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Comparison of In Situ and Ex Situ Equilibrium Passive Sampling for Measuring Freely Dissolved Concentrations of Parent and Alkylated Polycyclic Aromatic Hydrocarbons in Sediments

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Abstract: Equilibrium passive sampling methods (EPSMs) allow quantification of freely dissolved contaminant concentrations (C_{free}) in sediment porewater. Polydimethylsiloxane (PDMS) is a convenient sampling polymer that can be equilibrated in field (in situ) or laboratory (ex situ) sediments to determine C_{free}, providing reliable compound-specific PDMS–water partition coefficients ($K_{PDMS\text{-}water}$) are available. Polycyclic aromatic hydrocarbons (PAHs) are an important class of sediment contaminants comprised of parent and alkylated homologs. However, application of EPSM to alkylated PAHs is challenged by lack of $K_{PDMS\text{-}water}$ measurements. Our first objective was to obtain $K_{PDMS\text{-}water}$ for 9 alkylated PAHs and biphenyls using 3 different PDMS-coated fibers. Quantitative relationships were then established to define $K_{PDMS\text{-}water}$ for 18 parent and 16 alkyl PAHs included in the US Environmental Protection Agency's sediment quality benchmark method for benthic life protection based on additive toxic units. The second objective was to compare C_{free} in porewater obtained using both in situ and ex situ EPSMs at 6 Baltic Sea locations. The results indicated that in situ and ex situ C_{free} for alkyl PAHs generally agreed within a factor of 3. Further, all sites exhibited additive toxic units <1, indicating that PAHs pose a low risk to benthos. The results extend practical application of EPSMs for improved risk assessment and derivation of porewater-based remediation goals for PAH-contaminated sediments. *Environ Toxicol Chem* 2020;39:2169–2179. © 2020 The Authors. *Environmental Toxicology and Chemistry* published by Wiley Periodicals LLC on behalf of SETAC.

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INTRODUCTION

Equilibrium passive sampling methods (EPSMs) are increasingly being applied in analysis of contaminated sediments because concentrations of freely dissolved chemicals (C_{free}) in sediment porewater directly relate to chemical activity and provide a mechanistic basis for predicting adverse biological effects from sediment-associated contaminants when contrasted to traditional bulk sediment concentrations (Reichenberg and Mayer 2006). Accordingly, C_{free} is broadly recognized as an improved metric of exposure for sediment quality evaluation and risk assessment (Mayer et al. 2013). One important class of sediment-associated contaminants known to pose a hazard to benthic life are polycyclic aromatic hydrocarbons (PAHs). Because of their physicochemical properties (high organic carbon–water partition coefficient [K_{OC}] and high octanol–water partition coefficient [K_{OW}]), PAHs are likely to absorb to sediments and to bioaccumulate in lower trophic–level organisms which exhibit limited capability for biotransformation (Neff 1979; Witt 2002; Replinger et al. 2017). However, the concentration and composition of PAH pollution depend on the actual contribution of both pyrogenic (i.e., incomplete combustion processes that generate predominantly unsubstituted parent PAHs) and petrogenic (i.e., derived from crude oil or related petroleum substances which are dominated by alkylated PAHs) sources.

To address the risks of sediment-associated PAHs to benthic life, the US Environmental Protection Agency (USEPA) has developed a sediment quality benchmark relying on measurement of the fraction organic carbon (f_{oc}) and total concentrations (C_{total}) of 18 parent and 16 groups of alkyl PAHs (34 PAHs) in sediments. Using equilibrium partitioning (EqP) theory (Di Toro et al. 1991), these data are used to estimate C_{free} and PAH

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additive toxic units for evaluating risk to benthic organisms (US Environmental Protection Agency 2003, 2017a; Burgess 2009; Burgess et al. 2013). By definition, a toxic unit is the bioavailable concentration of a single PAH (i.e., C_{free} in porewater), divided by the corresponding final chronic value. Alternatively, EPSMs can be used to determine the C_{free} of PAHs, directly avoiding the need to invoke EqP assumptions that can significantly overstate bioavailability due to increased sorption capacities of heterogeneous carbonaceous phases in sediments (Apell and Gschwend 2016; Brennan and Johnson 2017). Guidance has also been developed for applying this procedure to derive porewater-based remediation goals (US Environmental Protection Agency 2017a). To use this approach, polymer to water partition coefficients are required for translating polymer measurements into C_{free} (Witt et al. 2010; Ghosh et al. 2014).

To date, polymer–water partition coefficients have primarily been reported for parent PAHs using different polymer materials (e.g., polydimethylsiloxane [PDMS], polyethylene [PE], polyoxymethylene; Lydy et al. 2014; US Environmental Protection Agency 2017b). However, lack of reliable partition coefficient data for alkylated PAHs limits the use of EPSMs in conducting site risk assessments and establishing risk-based remediation objectives.

To address this gap, the first objective of the present study was to experimentally determine the partitioning coefficients between PDMS and water ($K_{PDMS\text{-}water}$) for alkylated PAHs and biphenyl using PDMS fibers of 3 different formats. In this approach, PDMS-coated glass fibers (10- and 30-μm-thick coating) and a PDMS hollow fiber (40 μm wall thickness) served as sampling phases. The thin coating thicknesses (10–40 μm), coupled with a high surface area to volume ratio, ensures a reasonable time span for reaching equilibrium with sediment porewater, while providing sufficient quantity for proper analysis. These fibers have been used frequently for EPSMs given their low cost, durability, and commercial availability (Witt et al. 2013; Lang et al. 2015). During partition coefficient experiments, fibers "consume" the dissolved concentrations, which are "refilled" from a loaded silicone layer that serves as a passive donor. Because, in earlier published data, depletion of the water phase leads to questionable partitioning coefficients with values spanning 4 orders of magnitude (DiFillipo and Eganhouse 2010), this passive dosing–passive sampling design avoids depletion and ensures constant water concentrations during the experiment. Using these and previously reported $K_{PDMS\text{-}water}$ values for PAHs, quantitative linear free relationships were developed to obtain values for all 34 PAHs included in the USEPA's sediment quality benchmark.

