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Enhancement of toxic effects of phenanthrene to *Daphnia magna* due to the presence of suspended sediment

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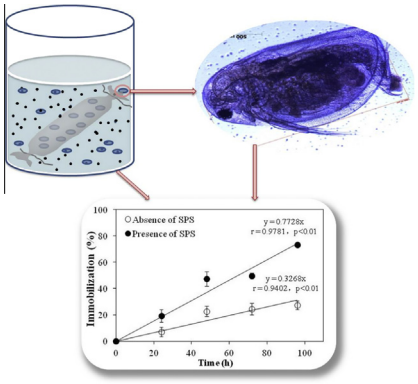
HIGHLIGHTS

- Immobilization of *Daphnia magna* caused by PHE was enhanced in the presence of SPS.
- PHE sorbed on SPS inhibited the total superoxide dismutase activity of *D. magna*.
- PHE sorbed on SPS (1–5 g L^{-1}) contributed to 37–63% of the immobilization of *D. magna*.
- The bioavailable fraction of PHE sorbed on SPS to *D. magna* ranged from 10% to 23%.
- HOCs sorbed on SPS should be considered in the establishment of water quality standard.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, the influences of suspended sediment (SPS) on the toxic effects of phenanthrene (PHE), one kind of polycyclic aromatic hydrocarbons, to *Daphnia magna* was studied using a dialysis bag simulation system, which equalized the freely dissolved concentration of PHE between outside the dialysis bag in the presence of SPS and inside the dialysis bag in the absence of SPS. The immobilization and total superoxide dismutase (T-SOD) activity of *Daphnia magna* caused by PHE (0–0.8 mg L^{-1}) were investigated under the influence of different SPS concentrations (0, 1, 3, 5 g L^{-1}) during a 96 h-exposure. The results showed that, compared to the absence of SPS, the presence of SPS (1–5 g L^{-1}) increased the immobilization of *Daphnia magna* by 1.6–2.7 times when the freely dissolved concentration of PHE was identical in both systems. The inhibition of T-SOD activity of *Daphnia magna* by PHE was significantly greater in the presence of SPS than in the absence of SPS ($p < 0.01$). This infers that the PHE sorbed on SPS might be bioavailable and enhanced the toxic effect of PHE to *Daphnia magna*. The bioavailable fraction of PHE sorbed on SPS ranged from 10.1% to 22.7%, and the contribution of PHE sorbed on SPS to the immobilization caused by total PHE in the exposure system increased with SPS concentration, with the contribution ratio increasing from 36.7% to 57.7% when SPS concentration increased from 1 to 5 g L^{-1}. This study suggests that only considering the concentrations of hydrophobic organic compounds in the water phase may underestimate their toxicity; and the hydrophobic organic compounds sorbed on SPS should not be ignored in assessment of water quality and the establishment of water quality standard in the future.

1. Introduction

Hydrophobic organic compounds (HOCs) are a class of organic chemicals characterized with high octanol–water partition

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coefficients and they have strong affinity for natural sorbents (Liu et al., 2004; Bolldarenko and Gan, 2009). Once HOCs enter into aquatic environment, they tend to be associated with deposited and suspended sediment (SPS) (Xia et al., 2006; Eek et al., 2010; Wang et al., 2011a,b). Therefore, the fate and behavior of HOCs and the water quality of rivers will be affected by the presence of SPS. High SPS concentration exists in many rivers around the world. For instance, the Mississippi River, the chief river of the largest drainage system in North America, has a SPS concentration of 5.1 g L^{-1} at St. Louis, MO (Sivakumar, 2002); the SPS concentration of the Delaware River, a major river on the Atlantic Coast of the United States, ranges from 0.1 to 11.7 g L^{-1} (Putnam and Pope, 2003). The Yellow River in China has an average SPS concentration of 22 g L^{-1} (WCC, 2010). Therefore, it is necessary to study the effect of SPS on the fate and bioavailability of HOCs in rivers, especially for the rivers with high SPS concentration.

It is commonly considered that only the freely dissolved HOCs are bioavailable to aquatic organisms (Haftka et al., 2010; Xia et al., 2013a). As a result, the water quality evaluation is only based on the dissolved concentrations of HOCs, and those attached with SPS have not been considered. However, Fisher et al. (2011) reported that eleven polycyclic aromatic hydrocarbons (PAHs) sorbed on sediment did cause acute toxicity to *Corpophium volutator* after exposure for 10 d. According to the research results reported by Tian et al. (2012), the uptake of polybrominated diphenyl ethers by carp (*Cyprinu carpio*) in water system in the presence of SPS was significantly higher/faster than that in the absence of SPS. Our previous study found that the biodegradation rates of PAHs increased with SPS concentrations in the water system (Xia et al., 2006; Xia et al., 2011). In addition, even black carbon associated phenanthrene (PHE) could be partly biodegraded by bacteria (Xia et al., 2010). Therefore, based on the above mentioned, the HOCs associated with SPS might be bioavailable and toxic to aquatic organisms, which is important for the evaluation of water quality and the establishment of water quality standard.

