4.80	4.81
CLM	7425±28	69.3	10,715	0.823±0.017	16	0.997	4.56	4.56	4.38	4.34	4.21	4.10
CLH	12,618±26	67.1	18,806	0.873±0.016	16	0.998	4.61	4.69	4.48	4.52	4.35	4.33

"na" means not applicable.

^a $K_{OC}=K_{FOC} C_e^{N-1}$; the unit of K_{OC} is (L/kg OC), C_e is the liquid-phase equilibrium concentration (mg/L).^b $K_{FOC}=K_F/F_{OC}$; the union of K_{FOC} and K_F is the sorption capacity coefficient [(mg/kg)/(mg/L)^N].^c F_{OC} : organic carbon fraction (dimensionless).^d Number of observations.^e Of char calculated, K_{OC} calculated = $(K_{OC}$ sample $- f_{NOM} * K_{OC}$ NOM) / ($f_{char} * F_{OC}$ char), F_{OC} char: organic carbon content of char (0.729), K_{OC} sample = $K_{FOC} C_e^{N-1}$.^f One standard deviation (σ).

calculated from the slope of the linear portion of the isotherms. The concentration-dependent K_{OC} (L/kg OC) was calculated based on the following equation:

$$K_{OC} = (K_F/F_{OC})C_e^{N-1} \quad (2)$$

where F_{OC} is the organic carbon content. The values of K_{OC} can be used to denote directly the sorption characteristics of heterogeneous sorbents. The resulting model parameters, along with their standard errors (σ), and the calculated K_{OC} values at $C_e=0.001$, 0.01 and 0.1 mg/L are presented in Table 3.

The Freundlich equation parameters suggested that the phenanthrene sorption isotherm of char was highly nonlinear, as evidence for N value far from 1.0 ($N=0.495$). The sorption isotherm of phenanthrene on lipid was linear, with the N value of 0.992. N value could be taken as an index of site energy distribution (Weber et al., 1992). Smaller N values represent more heterogeneous sorption sites in nature. Xing and Pignatello (1997) suggested that nanometer-size voids within the organic matrix provide complexation sorption sites. Sorption of HOCs to wood chars is dominated by adsorptive pore-filling processes (Nguyen et al., 2007). Zhu et al. (2004) demonstrated the overlap of π -electrons in the aromatic black carbon structure and the planar aromatic ring of PAH molecules, suggesting the importance of aromatic carbons in PAH sorption. Thus, the largest pore volume and relatively higher aromatic carbon content of char were assumed to explain the lowest N value. Sorption of HA and lipid attenuated the nonlinearity of the sorption isotherms. The N values of HA and lipid-coated char increased with increasing HA and/or lipid loading levels, which ranged from 0.601 to 0.792, and 0.678 to 0.873, respectively. The N values of HA coated chars were lower than those of lipid-coated chars, which was assumed to be ascribed to their relatively large pore volume (Table 1) and high aromatic carbon content (Table 2). Regression analysis showed the significant inverse correlation between the pore volume of micropore and mesopore and N values ($R^2=0.983$, $p<0.01$), and a positive correlation between the aliphaticity and N values ($R^2=0.750$, $p<0.05$) thereby further verifying our assumption.

Similar attenuation was also found for the carbon-normalized sorption coefficients K_{FOC} values. Further loading with HA and/or lipid resulted in further attenuation except those of CHH and CLH. The K_{FOC} values of HA- and lipid-coated chars were from 24,101 to 38,021 and from 10,715 to 30,247, respectively.

However, it should be noted that a precise comparison cannot be made according to the K_{FOC} values due to their different units as a result of nonlinearity. Therefore, the concentration-dependent organic carbon-normalized sorption coefficient K_{OC} values at the

