Effects of varying estuarine conditions on the sorption of phenanthrene to sediment particles of Yangtze Estuary

Jing Shang [a], Jing Chen [a,*], Zhenyao Shen [a], Ying Wang [a], Aidong Ruan [b]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Beijing Normal University, Beijing 100875, China
[b] State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering, Hohai University, Nanjing 210098, China

ARTICLE INFO

ABSTRACT

The sorption of phenanthrene on the Yangtze Estuary sediment was studied under varying conditions of particle size, sediment organic contents, salinity, and dissolved organic matter (DOM) concentrations. Small sediment particles showed higher trapping capacity for phenanthrene due to the higher organic contents associated. The organic carbon-based partition coefficient of phenanthrene to the Yangtze Estuary sediment was obtained as 7120 L/kg, lower than the values for other soils or sediments reported in previous studies. The magnitude and direction of the salt effect were complicated by the specific DOM studied. The sediment sorption capacity was greatly increased in saline water in the absence of DOM but decreased in the presence of DOM. Given the conditions in the Yangtze Estuary, the equilibrium sorption of phenanthrene would be decreased with increasing salinity. Overall, the nature and content of both sediment-bound and dissolved organic matter dominate the sorption of hydrophobic organic contaminants in the estuary.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Located at a junction area of river, sea, and land, the estuary environment is more strongly affected by human activities and natural processes than other areas, resulting in its fragility (Matamoros et al., 2009). The Yangtze Estuary is the lower, tide-affected part of the Yangtze River, the largest river in China with an average annual water discharge volume of 9.6×10^{11} m^3 to the sea (Gao et al., 2013). The water environment of the Yangtze Estuary undergoes considerable change in recent years due to the intense industrialization and urbanization in this area, upstream dam construction, and climate change (Wang et al., 2011; Dai et al., 2011). For example, the annual sediment discharge has been drastically decreased over the past decades due to dam construction and reforestation on the Yangtze River and the river channel in middle-lower reaches has changed from depositional to erosional (Xu and Milliman, 2009). As a result, the sorption behavior of organic pollutants to sediment particles and their fate in the estuary have been greatly affected, posing potential threat to local inhabitants (Turner and Millward, 2002).

Recently, it was frequently reported that persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) occurred in the surface sediments from the Yangtze Estuary (Guitart et al., 2010; Wang et al., 2013). Sorption is a key process controlling the fate of persistent organic pollutants in the estuary which tend to interact strongly with estuarine sediments. The sorption equilibrium of organic pollutants in the estuary is influenced by both the water properties, such as salinity, dissolved organic matter contents, temperature and pH (Jones and Tiller, 1999; Zhou et al., 2004; Yu et al., 2011), and the suspended particulate matter properties, such as grain size and particulate organic carbon contents (Yang et al., 2008, 2011). The changes of sorption equilibrium will affect the allocation proportion and exchange flux of organic contaminants between water and sediment particles, and thus affect the air–water exchange flux through the surface microlayer of the water body and the bioavailability of organic contaminants to sediment dwelling organisms in the estuary.

It is well documented that sorption of nonpolar (e.g., PAHs) and slightly polar (e.g., PCBs) hydrophobic organic contaminants (HOCs) is highly associated with sediment organic matter (Huang et al., 1997; Pan et al., 2006; Ghosh and Hawthorne, 2010). Both linear and nonlinear sorption isotherms have been established between HOCs and different sediment organic matter, dependent on the chemical and structural properties of the sediment organic matter (Gunasekara and Xing, 2003; Oren and Chefetz, 2005; Yang et al., 2008). The presence of black carbon may enhance the nonlinearity of HOC sorption to sediments (Bärring et al., 2002; Oen et al., 2006). A few size fractionation investigations of sediments have been conducted to further understand the distributions of HOCs in the field and their relations to organic matter characteristics

* Corresponding author. Tel./fax: +86 10 58804585.
E-mail address: jingchen@bnu.edu.cn (J. Chen).

(Ghosh et al., 2000; Rockne et al., 2002; Oen et al., 2006). However, different particle size dependence of HOC concentrations have been observed, mostly attributed to the various size distributions of sediment organic matter. For example, Oen et al. (2006) reported elevated concentrations of PAHs in the sand fraction of the Norwegian harbor sediments compared to the silt and clay fractions whereas Ghosh et al. (2000) found that the PAH concentrations in the Milwaukee Harbor sediment particles decreased with increasing particle size. In the Yangtze Estuary, the sediment particle size generally decreases from the inner estuary to the adjacent sea area. Besides, sediments carried from the Yangtze River have been composed of higher percentages of fine particles since the operation of the Three Gorges Dam. Elucidating the sorption behavior of HOCs in different size fractions of the sediments with varying organic matter characteristics would improve our understanding of the temporal and spatial variations of the HOC distributions as well as their fate in the sediments of the estuary.

In addition to sediment properties, the increase of salinity in the estuary during the transition from river to seawater could also greatly affect the sorptive behavior of HOCs. Increasing salinity reduces HOC solubility by "salting out" HOCs with high ionic strengths, which enhances the distribution of HOCs to solid phases (Brunk et al., 1997; Wu and Sun, 2010). The effect of salinity on HOC sorption becomes complicated in the presence of dissolved organic matter (DOM) in natural water bodies. DOM would facilitate the desorption of HOCs from sediments by enhancing the solubility of HOCs in water (Ke et al., 2009). However, DOM could also form hydrophobic coatings on suspended sediment particles as water salinity increases, which are favorable for the sorption of HOCs to sediments (Brunk et al., 1997). As the intrusion of salt water has become more frequent in the Yangtze Estuary (Gao et al., 2013), the magnitude and direction of the salt effect in the presence of DOM need to be clarified to better understand the pollution status of organic contaminants in the estuary.

