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Distribution characteristics of phenanthrene in the water, suspended particles and sediments from Yangtze River under hydrodynamic conditions

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ABSTRACT

The effects of aquatic sediment concentrations, grain size distribution and hydrodynamic conditions on sorption behavior of phenanthrene (PHE) on sediments collected from Yangtze River (Wuhan catchment) were investigated. The results showed that the sorption behavior of PHE was mainly affected by the organic carbon in different phases, i.e. organic carbon contents (f_{oc}) (w/w, organic carbon/dry weight sediment) in the sediments and dissolved organic carbon (DOC) in liquid phase. In this study, sediments were subjected to artificial resuspension under turbulent diffusion coefficients being 24.6, 29.5 and 46.2 $cm^2 s^{-1}$ corresponded to 0.4, 0.3 and 0.2 s $cycle^{-1}$ of the perforated grids, respectively, which were driven by variable speed motor with 150, 180 and 280 rotation per minute (rpm). The suspended particle concentration increased from 1.01 to 6.70 g L^{-1} as the hydrodynamic strength increased from 150 to 280 rpm, whereas PHE concentration in liquid phase decreased from 0.56 to 0.34 μg mL^{-1}. The amount of DOC was supposed to play an important role in the partition of PHE under hydrodynamic conditions. Moreover, a sorption dynamic model was developed based on the linear isotherm expression and law of conservation of mass. The model was validated by PHE sorption behavior acquired with three different hydrodynamic conditions and the predicted values displayed satisfying accordance with experimental data.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread pollutants with high toxicity and some of them are endocrine disrupting chemicals (EDCs) [1–4]. Once released into the aquatic environment, PAHs tend to bind to particles and subsequently deposit in the sediments due to their high hydrophobicity. Consequently, sediments act as a natural repository for these hydrophobic organic contaminants [5,6]. Unfortunately, under favorable conditions, PAHs will be released from the sediments, which results in a second contamination [7]. As the important source and sink of PAHs, sediment plays an important role in the transport and fate of these chemicals in the aquatic environment. Therefore, there has been considerable interest in the transport and fate of these contaminants in the water [3–5,8].

Investigation on the influence of sediment characteristics, pollutant properties and physicochemical properties of freshwater on sorption or desorption behavior of organic pollutants has been an issue for several years [9–13]. In the aquatic environment, hydrodynamic condition is a ubiquitous natural process and will induce the sedimentation of suspended particle and the sediment resuspension. A number of laboratory studies indicated that the hydrodynamic conditions could result in the release of organic contaminants into overlying water and could act as a potential pollution source to water column [7,12,13]. For example, Latimer et al. [12] found that variations of dissolved PAHs in the overlying water were not uniform because of different sediment compositions and complicated phase changes. Recently, Feng et al. [7] reported that the distribution of PAHs in the aquatic environment was significantly affected by aquatic particulates or aggregates of numerous complicated organic materials, and the desorption from the entrained particles was the primary source of dissolved PAHs in the liquid phase. Moreover, the composition of sediments is the major factor in determining the amount of released PAHs, more than the level of resuspension energy [9]. So far, the effects of hydrodynamic conditions on the remobilization and fate of PAHs are not fully understood. Especially, little was known about the effects of different hydrodynamic conditions on the distribution characteristics of PAHs in the water, suspended particles and sediments.

The body of literature investigating the absorptive linear partition of hydrophobic organic compounds into natural organic matter is extensive, owing largely to the pioneering work by Chiou,

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Karickhoff, and others [14–16]. These researchers correlated carbon-normalized or organic matter normalized partition coefficients (K_{oc} or K_{om}) with aqueous solubility (S_w) or octanol–water partition coefficient (K_{ow}) on the basis of theory derived from linear-solvation-energy relations (LSERs) [17]. Despite the widespread successes of the organic carbon contents (f_{oc})–K_{oc} paradigm, there are a number of important environmental scenarios (such as the sediment properties and hydrodynamic conditions) in which this paradigm is inadequate [18].

The objective of this study was to investigate the effect of hydrodynamic conditions on the sorption behavior of phenanthrene (PHE) in the sediments from the Yangtze River (Wuhan catchment) using a designed syntonic turbulence-simulation device. The influences of sediment concentrations and grain size on PHE distribution in static experiments were also studied. Moreover, based on the linear isotherm expression and law of conservation of mass, a sorption dynamic model was developed from the view of the hydrodynamic conditions.

2. Materials and methods

2.1. Chemicals

Standard PHE was purchased from the National Research Center for Certified Reference Materials of China. The PHE standard solutions (1.25 g L^{-1}) were prepared by diluting appropriate volumes of the standard PHE with methanol solution (HPLC grade, Merck, Germany). Other solvents and reagents included acetone (HPLC grade, Tedia, USA), dichloromethane, n-hexane (HPLC grade, Dikma, USA), and anhydrous sodium sulfate (analytical grade, Beijing Chemical Reagent Co., China). Anhydrous sodium sulfate was baked in a furnace oven at 650 °C for 6 h, kept in a sealed desiccator prior to use. Additionally, the background solution was prepared by $CaCl_2$ electrolyte, which was composed of 1 mM $CaCl_2$, and some of 100 mg L^{-1} NaN_3 as bacterial inhibitor, in order to make the aquatic environment condition close to the natural freshwater. All solutions were prepared using distilled water that was passed through a MilliQ UV-plus water purification system (Millipore, Bedford, MA, USA) with a specific resistivity of 18.2 MΩ cm.