Recommended $K_{PDMS\text{-}water}$ values were then applied to quantify equilibrium concentrations of target PAHs in sediment porewater using both in situ and ex situ deployments. Although in situ measurements reflect C_{free} values under natural conditions, such deployments can be time-consuming, costly, and subject to potential sampler losses. In contrast, ex situ EPSM measurements are typically more convenient because the costs and challenges of field deployment are avoided and mixing can be introduced to promote equilibrium conditions, thereby reducing the time required for data generation. However, ex situ EPSMs exclude natural field processes that can introduce local disequilibrium of contaminant partitioning between sediment and porewater, thus generating C_{free} values that are unrepresentative of actual field exposures. Therefore, as a second study objective, C_{free} values derived using both in situ and ex situ measurements were compared with sediments from 6 Baltic Sea field sites. Estimates of C_{free} determined using ex situ EPSMs were also compared with C_{free} predictions based on EqP predictions derived from organic carbon normalized total PAH sediment concentrations to assess the concordance of results. The present study is intended to provide a crucial contribution to the practical application of EPSMs to the USEPA's PAH sediment quality benchmark procedure.

MATERIALS AND METHODS

Test substances and PDMS fibers

Neat PAH standards were used for the loading solution. For calibration of the gas chromatography/mass spectrometry (GC/MS)-system, liquid standard solutions (Campro Scientific) were used. For selected parent PAHs, a standard mixture was available. Details are given in Supplemental Data, Table S1.

The equilibrium sampling experiments for alkylated PAHs were conducted with the following commercially available fibers: 1) GF10, 10-μm PDMS-coated glass fibers SPC 210/230 from Fiberguide Industries; 2) GF30, 30-μm PDMS-coated glass fibers from Polymicro Technologies; and 3) HF40, 40-μm silicone tubing Nagasep Hollow Fiber M-40 from Nagayanagi. Fiber properties are described in Supplemental Data, Table S2.

Determination of PAH partition coefficients

Preparation of the passive dosing vials was conducted based on previously published work (Mayer and Holmstrup 2008; Birch et al. 2010). Briefly, a silicone layer was cast into 60-mL glass vials with polytetrafluoroethylene screw caps using the medical-grade silicone elastomer kit (A-103 Platinum Silicone Elastomer; Factor II). Following the supplier's instructions, the elastomer was mixed with the crosslinker, and each vial was coated with 1.5 g (±0.5%) silicone at the bottom, which produced an approximately 2500-μm-thick layer. To eliminate bubbles in the PDMS, the vials were left in the refrigerator at 4 °C for 96 h, afterward at room temperature for at least 72 h, followed by 48 h at 110 °C. The resulting A103-silicone layer was cleaned of oligomers and impurities by shaking it 2 times for 48 h with ethanol and subsequently rinsing it several times with ultrapure water to remove the ethanol. Finally, the water was removed manually using a lint-free tissue.

To achieve the targeted concentration in the silicone layer, all alkylated PAHs were dissolved in n-hexane. Concentrations of the stock solutions were 3000 μg/mL for 1-methylnaphthalene, 3375 μg/mL for 2-methylnaphthalene, 3525 μg/mL for 2,6-dimethylnaphthalene, 1000 μg/mL for 2,3,5-trimethylnaphthalene, 625 μg/mL for 1-methylchrysene, and 1250 μg/mL for 3,6-dimethylphenanthrene (resulting

in stock solution I). Further, stock solution II contained 150 µg/mL for biphenyl, 300 µg/mL for 1-methylfluorene, 200 µg/mL for 4-methyldibenzo-thiophene, 300 µg/mL for 4,6-dimethyldibenzothiophene, and 400 µg/mL for 2-methylphenanthrene. Following the dissolution of all substances, 3 mL of the resulting stock solutions (1 mL of I and 2 mL of II) were added in 500-µL increments to the silicone layer of each vial. Using a nitrogen flow, the hexane was slowly evaporated between each step, allowing the PAHs to transfer into the silicone layer (Mayer et al. 1999; Gilbert et al. 2016). After all hexane was evaporated, 55 mL of ultrapure water were added to each vial. The vials were left at room temperature for 3 d to ensure chemical equilibrium between water and silicone (Smith et al. 2010). The experiment started by adding a total of 36 fibers (12 GF10, 12 GF30, 12 HF40) to each vial using a stainless steel holding fixture (precleaned in 50/50% n-hexane/acetone) to avoid contact between fibers themselves and between fibers and the passive dosing phase (Supplemental Data, Picture 1). Before use, the PDMS fibers were cut into approximately 10-cm pieces (5 cm for HF40), placed into an Accelerated Solvent Extraction (ASE) cell, and subsequently extracted 3 times with ethyl acetate using a Dionex ASE 200. After extraction, the cleaned fibers were washed 3 times for 15 min with ultrapure water using an ultrasonic bath. Prior to use, fibers were stored in ultrapure water at 4 °C. This experimental dosing system was designed to maintain freely dissolved concentrations by limiting depletion of PAHs from the silicone donor due to fiber uptake, as detailed in Supplemental Data, Appendix S1.

Measurement of PDMS fibers, water, and silicone donor

To measure the uptake kinetics, one fiber of each type (GF10, GF30, HF40) was removed at 12 different time points. Two replicate vials were sampled at each time point. With completion of the experiment, 2 additional vials that had not been previously sampled were used to provide 4 replicates for measurement at $t = 1440$ h (=60 d). A time span of 60 d was chosen based on previous work to provide sufficient time to achieve equilibrium between PDMS fibers and water (Cornelissen et al. 2001). The 10-cm-long fibers were cut into approximately 3-cm pieces, exactly measured with a caliper (for HF40, the weight was determined), and analyzed separately, yielding 3 analyses/fiber. Removal of fibers took place after 24, 52, 96, 190, 240, 336, 528, 720, 888, 1032, 1224, and 1440 h. The PAH concentrations in fibers (C_{PDMS}) were measured, using thermal desorption on a GC/MS (GC 7890B/MS 5977A) system from Agilent with an initial temperature of 70 °C (hold 15 min), ramped at 10 °C/min to 175 °C (hold 4 min), ramped at 3 °C/min to 235 °C (hold for 0 min), and subsequently ramped at 8 to 315 °C (hold 8 min) using an HP5-MS UI (30 m, 250 µm, 0.25 µm) column from J&W Scientific. This led to a total run time of 67.5 min.

Once all fibers were removed from the vials, PAH concentrations in the water were determined by extracting with 10 mL n-hexane, followed by 10 min of shaking in a 100-mL separatory funnel. This procedure was repeated 3 times, and extracts were then combined and evaporated to a volume of 800 µL, using a rotary evaporator (Heidolph; Laborata 4000 eff). The concentrated extracts were stored at 4 °C in the dark until analysis. After the water was removed, the PAH concentration of the silicone layer (dosing phase) was also determined to confirm negligible depletion. The silicone was extracted 3 times with each 10 mL n-hexane for each 48 h on a horizontal shaker. The n-hexane was then processed as previously described for water samples.

