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Combined temperature and salinity effects on the passive sampling of PAHs with an assessment of impacts to petroleum toxicity†

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In equilibrium-based passive sampling applications, the accuracy of estimating freely dissolved concentration (C_{free}) of hydrophobic organic compounds (HOCs) relies on the passive sampler–water partition coefficient (K_{PS-W}) values applied. The vast majority of K_{PS-W} are generated under standard conditions: 20 °C in deionized or freshwater. Few empirically derived values are available for non-standard conditions. In this study, polyethylene (PE)–water partitioning coefficients (K_{PE-W}) were experimentally determined for 15 polycyclic aromatic hydrocarbons (PAHs, comprising 9 parent and 6 alkylated compounds) under three different temperature (10, 20, 30 °C) and salinity (0, 18 and 36‰) regimes, the K_{PE-W} values were found to correlate strongly with a variety of molecular parameters (*e.g.*, octanol–water partition coefficients (K_{OW}), molecular weight (MW) and molecular volume (M_{VOL})). The effects of temperature and salinity on the magnitude of K_{PE-W} were found to be substantial. For temperature, the values range between −0.005 and −0.023 log units per °C; these values indicate that every 10 °C rise in temperature would potentially decrease the K_{PE-W} by a factor of between 0.4 to 1.6. For salinity, the values range from 0.0028 to 0.0057 log units per unit ‰, indicating that an 18‰ increase in salinity would likely increase the K_{PE-W} by a factor of between 0.28 and 0.82. Moreover, temperature and salinity were shown to be independent of each other and non-interacting. Temperature effects were chemical-specific and moderately dependent on hydrophobicity (expressed as the K_{OW}), whereas salinity effects were independent of hydrophobicity. We also assessed the combined impact of temperature and salinity, which showed increasing effects with the hydrophobicity of the PAHs studied. Based on the results, K_{PE-W} values adjusted for site-specific temperature and salinity can be calculated. The impact of applying such site-specific values was demonstrated using a PE-based field monitoring dataset for PAHs from coastal waters of Grand Isle (LA, USA) collected during the 2010 Deepwater Horizon oil spill. When K_{PE-W} values were adjusted to 10 °C and 30 °C, the final freely dissolved concentrations (C_{free}) decreased or increased depending on the adjustment. Use of the results of this investigation allow for adjusting existing PE-based datasets to site-specific conditions resulting in more accurate C_{free} values for estimating exposure and adverse ecological effects.

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Environmental significance

This study examines how temperature and salinity affect the estimation of freely dissolved concentrations (C_{free}) of hydrophobic organic compounds (HOCs) using polyethylene (PE)-based passive samplers. By determining partition coefficient (K_{PE-W}) values for polycyclic aromatic hydrocarbons (PAHs) under varying temperature and salinity conditions, we report significant temperature effects on K_{PE-W}, which are chemical-specific and moderately dependent on hydrophobicity. Salinity effects, on the other hand, are independent of hydrophobicity. These results highlight the need for site-specific adjustments to improve the accuracy of C_{free} estimations, crucial for assessing HOC exposure and ecological impacts in aquatic environments. Applying these adjustments to field monitoring datasets from areas affected by the 2010 Deepwater Horizon oil spill demonstrates the practical implications of our findings, aiding informed decision-making in environmental management and remediation efforts.

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Introduction

Several nonpolar organic compounds (NOCs) including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) preferentially sorb to sediments and particulate matter in the aquatic environment, making their freely dissolved concentrations (C_{free}) very low and difficult to be reliably measured. Whole water sampling as currently recommended in the European Union Water Framework Directive (EU WFD) yields total concentration (*i.e.*, total dissolved + colloidal bound + particulate) or when filtered yields total dissolved concentration (*i.e.*, freely dissolved + colloid bound). This conventional approach does not allow the distinct measurement of C_{free}, rather the measurement represents freely dissolved and absorbed concentrations which is a poor metric of a compound's chemical activity.[1,2] This challenge has been recognised resulting in the development and use of an alternative approach involving the estimation of C_{free} of nonpolar organic compounds from concentrations in other compartments (*e.g.*, sediment, biota) through equilibrium partitioning theory[3] and the relevant partitioning coefficients (*e.g.*, organic carbon–water partition coefficient (K_{OC}), bioaccumulation factor (BAF)). This approach is useful however it does have its own difficulties. For example, the natural variability in biota (*e.g.*, biomagnification, metabolism) and in sediment (*e.g.*, amount and quality of organic carbon content) may potentially influence K_{OC} and BAF ultimately confounding C_{free} estimates.[2]