2.2. Sample collection

Sediment samples were collected using a Van Veen stainless steel grab sampler (Eijkelamp, Netherlands) from Yangtze River (Wuhan catchment) in July 2005. The top 10 cm sections from five cores (8 cm in diameter) were combined and passed through a 500-μm mesh sieve to remove macrofauna. The sediment, which was black, fine-grained, muddy sand, was allowed to settle for 7 days at 4 °C prior to analysis and use in the microcosms.

2.3. Sorption experiments

Kinetics of PHE sorption onto the Yangtze River sediments was carried out in a series of conical flasks to determine the time required to reach the fast adsorption equilibrium. PHE (20 μL) dissolved in ethanol was added to each empty flasks for a total mass of 2.5 μg PHE per flask. After the ethanol evaporated, the equivalent sediment was added to each flask (2.0 g dry weight) along with 25 mL of $CaCl_2$ electrolyte. Flasks were sealed, and shaken at 150 rotation per minute (rpm) in darkness at 20 ± 1 °C for various periods of time ranging from 0.6 to 12 h. At the end of each agitation period, aliquots of 10.0 mL from duplicate flasks were collected, and centrifuged at 4000 rpm for 20 min. The supernatant was moved to a clean centrifuge tube, and the PHE concentration in the supernatant was analyzed with high-performance liquid chromatography (HPLC). In order to select an isotherm with the best validity and stability, the relative errors of partition coefficient (RE) and the coefficient of variation (CV) were used to test the stability of isotherms.

A series of mass of sediments with different grain size were added to conical flasks containing 0.8 mL L^{-1} of PHE $CaCl_2$ electrolyte. After the initial sorption phase was obtained, the PHE concentration was determined to exhibit the effects of sediment concentration and grain size on the sorption behavior of PHE.

2.4. Analytical methods

Prior to testing, the sediments were size fractionated using sequential sieve sizes to obtain the following fractions: >200 μm, 125–200 μm, 63–125 μm, 25–63 μm, and <25 μm. The grain size analysis of the sediment samples used for classification test was performed by X-ray sedigraphy using a SALD-3001 Particle Analyzer (0.269–2000 μm, RSD <3%) (Shimadzu, Japan). The total organic carbon (TOC) contents of sediment samples were determined using a Liqui TOC analyzer (Elementar, Germany) after treatment with 2N HCl to remove carbonate-containing minerals. The values of dissolved organic carbon (DOC) in liquid phase were also measured by Liqui TOC analyzer (Elementar, Germany) by detecting the organic carbon contents in solution samples.

The extraction procedure was a modification of the method described elsewhere [7]. Briefly, the sediments were extracted three times with 30 mL hexane/acetone mixture (1:1, v/v) for 1.0 h in an ultrasonic bath (KQ-502B, Kunshan Ultrasonic Instruments, China). The extract was partitioned against solvent-extracted, deionized water and reduced in volume to about 1.0 mL in a rotary evaporator (RV 05 basic, IKA, Germany). Cleanup of the extracts was performed using an open glass column containing 2 g of 5% deactivated silica gel (100–200 mesh, Qingdao Ocean Chemical Plant, China). Water samples were extracted with dichloromethane and the aqueous extracts were then reduced to a volume of about 2 mL, re-extracted with methanol, and again concentrated to 1.0 mL for analysis. Following the extraction from sediments or water samples, quantification analysis of PHE was performed on a Waters 1525 HPLC system (Waters, USA) equipped with fluorescence detector (excitation wavelengths were 292 nm, emission wavelength were 366 nm for PHE). The injector was a Rheodyne 7725 high-pressure manual injector valve with a 20-μL injection loop. Separation was carried out using a ChromSep guard column (10 mm × 4.6 mm, grain size 5 μm, Varian, USA) followed by a ChromSep C_{18} Column (250 mm × 4.6 mm, grain size 5 μm, Varian, USA). The elution was conducted with 95% acetonitrile/water (v/v). PHE quantification was based on an external standard (NIST SRM1647d). Extraction solvents were regularly checked for blank levels.

2.5. Turbulence-simulation device

In the natural aquatic environment, the adsorption of organic matter on sediments or suspended particles is carried out in the turbulent water rather than the still water. The improved syntonic turbulence-simulation device (ISTSD) was used to simulate the natural aquatic environment, and perform hydrodynamic experiments to estimate the effect of hydrodynamic condition on the adsorption of PHE on resuspended particles. As shown in Fig. 1, the improved ISTSD consists of a vertical acrylic cylinder ($\Phi = 25$ cm, $h = 60$ cm) and a set of oscillating vibratory grids driven by a variable speed motor. The positions of sample ports on the cylinder are 5 cm intervals from bottom to top.