Equilibrium confirmation

As described by Mayer et al. (2003) confirmation of equilibrium between PDMS and water was achieved using 2 different approaches. The first approach relied on examination of fiber uptake kinetics. After the kinetic phase of increasing uptake into the PDMS fibers, a plateau in the PDMS concentration indicates that equilibrium between PDMS and water is reached. Data were processed in R Statistics (Ver 1.1.419; R Development Core Team 2009–2018). To describe the uptake kinetics of PAHs into the PDMS fibers, a pseudo-first-order, one-phase association model was used:

$$Y = Yo + Ymax \times (1 - exp^{-K \times t}) \quad (1)$$

In Equation 1, *Yo* is the background concentration on the fiber at the test start (picograms per microliter of PDMS), *Ymax* is the maximum concentration on the fiber at equilibrium (picograms per microliter of PDMS), K is the desorption rate constant (per hour), and t is time (hours).

The second approach involved analysis of different PDMS fibers with varying coating thicknesses, and hence sampling rates, to confirm equilibrium, as described by Reichenberg et al. (2008). This approach relies on the fact that PDMS concentrations on the different fibers will differ at sampling times prior to equilibrium but converge to the same value when equilibrium is achieved.

Equilibrium concentrations of PAHs in the fibers (C_{PDMSeq}) and in the water (C_{water}) were used to calculate the partitioning coefficients between PDMS and water. For an equilibrated 2-phase PDMS–water system, the partitioning coefficient ($K_{PDMS-water}$) is defined as

$$K_{PDMS-water} = \frac{C_{PDMSeq}}{C_{water}} \quad (2)$$

where C_{PDMSeq} is the equilibrated concentration of the PAH of interest in the PDMS and C_{water} is the corresponding concentration in water (DiFillipo and Eganhouse 2010).

Quality assurance

All ex situ sediment samples were tested using at least 3 fibers per vial. In situ sediments were tested with 10 GF and

approximately 50 cm HF40 per sampler. Kinetic experiments were conducted with 12 fibers of each kind. New solid-phase microextraction fibers were used for all procedures described, and GC liners were checked for chemical purity during the course of experiments. Previous experiments have shown that PAHs exhibit good recovery using the extraction procedure used in the present study (Supplemental Data, Figure S1). Cleaned and unexposed fibers served as analytical blanks for method detection limits (MDLs) and quantification limits (MQLs). Method calibration was implemented with external standards (PAH- Mix 9 from Dr. Ehrenstorfer for parent PAHs; liquid standard solutions from Campro Scientific for alkylated PAHs).

Standard curves were derived by an external 10-point calibration (10 000–20 000 μg/L) with a correlation coefficient >0.99.

Method detection limits and MQLs were calculated using the average PAH mass in the blanks plus 10 times (MQL) or 3 times (MDL) the standard deviation and converted to C_{PDMS} (picograms per microliter). The detection limits ranged between 10 and 25 pg μL^{-1} PDMS for parent PAHs. Although the detection limits of alkylated naphthalenes ranged between 423.7 pg μL^{-1} PDMS (C3-naphthalene) and 3121.5 pg μL^{-1} PDMS (C2-naphthalene), the detection limits of all other investigated alkylated PAHs ranged between 0.8 pg μL^{-1} PDMS (C1-fluorene) and 124.1 pg μL^{-1} PDMS (biphenyl). Method quantification limits on a C_{free} basis (MQL_{free}) are orders of magnitude lower and decrease with increasing K_{PDMS}:

$$MQL_{free} = \frac{MQL_{PDMS}}{K_{PDMS}} \quad (3)$$

Investigation of Field Sediments

Sediment samples were collected from a former highly industrialized area of the Elbe River in Hamburg (Vernigkanal, Germany) in February 2017 and at 6 different stations at a brackish bay located in the Baltic Sea (Darß-Zingster Boddenkette: Ahrenshoop, Born am Darß, Daendorf, Wieck am Darß, Wustrow, and Zingst) in June 2017 (Supplemental Data, Table S4). The locations were expected to reflect a range of PAH contamination. Total organic carbon and PAH measurements for 16 parent and 8 alkyl PAHs have been previously reported for sediment collected at these stations (Supplemental Data, Table S5). Sediment samples for ex situ EPSM measurements were taken with a Van-Veen grab sampler and stored in cleaned (300 °C for 8 h) aluminum trays, transported to the Hamburg University of Applied Sciences, and stored at –20 °C until use.

To determine C_{free} of selected parent (naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, indeno[*1,2,3 cd*]pyrene, dibenzo[*ah*]anthracene, and benzo[*ghi*]perylene) and alkylated (2-methylnaphthalne, 1-methylnaphthalene, C2-naphthalenes, C3-naphthalenes, C1-fluorene, C1-phenanthrene, C2-phenenathrenes, C3-phenanthrenes, C1-fluoranthene/pyrene, and C1-chrysene) PAHs in sediments ex situ, 10 g of each of the 7 collected sediments were weighed into a chromacol vial (Thermo Scientific). Three GF10 fibers were placed into the sediments using a cannula to pierce through the septum of the cap. The vials were then placed in an overhead shaker for 21 d at 20 ± 2 °C in darkness. Witt et al. (2010) have shown that a 21-d period is sufficient to achieve an equilibrium between porewater and GF10 for all USEPA PAHs. Because it can also be shown that $t_{90\%}$ is correlated with the log K_{OW} and the molecular weight (Supplemental Data, Figure S3.1 and S3.2) and all alkylated PAHs, which are underestimated in the present study, are in the range of 16 EPA PAHs, a 21-d period was considered sufficiently long for this experimental setup. After 21 d, the experiment was stopped, and the fibers were removed, cleaned with ultrapure water, and wiped dry using lint-free tissues. The equilibrated fibers were stored at –20 °C until analysis.

In situ sampling with passive samplers was performed at 6 stations (excluding Vernigkanal) according to Witt et al. (2010) and Arthur and Pawlyszin (1990). The in situ sampling devices (described in Witt et al. 2013) were deployed in the field for 3 mo. Equilibrium was confirmed by comparing observed concentrations in different PDMS formats (HF40 and GF10). After collecting the devices, the GF10 and HF40 fibers were removed, cleaned with ultrapure water, and wiped dry using a lint-free tissue. The dry fibers were wrapped in heated aluminum foil and stored at –20 °C until measurement.

