**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-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.

Key words: SPMD, Membrane sampling rate, Bioavailability, Kaohsiung Harbor

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 sub-micron 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 ($\text{cm}^3 \text{ cm}^{-3}$), 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:

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

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; 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; Fang et al., 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]fluoranthene-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 x 2.5 cm, 70 to 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]fluoranthene-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

1 chromatography (GPC) to remove polyethylene and remaining co-dialyzed lipids. The
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4 GPC system consisted of HPLC (L-2130, Hitachi, Japan) with PL EnviroPrep organic
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7 GPC columns (19×300 mm, Varian, USA) and a UV detector
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10 (L-4200, Hitachi, Japan) at 254 nm. The mobile phase was dichloromethane, with a
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13 flow rate of 8 mL min^{-1} . The extract fractionated from the GPC system was eluted by
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16 petroleum ether through a column packed with aluminum oxide to remove the polar
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19 interferences. The extract was evaporated under a gentle stream of nitrogen to 0.5 mL.
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23 The XAD-2 resin was extracted in a Soxhlet apparatus for 24 h using acetone and
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26 hexane (1:1) with surrogate standards added. The subsequent extract was used in
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29 liquid-liquid extraction with 25 mL saturated sodium chloride and followed by two
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32 aliquots of Milli-Q water (25 mL) to remove the aqueous phase. Then the organic
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35 extract was concentrated by rotary evaporation and nitrogen stream to approximately
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38 0.5 mL. The extracted samples were further eluted by petroleum ether through a
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41 column packed with aluminum oxide to remove the polar interferences and reduced to
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44 0.5 mL under the gentle nitrogen stream.
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47 48 *2.4 Quantification and instrumental analysis* 49 50

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52 Three perdeuterated PAHs, fluorene-d10, fluoranthene-d10, and pyrene-d12, were
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55 added to each sample before extraction as surrogates to monitor the performance of
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58 the overall analytical procedure. The average recovery for fluorene-d10,
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1 fluoranthene-d10, and pyrene-d12 was $73\pm21\%$, $72\pm14\%$, and $65\pm12\%$ for the
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4 XAD-2 samples and $52\pm11\%$, $79\pm15\%$, and $82\pm11\%$ for the SPMD samples. The
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7 PAH concentrations measured in this study were corrected using surrogate recovery.
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10 For quantification, each extract was spiked with phenanthrene-d10,
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12 benzo[a]anthracene-d12, benzo[a]pyrene-d12, and benzo[g,h,i]perylene-d12 as the
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14 internal standards and was analyzed on an Agilent 6890 gas chromatograph with
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17 Agilent 5973N mass selective detector (GC/MSD) operating in the selected
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20 ion-monitoring mode.
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26 Laboratory and field blanks were incorporated in the analysis to quantify possible
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28 contamination due to collection, transport, and extraction. The mean detection limits
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30 (MDLs) were derived from the blanks and defined as the mean concentrations plus
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33 three times the standard deviation in the blank for each PAH compound. For the PAH
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36 compounds, the MDLs ranged from 0.012 to 0.521 ng L^{-1} and from 0.246 to 13.5
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39 ng/SPMD for the XAD-2 and SPMD samples, respectively. Data processing was
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42 performed using ZunZun (ZunZun.com, 2013) for weighted polynomial fitting and
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45 Statistical Product and Service Solutions (SPSS) for Kendall correlation coefficients
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48 and principal component analysis.
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54 The toxic equivalent factor (TEF) was used to estimate the TEQs and assess the
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57 PAH toxicity to aquatic organisms; PAH toxicity relative to benzo[a]pyrene was
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evaluated.

3. Results and discussion

3.1 Variation of PAHs in the water samples

Most concentrations from the conventional XAD-2 samples (C_w) had low values and were close to the MDL (Fig. 2). Some PAHs showed a few high outliers, and therefore, the means and standard deviation are a poor measure of the central value and dispersion. In such situations, medians can be a good estimate of central tendency and quartile descriptors of dispersion, and were used in the initial description of the XAD-2 PAH concentrations (C_w). However, where sums and means were needed, values below the detection limit were assigned 70% of the MDL value. The standard deviation can be inflated by outliers, implying variability larger than that shown by the majority of the data set and can suggest finite probability negative concentrations. The median and the interquartile range (IQR; i.e., the first quartile subtracted from the third quartile, $q_3 - q_1$) can be useful as they are less affected by the lowest or highest data values and can be applied to censored data.

