



Contribution ratio of freely to total dissolved concentrations of polycyclic aromatic hydrocarbons in natural river waters

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HIGHLIGHTS

- ▶ The ratios of freely to total dissolved concentrations of three polycyclic aromatic hydrocarbons (PAHs) were studied.
- ▶ The ratio sequence of the three PAHs was phenanthrene > pyrene > chrysene.
- ▶ The ratios were significantly negatively correlated with the $\log K_{ow}$ (octanol–water partition coefficient) values of PAHs.
- ▶ The ratios were negatively correlated with suspended sediment and dissolved organic carbon concentrations in river water.
- ▶ Characteristics of suspended sediment and dissolved organic carbon were also important factors affecting the ratios.

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ABSTRACT

The bioavailability and ecological risk of hydrophobic organic compounds (HOCs) in aquatic environments largely depends on their freely dissolved concentrations. In this work, the freely dissolved concentrations of polycyclic aromatic hydrocarbons (PAHs) including phenanthrene, pyrene, and chrysene were determined for the Yellow River, Haihe River and Yongding River of China using polyethylene devices (PEDs). The results indicated that the order of ratios of freely to total dissolved concentrations of the three PAHs was phenanthrene ($66.8 \pm 20.1\%$) > pyrene ($48.8 \pm 26.4\%$) > chrysene ($5.5 \pm 3.3\%$) for the three rivers. The ratios were significantly negatively correlated with the $\log K_{ow}$ values of the PAHs. In addition, the ratios were negatively correlated with the suspended sediment (SPS) and dissolved organic carbon (DOC) concentrations in the river water, and the characteristics of the SPS and DOC were also important factors. Simulation experiments showed that the ratio of freely to total dissolved concentrations of pyrene in the aqueous phase decreased with increasing SPS concentration; when the sediment concentration increased from 2 g L^{-1} to 10 g L^{-1} , the ratio decreased from 67.6% to 38.4% for Yellow River sediment and decreased from 50.4% to 33.6% for Haihe River sediment. This was because with increasing SPS concentration, more and more DOC, small particles and colloids ($<0.45 \mu\text{m}$) would enter the aqueous phase. Because high SPS and DOC concentrations exist in many rivers, their effect on the freely dissolved concentrations of HOCs should be considered when conducting an ecological risk assessment.

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Abbreviations: HOCs, hydrophobic organic compounds; PAHs, polycyclic aromatic hydrocarbons; K_{ow} , octanol–water partition coefficient; SPS, suspended sediment; DOC, dissolved organic carbon; PEDs, polyethylene devices; SPMDs, semi-permeable membrane devices; SPME, solid-phase micro-extraction; PCBs, polychlorinated biphenyls; DCM, dichloromethane; LDPE, low-density polyethylene; PRCs, performance reference compounds; TOC, total organic carbon; BC, black carbon; YDRA, first sampling site along the Yongding River; YDRB, second sampling site along the Yongding River; HRA, first sampling site along the Haihe River; HRB, second sampling site along the Haihe River; HRC, third sampling site along the Haihe River; HRD, fourth sampling site along the Haihe River; HRE, fifth sampling site along the Haihe River; YRA, first sampling site along the Yellow River; YRB, second sampling site along the Yellow River; YRC, third sampling site along the Yellow River; YRD, fourth sampling site along the Yellow River; YRE, fifth sampling site along the Yellow River; YRF, sixth sampling site along the Yellow River.

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1. Introduction

Freely dissolved concentration is a key parameter of bioavailability for hydrophobic organic compounds (HOCs) in aquatic environments. Many studies have demonstrated that the bioavailability and toxicity of HOCs are directly proportional to their freely dissolved concentrations (Mayer et al., 2003; Escher and Hermens, 2004; Anderson et al., 2008; Hu et al., 2009; Bao and Zeng, 2011). The total dissolved concentration of HOCs in aqueous environments includes the freely dissolved concentration and the colloid-, particle- and dissolved organic carbon (DOC)-associated HOCs that cannot be filtered from the water using a $0.45\text{-}\mu\text{m}$ filter. Some research has indicated that colloid- and particle-associated HOCs are not bioavailable (Gustafson and Dickhut,

1997; MacRae and Hall, 1998). Contaminants that are tightly bound to DOC may have reduced bioavailability because their uptake by organisms is prevented (Luellen and Shea, 2002; Anderson et al., 2008; Cornelissen et al., 2009). However, the poor correlation between the total dissolved concentration and the portion assimilated by organisms (Gomez-Eyles et al., 2011) has long been ignored; environmental and eco-toxicological risk analysis has been based on the total dissolved concentration of HOCs in aquatic environments. Many scientists have assayed HOC concentrations in natural water (Li et al., 2006; Anderson et al., 2008), characterizing samples chiefly by the total concentration or total dissolved concentration without considering the effects of colloids and DOC.

