

Research Article

Sorption and Desorption of Phenanthrene to Black Carbon on Crop Soil from the South-North Water Diversion Project in China

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Abstract: The water quality of South-North Water Diversion Project (SNWDP) has attracted more and more attention. Polycyclic Aromatic Hydrocarbons (PAHs) in soils strongly sorb to black carbon. In this study, adsorption and desorption characteristics and isotherm of phenanthrene to black carbon in SNWDP crop soils were studied extensively. The results showed that the sorption and desorption of phenanthrene to black carbon were nonlinear. Freundlich model could fit the sorption and desorption data of BC well. Meantime, desorption process exhibited varied apparent sorption-desorption hysteresis. It can be inferred that BC of crop soils in SNWDP plays a significant role in reducing the bioavailability and toxicity of phenanthrene through sorption capacity and desorption hysteresis.

Keywords: Black carbon, crop soil, phenanthrene, sorption, South-North water diversion project

INTRODUCTION

Black Carbon (BC) originates from incomplete combustion of fossil fuels and biomass (Goldberg, 1985). Black carbon in environment has been found to have essential implications in controlling fate and behaviors of Persistent Organic Pollutants (POPs) in soils and sediments (Cornelissen *et al.*, 2005; Koelmans *et al.*, 2006). As a result, BC attracts great interest for environmental studies.

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous contaminants in soils and are well known for their toxic, carcinogenic and mutagenic effects. China suffers serious PAH contamination from combustion of fossil fuel and biomass (Zhang and Tao, 2008). Soil is the primary environmental reservoir and sink for PAHs in the terrestrial environment. As the South-North Water Diversion Project, s (SNWDP) importance to the Chinese economic and societal development, the water quality has attracted more and more attention. PAH contamination of soil will have a direct effect on public health. Sorption is one of the key factors regulating the bioavailability and the toxicity of organic contaminants in soils. However, limited information on PAH sorption behavior of black carbon from this area, particularly desorption behavior of PAH to black carbon. A better understanding of the sorption behavior of organic contaminants to BC is crucial to assess the ecological risks of the chemicals. It was the aim of this study to investigate sorption-desorption characteristics PAHs to BC on SNWDP.

MATERIALS AND METHODS

Studying area and soil sampling: The Danjiangkou reservoir which is the source of water for the middle route of the well-known SNWDP in China was selected. The basin has a sub-tropical monsoon and annual precipitation is about 700-1000 mm. Before 1990s, the water quality of the area was very good, up to Class I or II of Chinese Surface Water Quality Standard. However, the rapid processes of urbanization and economic development brought about a swift deterioration of river water quality during the 1990s (Zhu *et al.*, 2008). Different Surface soil samples were collected from study area, then air-dried and sieved through 60-mesh screen.

BC determination procedures: In this study we used a wet chemical oxidation method, which was modified from the procedures appeared in Lim and Cachier (1996) and Song *et al.* (2002). The sequential steps for BC determination in soils were as follows:

- **Removal of carbonates and silicates:** About 3 g soil samples were treated with 15 mL of 3 M HCl for 24 h, then with 15 mL mixture of 10 M HF and 1 M HCl for 24 h.
- **Removal of organic carbon:** The residue from step a was oxidized with a 10 mL acid potassium dichromate solution (0.1 M $K_2Cr_2O_7$ and 2 M H_2SO_4) at $55\pm 1^\circ C$ for 60 h. Based on the above results of OC contents in soils, higher concentrations of dichromate may be needed to ensure that oxidation is complete for some soils.

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- **Analyses of BC:** The residue from step 2 was dried and weighted and its carbon content was determined by a CHN elemental analyzer.

Sorption and desorption equilibrium: In this study, phenanthrene was dissolved in methanol to form a 500 mg/L stock solution. Before use, the stock solution was diluted into a set of concentrations with an electrolyte matrix containing 0.1 M CaCl₂ and 200 ug/mL Na₃, which was added to inhibit aerobic biodegradation. All sorption experiments were conducted in triplicates in 30-mL glass centrifuge vials. After aliquots of BC were added, respectively, each vial received 20 mL background electrolyte solution containing various concentrations of phenanthrene. The vials were shaken at 200 rpm on a horizontal shaker at 25±1°C for 48 h. After the establishment of sorption equilibrium, sorbents and aqueous phases were separated by centrifugation at 3000 rpm for 20 min. An aliquot of 1 mL of the supernatant liquid was filtered through a 0.45 um Millipore-membrane. Then, the phenanthrene concentrations were analyzed using High Performance Liquid Chromatography (HPLC). The compound concentrations were quantified with an external standard method. Each reactor was then refilled with solute-free background solution for the subsequent desorption experiment. At the conclusion of the desorption experiment-the same procedure was repeated for sampling supernatants for analysis of solute concentrations under equilibrium desorption conditions.