This research simulated the equilibrium sorptive phenomena of HOCs in the estuarine environment to elucidate the effects of particle size, sediment organic contents, salinity, and DOM on HOC sorption to sediment particles. Phenanthrene, a three ring PAH, was chosen as a representative HOC for the sorption study because of its strong mobility and common existence in the Yangtze Estuary. The results of this research would provide evidence for the relative importance of different estuarine conditions in HOC trapping and useful parameters for modeling the sorptive behavior and fate of HOCs in a changing estuarine environment.

2. Materials and methods

2.1. Study area

Fig. 1 shows the study area of the Yangtze Estuary, which lies in the eastern subtropical monsoon climate region within the range of 30.5–32°N and 121–122.6°E. The Three Gorges Dam, the world's largest hydropower project in terms of installed capacity (22,500 MW), is around 1800 km upstream to the Yangtze Estuary. The sediment sample taken along the −20 m isobath in the adjacent sea was used in the simulated sorption experiments. The surface sediment sample was collected with a grab sampler in August 2010 and stored in a refrigerator at −20 °C before further treatments. In our previous study on the organic pollutant distribution in the surface sediments of the Yangtze Estuary (Gao et al., 2013), we measured the particle size distribution and TOC content of the surface sediments taken from 20 sites within the inner estuary and 10 sites along the −10 m and −20 m isobaths in the adjacent sea. According to our previous results, the surface sediment samples showed higher fine particle proportion and

TOC content in the adjacent sea. As the effects of fine particles and TOC contents on the sorption of phenanthrene to the sediments were the major concern in this research, the sample along the −20 m isobath in the adjacent sea was chosen and studied in the sorption experiments, which was representative of the surface sediments in the adjacent sea area in the Yangtze Estuary in terms of particle size distribution and TOC content. Besides, as the sorption of HOCs to the harbor sediments and river sediments have been extensively studied in the literature, the investigation of the sorption of HOCs to the sediment in the adjacent sea area would provide a full understanding of the transport change of HOCs from the river to the ocean.

2.2. Sediment pretreatment and characterization

The sediment sample collected from the Yangtze Estuary was freeze-dried and ultrasonically washed by methanol for 1 h and oxidized by 30% H_2O_2 for 12 h in order to remove the organic contents in varying degrees (Yang et al., 2011). Then the sediments with different organic contents were sequentially passed through the 100 mesh, 200 mesh, and 600 mesh sieves by wet sieving to obtain three size fractions in the range of <22 μm, 22–74 μm, and 74–150 μm. After the organic cleaning and size fractionation procedures, twelve samples with different organic contents and particle sizes were obtained, including $S_{o,0}$, $S_{o,1}$, $S_{o,2}$, $S_{o,3}$, $S_{m,0}$, $S_{m,1}$, $S_{m,2}$, $S_{m,3}$, $S_{h,0}$, $S_{h,1}$, $S_{h,2}$, $S_{h,3}$. S_o, S_m, and S_h represent the original sediment, the sediment washed by methanol and the sediment oxidized by 30% H_2O_2 respectively. The notation 0, 1, 2, 3 denote the sediment not size-fractionated and the sediments with small (<22 μm), medium (22–74 μm), and large (74–150 μm) grain sizes respectively.

The total organic carbon (TOC) content of each sample was determined by oxidation of the organic matter with an acidified potassium dichromate ($K_2Cr_2O_7$–H_2SO_4) solution at 170 °C for 30 min and titration of the unreacted potassium dichromate with ferrous sulfate (Yeomans and Bremner, 1988). The particle size distribution and median diameter of the samples were determined by a particle size analyzer (Microtrac S3500, USA).

2.3. Equilibrium sorption of phenanthrene

Batch sorption experiments were conducted to investigate the sorption behavior of phenanthrene to the sediment of the Yangtze Estuary. The treated sediments with different organic contents and particle sizes were used to determine the effects of particle size and TOC on phenanthrene sorption, and artificial seawater solution and humic acid (Alfa Aesar China Co., Ltd.) solution were used to elucidate the effects of salinity and DOM. The artificial seawater stock solution with a salinity of 35 g/L was prepared by dissolving 27.4309 g NaCl, 2.5312 g $MgCl_2$, 3.4288 g $MgSO_4$, 0.7499 g $CaCl_2$, 0.2090 g $NaHCO_3$, and 0.0859 g NaBr into 1 L deionized water. The phenanthrene stock solution was prepared by ultrasonically saturating deionized water with excess phenanthrene.

During the batch sorption experiment, 0.2 g sediment and 40 ml aqueous phenanthrene solution were added in a 50 ml conical flask, leaving a minimum headspace (Wang et al., 2011). The aqueous phenanthrene solution was obtained by diluting the phenanthrene stock solution to the environmentally relevant concentration range of 10–500 μg/L. The flask was then sealed and placed in a horizontal shaker to shake continuously for 24 h. For each particle class the sorption of phenanthrene was quite fast, and an apparent equilibrium was reached after 24 h. The solution containing sediment particles was then centrifuged at 4500 rpm for 10 min and analyzed for phenanthrene concentration at equilibrium. The mass balance of the batch experiments was checked in all cases through the control experiments. The system loss of