Measuring the freely dissolved concentrations of HOCs with traditional methods requires difficult phase separations (e.g., centrifugation and filtrations) and extraction of large volumes of water due to the low dissolved concentrations of HOCs in the environment. Therefore, many passive sampling techniques such as semi-permeable membrane devices (SPMDs) (Huckins et al., 1990; Allan et al., 2010), solid-phase micro-extraction (SPME) (Ouyang et al., 2007; Ghosh and Hawthorne, 2010), and polyethylene devices (PEDs), a passive and diffusion-based technique (Booij et al., 2003; Anderson et al., 2008), have been proposed to measure the freely dissolved concentrations of HOCs in aquatic environments. For example, Sower and Anderson (2008) measured the freely dissolved concentrations of 15 polycyclic aromatic hydrocarbons (PAHs) along 18.5 miles of the lower Willamette River (USA) during rainy season, a dry season with no rain, and a dry season with rain events from 2002 to 2006 using SPMDs. Ouyang et al. (2007) studied the freely dissolved concentrations of six PAHs in Hamilton Harbor, located on the western tip of Lake Ontario (Canada) using SPME. Adams et al. (2007) measured phenanthrene and pyrene at ng L^{-1} concentrations and 2,2',5,5'-tetrachlorobiphenyl at pg L^{-1} concentrations in Boston Harbor seawater with PEDs and suggested that PEDs are inexpensive and robust samplers that can accomplish in situ, time-averaged passive sampling with rapid equilibration times (\sim days) and simplified laboratory analysis. Anderson et al. (2008) measured the freely dissolved concentrations of PAHs, polychlorinated biphenyls (PCBs) and several pesticides in the lower Willamette River (USA) using PEDs. Bao et al. (2012) similarly studied the freely dissolved concentrations of 14 PAHs in four reservoirs of Guangdong Province in China using PEDs. According to these previous reports, the SPMD method, which consists of polyethylene bags filled with triolein, often leaked unknown amounts of triolein and required deployment time up to several months (Adams et al., 2007; Hu et al., 2009). The deployment time of PEDs and SPME methods is short, and the PEDs method is more suitable for in situ measurement than the SPME method (Adams et al., 2007). The feasibility of PEDs as passive samplers in aquatic systems has been demonstrated by many researchers (Carls et al., 2004; Tomaszewski and Luthy, 2008; Wang et al., 2011).

Although many studies have investigated the total dissolved concentration of HOCs in natural water, only a few studies have examined the freely dissolved concentration of HOCs in natural water, and no research reports have discussed the contribution ratio of freely to total dissolved concentrations of HOCs in natural waters including rivers. Little is known about the environmental factors affecting the contribution ratio of freely to total dissolved concentrations of HOCs.

In the present study, low-density polyethylene devices were used to study the freely dissolved concentrations of common environmental PAHs, including phenanthrene, pyrene, and chrysene, in natural river waters. The freely dissolved PAH concentrations, which do not include PAHs associated with DOC and colloids, were measured in situ for the Yellow River, the Haihe River and the

Yongding River, and the total dissolved concentrations of PAHs were measured simultaneously. The relationships between the freely dissolved concentrations of PAHs and the suspended sediment (SPS) concentration, as well as the DOC, were analyzed. In addition, pyrene was selected as a model PAH to investigate the influence of SPS concentration on the freely dissolved PAH concentration in simulation experiments.

2. Materials and methods

2.1. Chemicals and glassware

PAHs (phenanthrene, pyrene and chrysene) and deuterated PAHs (*d*10-phenanthrene, *d*10-pyrene and *d*12-chrysene) were obtained from JT Baker (Philipsburg, NJ, USA); these materials were purchased as solid phase reagents except for *d*10-phenanthrene and *d*12-chrysene. The physico-chemical properties of the studied PAHs are listed in Table S1 (Supplementary data). Dichloromethane (DCM) (HPLC grade), hexane (HPLC grade), 2-fluorobiphenyl (recovery standard) and meta-terphenyl (internal standard) were all acquired from J&K Scientific Ltd. (New Haven, C.T., USA). Hydrochloric acid, sodium azide and calcium chloride were of analytical grade and supplied by Beijing Chemical Inc. (Beijing, China). All glassware was prepared with sequential treatments in the following order: soaking in an acid solution for 24 h; washing with tap water, distilled water and ultrapure water (three times each) in sequence; drying in an oven ($105\text{ }^{\circ}\text{C}$); and heating at $350\text{--}400\text{ }^{\circ}\text{C}$ in a muffle furnace for 5 h.

2.2. PEDs preparation

Low-density polyethylene (LDPE) sheets ($51 \pm 3\ \mu\text{m}$ thick, Carlisle Plastics, Inc., Minneapolis, MN) were cut into small strips before use. The LDPE strips were soaked in DCM for 48 h and then methanol for 48 h, rinsed with ultrapure water and soaked in ultrapure water for 48 h. Approximately 30 g of LDPE were allowed to equilibrate with 3 L of a performance reference compound (PRC) solution (i.e., *d*10-phenanthrene, *d*10-pyrene, and *d*12-chrysene; each at a concentration of $10\ \mu\text{g L}^{-1}$) for at least three months before use. The PEDs method does not require targets to reach equilibrium because the LDPE strips have been spiked with PRCs.

To measure the concentrations of freely dissolved PAHs in water, a loss of at least 20% of the PRCs from the LDPE strips is desired so that the mass loss can be detected after considering the variation of the apparatus (Fernandez et al., 2009). According to the results shown in Fig. S1 (Supplementary Data), 8 h was sufficient for 20–29% of the PRCs to diffuse from the LDPE strips, and the presence of $10\ \text{g L}^{-1}$ SPS and DOC did not significantly influence the diffusion process of the targets and PRCs. Therefore, the exposure time was set at 8 h for each experiment.

2.3. Field deployment of PEDs in river water

The freely and total dissolved concentrations of PAHs in the Yellow River, the Haihe River and the Yongding River were studied. The Yellow River is the second-longest river in China and the fifth longest in the world with a length of 5464 km and a drainage area of $752444\ \text{km}^2$. It is located in northern China and flows through nine provinces with an average discharge of $2571\ \text{m}^3\ \text{s}^{-1}$. The Haihe River, located in northern China with a length of 1090 km and an area of $263631\ \text{km}^2$, is an important resource for drinking water for the Tianjin area; its annual flow is only half that of the Yellow River. The Yongding River, the largest river flowing through Beijing, with a maximum discharge of $5200\ \text{m}^3\ \text{s}^{-1}$, is 650 km in length and

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