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Measuring bioavailable PAHs in estuarine water using semipermeable membrane devices with performance reference compounds

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ABSTRACT

Bioavailable polycyclic aromatic hydrocarbon (PAH) concentrations in the estuarine water of Kaohsiung Harbor were measured using XAD-2 resin and semipermeable membrane devices (SPMDs) calibrated with performance reference compounds (PRCs). The sum of the PAH concentrations from XAD-2 resin (C_w) in the surface and bottom water samples was 6.63 and 9.58 ng L^{-1}, respectively. The variation in PAHs was higher in surface water. Cubic polynomial regressions using the sampling rate for five PRCs ($R_{s\text{-PRC}}$) provided estimated *in situ* sampling rates (R_s). The turbulent condition in the surface water was important in enhancing R_s; however, diffusion was relevant to the bottom water, which was less turbulent and showed decreasing R_s at high MW PAHs. The sum of the dissolved PAH concentrations estimated with the SPMDs (C_{SPMD}) was 5.87 and 9.15 ng L^{-1} in the surface and bottom water samples, respectively. The surface and bottom water PAHs were derived from different sources.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are found throughout the environment and are of great concern due to their toxicity, carcinogenicity, and mutagenicity. The bioavailable concentration of PAHs in the marine environment is of paramount importance when assessing their potential to harm aquatic organisms. In aquatic systems, free or dissolved PAHs are easily bound to hydrophobic particles; the effective toxicity is reduced because only free PAHs are bioavailable to diffuse across biomembranes and enter organisms (Hamelink et al., 1994; Oris et al., 1990). The concentration of dissolved PAHs is frequently below conventional detection limits; therefore, large volumes of water must be filtered through submicron filters and extracted with solvents for further analysis (Fang et al., 2012). Thus, direct measurements of free PAHs in water samples offer the potential for effective estimates of available concentrations for uptake by marine biota.

The semipermeable membrane device (SPMD), a passive sampler, was developed in 1990 and is widely used as a monitoring tool for assessing organic contaminants in aquatic environments (Huckins et al., 2006). The SPMD has shown excellent performance in estimating the bioavailable concentrations of persistent hydrophobic chemicals in water (Djedjibegovic et al., 2010; Grabic et al., 2010; Luellen and Shea, 2002; O'Brien et al., 2012). Time-weighted average PAH concentration via the SPMD (C_{SPMD}) in aquatic systems is estimated directly by measuring PAHs that have accumulated in the SPMD, according to Eq. (1):

$$C_{SPMD} = N/K_{sw}V_s[1 - \exp(-R_s t/K_{sw}V_s)] \quad (1)$$

where N is the amount of PAHs in the SPMD (ng), K_{sw} is the SPMD/water partition coefficient ($cm^3\ cm^{-3}$), V_s is the SPMD volume (L), R_s is the sampling rate (L d^{-1}), and t is the sampling period in days (d). For the short-term uptake exposure of the SPMD, C_{SPMD} can be expressed as:

$$C_{SPMD} = N/R_s t \quad (2)$$

The sampling rate (R_s) is the key variable for estimating the C_{SPMD}, which is used to approximate the bioavailable concentration of hydrophobic organic contaminants. This parameter, R_s, as shown in other papers, depends on parameters such as the temperature (Booij et al., 2003; Huckins et al., 2002), water flow velocity (Booij et al., 1998; O'Brien et al., 2012; Vrana and Schuurmann, 2002), bio-fouling (Booij et al., 2006; Richardson et al., 2005;

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Huckins et al., 2002), and geometry of the mounting cages. Booij et al. (2003) found that the sampling rate at 30 °C is about three times higher than that at 2 °C. Several researchers have suggested using performance reference compounds (PRCs) to obtain a more reliable *in situ* sampling rate (Booij et al., 2003; Booij and Smedes, 2010; Ellis et al., 1995; Huckins et al., 2006).

The samples here were collected from Kaohsiung Harbor, located in southern Taiwan adjacent to Kaohsiung, the largest industrial city in Taiwan. Kaohsiung Harbor receives the outflow from Love River, which passes through the metropolitan area of Kaohsiung and is polluted by municipal and industrial waste. PAHs in the atmosphere, water, and sediments from the harbor and nearby coastal environment have been measured (Fang et al., 2007, 2012; Jiang et al., 2009). Fang et al. (2012) showed that the dissolved PAHs amounted to 60% of the sum of the dissolved and particulate PAHs in Kaohsiung Harbor.

In this study, we compare the dissolved PAH concentrations determined using conventional XAD-2 resin (C_w) and SPMD (C_{SPMD}). The on-site sampling rates are obtained by using PRCs specific to Kaohsiung Harbor. In addition, principal component analysis (PCA) was applied to identify the possible sources of PAHs in Kaohsiung Harbor, and the toxic equivalent quotients (TEQs) of the bioavailable PAHs for the water were estimated.

2. Materials and methods

2.1. Chemicals

Organic solvents used in this study were SupraSolv grade purchased from Merck Co., Germany. Sodium sulfate was pre-cleaned by refluxing with 1:1 hexane and acetone in Soxhlet and baked at 150 °C before use. Aluminum oxide was baked at 550 °C before use. Perdeuterated standards including phenanthrene-d10, acenaphthene-d10, and benzo[a]anthracene-d12 were purchased from Supelco, USA. Perylene-d12, fluorene-d10, fluoranthene-d10, and benzo[a]pyrene-d12 were purchased from Chem Service, USA. Benzo[g,h,i]perylene-d12, anthracene-d10, benzo[K]fluoranthen-d12, pyrene-d10, and indeno[1,2,3-CD]pyrene-d12 were purchased from Cambridge Isotope Laboratories, USA. PAH calibration standards were purchased from AccuStandard, USA.

