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Sorption behavior of phenanthrene in Yangtze estuarine sediments: Sequential separation

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ABSTRACT

In the present study, phenanthrene was chosen as the probe compound for determining the sorption of PAHs in sediments from Yangtze estuary and nearby coastal area, China. Sorption isotherms were fitted well by the Freundlich and dual models, respectively. Selected sediments were further sequentially separated to remove the carbonate and organic carbon (OC). Calculated OC sorption capacity values based on both H_2O_2 oxidization and 375 °C combustion methods were similar and comparable to the K_{oc} values estimated by the empirical linear sorption equations. Both sorption models and sorption data using sequentially separated samples achieve the similar conclusions: (1) the partition behavior dominated by OC in sediments with $f_{oc} > 0.01$; (2) for sediments with $0.001 < f_{oc} < 0.01$, OC dominated sorption at relatively high aqueous concentration; whereas mineral phase adsorption dominated sorption at lower concentration especially when C_w/S_w was in the range of 0.0001–0.001 in natural aqueous system.

1. Introduction

The study of hydrophobic organic contaminants (HOCs) in coastal marine environments and especially in estuarine systems is of great importance since these areas are biologically productive and receive considerable pollutant inputs from land-based sources via river runoff and sewage outfalls. Recently, the occurrence of HOCs including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in tidal surface sediments from the Yangtze estuary, China had been reported (Zhou et al., 2001; Liu et al., 2001, 2004).

Due to the nature of HOCs, they tend to interact strongly with estuarine sediments. It is well documented that sediment organic carbon (OC) predominantly controls the sorption of HOCs, such as PAHs in aquatic sediments (Luthy et al., 1997; Accardi-Dey and Gschwend, 2002; Schwarzenbach et al., 2003). Compared to predictions based on the classic linear OC-dependent sorption coefficient, enhanced sorption was often found in the natural geosorbents due to the occurrence of black carbon (BC) (Accardi-Dey and Gschwend, 2003; Cornelissen et al., 2005), coal particles (Cornelissen and Gustafsson, 2005; Yang et al., 2008) and kerogens (Ran et al., 2004; Xiao et al., 2004) in sediments. Two types of OCs, including "soft carbon" and "hard carbon", have been considered as the two sorption domains in concentration-dependent sorption isotherms. Consequently more and more attention has been paid to "hard carbon" with high sorption enthalpies, nonlinear sorption behavior, competitive sorption, slow kinetics, and possible sorption–desorption hysteresis (Huang et al., 2003; Cornelissen et al., 2005; Jonker et al., 2005). Although mineral phase was found in large amount in the sediment, its contribution to HOCs sorption was often omitted, especially when OC amount was greater than 0.1% of the sediments (Piatt et al., 1996; Mader et al., 1997). However, this approach may be too simplistic as the minerals may play an equally important role in the accumulation of HOCs in sediments.

Considering the uncertainty in our understanding of the sorption of HOCs in estuarine sediments, selected sediment samples were further sequentially treated to remove carbonate and OC. The overall objectives of the work are to investigate the sorption behavior of PAHs with phenanthrene (Phen) as the probe compound and to elucidate the generic mechanism of HOC sorption.

2. Material and methods

2.1. Sample collection

Surface sediment samples were collected along the Yangtze river estuary and its nearby coastal areas in March 2009 and the sampling sites included Liuhekou (LHK), Shidongkou (SDK), Wusongkou (WSK), Bailonggang (BLG), Laogang (LG), Fengxin (FX), Jinshan (JS) and Chongming (CM) (Fig. 1). To ensure a greater homogeneity, triplicate sediment samples were combined, rendering the total sediment wet mass of at least 2 kg for each sample. All sediment samples were packed in brown glass bottles (pre-heated

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Fig. 1. Map of the Yangtze estuary and the sampling locations.

at 400 °C, 5 h) and immediately stored at −20 °C until further processing.

2.2. Sediment characterization

All samples were freeze-dried, pulverized for about 30 min in a zirconium oxide mill and passed through a 200 mesh sieve. PAHs were extracted from sediment samples using an accelerated solvent extractor (ASE 300, Dionex) subsequently under high-pressure (100 bars) and high temperature (100 °C with acetone and 150 °C with dichloromethane) in duplicate. Copper powder (1 g) was then added to each ASE cell to remove sulfur in the sediment. Each extract was then reduced into about 2 mL and cleaned up by a silica gel column. The polar compounds were eluted with 15 mL n-hexane and target compounds were eluted with 70 mL dichloromethane and acetone mixture (3:7 v/v). The extract was then reduced and the solvent was exchanged by hexane and concentrated to a volume of 1 ml with gentle nitrogen gas. A mixture of naphthalene-d8, anthracene-d10, phenanthrene-d10, chrysene-d10, and perylene-d12) was used as internal standard. Sixteen PAHs including naphthalene [Nap], acenaphthylene [Any], acenaphthene [Ace], fluerene [Fln], phenanthrene [Phen], anthracene [Ant], fluoranthene [Fth], pyrene [Py], benz(*a*)anthracene [BaA], Chrysene [Chr], benzo(*b*)fluoranthene–benzo(*k*)fluoranthene [BbF–BkF], benzo(*e*)-pyrene [BeP], benzo(*a*)pyrene [BaP], indeno(*1,2,3-cd*)pyrene [InP], dibenz(*a,h*)anthracene [DahA], benzo(*ghi*)perylene [BghiP] were determined by gas chromatography–mass spectrometry (GC–MS). Quantitation of PAHs was performed via the internal standard with relative response factors determined by calibration with 16 PAHs mix. The separation and analysis were achieved with Agilent 6890 GC equipped with 5975 MS. A DB-5 column (30 m, 0.25 mm i.d.) was used with helium as the carrier gas. All results were expressed on a dry weight basis. PAH recoveries ranged from 79%-107%. The limit of detection (LOD) ranged from 1 to 5 ng/g, and the relative standard deviation for each compound was below 22%.

The BC content in each sample was determined according to the direct high temperature oxidation method (CTO-375) (Gustafsson et al., 2001). Samples were treated with a dilute HCl acid to remove carbonates. About 20 mg of each sample was oxidized for 24 h under air in muffle furnace at 375 ± 2 °C. TOC and BC fractions of both heat-treated and untreated samples were determined by elemental analysis (Vario EL, Elementar). Sediment samples were also prepared for XRD analysis. Powdered samples were examined at room temperature using a Philips X'Pert Pro X-ray diffractometer with a Cu tube (current = 25 mA; voltage = 35 kV), graphite crystal monochromator and proportional counter. Diffraction data were processed by the Philips X'Pert Software. The relative intensities of X-ray diffraction lines were compared with the literature values.

2.3. Sequential separation procedures

Sequential separation procedures were performed to sequentially get S_1, S_2 and S_3 fractions in WSK and LG samples (Wang et al., 2008). (1) S_1 fractions were achieved by removing carbonate from original sediments (S_0) using 1 M HCl repeatedly, and then the samples were thoroughly washed with de-ionized water. (2) H_2O_2 solution (30%) was added dropwise to S_1 fractions in order to remove the OC, and the mixture was intermittently agitated at 40 °C and then evaporated. The second step was repeated three times to achieve S_2 fractions. (3) S_1 fractions were oxidized for 24 h under air in muffle furnace at 375 ± 2 °C in order to thoroughly remove OC and achieve S_3 fractions. All fractions were lyophilized and ready for the sorption experiments.