However, there is few research report about the toxicity of HOCs attached with SPS to aquatic organisms, and there lacks the information regarding the effect of SPS concentration on the toxicity of HOCs. PAHs are a class of HOCs; they are most widely detected in the environment (Feng et al., 2007; Fernandez et al., 2009) and have been studied by many scientists for their mutagenic and carcinogenic characteristics. Furthermore, the fate of PAHs in natural waters is strongly influenced by the presence of SPS (Li et al., 2006). *Daphnia magna* is a kind of filter feeder in overlying water and they have been widely used as a standard testing organism to study the biotoxicity of PAHs, which contributes to the establishment of water quality standard (USEPA, 2003).

In this research, we chose PHE, which is widely used as a model compound to investigate the environmental behavior of PAHs, to study the effect of SPS on the toxicity of HOCs to *D. magna* in water system. The main objective of this study was to investigate the impacts of different SPS concentrations on toxicity of PHE to the immobilization and total superoxide dismutase (T-SOD) activities of *D. magna*. The dialysis bag was used to establish two systems with an identical dissolved concentration of PHE while one in the presence of SPS and the other in the absence of SPS. The freely dissolved concentration (C_{fw}) of PHE was measured using low-density polyethylene (LDPE) devices which is practicable and accurate, and has been employed and approved by many studies (Vrana et al., 2005; Wang et al., 2011b). The contribution of SPS associated PHE to the toxicity caused by total PHE in water system was evaluated. In addition, the importance of SPS in the evaluation of water quality and the establishment of water quality standard for HOCs was discussed.

2. Materials and methods

2.1. Chemicals and materials

PHE was purchased as solid phase from AccuStandard Inc. (New Haven, USA). The stock solution of 1000 mg L^{-1} PHE was obtained by dissolving 100 mg solid PHE in 100 mL methanol (HPLC grade), which was purchased from JT Baker. Di-fluoro-biphenyl used as recovery standard and meta-terphenyl used as internal standard were obtained from J&K Scientific Ltd. (Beijing, China). GC–MS grade dichloromethane (DCM), hexane and acetone were purchased from J&K Scientific Ltd. (Beijing, China). Other analytical grade reagents and chemicals were from Beijing Chemical Reagents Company (Beijing, China). Spectra Por 6 7000 Da MW cutoff dialysis bag (28 mm × 5 m) was from Viskase Companies, Inc. Before the experiment, the dialysis bag was cut into 10 cm length and then boiled in the boiling water for 10 min; then it was washed by hot deionized water (60–80 °C) and room temperature deionized water twice. Low-density polyethylene sheets (51 ± 3 μm thick) were purchased from Carlisle Plastics, Inc. (Minneapolis, USA). Glassware were prepared by sequential treatments in following order: soaked in an acid solution for 24 h, then washed with tap water, distilled water and ultrapure water (each for three times) in sequence; afterwards dried in oven (105 °C) and heated at 350–400 °C in a muffle furnace for 5 h.

2.2. Sediment sampling and characterization

The surface sediments were collected from the Huayuankou Hydrological Station near Zhengzhou which is in the middle reach of the Yellow River. The samples were placed in a cooler and transported to the laboratory. They were dried in a freeze drier, and then sieved through a 2 mm sieve. The particle size distribution of the sediment samples was determined with a Microtrac S3500 Laser Particle Size Analyzer (Microtrac Inc., Montgomeryville, PA). In addition, total organic carbon (TOC) of the sediment was determined using an elemental analyzer (Vario El, Elementar Analysensysteme GmbH, Germany). The physico-chemical properties of the sediment are listed in Table S1.

2.3. D. magna cultivation

The tested *D. magna* were purchased from the Chinese Center for Disease Control and Prevention, which have been cultured in laboratory conditions for at least 10 years. The *D. magna* were cultured in the Artificial freshwater with the conditions described in the guideline of Organization for Economic Cooperation and Development for the testing of chemical (OECD, 2008). The detailed procedure has been described in our previous study (Dai et al., 2012).

2.4. Biological experiment

2.4.1. Design of biological experiment system

The experiments were conducted in 500 mL beakers. The total volume of the exposure solution is 300 mL; the dialysis bag was placed into each beaker with 20 mL solution inside the bag and 280 mL solution outside the bag. Then, varied amount of sediment was added in the outside of the dialysis bag, obtaining different concentrations of sediment. The schematic of that was shown in Fig. S1. In such systems, the C_{fw} of PHE inside the dialysis bag in the absence of SPS and outside in the presence of SPS should be identical. Before biological experiments, the beakers were covered by parafilm, which is water proof but ventilated, and equilibrated on a magnetic stirrer at room temperature for 48 h. After that,