Environmental Pollution xxx (2017) 1–9

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Strong binding of apolar hydrophobic organic contaminants by dissolved black carbon released from biochar: A mechanism of pseudomicelle partition and environmental implications☆

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ARTICLE INFO

Article history:
Received 2 June 2017
Received in revised form
7 September 2017
Accepted 17 September 2017
Available online xxx

Keywords:
Dissolved black carbon
Hydrophobic organic contaminants
Pseudomicellar structures
Hydrophobic partition

ABSTRACT

Dissolved black carbon (DBC), the soluble fraction of black carbon (BC), is an important constituent of dissolved organic matter pool. However, little is known about the binding interactions between hydrophobic organic contaminants (HOCs) and DBC and their significance in the fate process. This study determined the binding ability of DBC released from rice-derived BC for a series of apolar HOCs, including four polycyclic aromatic hydrocarbons and four chlorinated benzenes, using batch sorption and solubility enhancement techniques. Bulk BC and a dissolved soil humic acid (DSHA) were included as benchmark sorbents. The organic carbon-normalized sorption coefficient of phenanthrene to DBC was slightly lower than bulk BC, but was over ten folds higher than DSHA. Consistently, DBC was more effective than DSHA in enhancing the apparent water solubility of the tested HOCs, and the enhancement positively correlated with solute *n*-octanol-water partition coefficient, indicating the predominance of hydrophobic partition. The much higher binding ability of DBC relative to DSHA was mainly attributed to its higher tendency to form pseudomicellar structures as supported by the fluorescence quenching and the pH-edge data. Our findings suggest that DBC might play a significant role in the environmental fate and transport of HOCs as both sorbent and carrier.

1. Introduction

Sorption to natural dissolved organic matter (DOM) is a key process affecting the mobility, reactivity, and bioavailability of hydrophobic organic contaminants (HOCs) in aquatic and soil environments (Chiou et al., 1986; Johnson and Amy, 1995; Kukkonen and Oikari, 1991). An extensive effort has been devoted to understanding sorptive interactions between HOCs and natural DOM, particularly, the structure–activity correlations (Chin et al., 1997; Gauthier et al., 1987; Kopinke et al., 2001). Many studies reported that sorption of apolar HOCs (e.g., polycyclic aromatic hydrocarbons/PAHs, halogenated compounds, etc.) to DOM positively correlated to its aromaticity, which was attributed to the facilitated van der Waals (dispersion) and/or π-π interactions in sorption (Chin et al., 1997; Gauthier et al., 1987; Jin et al., 2017; Kopinke et al., 2001; Laor et al., 1998; Uhle et al., 1999; Wang and Zhang, 2014). However, the strong correlation between HOCs sorption affinity and DOM aromaticity was not observed in several other studies (Eriksson et al., 2004; Ilani et al., 2005). Instead, the aliphatic content of DOM was suggested to play a more important role in sorption of apolar HOCs (Eriksson et al., 2004; Ilani et al., 2005). Additionally, the sorption affinity of apolar HOCs was often found to be inversely proportional to the polarity of DOM (e.g., indexed by the atomic ratios of (O+N)/C), suggesting the dominant role of hydrophobic partition (Chiou et al., 1986; Jin et al., 2017; Kopinke et al., 2001; Wang and Zhang, 2014). A positive influence of increasing molecular weight of DOM on sorption of apolar HOCs has also been observed (Chiou et al., 1986; Chin et al., 1997).

It was proposed that DOM molecules could arrange into micelle-like structures in aqueous solutions with hydrophobic interior domains shielding by hydrophilic exterior regions (Conte and Piccolo, 1999; Sutton and Sposito, 2005), creating hydrophobic domains for the partition of HOCs (Kopinke et al., 2001; Marschner et al., 2005;

☆ This paper has been recommended for acceptance by Baoshan Xing.