The ability of nonpolar passive sampling devices (PSDs) to effectively measure the C_{free} of NOCs has been adequately demonstrated.[4,5] Nonpolar PSDs mostly find use in measuring the C_{free} of NOCs of environmental concern including PAHs, PCBs, hexachlorobenzene (HCB), and polybrominated diphenyl ethers (PBDEs)[6–9] and other HOCs of emerging concern including triclosan,[10,11] alkylphenols[11] and organophosphate pesticides.[12] Several types of nonpolar PSDs have been developed. The pioneer nonpolar PSD was biphasic (*e.g.*, semipermeable membrane device (SPMD)) and filled with the synthetic lipid triolein. This type of sampler was used on a considerable scale in the early applications of passive sampling. Single phase polymeric materials (*e.g.*, polyethylene (PE), polyoxymethylene (POM), polydimethylsiloxane (PDMS), silicon rubber (SR)) have been used more frequently recently. The initial group (*i.e.*, the biphasic) are gradually being phased out by the latter (*i.e.*, single phase polymers). This is in part, because, the single phase polymers allow simpler modelling of polymer–water kinetics and are less susceptible to damage in that they have no associated risk of lipid/triolein leakage during exposure and/or extraction.[13,14]

Single phase polymers when exposed to the aquatic environment act as a sorption phase by accumulating target compounds until system equilibrium is reached or polymer exposure terminated. The C_{free} of the target compounds can be determined using the model (eqn (1)) from Huckins *et al.*[1] and Smedes & Booij:[15]

$$C_{\text{free}} = \frac{N_{\text{PS}}}{m_{\text{p}} \times K_{\text{PS-W}} \times \text{DEQ}} \tag{1}$$

where C_{free} is in units of μg L^{-1}, N_{PS} is the target compound accumulated in the polymer (μg), and m_{p} represents polymer mass (g) while $K_{\text{PS-W}}$ and DEQ are the polymer–water partition coefficient (L kg^{-1}) and the degree of equilibrium (unitless) reached during deployment, respectively. The DEQ term is used to account for non-equilibrium conditions and it is based on the use of performance reference compounds (PRCs).[16–18] PRCs are non-naturally occurring compounds spiked into the polymer prior deployment.[15,17] The PRC method operates based on the assumption that PRC release and target compound uptake during polymer deployment follow an isotropic exchange process (*i.e.*, same release and uptake rate constants).[19] DEQ can be estimated using the mass transfer model (eqn (2)):

$$\text{DEQ} = 1 - \exp\left(\frac{R_{\text{s}} \times t}{m_{\text{p}} \times K_{\text{PS-W}}}\right) \tag{2}$$

where R_{s} is the (equivalent) water sampling rate (L per d) and t represents the deployment period (d).

As seen in eqn (1) and 2, knowledge of $K_{\text{PS-W}}$ is crucial to the precise estimation of C_{free}. For this reason, many investigations have been carried out to determine compound-specific $K_{\text{PS-W}}$ for several polymers including PE,[6,14,20–25] POM,[6,25–28] SR,[21,29,30] and PDMS.[25,31–36] The vast majority of $K_{\text{PS-W}}$ for all the types of passive samplers were experimentally determined or modelled under standard conditions (20 °C, deionized water).

Based on thermodynamic theory it is recognised that the partitioning of NOCs in a two-phase environmental system such as water and a solid phase is influenced by environmental parameters including temperature and salinity. At low temperatures and high salinity, the aqueous solubility of non-polar compounds decreases thereby increasing their hydrophobicity and preferential sorption to the solid phase such as a passive sampling polymer. This means, the use of $K_{\text{PS-W}}$ derived under standard conditions to estimate C_{free} of compounds from laboratory experiments or field-deployments carried-out under non-standard conditions would likely yield inaccurate results.