three-selected concentration ($C_e=0.001$, 0.01, and 0.1 mg/L) were employed to compare the sorption capacity (Table 3). Overall, K_{OC} was a concentration-dependent sorption coefficient, and lower C_e concentrations would result in higher K_{OC} values, as a result of nonlinear sorption. For char, the log K_{OC} values at 0.001 mg/L was 6.47, which is consistent with literature values (5.4–7.3) for laboratory wood char (James et al., 2005). For char coated with HA and CLL, the log K_{OC} values at 0.001 mg/L were in the range of 5.02–5.78, which is in conformity with the values (5.0–6.4) reported for field chars (James et al., 2005). For CLM and CLH at 0.001 mg/L, the log K_{OC} values were 4.56 and 4.61, respectively, which are about 0.5 orders of magnitude lower than those of HA coated char. Assuming that the K_{OC} of HA and lipid is unaffected by the char, the log K_{OC} of char calculated decreased with increasing HA loading (Table 3). However, for CHH, the log K_{OC} of char calculated was equivalent to that of CHM. This phenomenon was in accord with the SSA for HA coated chars that when loading level increased from 0.25 to 0.50 g HA/g char, SSA didn't decreased (Table 1). This finding further demonstrated the formation of organic cluster on the char surface. The log K_{OC} of char calculated for CLH was not lower and even higher than that of CLM. Chen and Xing (2005) examined the sorption of phenanthrene on lipid-coated montmorillonite, and also found that the organic carbon-normalized sorption coefficients (K_{OC}) increased with increasing lipid loading on clay. They attributed those to the different physical conformations of lipid. Lipid is reported to be a multiphase system consisting of crystalline and amorphous zones. The amorphous zones are subdivided into a solid zone and a mobile zone. The two NMR peaks of 32 ppm for crystalline and amorphous aliphatic carbons and 29 ppm for mobile or liquid amorphous aliphatic carbons were used to characterize the physical conformation of lipid. They could be observed clearly for CLH (Fig. 3), demonstrating the coexistence of amorphous and crystalline microdomains. In FTIR spectra of lipid (Fig. 2), a peak at 1720 cm⁻¹ (–COOH) was observed, but the –COOH peak in the ¹³C NMR spectra of 165–190 ppm was very weak. Mao et al. (2002) reported that the sp² carbons (110–220 ppm) or –COOH tend to be underrepresented by CP MAS ¹³C NMR due to their longer relaxation times (T_1 , spin-lattice relaxation time). According to this observation, –COOH of the lipid may be in rigid domains, corresponding to longer T_1 (Hu et al., 2000; Mao et al., 2000). When lipid was coated on char, a small peak at 167 ppm (–COOH) appeared and even more intensive with increasing coated lipid, indicating that some rigid domains changed to more mobile domains, corresponding to the reduced T_1 of ¹³COOH. Chen and Xing (2005) suggested that when lipid interacted with the mineral surface, polar portion of the lipid molecule was likely to displace water molecules near polar functional group of mineral

surface and allow the aliphatic portions to be retained near the uncharged region on the mineral surfaces by van der Waals interactions. At low lipid loads, a large volume fraction of the lipid molecules is supposed to form an ordered structure near the char surface. As loading increases and the availability of an ordered template (the char surface) limits, more and more lipid molecules assume the “mobile” conformation. The phenanthrene sorption capacity of mobile domain was higher than that of rigid domain of lipid. Although the functional group of char is limited, the shift of carboxylate COO^- of CLL, CLM and CLH from 1720 to 1700 cm^{-1} suggested the important roles of lipid COO^- functional groups in the interaction between lipid and char. Moreover, the appearance of peak in 167 ppm and the higher $\log K_{oc}$ value of CLH compared with CLM provide evidence of the interactions between polar portions of the lipid molecule and char surface and the different physical conformations of lipid.

4. Conclusion

NOM co-evaporated with char could increase the aliphaticity and polarity, decrease the SSA, pore volume of char, and thus attenuate the sorption capacity and sorption isotherm nonlinearity of phenanthrene on char. Compared with HA the attenuation effect of lipid was much pronounced which may be due to its relatively lower molecular weight and higher aliphatic carbon contents. This suggested that not only the amount, but also the nature of NOM played an important role in affecting the sorption behavior of char.

At the initial stages of surface loading there is a strong decrease in N_2 -assessible SSA with increasing surface coverage by NOM. This is most likely due to preferential sorption at reactive sites. After those sites have been occupied, further sorption of organic matter results in a smaller loss of SSA. Preferential binding at reactive sorption sites favors the surface accumulation of organic matter in the form of cluster rather than in a continuous coating. It should be mentioned that this work was conducted using a single nonpolar contaminant. Sorption of other types of contaminants, such as polar and ionized organic pollutants on char needs to be evaluated.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (Grant: 40730740, 20890110) and the Knowledge Innovation Program of the Chinese Academy of Sciences (Grant Kzcx-1-YW-06-03).

References

Baigorry, R., Fuentes, M., Gonzalez-Gaitano, G., Garcia-Mina, J.M., 2007. Simultaneous presence of diverse molecular patterns in humic substances in solution. *J. Phys. Chem. B* 111, 10577–10582.

