Effects of humic acid coatings on phenanthrene sorption to black carbon

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Abstract

Black carbon (BC) can strongly adsorb hydrophobic organic compounds (HOCs). The HOC sorption to coated BC could be attenuated in soil and sediment compared with that of the parent BC. To study the potential causes of the sorption attenuation, humic acid (HA) and BC were isolated. Phenanthrene (PHE) was selected as the representative of HOCs. BC was coated with the precipitated HA. The PHE sorption to the HA-coated BC was determined. The HA coatings on BC could result in the significant sorption attenuation of PHE to BC. The attenuation varied in different HA origin and was positively correlated to the aromaticity of HA. The attenuation could be explained by the direct competition between HA and PHE for the available sorption sites on BC and the reduction of the available sorption sites as a result of the pore blockage of BC caused by the HA coatings. Therefore, the HA coatings on BC was one potential cause of the attenuation of HOC sorption to BC in soil and sediment.

Key words: black carbon; humic acid; phenanthrene; sorption; attenuation

Introduction

The pyrogenic carbon particles like soot and charcoal (collectively termed black carbon (BC)) are ubiquitous and frequently constitute 1%–20% of total organic carbon (TOC) in soil and sediment (Accardi-Dey and Gschwend, 2003). The sorption to BC has been observed to be up to 10–1000 times higher than the sorption to the non-BC organic carbon for the planar compounds like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polybrominated diphenylethers (Cornelissen and Gustafsson, 2004; Jonker and Koelmans, 2002) and even for nonplanar pesticide diuron (Yang and Sheng, 2003).

However, some recent studies showed that the sorption of hydrophobic organic compounds (HOCs) to BC in soil and sediment could be attenuated. The PAHs sorption to BC in the presence of natural organic matter (NOM) in a contaminated sediment was much weaker than the sorption to the BC isolated from the natural sediment (Cornelissen and Gustafsson, 2004). Moreover, the *in situ* affinity of BC for PAHs in sediment was weaker than the predicted affinity (Cornelissen and Gustafsson, 2005). In addition, the sorption of PCBs to a commercial char-sediment mixture was also weaker than that calculated based on the literature values (Jonker *et al.*, 2004). The attenuation was attributed to either the competition for

the limited sorption sites on BC between added HOCs and native HOCs or the blockage of BC sorption sites by NOM (Jonker *et al.*, 2004; Cornelissen and Gustafsson, 2005). The coating of humic acid (HA) on BC should result in competition between HA and HOCs for the limited sorption sites on BC, blockage of available sorption sites on BC, and decrease in the HOC sorption to BC, and at present, the studies on the effect of HA on HOC sorption to BC are scarce. In the present study, to examine the effect of HA on HOC sorption to BC, the BC and HA were isolated. The BC was coated with the HA. Phenanthrene (PHE) was selected as the representative of HOCs. The PHE sorption to BC was measured in the presence of precipitated HA coatings, and the correlation between PHE sorption to BC and HA properties was studied.

1 Materials and methods

PHE (>98%) was from Chem. Service, USA. Organic solvents (pesticide grade) were from Tedia, USA. Other reagents (analytical grade) were from Beijing Chemical Reagent, China.

1.1 Isolating HA and BC

HAs were isolated from the air-dried, 2-mm-sieved substrates (e.g. compost, soil and peat) according to the conventional procedures: extraction by a solution of NaOH and $Na_4P_2O_7$, precipitation by HCl at pH 2, mild purification by successive NaOH dissolution and HCl precipitation, washing using water, and final freeze-drying

step (Schnitzer, 1982). The HAs isolated from the compost, soil, and peat were denoted by compost HA (CHA), soil HA (SHA), and peat HA (PHA), respectively. The C, H, O, and N contents of HA were determined by the 1110 Elemental Analyzer (Carco Erba, Italy).

BC was obtained by purifying the charred wheat (*Triticum aestivum* L.) residue as follows. In an open field, under natural conditions the wheat straw was burned in the air on a stainless steel plate. The char (10 g) was treated four times with 200 ml of 1 mol/L HCl and with 200 ml HCl-HF (1 mol/L and 1 mol/L) followed by a thorough washing with distilled water four times. It was then dried for 2 d at 105°C, ground carefully with a mortar and pestle, and dried again for more than 2 d at 105°C. Such purification has been proven effective in removal of Si and salts and in enrichment of BC obtained from wheat (Yang *et al.*, 2004).