Numerous passive sampling based studies focused on assessing C_{free} of NOCs have been performed in non-standard environments including deep ocean waters[37,38] and cold waterbodies.[20,28,39,40] In these studies, the effects of changes in temperature and salinity on $K_{\text{PS-W}}$ were mostly corrected using the Van' t Hoff equation and the Setschenow constant, respectively. This correction approach is valid and useful for adjusting the individual effect of temperature and salinity; however, the method may not be appropriate for correcting for combined effects or assessing possible interacting effects of both temperature and salinity on $K_{\text{PS-W.}}$ Lohmann[41] provided a comprehensive review of these correction methods, which forms a valuable basis for understanding how temperature and salinity individually affect $K_{\text{PS-W.}}$

Alternative means using different single phase polymeric materials have been presented through laboratory studies. This new method based on empirical studies, depending on the experimental design, allows for the quantification and correction for both individual and combined effects of temperature and salinity on $K_{\text{PS-W.}}$ Furthermore, it also allows for the investigation of possible interacting effects between both parameters.

Currently, there are two issues with this alternative empirical approach. First, the results reported from several laboratory studies (using different polymers) are inconsistent. For example,[16,30,32,42] using polymers including SR, PE and PDMS found substantial temperature effects on $K_{\text{PS–W}}$ values for low molecular weight (LMW) PAHs and PCBs. Interestingly, against theoretical principles, enhanced partitioning with increasing temperature was observed for methyl-triclosan, *n*-nonylphenol and some high molecular weight (HMW) PAHs and PCBs for PE.[11] Conversely, no substantial temperature effects were observed in the sorption of some PAHs to PDMS, POM[28] and PE,[20] and the partitioning of triclosan and selected *n*- and *t*-octylphenols to PE.[11] Similarly, substantial salinity effects have been reported on the partitioning of PAHs and PCBs to SR[30] and PAHs sorption to PDMS[28] and PE[16] have been reported. In contrast, minor salinity effects on the partitioning of LMW PAHs, and sorption of methyl-triclosan and n-nonylphenol to PE[11,22] have been observed. Overall, the mixed results are surprising given the effects of changes in temperature and salinity on $K_{\text{PS–W}}$ are supposedly driven by a compound's aqueous solubility and not by the differences in polymer properties.[30] Variations in experimental design such as temperature ranges, salinity levels, equilibration times, and the presence of organic matter can significantly impact partitioning outcomes. Small differences in these experimental variables across studies can contribute to the observed inconsistencies.

A second concern with many of these laboratory studies except that of Jonker *et al.*[30] is that they have largely focused on quantifying the individual effects of temperature and salinity leaving out the assessment of combined and possible interacting effects. Results from Jonker *et al.* show the effects of temperature and salinity on SR–water partition coefficients ($K_{\text{SR–W}}$) of PAHs and PCBs are independent and non-interacting but their combined effects increase with chemical hydrophobicity.

Considering the current non-consensus in the literature on temperature and salinity effects on $K_{\text{PS–W}}$, further studies focused on the quantification of not only individual effects, but also combined and possible interacting effects are needed for more commonly used nonpolar passive sampling polymers. Also, as noted earlier, the vast majority of $K_{\text{PS–W}}$ were determined under standard conditions (*i.e.*, 20 °C in freshwater or deionized water). Consequently, an area of passive sampling application that needs further research is expansion of the experimental and modelling efforts for deriving these partition coefficients at temperatures and salinities beyond these narrow conditions. Access to $K_{\text{PS–W}}$s at higher salinities along a wider range of temperatures would expand the usefulness of passive sampling (*e.g.*, in polar and tropical locations). To this end, the following exercises were carried out in this study: (1) using PE as the passive sampling polymer, we experimentally determined the PE–water partitioning coefficient ($K_{\text{PE–W}}$) for 15 PAHs (10 parent, 5 alkylated) under three different temperature (10, 20, 30 °C) and salinity (0, 18 and 36‰) regimes while varying experimental temperatures and salinities on $K_{\text{PE–W}}$, (2) assessed the joint effects of temperature and salinity on $K_{\text{PE–W}}$ values on the target compounds, and (3) using the relationships derived between temperature and salinity and $K_{\text{PE–W}}$ a field PE dataset collected during an oil spill was adjusted for site-specific conditions. Results of this investigation should allow for more accurate determinations of C_{free} for estimating exposure and adverse ecological effects for a range of temperature and salinity conditions.