Data evaluation: All sets of equilibrium sorption and desorption data collected in this study were fitted to the Freundlich isotherm model having the following form:

$$\log q_e = \log KF + n \log C_e \quad (1)$$

where, KF (lg/g) and n are the Freundlich isotherm coefficient and the isotherm nonlinearity index, respectively. A linear regression procedure with SYSTAT software (Version 10.0) was used for fitting the logarithmically transformed sorption or desorption data collected for each sorbent-sorbate system to Eq. (1).

The apparent sorption-desorption hysteresis was quantified for each sorbent-solute system using the Hysteresis Index (HI) defined by Huang *et al.* (2003):

$$\text{Hysteresis Index (HI)} = q_d \quad (2)$$

where, q_{se} and q_{de} are the solid-phase sorbate concentrations for the sorption and single-cycle desorption experiments, respectively and the subscripts T and C_e specify conditions of constant temperature and residual solution phase concentration. This equation was invoked for eliminating artifacts resulting from the impacts of isotherm nonlinearity on apparent desorption hysteresis. Hysteresis indices at constant temperature (25°C) and at different concentration levels were calculated for each sorbate-sorbent system using the Freundlich parameters.

RESULTS AND DISCUSSION

Sorption dates of phenanthrene to five black carbon were plotted in Fig. 1, while the parameters by FM were listed in Table 1. The FM described all the sorption isotherm data well with R² ranging from 0.929 to 0.984 and the N values were 0.649-0.926 for phenanthrene, indicating that all the isotherm curves were nonlinear. As shown in Table 1 and Fig. 1, the sorption behavior of phenanthrene at different black carbon were different. This result showed that the black carbon varying in characteristics could not be combined together for the prediction of adsorption capacity as such because of the heterogeneity of the black carbon. The phenanthrene

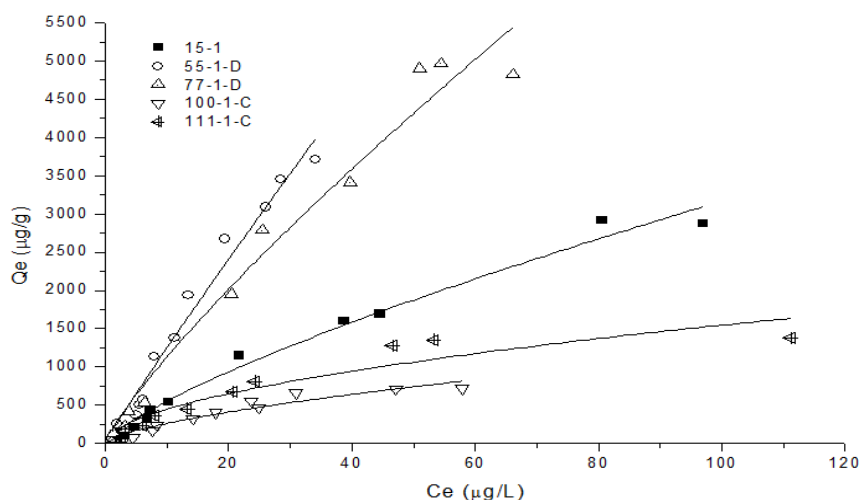


Fig. 1: Sorption isotherms of Ph to BC

Q_e: The amount of Ph sorbed per mass of BC; C_e: The equilibrium Ph concentration