The sum of the PAH concentrations from XAD-2 resin (C_w) in each surface water and bottom water sample ranged from 4.32 to 30.0 ng L⁻¹ (sum of the PAH means, 9.31 ± 7.50 ng L⁻¹; sum of the PAH medians, 6.63 ng L⁻¹; n = 10) and from 6.63 to

13.2 ng L⁻¹ (sum of the PAH means, 10.1 ± 2.14 ng L⁻¹; sum of the PAH medians, 9.58 ng L⁻¹; n = 10), respectively. The coefficient of variation, the IQR/median, calculated from the surface water samples, is higher than that of the bottom water samples, which are shown in Fig. 2. This shows that the variation from the surface water is higher than that from the bottom water. Surface water is a more disturbed environment than bottom water due to shipping activity, river and pollutant input, and wave action. The dissolved PAH concentrations (C_w) were also comparable with measurements made in Raritan Bay in 1998 and Narragansett Bay in 2006 in the United States (Gigliotti et al., 2002; Lohmann et al., 2011).

The dissolved PAH compositional pattern in Kaohsiung Harbor was dominated by pyrene (14.8–36.4%), followed by fluoranthene (13.3–21.3%) and phenanthrene (6.06–21.8%). Larsen and Baker (2003) identified these compounds as the main PAH compounds emitted from coal-power plants (Larsen and Baker, 2003), which are found in the local area.

3.2 PRC estimate of the field sampling rate constant

Five PRCs were added to each SPMD before exposure to simulate the *in situ* exchange processes. The PRCs correct for the effects of environmental factors. The exchange kinetics established by the exchange of PRCs defines the release and uptake rates. The PRCs allow us to estimate the *in situ* release rate constant k_{e-PRC} (Booij et al.,

2003; Huckins et al., 2002). Huckins et al. (2006) provided a PRC-based methodology for calibrating field sampling rates. The PRC dissipation rate constant ($k_{e\text{-PRC}}$) was estimated (Huckins et al., 2006) according to the first-order exchange process:

$$k_{e\text{-PRC}} = -\ln(N/N_0)/t \quad (3)$$

where t is the exposure time (d) during deployment, N is the PRC amount (ng) present in the SPMD after dissipation, and N_0 is the initial amount (ng) at $t = 0$. The recovery rates (N/N_0) of all PRCs for surface water and bottom water are in the range of 4.85–68.7% and 8.48–90.3%, respectively (Table 1). All $k_{e\text{-PRC}}$ values are higher in the surface water than in the bottom water (Table 1).

The PRC sampling rate was estimated with Eq. (4):

$$R_{s\text{-PRC}} = V_{\text{SPMD}} k_{e\text{-PRC}} K_{sw} \quad (4)$$

where V_{SPMD} is the total volume of the SPMD (L) and K_{sw} is the SPMD-water partition coefficients, which are obtained from a quadratic regression for PAH compounds (Huckins et al., 2002) as:

$$\log K_{sw} = -0.16181 \log K_{ow}^2 + 2.321 \log K_{ow} - 2.61 \quad (5)$$

Huckins et al. (2006) showed that $\log(R_s)$ has a cubic relationship with $\log(K_{ow})$.

This relationship helps calculate the R_s values for any given PAH. However, the coefficients must be determined. This has been done for the samples collected from Kaohsiung Harbor using the five PRCs listed in Table 1. The R_s values calculated

1 based on five R_{s-PRC} using Huckins's method are shown in Fig. 3 (Huckins et al.,
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4 2006). Although the R_s shape from different PRCs is the same, they are ranked
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7 differently. We considered that when using PRCs to calculate the R_s values of other
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10 compounds, a range of PRCs that embrace the compounds being estimated is needed.
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13 The $\log (R_s)$ values calculated from the PRCs in the surface water were fit to a
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16 cubic polynomial as a heavy solid line in Fig. 4. Such fits are simply to provide an
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19 estimate of R_s for additional PAHs and should not be assumed to have any theoretical
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22 value. The regression was performed using ZunZun (ZunZun.com, 2013), which
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25 allowed the individual R_s values for PRCs to be weighted according to the percentage
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28 recovery $Pr = (100 N/N_0)$ of the PRC with weights (w) estimated: $w = Pr/5$ where Pr is
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31 less than 50% and $w = (100- Pr) /5$ where Pr is greater than 50%. These weights allow
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35 for the decreased reliability of R_s when recovery is low or high. Dividing by 5 acts as
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38 a scaling factor that led to weights that range between 1 and 10, but this choice was
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41 arbitrary and does not affect the fit. The weighted polynomial fit to the bottom water
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44 PRCs (heavy dashed line) was not as successful as it required a slight linearization at
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47 $\log (K_{sw})$ below 4.5.
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51 The shape of the surface water and bottom water polynomials are quite different.
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54 The surface water showed $\log (R_s)$ increased as $\log (K_{ow})$ increased and no clear
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57 maximum, while that for the bottom water showed a maximum around $\log (K_{ow})$ 6.
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Huckins et al. (2006) fitted $\log(R_s)$ data from nine studies to a third-order polynomial in $\log(K_{ow})$. This equation has often been used to determine R_s as it can yield the R_s of many compounds with perhaps only one or two PRCs (Huckins et al., 2006). However, different experimental conditions lead to R_s values of quite different magnitude (fine lines in Fig. 4), and these fits can also have different shapes. The regression curves we used were tuned to conditions in Kaohsiung Harbor; therefore, the shape and magnitude are likely the best representation of our sampling rates.