Materials and methods

Test materials

A standard solution of 15 target compounds 2-methylnapthalene, acenapthene, 2,6-dimethynapthalene, fluorene, phenanthrene, 1-methylflourene, fluoranthene, pyrene, 2-ethylanthracene, 1-methylpyrene, benzo(*a*)anthracene, benzo[*e*]pyrene, benzo(*a*)pyrene, 7,12-dimethylbenz [*a*] anthracene and benzo[*ghi*]perylene in acetonitrile was purchased from Neochema GmbH (all >98% purity; Bodenheim, Germany). Solvents used in this study were cyclohexane (99.5% purity; Th. Geyer GmbH & Co. KG, Renningen, Germany), methanol and acetone (GC grade; Sigma-Aldrich, Steinheim, Germany) and deionised water (Sigma-Aldrich, Steinheim, Germany). Internal standards (d10-acenaphthene, d12-chrysene, d8-napthalene, d12-perylene, d10-phenathrene and d10-pyrene) all with a purity of >99% were purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany).

Salts used in this study included sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium tetraborate (Na_2B4O_7), calcium chloride ($CaCl_2\cdot 2H_2O$), strontium chloride ($SrCl_2\cdot 6H_2O$), sodium carbonate ($NaHCO_3$), potassium chloride (KCl), potassium bromide (KBr), magnesium chloride ($MgCl_2\cdot 6H_2O$), and sodium azide (NaN_3). All salts were of extra pure quality obtained from Merck KGaA (Darmstadt, Germany), Carl Roth Gmbh & Co. KG (Karlsruhe, Germany), and Sigma-Aldrich (Steinheim, Germany). Tables S1 and S2 in the ESI† contains additional information on the salt composition and the target compounds.

Polyethylene (PE) (70 μm thickness) was obtained from Brentwood Plastics (St. Louis, MO, USA) kindly supplied by K. Booij (PaSOC, The Netherlands). The PE was resized into several small square-shaped strips (0.05 g per strip) and the strips were cleaned by soaking twice in cyclohexane by shaking at 150 rpm. Each precleaning cycle lasted 24 hours.

Polyethylene–water partitioning coefficient ($K_{\text{PE–W}}$)

Chemical-specific $K_{\text{PE–W}}$ were determined under three different temperature regimes (*i.e.*, 10, 20 and 30 °C) and at three different salinity levels (*i.e.*, 0, 18 and 36‰), representing freshwater, brackish and seawater, respectively.

The $K_{\text{PE–W}}$ experiment was carried out using the desorption approach. This approach involved a first step that loaded the precleaned PE strips with fixed amount of target compounds (Table S2†) prior to the PE–water equilibration step. The loading process was carried out following the procedures detailed in the study by Booij *et al.*[17] Briefly, PE strips were incubated in a target compound-spiked methanol/water (80/20) (V/V) mixture, the water content was increased in 10% steps (over 13 days mixed at 150 rpm) until a 50/50 methanol/water content was reached. Clean laboratory tissue paper was used to remove traces of methanol from the PE strips. Along with the methanol swelling the polymer to enhance HOC partitioning, the increasing aqueous fraction encourages the HOCs into the polymer rather than staying in the methanol.

Amber bottles (250 mL) were prepared by dishwashing twice with solvent and distilled water and oven dried for a 6 h period. Thereafter, 220 mL of aqueous solution was poured into each bottle followed by the addition of a piece of the loaded PE strips. The aqueous solution consisted of 50 mg L^{-1} sodium azide (to inhibit microbial growth) and sufficient salt contents for the treatments of 18‰ and 36‰ salinity levels. The filled amber bottles were swiftly closed by glass stoppers and transferred to corresponding rotating orbital shakers placed in temperature-controlled rooms. In total, there were three shakers, one each for the three different temperature regimes. Each treatment (*i.e.*, combination of temperature and salinity level) was replicated three times. The overall shaking period for the partitioning experiment lasted 11 week.