Freely dissolved PAH concentrations were calculated using $K_{PDMS-water}$ derived from the present study:

$$C_{free,i} = \frac{C_{PDMSeq,i}}{K_{PDMS-water}} \quad (4)$$

C_{free} for PAH_i can then be used to calculate toxic unit (TU)

$$TU_{FCV,i} = \frac{C_{free,i}}{FCV,i} \quad (5)$$

where FCV,*i* is the PAH-specific final chronic value (USEPA, 2012, 2017b).

The additive toxic units for all PAHs derived using direct C_{free} measurements were compared with additive toxic units derived via EqP theory.

$$C_{EqP\ free,i} = \frac{C_{sediment,i}}{K_{OC,i} \times f_{OC}} \quad (6)$$

where the K_{OC} for each PAH is estimated from the K_{OW} (Burgess et al. 2013).

RESULTS

Uptake kinetics and equilibrium confirmation

The uptake profiles of target substances into the PDMS were generated through fitting a pseudo-first-order association model (Equation 2) to the time series data measured during the 60-d passive dosing–passive sampling experiment. This model was used to describe the experimental data (Figure 1) to estimate the time to reach 90% of the equilibrium concentration in

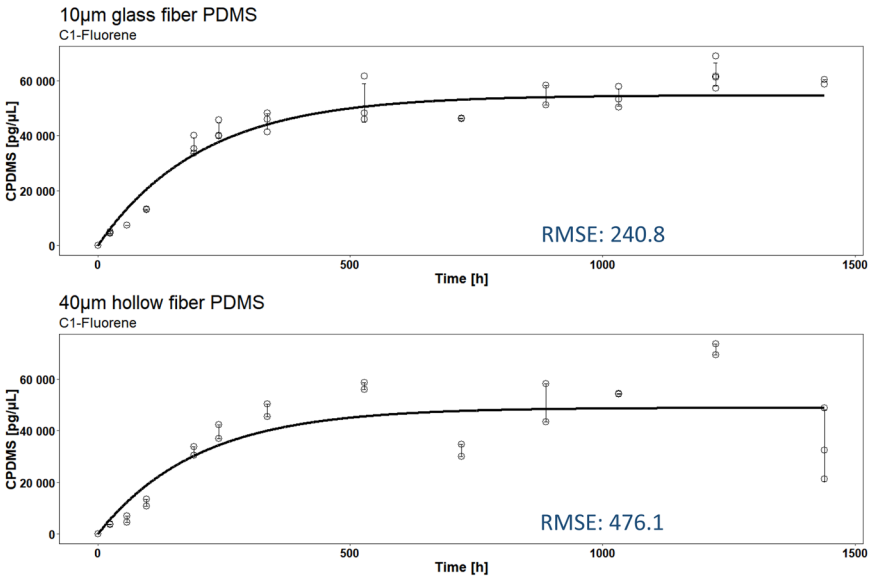

FIGURE 1: Example uptake profiles of C1-fluorene into the GF10 and HF40 polydimethylsiloxane fibers (additional kinetic plots are provided in Supplemental Data, Figure S2). CPDMS = concentration of PDMS; PDMS = polydimethylsiloxane; RMSE = root mean square error.

PDMS. Using the rate constant k, the time t needed to reach near (90%) of the equilibrium concentration ($C_{PDMSmax}$) in the PDMS can be estimated as follows:

$$t_{90\%} = \frac{\ln(10)}{k} \quad (7)$$

The $t_{90\%}$ was reached between 150 h (C1-chrysene) and 1027 h (C2-DBT) in 10-µm fibers. All $t_{90\%}$ values for 10-µm fibers are shown in Table 1. Time to reach 90% of equilibrium was also correlated to molecular weight ($r^2 = 0.838$) and log K_{OW} ($r^2 = 0.818$; C1-chrysene excluded; Supplemental Data, Figures S3.1 and S2.2). After 1440 h for most substances, no obvious concentration differences between the GF10, GF30, and HF40 fibers were observed, indicating that equilibrium was reached in the fiber–water system for all PDMS types (as mean of 4 replicates; Supplemental Data, Figure S4). Again, after 1440 h, C1-naphthalene, C2-naphthalene, and biphenyl concentrations in 40-µm fibers were elevated compared to 10-µm fibers (HF40/GF10 = 9.83 for C1-naphthalene, 2.49 for C2-naphthalene, and 2.82 for biphenyl). Concentration ratios of 40- and 10-µm fibers for the remaining substances ranged between 0.91 (C1–C3-naphthalene) and 0.49 (C2-phenanthrene). Ratios for 30- and 10-µm fibers (GF30/GF10) ranged from 4.32 (C1-naphthalene) to 0.84 (C2-phenanthrene), whereas 40- and 30-µm fibers (HF40/GF30) ranged from 1.81 (C1-naphthalene) to 0.52 (C1-chrysene).

An overall higher variation in biphenyl, C1-naphthalene, and C2-naphthalene measurements in GF10 was seen throughout the experiment. We assume that the surface area to volume ratio of the fibers (a/v = 8329 $cm^2\ cm^{-3}$ for GF10, 4492 $cm^2\ cm^{-3}$ for GF30, and 2536 $cm^2\ cm^{-3}$ for HF40) affects the reliability of measurements for the more volatile substances. After removing the fibers from the test system, the fibers were stored at –20 °C immediately prior to analysis to minimize such losses. Further, during measurement the fibers were placed in the GC/MS rack in sets of 2, to avoid longer uncooled phases. Nonetheless, it appears that an increased partial desorption of the more volatile substances from fibers with higher a/v ratios likely occurred prior to analysis.

Partition coefficients

To derive PDMS–water partition coefficients, C_{water} measurements obtained for each of the 4 vials at the completion of the experiment (1440 h) were used in conjunction with the different fibers and the silicone layer concentration measurements obtained from the same vial for each test PAH. The results are summarized in Table 1. Measured water concentrations between replicates showed moderate variations with a coefficient of variation (*CV*) of approximately 25% based on the mean of all substances, excluding C1-chrysene. These variations are likely due to the different handling of 2 out of the 4 vial replicates. For replicates 1 and 2, fibers were repeatedly taken for the kinetic measurements (opening the vial, removing fibers), whereas replicates 3 and 4 were left untouched until experiment termination. For example, the standard deviation (for C_{water}, without C1-chrysene) between 2 identically treated replicates showed lower mean *CV*s of 10.65% (untouched replicates 3 and 4) and 12.92% (replicates 1 and 2), respectively. Negligible depletion criteria were met in the untouched replicates for all substances (excluding C1-chrysene), with the highest depletion for biphenyl (4.82% replicate 3 and 4.24% replicate 4). For the first 2 replicates, depletion ranged between 4.18% (C1-naphthalene, replicate 1) and 17.06% (C1-fluorene, replicate 2) with a mean depletion for all substances and both vials of 9.92% (Supplemental Data, Table S6). In contrast, C1-chrysene showed a much higher and unexplained variation in measured water concentrations than the other test substances (*CV* = 130.1%, further data given in Supplemental Data, Table S7).