Braida, W.J., Pignatello, J.J., Lu, Y., Ravikovitch, P.I., Neimark, A.V., Xing, B., 2003. Sorption hysteresis of benzene in charcoal particles. *Environ. Sci. Technol.* 37, 409–417.

Brown, R.A., Kercher, A.K., Nguyen, T.H., Nagle, D.C., Ball, W.P., 2006. Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. *Org. Geochem.* 37, 321–333.

Burdon, J., 2001. Are the traditional concepts of the structures of humic substances realistic. *Soil Sci.* 166, 752–769.

Chen, B., Xing, B., 2005. Sorption and conformational characteristics of reconstituted plant cuticular waxes on montmorillonite. *Environ. Sci. Technol.* 39, 8315–8323.

Cornelissen, G., Gustafsson, Ö., 2004. Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates. *Environ. Sci. Technol.* 38, 148–155.

Cornelissen, G., Gustafsson, Ö., 2006. Effects of added PAHs and precipitated humic acid coatings on phenanthrene sorption to environmental black carbon. *Environ. Pollut.* 141, 526–531.

Cornelissen, G., Gustafsson, Ö., Bucheli, T.D., Jonker, M.T.O., Koelmans, A.A., Noort, P.C.M.V., 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.* 39, 6881–6895.

Gun'ko, V.M., Betz, W.R., Patel, S., Murphy, M.C., Mikhailovsky, S.V., 2006. Adsorption of lipopolysaccharide on carbon sieves. *Carbon* 44, 1258–1262.

Drori, Y., Lam, B., Simpson, A., Aizenshtat, Z., Chefetz, B., 2006. The role of lipids on sorption characteristics of freshwater- and wastewater-irrigated soils. *J. Environ. Qual.* 35, 2154–2161.

Drori, Y., Aizenshtat, Z., Chefetz, B., 2008. Sorption of organic compounds to humin from soils irrigated with reclaimed wastewater. *Geoderma* 145, 98–106.

Hansen, J., Nazarenko, L., 2004. Soot climate forcing via snow and ice albedos. *P. Natl. Acad. Sci.* 101, 423–428.

Hu, W.G., Mao, J., Xing, B., Schmidt-Rohr, K., 2000. Poly(methylene) crystallites in humic substances detected by nuclear magnetic resonance. *Environ. Sci. Technol.* 34, 530–534.

Huang, W., Peng, P., Yu, Z., Fu, J., 2003. Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *Appl. Geochem.* 18, 955–972.

James, G., Sabatini, D.A., Chiou, C.T., Rutherford, D., Scott, A.C., Karapanagioti, H.K., 2005. Evaluating phenanthrene sorption on various wood chars. *Water Res.* 39, 549–558.

Jonker, M.T.O., Hoenderboom, A.M., Koelmans, A.A., 2004. Effects of sedimentary sootlike materials on bioaccumulation and sorption of polychlorinated biphenyls. *Environ. Toxicol. Chem.* 23, 2563–2570.

Kaiser, K., Guggenberger, G., 2003. Mineral surfaces and soil organic matter. *Eur. J. Soil Sci.* 54, 219–236.

Kaal, J., Brodowski, S., Baldock, J.A., Nierop, K.G.J., Cortizas, A.M., 2008. Characterisation of aged black carbon using pyrolysis-GC/MS. *Org. Geochem.* doi:10.1016/j.orggeochem.2008.06.011.

Koelmans, A.A., Jonker, M.T.O., Cornelissen, G., Bucheli, T.D., Van Noort, P.C.M., Gustafsson, Ö., 2006. Black carbon: the reverse of its dark side. *Chemosphere* 63, 365–377.

Kohl, S.D., Rice, J.A., 1999. Contribution of lipids to the nonlinear sorption of polycyclic aromatic hydrocarbons to soil organic matter. *Org. Geochem.* 30, 929–936.

Kwon, S., Pignatello, J.J., 2005. Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): pseudo pore blockage by model lipid components and its implications for N_2 -probed surface properties of natural sorbents. *Environ. Sci. Technol.* 39, 7932–7939.

Laird, D.A., Chappell, M.A., Martens, D.A., Wershaw, R.L., Thompson, M., 2008. Distinguishing black carbon from biogenic humic substances in soil clay fractions. *Geoderma* 143, 115–122.

Mao, J.D., Hu, W.G., Schmidt-Rohr, K., Davies, G., Ghabbour, E.A., Xing, B., 2000. Quantitative characterization of humic substances by solid-state carbon-13 nuclear magnetic resonance. *Soil Sci. Soc. Am. J.* 64, 873–884.