Polyethylene and water – phase extraction

Upon the completion of the shaking period, accumulated PAHs in the PE and water phases was extracted from each bottle. The PE was extracted by submerging and soaking sequentially twice for 24 hours in cyclohexane and the extracts combined. The water phase was extracted with three sequential and composited aliquots (40 mL) of cyclohexane. Internal standards were added before the initial extraction of each phase. The extracts from both phases were reduced to appropriate volumes for gas chromatograph (GC) and mass spectrometry (MS) (GC/MS) analysis using a stream of nitrogen gas. Prior to analysis, the extracts were stored in 1.8 mL amber vials in the dark at 4 °C.

Instrumental analysis

Chemical analysis of the target compounds was performed on an Agilent 6890 GC equipped with a 5973-mass selective detector (Agilent Technologies, Inc., Santa Clara, CA, USA) operated in select ion monitoring mode. Analytes and internal standards were separated using an Agilent DB – 5MS capillary column (30 m length, 250 μm diameter, 0.25 μm thickness, Agilent J&W Scientific, Santa Clara, CA, USA) and quantified with a 5- or 6-point calibration curve. The oven temperature was set at 40 °C for 3 min, then elevated to 280 °C at the rate of 10 °C min^{-1} (holding at each step for 6 min). The samples were injected in spitless mode. The temperatures of the injector, electron ionisation source, and analyzer were set to 250, 230 and 150 °C, respectively.

Deepwater horizon dataset

Over a period of 13 months, the study by Allan *et al.*.involved PE-based sampling conducted at four coastal locations: Grand Isle, Louisiana (LA); Gulfport, Mississippi (MS); Gulf Shores, Alabama (AL); and Gulf Breeze, Florida (FL).[43] These sampling events encompassed the period before, during, and after the 2010 Deepwater Horizon oil spill. The study included a total of nine distinct sampling events, each assigned shorthand names such as 'May 2010' (May 10–13, 2010), 'June 1 2010' (June 8–11, 2010), 'June 2 2010' (June 11–July 7, 2010), 'July 2010' (July 7–August 5, 2010), 'August 2010' (August 5–September 8, 2010), 'September 2010' (September 8–October 13, 2010), 'March 2011' (February 9–March 15, 2011), 'April 2011' (March 15–April 29, 2011), and 'May 2011' (April 29–June 8, 2011).

For the analysis in this study, only data from Grand Isle, Louisiana (LA) was investigated. For the specific data related to Grand Isle, Louisiana (LA), it should be noted that samplers were lost from Grand Isle in July 2010. The duration of sampling deployments at Grand Isle varied ranging from 3 to 41 days (Table S3†). The PAHs monitored at Grand Isle consisted mainly of 33 parent and alkylated PAHs (Table S4†). Throughout the sampling events at Grand Isle, the average temperature exhibited a range from 24.85 to 32.85 °C, with the salinity of the water consistently measured at 35 (‰). Detailed passive sampling conditioning, construction, cleanup, extraction and subsequent chemical analyses at Grand Isle are described in Tidwell *et al.*[44] Briefly, approximately one meter long PSDs made from low-density PE (LDPE) tubing were fortified with deuterated PAHs (PRCs) for water sampling rate calculations. PRCs spanned a range similar to the target PAHs, with the most similar used for quantification. PSDs were transported in sealed polytetrafluoroethylene (PTFE) bags and stored at 4 °C until extraction within two weeks. All solvents were Optima grade or better, and standards had purities of ≥97%. PSDs were extracted as a composite sample for increased sensitivity, using *n*-hexane dialysis, and stored in amber glass vials at −20 °C until analysis.

Quality control

Laboratory blanks for the PE samplers and water phase ($n = 3$ per phase) were prepared, extracted, and analysed as described above. No PAHs were detected in the blanks above the limit of detection (LOD). Instrument LOD and quantitation (LOQ) were determined according to the German standard method DIN 32645.[45] For this purpose, a calibration of 6–10 points with several points close to the expected limits was performed. For recovery determination, complete chemical recovery from PE was confirmed through repeated extraction. For the water phase, recovery of chemicals was verified by spiking a defined quantity of an independent PAH mixture (1000 ng) into clean water ($n = 3$). The mixture was then extracted, measured and evaluated analogously to the aqueous samples. The recovery rates were calculated by comparing analytically measured concentrations in the extract with the nominal concentrations of the spiked mixture.