TABLE 1: Molecular weight, log K_{OW}, and calculated log $K_{PDMS\text{-}water}$ for GF10, GF30, and HF40 fibers and A-103 silicone coating for the polycyclic aromatic hydrocarbons investigated in the present study[a]

	MW	Log K_{OW}	Log $K_{PDMS\text{-}water}$ GF10	Log $K_{PDMS\text{-}water}$ GF30	Log $K_{PDMS\text{-}water}$ HF40	Log A-103	$t_{90\%}$ (hours) 10-µm fiber
C1-Naphthalene	142.20	3.80	1.86 ± 0.44	2.69 ± 0.12	2.92 ± 0.13	3.00 ± 0.07	179
Biphenyl	154.20	3.94	2.746 ± 0.26	3.24 ± 0.10	3.28 ± 0.11	3.06 ± 0.09	185
C2-Naphthalene	156.23	4.30	3.42 ± 0.16	3.78 ± 0.05	3.82 ± 0.10	3.54 ± 0.08	231
C1-Fluorene	180.25	4.72	4.34 ± 0.21	4.33 ± 0.12	4.20 ± 0.08	3.61 ± 0.06	359
C3-Naphthalene	170.25	4.80	4.34 ± 0.19	4.44 ± 0.08	4.30 ± 0.08	3.81 ± 0.08	399
C1-DBT	198.30	4.86	4.74 ± 0.19	4.70 ± 0.11	4.54 ± 0.08	3.98 ± 0.07	513
C1-Phenanthrene	192.26	5.04	4.75 ± 0.23	4.69 ± 0.11	4.54 ± 0.08	3.96 ± 0.07	528
C2-DBT	212.30	5.33	5.25 ± 0.25	5.21 ± 0.14	5.07 ± 0.13	4.50 ± 0.12	1027
C2-Phenanthrene	206.39	5.46	5.19 ± 0.18	5.15 ± 0.14	4.90 ± 0.11	4.36 ± 0.08	912
C1-Chrysene	242.32	6.14	4.54 ± 0.82	4.56 ± 0.46	4.40 ± 0.51	3.62 ± 0.67	150

[a]Error in log $K_{PDMS\text{-}water}$ is determined based on 4 replicates, and $t_{90\%}$ values are reported for GF10 fibers.
K_{OW} = octanol–water partition coefficient; $K_{PDMS\text{-}water}$ = polydimethylsiloxane–water partition coefficient; MW = molecular weight; $t_{90\%}$ = time to reach 90% of equilibrium.

Gilbert et al. (2016) and Rusina et al. (2007) suggested that within one class of silicone polymers, the sorption capacity can vary by up to 0.4 log units. In this experiment log $K_{PDMS\text{-}water}$ values vary between GF10, GF30, and HF40, with the highest variation found for substances with lower molecular weights/log K_{OW} values (1.06 log units for HF40 vs GF10 and 0.76 log units for GF30 vs GF10 for C1-naphthalene, 0.49 log units for HF40 vs GF10 and 0.45 log units for GF30 vs GF10 for naphthalenes). However, higher molecular weights/log K_{OW} produced more consistent log $K_{PDMS\text{-}water}$ values. Variation between HF40 and GF30 ranged between 0.25 and 0.03 log units. DiFilipo and Eganhouse (2010) found that most variation in published $K_{PDMS\text{-}water}$ values resulted from methodological failures but may also be to a certain extent due to uncertainties in fiber coating thickness and fiber source. The well-defined A-103 silicone layer as well as the HF40 (coating defined via weighing) showed variation in $K_{PDMS\text{-}water}$ between 0.06 and 0.13 log units for all substances except C1-chrysene. Given that the negligible depletion criterion was not met coupled with the high variability in water concentrations and anomalous $t_{90\%}$ and $K_{PDMS\text{-}water}$ values obtained for C1-chrysene, results for this compound are considered unreliable and were excluded in further analysis.

With C1-chrysene as the heaviest investigated substance, it is suspected that an incomplete thermal desorption from the fibers caused the inconsistency of data.

When plotted against the respective K_{OW} (Burgess et al. 2013; Supplemental Data, Table S8), the experimentally measured $K_{PDMS\text{-}water}$ values for alkylated PAHs and previously published data for parent PAHs (provided by Witt et al. 2010) showed high r^2 values for the PDMS fibers and silicone donor: GF10, 0.82; GF30, 0.87; HF40, 0.92; A103-PDMS, 0.95 (without C1-chrysene; Supplemental Data, Figure S5). The lower r^2 value for GF10 is in part attributable to the lower-molecular weight substances because when the regression is performed without these substances (C1-naphthalenes and biphenyl), r^2 for GF10* increases to 0.86. Because the r^2 values for other fibers and A103-PDMS do not appreciably change (GF30*, 0.87; GF40*, 0.91; A103-PDMS*, 0.94) when calculated if these substances are excluded, this finding further supports a likely loss of the more volatile substances from the thinner fibers with higher a/v ratios. When using only the measured data for alkylated PAHs in the linear regression, even higher r^2 values are obtained (GF10, 0.94; GF30, 0.96; HF40, 0.97; A130, 0.95, without C1-chrysene).

Figure 2 shows the close relationship ($r^2 = 0.8895$) between log K_{OW} and log $K_{PDMS\text{-}water}$ for pooled data generated across different PDMS fibers including 9 groups of alkylated PAHs (black circles) and 16 parent PAHs (open circles). Data for C1-naphthalene and biphenyl are based on results for GF30 and HF40, with GF10 data excluded because of the apparent volatility losses previously discussed.

Previous investigations have shown that both the slope and the r^2 of the regression as a double log plot are very close to unity for parent PAHs, which is equivalent to proportionality between $K_{PDMS\text{-}water}$ and K_{OW} (Mayer et al. 2000; Witt et al. 2009). Although separate regressions could be developed for parent and alkyl PAHs, given the limited number and uncertainty in measured values for individual PAHs, we elected to pool these data sets for use in regression analysis. Therefore, the resulting linear regression equation reported in Figure 2 was used to estimate $K_{PDMS\text{-}water}$ for all 34 PAHs included in the USEPA's sediment quality benchmark (Supplemental Data, Table S9).