The R_s trend in surface water in our study (Fig. 4) is similar to the trend fitted to Booij's data (Booij et al., 2003), which was under flow conditions (90 cm s^{-1}) at 30°C . Our measurements were under relative high flow conditions: mean flow rate 49.4 cm s^{-1} (Su and Liaw, 2013) and a mean temperature of 25.4°C (CWBT, 2011). The bottom site from our study is less turbulent and has a slightly lower curve in Fig. 4, but is still higher than the two curves fitted to Luellen and Huckins's (Huckins et al., 2004; Luellen and Shea, 2002) data, collected at lower temperature (16.5°C and 25°C) and water flow rates (0.1 cm s^{-1} and 0.5 cm s^{-1}).

Not only the relative magnitude of these curves changes; the shapes are also different. In particular, the curves get shallower as the systems become more turbulent and the peak shifts to higher $\log(K_{ow})$. The changes in the shape and magnitudes of the curves can be understood in terms of the increasing turbulence and factors that

control the transfer of PAHs into the SPMD. As the molecular weight of the PAH increases, so does its $\log(K_{ow})$, and thus, its solubility in the SPMD lipid; however, conversely, the PAH's diffusion rate then decreases. These two competing factors could explain the increase in R_s at low molecular weights and the subsequent decrease at higher molecular weights in systems that have relatively low turbulence (Fig. 4, lower fine dotted lines). Under more turbulent conditions, the increasing solubility in the SPMD medium is still an important factor in increasing the R_s , but diffusion is less important; thus, there is not such a distinct decline in R_s with $\log(K_{ow})$ or molecular weight.

The relationship of R_s with turbulence implies that the values should generally be higher in the surface water than in the bottom water. Our study illustrates this since the R_s decreases between the surface water (turbulent and subject to shipping and tidal action) and the bottom water (less disturbed).

3.3 Comparison of PAH results from PRC-based SPMD and XAD-2

The sum of the dissolved PAH concentrations in the harbor water as estimated from SPMDs, C_{SPMD} , was 5.87 and 9.15 ng L⁻¹ in the surface and bottom water (Table 2), respectively, as calculated using the R_s values derived in this study. The C_{SPMD} using Luellen's R_s values in Fig. 5 significantly over-estimated concentrations in most cases, compared with the dissolved concentrations measured (Luellen and Shea, 2002).

1 Luellen's R_s values are from laboratory conditions. They differ from the natural
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4 environment conditions as shown by the results of this study (see also Vrana and
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7 Schuurmann, 2002). Using internal PRCs can help estimate more reasonable R_s values
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10 for the field environment. A comparison of R_s values based on five PRCs with
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13 Huckins's method (Fig. 2) and cubic regressions (Fig. 3) is shown as C_{SPMD} and C_w in
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16 Fig. 6. A related-sample Kendall's coefficient of concordance was used and showed
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19 that the two C_{SPMD} had similar rankings. These results show that C_{SPMD} from cubic
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22 regressions with C_w are comparable to each other.
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26 The C_{SPMD}/C_w ratios as a function of $\log(K_{ow})$ are shown in Fig. 7 and compare
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29 the water concentrations from SPMD-based PRC cubic regressions and XAD-2. In
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32 general, the ratios are close to one, showing that the methods yield comparable results.
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35 However, three PAHs, anthracene, phenanthrene, and 2,3,5-trimethylnaphthalene, tend
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38 to have ratios above 1.5 in surface and bottom water. Anthracene showed the best
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41 agreement probably because it is a PRC. Also notable, benzo(a)pyrene has a much
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44 larger C_{SPMD} value than C_w value, which is significant because this PAH has a high
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47 TEQ.
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51 *3.4 Principal component analysis and toxicity*