Data analysis

The concentrations of the target compounds in the PE samplers and the water were determined, and K_{PE-W} values were calculated for each treatment by dividing concentrations in PE (C_{PE}) extracts by concentrations in the aqueous phase extracts (C_w). A number of molecular parameters including molecular weight (MW), octanol–water partition coefficients (K_{OW}), and molecular volume (M_{VOL}) were used to correlate with the experimentally determined $K_{\text{PE-W}}$ values. Values for the molecular parameters used for the correlations are listed in Table S5.† Log K_{OW} used were mostly sourced from Jonker[35] a data review Ma *et al.*[46] and from the U.S. EPA's EPI suite (Estimation Programs Interface Suite, v. 4.10). While MW and M_{VOL} were sourced from the Molinspiration property calculator -MIPC- (**https://molinspiration.com**, accessed January 2022). Data processing, calculations and graphing were conducted using OriginPro 2021b (OriginLab Corporation USA, Northampton, MA, USA).

Results and discussion

Polyethylene and water partitioning coefficient ($K_{\text{PE-W}}$)

Experimentally-determined $\log K_{\text{PE-W}}$ values for the PAHs investigated in this study are presented in Table 1. The standard deviation of the triplicate measurements are primarily within 0.1 log unit suggesting good reproducibility of the measurements. Plots of the $\log K_{\text{PE-W}}$ values (determined under standard conditions: 20 °C in freshwater) *versus* $\log K_{\text{ow}}$, molecular weight and molecular volume are shown in Fig. 1. The regression plots indicate good linear relationships with coefficients of determination (r^2) greater than 0.931 suggesting these parameters are relatively good predictors of PAH $\log K_{\text{PE-W}}$ values. Molecular weight values show a better correlation with $\log K_{\text{PE-W}}$ than those of $\log K_{\text{OW}}$ and molecular volume:

$$\log K_{\text{PE-W}} = 0.0264\ \text{MW} - 0.3705\ (r^2 = 0.96, n = 15) \tag{3}$$

As seen in Fig. 1, $\log K_{\text{PE-W}}$ values increase with increasing values of the individual molecular parameters, except for 7,12-dimethylbenz[*a*]anthracene which showed an unusual interaction with the test polymer. Causes of the anomalous behaviour of this chemical are unclear but was noticed in all experimental treatments (Fig. S1†) and in the additional systems set-up for confirming partitioning equilibrium. The unusual behavior of 7,12-dimethylbenz[*a*]anthracene with the test polymer may be due to unique steric hindrance created by the methyl groups at the 7 and 12 positions, altering its conformation and interaction with the polymer in ways not seen with other methylated PAHs. Additionally, these specific positions uniquely alter the electron density, affecting interaction with the polymer differently. Unique non-covalent interactions, such as van der Waals forces or π–π stacking, may also occur between the polymer and the 7,12-dimethyl substituents, which are absent in other methylated PAHs.

For the PAHs in this study, addition of a methyl group to the ring structure consistently adds 0.4–0.5 log unit to the $K_{\text{PE-W}}$ values (Fig. S2†) but the expected ~1.2 log unit increase for 7,12-dimethyl-benz(*a*)anthracene *versus* benz(*a*)anthracene is not observed, and, actually, becomes negative at higher temperatures (*i.e.*, $K_{\text{PE-W}}$ values for 7,12- dimethyl-benz(*a*)anthracene are lower than those of benz(*a*)anthracene). This behaviour is inconsistent with theory, and it is also not supported by any of the other measurements (*e.g.*, 2-ethylanthracene which is 1.2 log unit higher than phenanthrene has a similar $\text{K}_{\text{PE-W}}$ as anthracene (Figure S2†)). This observed inconsistency in the 7,12-dimethyl-benz(*a*)anthracene $K_{\text{PE-W}}$ values further supports the earlier mentioned unexpected behaviour of the compound with the test polymer.