Application of EPSMs to Baltic Sea sediments

Figure 3 shows the log–log plot of the measured concentrations of in situ C_{free} alkylated PAHs against the respective ex situ C_{free} values across 6 stations. The plot includes 12 measured alkylated PAHs and biphenyl. Ex situ and in situ methods show comparable porewater concentrations, with 86% of the mean values within a factor of 3 (dashed red lines) and 94% of the mean values within a factor of 5. Witt et al. (2013) proved that under static conditions (e.g., in situ) a thermodynamic equilibrium between field sediments and PDMS fibers will be established within 5 to 20 d for parent PAHs. Given the comparability of C_{free} data in situ and ex situ, these findings suggest that a 90-d incubation period in situ is sufficient to reach equilibrium for all investigated PAHs. Ex situ C_{free} results for one site (Born) tend to be higher than in situ C_{free} data (Figure 3). The largest

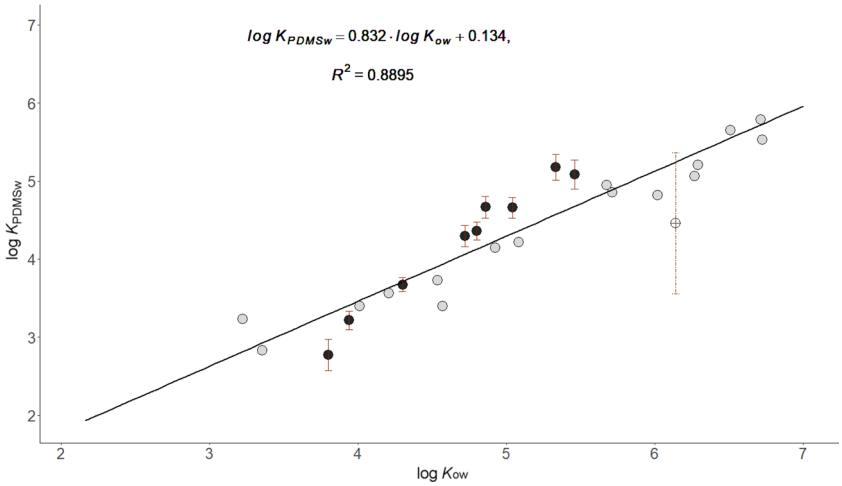

FIGURE 2: Relationship between log K_{OW} and log mean $K_{PDMS\text{-}water}$. Pooled data from GF10, GF30, and HF40 (each $n = 4$) except C1-naphthalenes and biphenyl (GF30 and HF40) with 1 standard deviation as error bars. C1-chrysene (⊖) data judged unreliable and excluded from regression. ● = alkylated polycyclic aromatic hydrocarbons; ● = parent polycyclic aromatic hydrocarbons; K_{OW} = octanol–water partition coefficient; K_{PDMSw} = polydimethylsiloxane–water partition coefficient.

differences can be seen at Daendorf (C1-chrysene) with a 6.22 times higher in situ value and at Born (C1-fluoranthene) with a 7.75 times higher ex situ value. Figure 4 shows the comparable log–log plot of measured in situ and ex situ C_{free} for 16 parent PAHs (if detected). Both laboratory- and field-based EPSM deployments show comparable porewater concentrations, with 61% of the mean values within a factor of 3 (dashed red lines) and 80% of the mean values within a factor of 5. Thus, parent PAHs exhibited a higher variation between in situ and ex situ deployments than observed for alkylated PAHs. The higher variability in parent PAHs may reflect greater heterogeneity in the bioavailability of this class due to the contribution of both pyrogenic and petrogenic sources as well as potential variation in atmospheric deposition of emissions that may alter porewater concentrations during the 90-d field deployment.

Because of strong currents and shipping activities, sediments at these sampling stations are of highly dynamic character. Thus, it remains unclear whether differences are related to sampling methods (e.g., snapshot character of grab sampling ex situ, bioirrigation and long-term sampling in situ) or if discrepancies reflect actual concentration fluctuations in the sediment during the sampling time (Apell et al. 2018). Apell and Gschwend (2016) found that ex situ C_{free} measurements for polychlorinated biphenyls (PCBs) tended to be higher than in situ data. They concluded that the constant shift toward higher ex situ measurements was not due to measurement imprecision

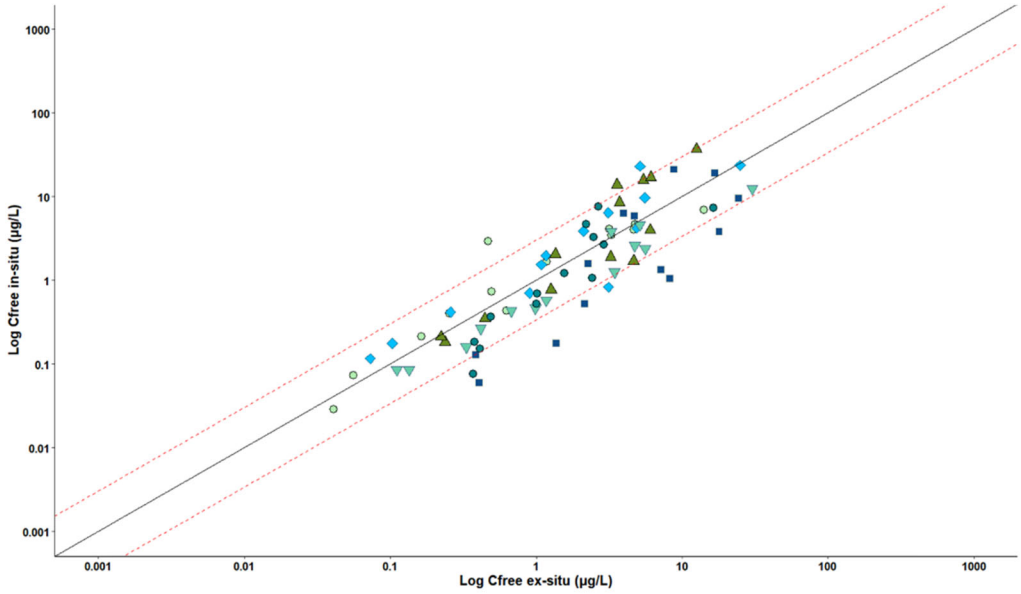

FIGURE 3: In situ versus ex situ data obtained at 6 stations for alkylated polycyclic aromatic hydrocarbons. Data points above the 1:1 line (solid line) indicate higher results for the in situ measurement method, and data points below the 1:1 line indicate higher results for the ex situ measurement method. Dashed lines show a factor of 3 of the 1:1 line. Cfree = freely dissolved concentration; ♦ = Ahrenshoop; ■ = Born; ● = Daendorf; ▲ = Wieck; ▼ = Wustrow; ● = Zingst.