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55 Using specific PAHs to identify the PAH sources can seem too arbitrary, so we
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58 used concentration measurements for 19 PAHs to represent the major sources in
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1 Kaohsiung Harbor. PCA was used as an exploratory analysis to suggest possible
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4 sources for the PAHs. Transforming the variable values corresponding to a particular
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7 data point, we can easily obtain each score for the variable set. Thus, we can better
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10 explain the PAH sources in the data from the field sampling.
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13 Four principal components were extracted for the water samples, and each
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16 accounted for more than 10% (i.e., 25.1%, 17.3% 12.2%, and 10.6%, Table 3), which
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19 explained 65.2% of the total variance. Those factors corresponding to correlation
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22 matrix eigenvalues of >1 are considered meaningful and are listed in Table 3. PC1 had
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25 significant positive loading for phenanthrene, 2-methylanthracene,
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28 3-methylanthracene, and 2-methylphenanthrene, all of which were probably related to
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31 volatilization or spillage of petroleum-related products (Huang et al., 2012; Lai et al.,
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34 2011; Larsen and Baker, 2003). Fluoranthene is associated with significant negative
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37 loading in PC1, and likely represents coal burning (Fang et al., 2007; Larsen and
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40 Baker, 2003). PC2 showed positive loading for acenaphthene and fluorene
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43 representing volatilization or petroleum-related spills (Huang et al., 2012; Lai et al.,
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46 2011; Larsen and Baker, 2003), but the negative loading for pyrene and
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49 benz[a]anthracene in PC2 probably represents vehicle emissions (Fang et al., 2007;
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52 Larsen and Baker, 2003). PC3 shows the dominance of benzo[k]fluoranthene and
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55 benzo[e]pyrene related to incomplete combustion of organic matter such as coal or
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1 crude oils (Benner et al., 1989; Budzinski et al., 1997). PC4 has significant loading for
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3 acenaphthylene and 2,3,5-trimethylnaphthalene representing spillage of
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5 petroleum-related products (Huang et al., 2012; Lai et al., 2011; Larsen and Baker,
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7 2003). Consequently, the PAH compositional pattern in Kaohsiung Harbor water
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9 samples could be categorized into four predominant sources: volatilization or spill of
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11 petroleum-related products, coal burning, vehicle emissions, and incomplete
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13 combustion of organic matter such as coals, fuel, fossil, or crude oils.
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23 After the PCA data analysis was conducted, the PCA scores were multiplied by
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25 C_w . The median values of the C_w scores were multiplied by C_{SPMD} to give new
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27 components EC1 and EC2 as shown in Fig. 8. The PAHs in the water samples were
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29 separated into two groups: the surface water group and the bottom water group. The
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31 PAHs in the bottom water samples seem more dependent on coal burning and vehicle
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33 emissions while those in the surface water samples were derived more from
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35 volatilization or spills of petroleum-related products. Source identifications from the
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37 SPMD and XAD-2 concentrations were similar and comparable.
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48 The bioavailable PAH TEQ is the sum of the 12 toxic equivalents from PAHs
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50 that gives the samples normalized to benzo[a]pyrene (Table 2). The total bioavailable
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52 PAH TEQ from the XAD-2 samples calculated from the surface water and bottom
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54 water samples was 0.061 and 0.086 ng L⁻¹, respectively. In contrast, that calculated
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from the SPMDs was 0.049 in the surface water and 0.155 ng L⁻¹ in the bottom water. The bioavailable toxicity of the bottom water is greater than that of the surface water in Kaohsiung Harbor. The bioavailable toxicity estimated with the SPMD for bottom water is greater than that from the XAD-2 resin, largely because SPMD samples the high molecular weight PAHs more effectively, and they are often very toxic. This is particularly true of benzo(a)pyrene, which has a much higher concentration (2.5 times) when measured with an SPMD.