1.2 Coating BC with HA

A total of 100 mg HA was dissolved in 50 ml of 0.01 mol/L KOH, then 2 g BC was added, the solution was acidified to pH 2 with 1–2 ml of 1 mol/L HCl. After 15 min of gentle magnetic stirring, the precipitating HA was allowed to settle for 24 h. The suspensions were centrifuged, and the supernatants were decanted and discarded. The HA-coated BC (referred to as "BC+HA") was dried for 2 d at 105°C, ground carefully with a mortar and pestle, and dried again for more than 2 d at 105°C.

The N_2-based Brunaer Emmett Teller (BET) surface area and pore-size distribution of parent BC and HA-coated BC were determined by the NOVA4200e Surface Area Analyzer (Quantachrome, USA). To determine the amount of HA that was coated on BC, the TOC of different solution was determined by the TOC Carbon-Analyzer 5050 (Shimadzu, Japan). First, the TOC (TOC1) of solution that was composed of 100 mg HA and 50 ml of 0.01 mol/L KOH was determined, the TOC (TOC2) of the remaining supernatant after coating BC with HA was then determined, the amount of HA that was coated on BC was calculated on the basis of TOC1 and TOC2.

1.3 Sorption experiment

The sorption experiments were carried out as follows: 0.01 mol/L $CaCl_2$ aqueous solution was prepared containing the following initial concentrations (C_0): 0.1–1.0 mg/L for PHE and 100 mg/L for $HgCl_2$. A total of 0.5 g BC, HA or BC + HA and 0.025 L $CaCl_2$ solution were placed in several stoppered conical flasks and shaken up to the equilibrium in a thermostatted shaker bath at 25.0±0.1°C. The preliminary experiments showed that 10 d were long enough for PHE to reach the sorption equilibrium. After shaking, the solution was centrifuged and filtered through 0.45-μm nylon filters. The concentration of PHE in the supernatant was determined by the Agilent 1100 HPLC system equipped with a G1321A Fluorescene Detector (FLD). The HPLC operating conditions were as follows: the separation of isocratic elution was performed on a 4.6-mm × 250 mm Zorbax 80 nm Extend-C18 bonded-phase column (Agilent, USA), the mobile phase was a solution of acetonitrile and water with the ratio 9:1 (v/v) at the flow rate of 1.0 ml/min, and the optimum conditions for the FLD were excitation at 250 nm and emission at 410 nm, and the volume of the injected sample was 20 μl.

The preliminary experiment showed that the mass loss of PHE was lower than 3% during the sorption, thus the concentration difference between the initial and final equilibrium solutions was assumed to result from the sorption. Three replicates were done. The differences between the three replicates were always lower than 5%. Blanks were used for each series of experiment.

2 Results and discussion

2.1 Elemental composition and pore surface

The elemental composition and atomic ratios of HA are shown in Table 1. The molar H/C or molar O/C ratios of HA was negatively related to the humification and aromaticity of HA (Rebecca and Garrison, 2005). Table 1 shows that the molar H/C and molar O/C ratios of the three HAs decreased in the order of CHA > SHA > PHA, indicating the humification and aromaticity of HA varied in different HA origin and increased in the order of CHA < SHA < PHA (Rebecca and Garrison, 2005).

The determination showed that almost 95% HA from the incipient HA (100 mg) was coated on BC and the coated HA accounted for less than 5% (w/w) of the BC + HA. The surface area of BET and the pore-size distribution of parent BC and HA-coated BC are listed in Table 2. It

Table 1 Elemental composition and atomic ratios of humic acid (HA)

HA	C (%)	H (%)	O (%)	N (%)	Molar C/N	Molar H/C	Molar O/C
CHA	40.7	5.3	30.5	2.9	16.37	1.56	0.56
SHA	52.6	4.6	32.1	1.6	38.35	1.05	0.46
PHA	61.2	3.8	27.3	1.1	64.91	0.75	0.33

CHA: compost HA; SHA: soil HA; PHA: peat HA.

Table 2 BET surface area and pore size distribution of parent BC and HA-coated BC

Sample	BC	BC+CHA	BC+SHA	BC+PHA
BET surface area (m^2/g)	203.5	35.9	30.6	26.1
Total pore volume (ml/g)	0.6012	0.1812	0.1801	0.1789
Pore size (nm)	21.72	32.58	33.12	34.09
Most probable pore diameter (nm)	18–23	27–32	28–32	28–33

shows that the surface area and total pore volume of HA-coated BC were lower than those of parent BC, and the pore size and most probable pore diameter of HA-coated BC were higher than those of parent BC, which meant that the HA coating could cause more pore blockage of HA-coated BC compared to that of parent BC. The coating of PHA resulted in the most pore blockage of HA-coated BC and the coating of CHA resulted in the least. The decrease in the surface area and the pore blockage of HA-coated BC was analogous to that of BC in soil and sediment (Cornelissen and Gustafsson, 2005; Seokjoon and Josephj, 2005).