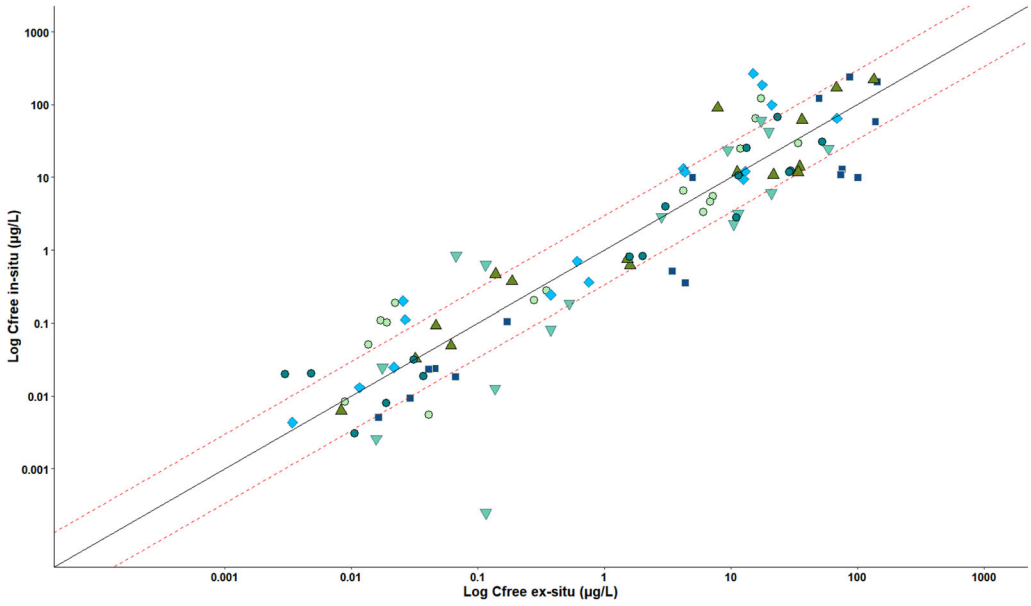

FIGURE 4: In situ versus ex situ data obtained at 6 stations for parent polycyclic aromatic hydrocarbons. Data points above the 1:1 line (solid line) indicate higher results for the in situ measurement method, and data points below the 1:1 line indicate higher results for the ex situ measurement method. Dashed lines show a factor of 3 of the 1:1 line. Cfree = freely dissolved concentration; ♦ = Ahrenshoop; ■ = Born; ● = Daendorf; ▲ = Wieck; ▼ = Wustrow; ● = Zingst.

but instead that in situ samplers are actually measuring lower C_{free}. These findings are consistent with the results of Fernandez et al. (2009), who found that the use of an in situ PE passive sampler led to approximately 5 times lower PAH porewater concentrations than the corresponding ex situ results. However, no consistent systematic biases between in situ and ex situ measurements across all sites were observed in the present study (Supplemental Data, Figure S6). Further, our findings are consistent with a recent study by Khairy and Lohmann (2020), who reported good agreement of C_{free} measurements for polychlorinated dibenzodioxin/furans and PCB congeners derived with PE passive samplers using both in situ and ex situ approaches.

Using in situ and ex situ measurements, additive toxic units were calculated (Equation 5) and compared for the 6 Baltic Sea stations and Veringkanal (C_{PDMS}, C_{free}, and additive toxic units data given in Supplemental Data, Table S10).

The highest value of 0.072 toxic unit was calculated for Veringkanal. Given that Veringkanal is a former highly industrialized area of the Elbe River in Hamburg, this station was expected to be more contaminated and to include a high contribution of petrogenic PAHs. For the Darß stations, toxic units were lower (<0.06) and suggested a variable pyrogenic and petrogenic source signature (Figure 5). However, given that toxic units are well below those based on both laboratory and field EPSM data, the results indicate that the PAHs investigated at these stations are not sufficiently bioavailable to pose a significant risk to benthic life.

For additional comparison, C_{free} values determined by EqP theory using Equation 6 for the 6 sampling stations were calculated and compared with C_{free} values determined using in situ EPSM. For this analysis, only PAHs for which both organic carbon–normalized total sediment concentrations and EPSM measurements were considered (Supplemental Data, Table S11). When the ratio $C_{EqP,free}$ to $C_{free,in\ situ}$ is plotted for both alkylated and parent PAHs as a function of log K_{OW}, EqP predictions exhibit a systematic trend in the extent of C_{free} overestimation (Supplemental Data, Figure S7). The positive slope of the observed (red) trendline shows that the extent to which EqP overestimates C_{free} increases with log K_{OW}. For lower log K_{OW} (3.26–4.73), this trend cannot be observed (Figure 6). Fernandez et al. (2009) found much higher EqP estimates than those measured via passive sampling. Because they investigated substances with log K_{OW} of 4.5 and higher (phenanthrene, log K_{OW} 4.57; pyrene, log K_{OW} 4.92; and chrysene, log K_{OW} 5.71), these earlier findings are consistent with the present study.

Lohmann et al. (2005) reported that the presence of black carbon, besides organic carbon, may play a dominant role in the sorption of PAHs to sediments. Because no black carbon measurement was performed in the present study, we cannot rule out the presence or effect of black carbon for this comparison which could help explain the underestimated sorption of higher-log K_{OW} substances. Several studies (Accardi-Dey and Gschwend 2002; Koelmans et al. 2006; Ghosh 2007; Brennan and Johnson 2017; Endo et al. 2020) underpin the hypothesis that the widespread occurrence of black carbon may reduce in situ bioavailability and thereby lead to order-of-magnitude discrepancies between measured in situ concentrations and EqP-computed porewater concentrations noted in the present and previous studies.