4. Conclusions

SPMD and conventional XAD-2 resin sampling helped measure bioavailable PAHs in the estuarine water of Kaohsiung Harbor. The PAHs sources in the bottom and surface water appear to be different regardless of the sampling method used. SPMD and conventional XAD-2 resin showed similar distributions although somewhat different estimates of total toxicity, possibly because the SPMD samples high molecular weight PAHs more effectively. However, the sampling rate of the SPMDs appears to be sensitive to environmental conditions such as temperature and turbulence. Additionally, the sampling rates appear to be dependent on the solubility of the PAHs in the sampling medium (i.e., R_s values increase with the values of the $\log(K_{ow})$). Diffusion through the membrane appears less dominant as a control except

1 under stagnant conditions with high molecular weight PAHs. Calibration is critically
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4 important, and a number of reference compounds should be used to reflect the
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7 subtlety of the changing environmental conditions and the effect they have on
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10 capturing a wide range of PAHs. Thus, it seems important to calibrate systems with
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13 more than one reference PAH and to repeat this for various sampling regimes to
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16 establish the most likely sampling rate to provide estimates of bioavailability.
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Figure Caption

Fig. 1. Sampling site No. 10 Wharf in the Kaohsiung Harbor lagoon.

Fig. 2. (a) box plot of PAH concentrations in surface water; (b) box plot of PAH concentrations in bottom water; (c) IQR/median (a non-parametric equivalent of the coefficient of variation) of surface water and bottom water.

Fig. 3. Log sampling rate $\log(R_s)$ as a function of $\log(K_{ow})$ calculated from five PRCs from (a) surface water and (b) bottom water (circles: $\log(R_s)$ from Acen, diamonds: $\log(R_s)$ from An, square: $\log(R_s)$ from Py, triangles: calculated $\log(R_s)$ from BkFa, cross: $\log(R_s)$ from INP).

Fig. 4. Log sampling rate $\log(R_s)$ as a function of $\log(K_{ow})$ for PAHs. The bold solid line is from the cubic polynomial regressions using five R_{s-PRC} with weights from surface water in this study; the bold dashed line is from the cubic polynomial regressions using five R_{s-PRC} with weights from bottom water in this study; the fine solid line is fitted from Booiij's data; the fine dotted line is fitted from Luellen's data; the fine dashed line is fitted from Huckins's data. (Note: Fitting equation: $\log R_s = -0.008 \log K_{ow}^3 - 0.008 \log K_{ow}^2 + 1.09 \log K_{ow} - 2.49$, bold solid line: $\log R_s = -0.193 \log K_{ow}^3 + 2.93 \log K_{ow}^2 - 14.3 \log K_{ow} + 24.0$, bold dashed line: $\log R_s = -0.012 \log K_{ow}^3 + 0.127 \log K_{ow}^2 - 0.200 \log K_{ow} + 1.36$, fine solid line: $\log R_s = 0.017 \log K_{ow}^3 - 0.424 \log K_{ow}^2 + 2.95 \log K_{ow} - 5.51$, fine dotted line: $\log R_s = 0.067 \log K_{ow}^3 - 1.12 \log K_{ow}^2 + 6.04 \log K_{ow} - 10.3$, fine dashed line.)

Fig. 5. Nineteen PAH concentrations from XAD-2 (C_w) and SPMD (C_{SPMD}) samples from (a) surface water and (b) bottom water (circles: PAH concentrations from XAD-2 resin (C_w), triangles: calculated PAH concentrations using R_s values established in this study (C_{SPMD}), diamonds: calculated PAH concentrations (C_{SPMD}) using R_s values from Luellen and Shea, 2002).

Fig. 6. Nineteen PAH concentrations from XAD-2 (C_w) and SPMD (C_{SPMD}) samples from (a) surface water and (b) bottom water (circles: PAH concentrations from XAD-2 resin (C_w), triangles: calculated PAH concentrations (C_{SPMD}) using R_s values from cubic regressions using the five PRCs, crosses: calculated PAH concentrations (C_{SPMD}) using R_s values from Huckins's method; Huckins et al., 2006).

Fig. 7. The ratios (C_{SPMD}/C_w) of PAH water concentrations from SPMD (C_{SPMD}) and XAD-2 (C_w) as a function of $\log(K_{ow})$ for PAHs in (a) surface water and (b) bottom water.

Fig. 8. Estimated scores plot of the two principal components EC1 and EC2 from Kaohsiung Harbor. The solid line encloses the surface water group; the dashed line encloses the bottom water group.

Table 1
SPMD field calibration data.