Mao, J.D., Hundal, L.S., Thompson, M.L., Schmidt-Rohr, K., 2002. Correlation of poly(methylene)-rich amorphous aliphatic domains in humic substances with sorption of a nonpolar organic contaminant, phenanthrene. *Environ. Sci. Technol.* 36, 929–936.

Mitra, A.P., Sharma, C., 2002. Indian aerosols: present status. *Chemosphere* 49, 1175–1190.

Moermond, C.T.A., Zwolsman, J.J.G., Koelmans, A.A., 2005. Black carbon and ecological factors affect in situ biota to sediment accumulation factors for hydrophobic organic compounds in flood plain lakes. *Environ. Sci. Technol.* 39, 3101–3109.

Nelson, D.W., Sommers, L.E., 1982. Total carbon, organic carbon, and organic matter. *Methods of Soil Analysis, Part 2. ASA and SSSA, Madison, WI.* 539–579 pp.

Nguyen, T.H., Cho, H.H., Poster, D.L., Ball, W.P., 2007. Evidence for a pore-filling mechanism in the adsorption of aromatic hydrocarbons to a natural wood char. *Environ. Sci. Technol.* 41, 1212–1217.

Olivier, J.P., 1998. Improving the models used for calculating the size distribution of micropore volume of activated carbons from adsorption data. *Carbon* 36, 1469–1472.

Pignatello, J.J., Kwon, S., Lu, Y., 2006. Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): attenuation of surface activity by humic and fulvic acids. *Environ. Sci. Technol.* 40, 7757–7763.

Schnitzer, M., Hindle, C.A., Meglic, M., 1986. Supercritical gas extraction of alkanes and alkanolic acids from soils and humic materials. *Soil Sci. Soc. Am. J.* 50, 913–919.

Shinozuka, T., Shibata, M., Yamaguchi, Y., 2004. Molecular weight characterization of humic substances by MALDI-TOF-MS. *J. Mass. Spectrom. Soc. Jpn.* 52, 29–32.

Swift, R.S., 1996. Organic matter characterization. In: Sparks, D.L., et al. (Ed.), *Methods of Soil Analysis, Part 3. Chemical Methods*. Soil Sci. Soc. Am. Book Series, vol. 5. SSSA, Madison, WI, pp. 1018–1020.

Thorsen, W.A., Cope, W.G., Shea, D., 2004. Bioavailability of PAHs: effects of soot carbon and source. *Environ. Sci. Technol.* 38, 2029–2037.

Tremblay, L., Kohl, S.D., Rice, J.A., Gagne, J.-P., 2005. Effects of lipids on the sorption of hydrophobic organic compounds on geosorbents: a case study using phenanthrene. *Chemosphere* 58, 1609–1620.

Weber, W.J., McGinley, P.M., Katz, L.E., 1992. A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments. *Environ. Sci. Technol.* 26, 1955–1962.

Wen, B., Zhang, J.J., Zhang, S.Z., Shan, X.Q., Khan, S.U., Xing, B., 2007. Phenanthrene sorption to soil humic acid and different humin fractions. *Environ. Sci. Technol.* 41, 3165–3171.

Wiesenberg, G.L.B., Schwarzbauer, J., Schmidt, M.W.I., Schwark, L., 2004. Source and turnover of organic matter in agricultural soils derived from n-alkane/n-carboxylic acid compositions and C-isotope signatures. *Org. Geochem.* 35, 1371–1393.

Xiao, B.H., Yu, Z.Q., Huang, W.L., Song, J.Z., Peng, P.A., 2004. Black carbon and kerogen in soils and sediments. 2. Their roles in equilibrium sorption of less-polar organic pollutants. *Environ. Sci. Technol.* 38, 5842–5852.

Xing, B., Pignatello, J.J., 1997. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environ. Sci. Technol.* 31, 792–799.

Yu, X.Y., Ying, G.G., Kookana, R.S., 2006. Sorption and desorption behaviors of diuron in soils amended with charcoal. *J. Agric. Food Chem.* 54, 8545–8550.

Zhu, D., Hyun, S., Pignatello, J.J., Lee, L.S., 2004. Evidence for π - π electron donor-acceptor interactions between π -donor aromatic compounds and π -acceptor sites in soil organic matter through pH effect on sorption. *Environ. Sci. Technol.* 38, 4361–4368.