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https://doi.org/10.1016/j.envpol.2017.09.053
0269-7491/

Pan et al., 2007a, 2008). The pesudomicellar conformation of DOM is affected by its chemical and structural properties (e.g., aromaticity/aliphaticity, polarity, and molecular weight) as well as solution chemistry conditions such as pH (Guo and Ma, 2006; Pace et al., 2012; Pan et al., 2008; Šmejkalová and Piccolo, 2008; Sutton and Sposito, 2005; Tombácz, 1999). For instance, Tombácz (1999) found that humic acid fractions with larger hydrocarbon content had higher critical micelle concentration. Šmejkalová and Piccolo (2008) proposed that the conformational arrangement of humic substances was mainly driven by the association of hydrophobic aromatic moieties based on the results of diffusion ordered nuclear magnetic resonance (NMR) spectra. Low pH was expected to facilitate the formation of pesudomicellar structures due to the reduced repulsion among functional groups and the aggregates of discrete hydrophobic microdomains (Guo and Ma, 2006; Pace et al., 2012; Pan et al., 2008).

Natural DOM pool is a very complex mixture of humic substances, carbohydrates, proteins, and a variety of acidic and lower molecular weight species (Beck et al., 1993). The observed complex and sometimes inconsistent sorption properties of DOM can be partially reconciled by the diversity of DOM investigated which differs in carbon sources, humification conditions as well as the preparation and purification methods (Burkhard, 2000; Raber et al., 1998). Recent studies revealed that dissolved black carbon (DBC), the water soluble fraction of black carbon (BC), is an important constitute of the natural DOM pool (Jaffé et al., 2013; Mannino and Harvey, 2004; Masiello and Druffel, 1998). It was estimated that DBC comprises as much as 4–22% of marine DOM (Masiello and Druffel, 1998), 4–7% of coastal marine DOM (Mannino and Harvey, 2004), and 0.1–17.5% of freshwater DOM (Jaffé et al., 2013). A recent global survey suggested that DBC can account for approximately 10% of the global riverine flux of dissolved organic carbon to the oceans (Jaffé et al., 2013). It is also noteworthy that using biochar as a soil amendment for fertility enhancement, carbon sequestration, as well as pollutant immobilization has drawn increasing attention (Beesley et al., 2010, 2011; Cao et al., 2009). DBC can be readily released from bulk BC such as char, charcoal, and biochar by infiltration and surface runoff (Dittmar et al., 2012; Jaffé et al., 2013), and is mobile in aqueous media as suggested by column experiments (Wang et al., 2013). This highlights the potential role of DBC as sorbent and carrier for HOCs in the environment, which also confounds the feasibility of using biochar as amendments to sequester HOCs in contaminated soil/sediments. Thus, understanding the sorption behaviors of HOCs to DBC is essential to the prediction of the environmental fate process of HOCs as well as the assessment of the application potential of biochar in sequestration of organic contaminants. Due to the different carbon sources and formation processes, DBC and well-studied humic substances differ pronouncedly in chemical and structural properties. As demonstrated in our previous studies (Qu et al., 2016), DBC released from biochar comprised mainly of small aromatic clusters substituted by carboxylic groups, and by phenolic groups to a less extent. The unique properties of DBC likely lead to significantly different sorption properties as compared with the well-studied humic substances.

In the present study, the sorption affinity of a series of apolar HOCs (PAHs and chlorinated benzenes) varying in hydrophobicity and electronic polarizability by DBC released from rice-derived BC was investigated. The source bulk BC and a dissolved soil humic acid were included as benchmark sorbents for better understanding of the sorption mechanisms. The sorption mechanisms were also probed by the solubility enhancement, fluorescence quenching, and pH-edge experiments. The main objectives were to compare the HOC sorption affinity to DBC with bulk BC and soil humic acid, and to discern the sorption mechanisms.