Compounds	log K_{sw}	N/N_0 (%)		K_{e-PRC} (d ⁻¹)		R_{s-PRC} (L/d)	
		Surface water	Bottom water	Surface water	Bottom water	Surface water	Bottom water
Acen	4.00	4.85	8.48	0.303	0.247	14.9	12.1
An	4.56	19.1	45.3	0.166	0.079	29.4	14.0
Py	4.95	31.4	63.3	0.116	0.046	50.6	20.0
BkFa	5.53	59.7	74.3	0.052	0.030	85.8	49.4
INP	5.67	68.7	90.3	0.037	0.010	85.8	23.4

Table 2
Concentrations and TEQs of 19 dissolved PAHs (ng L⁻¹).

Compounds	Abbr.	TEF	XAD-2 water samples				SPMD			
			Surface water		Bottom water		Surface water		Bottom water	
			TEQ	TEQ	TEQ	TEQ	TEQ	TEQ	TEQ	TEQ
Acenaphthylene	Aceny	0.001	0.080	0.000	0.099	0.000	0.084	0.000	0.028	0.000
Acenaphthene	Acen	0.001	0.211	0.000	0.176	0.000	0.220	0.000	0.091	0.000
Fluorene	Fluo	0.001	0.308	0.000	0.231	0.000	0.360	0.000	0.171	0.000
Dibenzothiophene	DBT	–	0.364	–	0.364	–	0.200	–	0.324	–
Anthracene	An	0.01	0.161	0.002	0.149	0.001	0.297	0.003	0.315	0.003
Phenanthrene	Ph	0.001	0.492	0.000	0.581	0.001	1.295	0.001	0.926	0.001
2,3,5-trimethylnaphthalene	235TMNaP	–	0.166	–	0.317	–	0.485	–	0.697	–
Pyrene	Py	0.001	1.943	0.002	3.485	0.003	0.854	0.001	2.727	0.003
2-methylanthracene	2MeA	–	0.161	–	0.177	–	0.135	–	0.196	–
3-methylphenanthrene	3MeP	–	0.237	–	0.324	–	0.328	–	0.544	–
Fluoranthene	Flt	0.001	1.241	0.001	2.041	0.002	0.769	0.001	1.456	0.001
2-methylphenanthrene	2MeP	–	0.636	–	0.775	–	0.492	–	0.543	–
Benzo[b]fluoranthene	BbFa	0.100	0.126	0.013	0.113	0.011	0.044	0.004	0.145	0.015
Chrysene+triphenylene	ChryTriphe	0.010	0.206	0.002	0.244	0.002	0.116	0.001	0.237	0.002
Benz[a]anthracene	BaA	0.100	0.116	0.012	0.234	0.023	0.076	0.008	0.238	0.024
Benzo[a]pyrene	BaPy	1.000	0.025	0.025	0.035	0.035	0.026	0.026	0.096	0.096
Benzo[k]fluoranthene	BkFa	0.100	0.041	0.004	0.062	0.006	0.033	0.003	0.099	0.010
Perylene	Pery	–	0.025	–	0.041	–	0.016	–	0.108	–
Benzo[e]pyrene	BePy	–	0.089	–	0.135	–	0.042	–	0.211	–
19PAHs			6.625	0.061	9.583	0.086	5.871	0.049	9.151	0.155

‘-’ No available TEFs

Table 3

Rotated component loadings of PAHs in Kaohsiung harbor. Values in bold indicate those greater than absolute value of 0.65. Factors corresponding to correlation matrix eigenvalues of >1 are considered meaningful.

Total variance explained	PC1	PC2	PC3	PC4
	25.1	17.3	12.2	10.6
Aceny	0.016	0.208	-0.263	0.662
Acen	-0.499	0.729	-0.132	-0.183
Fluo	-.044	0.929	0.043	0.219
DBT	0.187	0.064	0.002	0.167
An	0.427	0.594	-0.059	-0.506
Ph	0.920	0.207	0.226	-0.031
235TMNaP	0.125	0.021	-0.082	0.952
Py	-0.378	-0.858	0.075	-0.099
2MeA	0.666	0.088	-0.317	-0.268
3MeP	0.859	0.017	-0.234	0.335
Flt	-0.866	0.072	-0.041	-0.079
2MeP	0.904	0.193	-0.235	-0.074
BbFa	0.274	-0.095	0.230	-0.047
ChryTriphe	-0.508	-0.133	0.265	0.117
BaA	-0.422	-0.733	0.022	0.125
BaPy	-0.107	0.055	0.057	-0.124
BkFa	-0.018	0.017	0.958	-0.189
Pery	-0.028	-0.290	0.081	0.118
BePy	-0.144	-0.096	0.946	0.008

Figure(1)

Figure(2)

Figure(3)

Figure(4)

Figure(5)

Figure(6)

Figure(7)

Figure(8)