The SPMDs and stainless steel mesh cages were purchased from EST, St. Joseph, MO, USA. Standard size SPMDs were constructed of low-density polyethylene tubes (91.4 × 2.5 cm, 70–95 μm wall thickness) and contained 1 mL (0.91 g) of triolein. Each SPMD in the experiment was spiked with 1 μg acenaphthene-d10, anthracene-d10, benzo[K]fluoranthen-d12, pyrene-d10, and indeno[1,2,3-CD]pyrene-d12 as performance reference compounds (PRCs).

2.2. Sampling

The sampling site (water depth about 6 m) was located off No. 10 Wharf (22°36′51.48″N, 120°17′18.19″E) of the Kaohsiung Harbor basin as shown in Fig. 1. The SPMDs were deployed for 10 days, at 1 (surface) and 5 m (bottom) water depth, from 17 to 27 April 2011. During the deployment, water samples were taken every two days according to the stage of the tidal cycle. Two standard SPMDs, one with PRCs and the other without a PRC, were suspended in a stainless steel mesh cage at the sampling site. The SPMDs were removed approximately every two days and placed back in the position after the individual SPMD was wiped clean and dipped in a mixture of copper sulfate (3–5 mg L^{-1}). After collection, the SPMD was wrapped individually in aluminum foil and kept frozen (−20 °C). During SPMD deployment, water samples were collected with a 20 L pre-cleaned polished stainless steel can. Twenty water samples, including 10 surface water and 10 bottom water samples, were collected. Water samples were forced by pressurized nitrogen (purified by activated carbon) through a 293 mm diameter pre-ashed GFF filter placed inside a stainless steel filter holder. The filtered water was then passed through a glass column (30 cm × 5 cm ID) packed with Amberlite XAD-2 resin (Supelco, USA) with a flow rate of 160–200 mL min^{-1} to retain the dissolved PAHs in the water samples.

2.3. Analysis and sample processing

Before the SPMD was extracted, fouling was removed with Kimwipes tissue. The SPMD was then rinsed with Milli-Q water and soaked in 150 mL of n-hexane with surrogate standards added in a pre-cleaned amber glass bottle for 18 h at 18 °C in the dark. Extraction was repeated for an additional 6 h with a new portion of solvent. These two fractions were combined and concentrated to about 1.5 mL by rotary evaporation. Concentrated extracts were cleaned up using gel permeation chromatography (GPC) to remove polyethylene and remaining co-dialyzed lipids. The GPC system consisted of HPLC (L-2130, Hitachi, Japan) with PL EnviroPrep organic GPC columns (19 × 300 mm, Varian, USA) and a UV detector (L-4200, Hitachi, Japan) at 254 nm. The mobile phase was dichloromethane, with a flow rate of 8 mL min^{-1}. The extract fractionated from the GPC system was eluted by petroleum ether through a column packed with aluminum oxide to remove the polar interferences. The extract was evaporated under a gentle stream of nitrogen to 0.5 mL.

The XAD-2 resin was extracted in a Soxhlet apparatus for 24 h using acetone and hexane (1:1) with surrogate standards added. The subsequent extract was used in liquid–liquid extraction with 25 mL saturated sodium chloride and followed by two aliquots of Milli-Q water (25 mL) to remove the aqueous phase. Then the organic extract was concentrated by rotary evaporation and nitrogen stream to approximately 0.5 mL. The extracted samples were further eluted by petroleum ether through a column packed with aluminum oxide to remove the polar interferences and reduced to 0.5 mL under the gentle nitrogen stream.

2.4. Quantification and instrumental analysis

Three perdeuterated PAHs, fluorene-d10, fluoranthene-d10, and pyrene-d12, were added to each sample before extraction as surrogates to monitor the performance of the overall analytical procedure. The average recovery for fluorene-d10, fluoranthene-d10, and pyrene-d12 was 73 ± 21%, 72 ± 14%, and 65 ± 12% for the XAD-2 samples and 52 ± 11%, 79 ± 15%, and 82 ± 11% for the SPMD samples. The PAH concentrations measured in this study were corrected using surrogate recovery. For quantification, each extract was spiked with phenanthrene-d10, benzo[a]anthracene-d12, benzo[a]pyrene-d12, and benzo[g,h,i]perylene-d12 as the internal standards and was analyzed on an Agilent 6890 gas chromatograph with Agilent 5973N mass selective detector (GC/MSD) operating in the selected ion-monitoring mode.

Laboratory and field blanks were incorporated in the analysis to quantify possible contamination due to collection, transport, and extraction. The mean detection limits (MDLs) were derived from the blanks and defined as the mean concentrations plus three times the standard deviation in the blank for each PAH compound. For the PAH compounds, the MDLs ranged from 0.012 to 0.521 ng L^{-1} and from 0.246 to 13.5 ng/SPMD for the XAD-2 and SPMD samples, respectively. Data processing was performed using ZunZun (ZunZun.com, 2013) for weighted polynomial fitting and Statistical Product and Service Solutions (SPSS) for Kendall correlation coefficients and principal component analysis.