2.2 Sorption to HA and BC

The sorption isotherms of PHE to HA and BC are shown in Fig.1, where the C_S is the sorbed PHE solid-phase concentration (mg/g) and the C_W is the PHE liquid-phase equilibrium concentration (mg/L). For the selected HA and BC, Fig.1 shows the C_S increased in the order of CHA < SHA < PHA < BC at the given C_W, indicating that the sorption capacity of PHE to BC was much higher than that to HA, the sorption capacity of PHE to HA varied in different HA origin and increased in the order of CHA < SHA < PHA.

All sorption data in this study were fitted to the following logarithmic form of the Freundlich equation:

$$\lg C_S = \lg K_F + n_F \times \lg C_W \tag{1}$$

where, C_S is the solid-phase concentration (mg/g) and C_W is the liquid-phase equilibrium concentration (mg/L). The parameters K_F for sorption capacity coefficient $((mg/g)/(mg/L)^{n_F})$ and n_F (dimensionless) indicating isotherm nonlinearity were determined by linear regression of log-transformed data.

The fitted Freundlich sorption coefficients of PHE to HA and BC are summarized in Table 3. Table 3 shows that
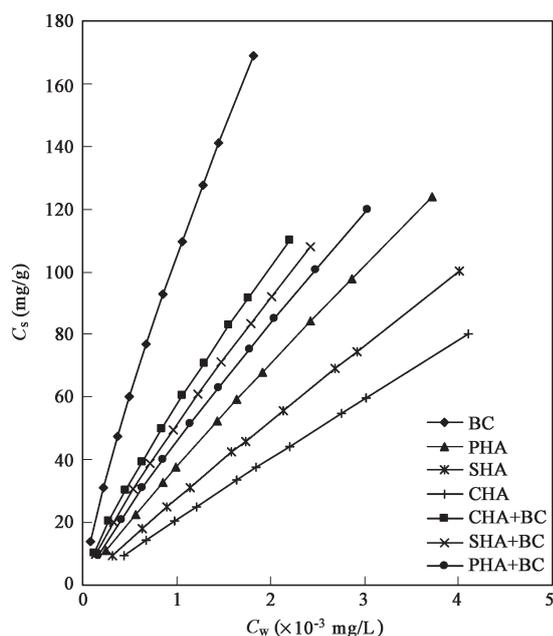
Table 3 Freundlich coefficients of PHE sorption to BC and HA

Sorbent	$\lg K_F$	n_F	r^2
BC	5.02±0.01	0.80±0.02	0.996
CHA	4.32±0.04	0.95±0.03	0.994
SHA	4.44±0.02	0.93±0.02	0.993
PHA	4.58±0.02	0.90±0.03	0.991

the sorption nonlinearity (n_F) and capacity (K_F) of PHE to the three HAs were less than those of PHE to BC, and increased in the order of CHA < SHA < PHA, which was the same as the aromaticity order (CHA < SHA < PHA) of the three HAs, indicating that the sorption capacity of PHE to HA varied in different HA origin. It can be seen from Tables 1 and 3 that there is a positive correlation between the aromaticity of HA and the sorption nonlinearity (n_F) and sorption capacity (K_F) of PHE to HA (Irinav *et al*., 1999).

2.3 Sorption to BC + HA

The sorption isotherms of PHE to BC+HA are shown in Fig.1. For the HA-coated BC, Fig.1 shows the C_S increased in the order of PHA+BC < SHA+BC < CHA+BC at the given C_W, indicating that HA coatings can significantly lower the PHE sorption to BC, the attenuation of the PHE sorption to the HA-coated BC compared with the parent BC varied in different HA origin. It can be seen from Section 2.2 and Table 3 that the coated HA accounted for less than 5% (w/w) of the BC + HA, and the sorption capacity (K_F) to the parent BC was several times higher than that to HA for PHE. Therefore, the contribution of HA to the PHE sorption to the BC + HA could be reasonably ignored, and the PHE sorption to the BC + HA could be regarded as the sorption only to the parent BC. The sorption results are listed in Table 4.