2. Experimental

2.1. Materials

Solutes include four PAHs, naphthalene (99%, Sigma-Aldrich, USA), phenanthrene (98%, Sigma-Aldrich), anthracene (>99%, Fluka, Switzerland), and pyrene (98%, Sigma-Aldrich), and four chlorinated benzenes, 1,4-dichlorobenzene (1,4-DCB, >99%, Fluka), 1,3,5-trichlorobenzene (1,3,5-TCB, 99%, Sigma-Aldrich), 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB, 98%, Sigma-Aldrich), and pentachlorobenzene (PtCB, 98%, Sigma-Aldrich). Their water solubilities (S_W) and n-octanol-water partition coefficients (K_{OW}) are listed in Table S1, Supplementary Information (SI).

Samples of bulk BC and DBC were prepared using the same procedures as described in our previous studies (Qu et al., 2016). Biochar was prepared by pyrolyzing the powder of rice straw (Nantong, Jiangsu Province, China) at 400 °C for 3 h. The resulting biochar was ground into powder, passed through a 100-mesh sieve, and designated as bulk BC. DBC was fractionated from the water extract of bulk BC. Briefly, 30 g of bulk BC was added to 3-L deionized water and stirred at 200 rpm for 48 h at room temperature. The suspension was then filtered through a 0.45 μm membrane (Pall, USA). The filtrate was mixed with 1 M HCl and 1 M HF and stirred at 200 rpm for 4 h to remove the minerals. After neutralized with 1 M NaOH, the mixture was dialyzed using dialysis bags (500 Da, Union Carbide, USA). The same treatment was repeated twice and the resulting solution was collected and freeze-dried. The obtained material was referred to as DBC. To investigate the effect of the associated minerals on the sorption properties of DBC, a portion of the filtrate was directly freeze-dried without demineralization treatment and was referred to as ML-DBC. Soil humic acid was extracted from a surface soil collected from Shenyang, Liaoning Province, China using a standard base extraction method according to the literature (Sparks, 1996). After base extraction, the obtained humic acid was demineralized by mixing with HCl/HF and was dialyzed using dialysis bags (500 Da, Union Carbide). To prepare dissolved soil humic acid (DSHA), 100 mg of soil humic acid was dissolved in 1-L deionized water with the aid of 5 mL of 0.1 M NaOH (Jones and Tiller, 1999). Then, the solution was adjusted to pH 6.0 using HCl, followed by filtration through a 0.45-μm membrane (Pall). The filtrate was freeze-dried and the resulting material was collected as DSHA.

2.2. Characterization of sorbents

Bulk BC, DBC, and ML-DBC were characterized by elemental analysis, quantitative ^{13}C direct polarization/magic angle spinning (DP/MAS) NMR and UV-visible absorption spectra in our previous studies (Qu et al., 2016). DSHA was newly characterized using the same techniques. The carboxyl and phenolic hydroxyl contents of DBC and DSHA were determined by the acid-base titration method using HCl and NaOH on an automatic titration device (877 Titrino Plus, Metrohm, Switzerland) (detailed procedure presented in SI). Molecular size distributions of DBC and DSHA were analyzed by a gel permeation chromatography (GPC) column (PSS MCX 1000 Å, 8 mm × 300 mm) (Polymer Standards Service GmbH, Germany) on a high-performance liquid chromatography equipped with a diode array detector (HPLC-DAD, Agilent 1100) (Agilent Technologies, USA). Polystyrenesulfonate sodium salts of known molecular sizes (208 D, 1100 D, 2290 D, 6430 D, 13000 D, and 45100 D) were used as standards. The elution was performed using 0.6% K_2CO_3 at a flow rate of 0.1 mL/min at 40 °C, and the detection wavelength was set to be 254 nm (Li et al., 2012). Particle sizes of DBC, ML-DBC, and DSHA at different pH (in the range of 3.3–11.2) were determined in solutions containing 0.02 M NaCl by dynamic light scattering

Please cite this article in press as: Fu, H., et al., Strong binding of apolar hydrophobic organic contaminants by dissolved black carbon released from biochar: A mechanism of pseudomicelle partition and environmental implications, Environmental Pollution (2017), https://doi.org/10.1016/j.envpol.2017.09.053