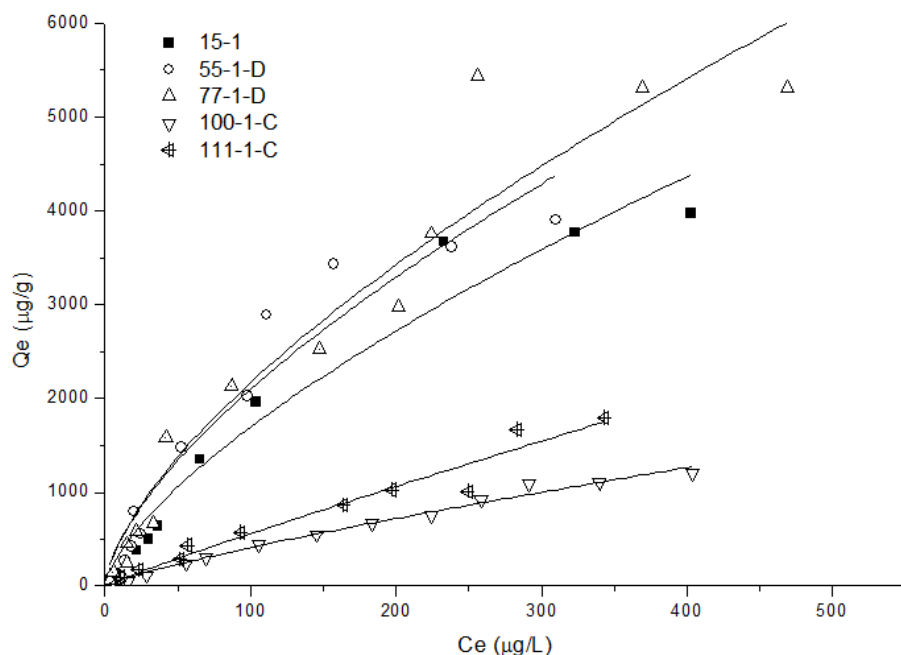


Fig. 2: Desorption isotherm of Ph to BC
 Qe: The amount of Ph sorbed per amount of BC; Ce: The equilibrium Ph concentration

Table 1: Sorption and desorption isotherm parameters and hysteresis indices

	Sorption			Desorption			HI			
	logKf	n	R ²	logKf	n	R ²	5 µg/L	50 µg/L	100 µg/L	500 µg/L
15-1	1.863	0.683	0.961	1.986	0.757	0.982	0.50	0.78	0.87	1.11
55-1-D	2.023	0.649	0.929	2.153	0.944	0.975	1.17	3.27	4.24	7.43
77-1-D	2.020	0.658	0.932	2.224	0.830	0.972	1.11	2.14	2.53	3.66
100-1-C	0.993	0.810	0.984	1.776	0.643	0.900	3.64	2.16	1.82	1.16
111-1-C	0.895	0.925	0.956	2.113	0.537	0.887	7.85	2.62	1.77	0.48

sorption isotherms measured in our study have n values slightly higher than the n values reported in the literature for sorption by different origins black carbon (Bornemann *et al.*, 2007; Luo *et al.*, 2011). There are many mechanisms to explain the sorptive observations: surface coverage, multilayer adsorption, condensation in capillary pores and absorption into the polymeric matrix (Huang *et al.*, 2003). The hole-filling adsorption was considered as the important contribution to sorption capacity of HOCs at relatively low and high concentrations (Burgess *et al.*, 2006; He *et al.*, 2006; Cornelissen *et al.*, 2005; Bornemann *et al.*, 2007). But the surface adsorption was also one of the sorption mechanism in some study (Bucheli and Gustafsson, 2000). In fact, the sorption capacity of BC sample seems to be positively related to the surface area and porosity. As stated previously, it is hard to infer which was the main sorption mechanism between hole-filling and surface adsorption, or both of them were sorption mechanisms in the sorption process. Therefore, further researches on sorption mechanisms of HOCs to BCs will still be needed.

The desorption isotherms for five black carbon were shown in Fig. 2. All the desorption data could be well described by the Freundlich model, with R² ranging

from 0.887 to 0.982 and every desorption isotherm was nonlinear with N value 0.538-0.944. When compared with adsorption isotherms, all the BC particles exhibited varied apparent sorption-desorption hysteresis. This was in accord with previous report (Luo *et al.*, 2011; Jonker *et al.*, 2005; Jonker and Koelmans, 2002; Braida *et al.*, 2003). It was proposed that the sorption-desorption hysteresis observed could contribute to the irreversible entrapment and/or slow rate of desorption of sorbed molecules within porous structures of condensed SOM (soil/sediment organic matter) domains. Jonker and Koelmans (2002) demonstrated that PAHs tightly bound on soot and charcoal particles cannot even be extracted with organic solvents or solvent mixtures if they cannot swell the BC matrices. Braida *et al.* (2003) explained that entrapment of sorbate molecules within pore network deformed during sorption process could be the dominant mechanism for the observed strong hysteresis in the sorption-desorption of benzene by a charcoal material. The study by Yang *et al.* (2004) indicated that BC exhibit greater sorption-desorption hysteresis. Furthermore, the pore-deformation mechanism as been hypothesized as the main cause of the irreversible sorption of organic compounds to macromolecular NOM (Natural Organic Matter) in recent studies

(Lennartz and Louchart, 2007). They argued that this is likely because these materials have few aliphatic moieties and more porous structures that could result in difference of binding energies between sorption and desorption processes in ink-bottle shaped or sorbate-deformed pores. Due to the complex nature of this phenomenon, further studies using integrated technologies such as FTIR and Carbon Nuclear Magnetic Resonance (CNMR) spectroscopy, will still need to be carried out after sorption-desorption completed to clarify the true mechanisms of the sorption-desorption hysteresis.

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