Table 4 Freundlich coefficients of PHE sorption to BC+ HA

HA+BC	$\lg K_F$	n_F	r^2
CHA+BC	4.76±0.01	0.82±0.03	0.992
SHA+BC	4.71±0.03	0.84±0.02	0.995
PHA+BC	4.66±0.02	0.87±0.02	0.991

Tables 3 and 4 show that the sorption nonlinearity (n_F) and capacity (K_F) of PHE to the HA-coated BC were less than those of PHE compared to the parent BC, and increased in the order of PHA+BC < SHA+BC < CHA+BC, which was opposed to the aromaticity order (CHA < SHA < PHA) of the HAs, indicating that HA coatings can significantly lower the PHE sorption to HA-coated BC compared with the parent BC, and the reduction of PHE sorption to the HA-coated BC varied in different HA origin.

To show the effect of HA coatings on PHE sorption to BC, the C_S of PHE to BC and BC+HA was calculated from the Freundlich coefficients (in Tables 3 and 4) at the four given C_W of PHE (C_W = 0.01, 0.1, 1, 10 µg/L), which is the environmentally relevant range, and the inhibitory rate (IR) of HA coatings on PHE sorption to HA-coated

Fig. 1 Sorption isotherms of PHE to HA, BC and BC+HA.

BC compared with the parent BC was calculated from the difference between the C_S of PHE to BC and BC+ HA at the above-mentioned C_W of PHE respectively. Table 5 shows HA coatings can significantly lower the PHE sorption to HA-coated BC, the IR was from 42.5% to 68.4% at the above-mentioned C_W of PHE for the three HA coatings, the IR decreased for the given HA coating when the C_W increased, and the IR increased in the order of CHA < SHA < PHA at the given C_W that was the same as the aromaticity order (CHA < SHA < PHA) of the three HAs, and the attenuation of PHE sorption to the HA-coated BC varied in different HA origin.

Table 5 Inhibitory rate (IR) of HA coatings on PHE sorption to BC at the given C_W

C_W ($\times 10^{-3}$mg/L)	0.01	0.1	1	10
IR of CHA coating (%)	49.9	47.5	45.0	42.5
IR of SHA coating (%)	59.3	55.3	51.0	46.3
IR of PHA coating (%)	68.4	62.8	56.3	48.7

Some HA coated on BC should be confined to the external surface sites, the shallow pores, and the mouths of longer pore networks of BC (Seokjoon and Josephj, 2005). Compared with the parent BC, the surface area of HA-coated BC was reduced, some access of PHE molecule to the internal pore networks of BC was blocked (Table 2), which could depend on whether the coating HA molecule was smaller or larger than the pore apertures of BC. The coatings of HA would decrease the potential for HOC sorption to BC, thus attenuating the sorption. In addition, some bulky HA molecules could approach the sorption sites on BC so closely that some PHE molecules were refrained from reaching the available sorption sites on BC. The diffusion of PHE through HA coatings could be retarded so that the PHE sorption to BC was hindered. Some HA molecules could compete with PHE molecule for the limited sorption sites on BC. Thus the PHE sorption to BC was attenuated by the precipitated HA coatings.

Different HA was expected to cause different pore blockage and sorption site competition on BC (Table 2), the BC coated with different HA should have different affinity for added HOCs (Seokjoon and Josephj, 2005). The HA of the higher aromaticity should have more affinity for BC (Irinav *et al.*, 1999; Seokjoon and Josephj, 2005). As the coating HA was of the higher aromaticity, more pores on BC were blocked, the more sorption sites on BC were occupied, and the sorption attenuation of PHE to BC was more. Among the three HAs studied, PHA was of the highest aromaticity and CHA was of the lowest. Thus, PHA could cause the highest sorption attenuation of PHE to BC and CHA could cause the lowest. Apparently, the attenuation could be significant only when enough HA was precipitated on BC.

3 Conclusions

In the present study, it was showed that the HA coatings on BC could result in the significant sorption attenuation of PHE to BC, and the attenuation varied in the different HA origin and was positively correlated to the aromaticity of HA. Moreover, the attenuation can be explained by the direct competition between HA and PHE for the available sorption sites on BC, and the reduction of the available sorption sites on BC as a result of the pore blockage of BC caused by the coatings of HA. However, this was tested only for the three HAs, and other natural organic materials (e.g. proteins, cellulose, lignin, fulvic acids, and humin) have to be tested to find out whether the current observation could be generalized.

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