CONCLUSION

Direct measurement of C_{free} from sediments using EPSM is a powerful tool to estimate potential risks of adverse

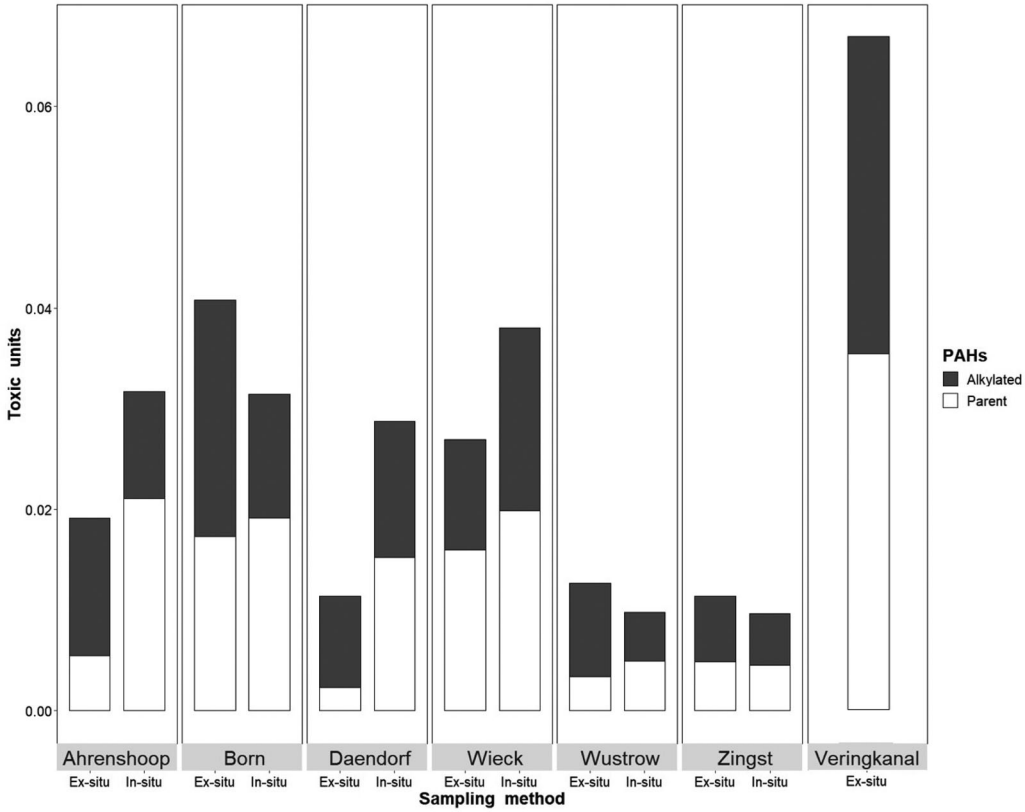

FIGURE 5: Additive toxic units derived from in situ and ex situ data for 6 Baltic Sea stations and Veringkanal. For each Baltic Sea station, left and right bars represents ex situ and in situ data, respectively. For Veringkanal, only ex situ values are available. The unfilled bar represents the contribution from the sum of the parent polycyclic aromatic hydrocarbons (PAHs), whereas the gray bar represents the sum of alkylated PAHs.

biological effects from sediment-associated contaminants and to establish risk-based porewater remediation objectives. Partition coefficients provided in the present study allow access to a wide range of possible applications for improving assessment and management of PAH-contaminated sediments. To illustrate practical applications in situ and ex situ, EPSMs led to comparable porewater concentrations for 6 sampling stations, with mean values typically within a factor

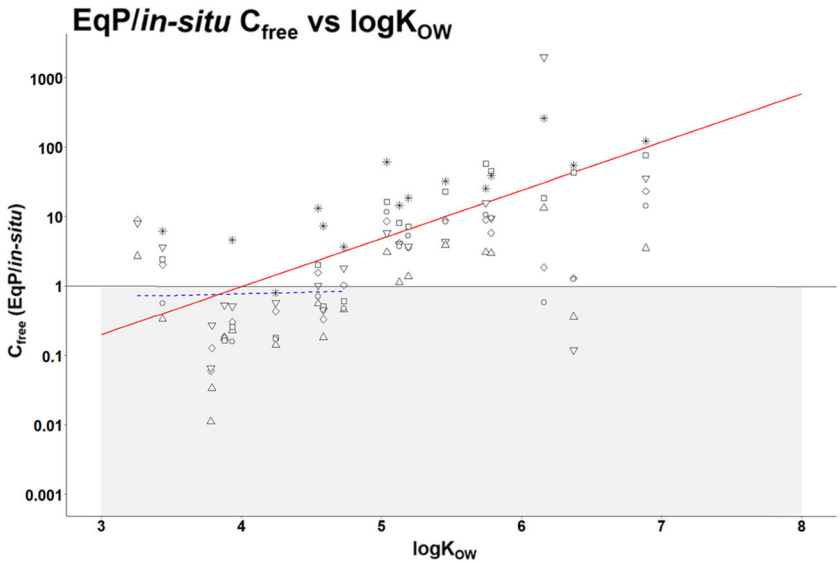

FIGURE 6: Ratio of freely dissolved concentration (C_{free}) calculated by equilibrium partitioning (EqP) and measured by in situ passive sampling as a function of the log K_{OW}. Data points below the unity line indicate higher values for C_{free} measured via passive sampling, whereas data points above the unity line indicate higher values for C_{free} calculated via EqP. Solid diagonal line indicates log K_{OW} 3.26 to 6.89; dashed line indicates log K_{OW} 3.26 to 4.73. K_{OW} = octanol–water partition coefficient; ◇ = Ahrenshoop; □ = Born; ○ = Daendorf; △ = Wieck; ▽ = Wustrow; * = Zingst.

of 3 for alkyl PAHs and 5 for parent PAHs. Calculated additive toxic units based on measured C_{free} yielded a consistent characterization, demonstrating that risks to benthos posed by the measured PAHs across the stations investigated were low and acceptable. Comparison of the C_{free} determined by EPSM and computed via EqP highlights the extent of conservatism that can be introduced in risk assessment of contaminated sediments, particularly for more hydrophobic PAHs. Our findings highlight the important misallocation of resources that may ensue if remedial decisions are based on total sediment concentrations that do not include a more realistic quantitative appraisal of PAH bioavailability. To circumvent such uncertainties and improve risk assessment, the measurement of C_{free} using EPSM serves as a logical and increasingly accepted regulatory strategy (US Environmental Protection Agency 2017a). The results of the present study are intended to deliver a crucial contribution to such efforts by extending the practical application of EPSM to PAH-contaminated sediments. Given the lack of a systematic bias between ex situ versus in situ results observed in the present study, the lower cost and practical advantages of laboratory-based over field deployment of EPSM appears particularly attractive for use in future sediment quality evaluation studies. Recent efforts to provide a standardized test protocol for ex situ passive sampling of contaminated sediment (Jonker et al. 2020) further support the use and acceptance of C_{free} measurements in decision-making.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at https://doi.org/10.1002/etc.4849.

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