Linear correlations between $\log K_{\text{PE-W}}$ values and the molecular parameters (Fig. 1) indicates the reliability of the PAH $K_{\text{PE-W}}$ values determined in this investigation. To further validate the reliability of the results determined under standard conditions, the $K_{\text{PE-W}}$ values from this study and those reported

Table 1 Experimentally determined $\log K_{\text{PE-W}}$ (average ± standard deviation) under different temperatures and salinities

	10 °C			20 °C			30 °C		
PAH	0‰	18‰	36‰	0‰	18‰	36‰	0‰	18‰	36‰
2-Methyl naphthalene	3.40 ± 0.02	3.49 ± 0.07	3.56 ± 0.04	3.39 ± 0.09	3.44 ± 0.01	3.46 ± 0.01	3.28 ± 0.02	3.36 ± 0.04	3.46 ± 0.02
Acenaphthene	3.65 ± 0.01	3.75 ± 0.07	3.81 ± 0.02	3.63 ± 0.09	3.67 ± 0.02	3.69 ± 0.02	3.53 ± 0.05	3.59 ± 0.01	3.68 ± 0.00
2,6-Dimethyl naphthalene	4.00 ± 0.01	4.12 ± 0.07	4.19 ± 0.04	3.99 ± 0.09	4.05 ± 0.01	4.08 ± 0.02	3.89 ± 0.05	3.96 ± 0.03	4.05 ± 0.02
Fluorene	3.81 ± 0.00	3.89 ± 0.07	3.95 ± 0.02	3.76 ± 0.09	3.8 ± 0.03	3.83 ± 0.03	3.65 ± 0.04	3.71 ± 0.03	3.8 ± 0.00
Phenanthrene	4.26 ± 0.02	4.36 ± 0.08	4.42 ± 0.02	4.21 ± 0.09	4.24 ± 0.01	4.28 ± 0.03	4.07 ± 0.05	4.12 ± 0.02	4.22 ± 0.03
1-Methylfluorene	4.4 ± 0.00	4.49 ± 0.07	4.55 ± 0.01	4.34 ± 0.09	4.38 ± 0.01	4.43 ± 0.03	4.22 ± 0.04	4.27 ± 0.02	4.36 ± 0.00
Fluoranthene	4.95 ± 0.01	5.03 ± 0.09	5.08 ± 0.02	4.84 ± 0.08	4.86 ± 0.00	4.92 ± 0.05	4.7 ± 0.03	4.74 ± 0.04	4.81 ± 0.01
Pyrene	5.09 ± 0.01	5.16 ± 0.08	5.21 ± 0.02	4.97 ± 0.08	5.00 ± 0.00	5.05 ± 0.05	4.84 ± 0.03	4.86 ± 0.05	4.93 ± 0.01
2-Ethylanthracene	5.52 ± 0.04	5.6 ± 0.07	5.65 ± 0.02	5.41 ± 0.09	5.42 ± 0.01	5.51 ± 0.04	5.32 ± 0.06	5.33 ± 0.04	5.46 ± 0.08
1-Methylpyrene	5.6 ± 0.02	5.75 ± 0.07	5.8 ± 0.02	5.51 ± 0.12	5.52 ± 0.01	5.58 ± 0.03	5.32 ± 0.07	5.36 ± 0.01	5.48 ± 0.02
Benzo(*a*)anthracene	5.77 ± 0.01	5.85 ± 0.06	5.9 ± 0.03	5.64 ± 0.09	5.66 ± 0.00	5.71 ± 0.03	5.46 ± 0.07	5.5 ± 0.01	5.6 ± 0.02
Benzo[*e*]pyrene	6.31 ± 0.02	6.49 ± 0.12	6.52 ± 0.04	6.29 ± 0.06	6.36 ± 0.04	6.15 ± 0.09	6.1 ± 0.10	6.12 ± 0.01	6.22 ± 0.02
Benzo(*a*)pyrene	6.78 ± 0.16	6.80 ± 0.15	6.83 ± 0.08	6.52 ± 0.06	6.56 ± 0.09	6.61 ± 0.07	6.34 ± 0.11	6.38 ± 0.05	6.46 ± 0.03
7,12-Dimethylbenz[*a*] anthracene	6.19 ± 0.09	6.31 ± 0.15	6.46 ± 0.03	5.69 ± 0.27	5.68 ± 0.11	5.76 ± 0.03	5.43 ± 0.05	5.29 ± 0.13	5.42 ± 0.24
Benzo[*ghi*]perylene	6.15 ± 0.22	7.17 ± 0.27	7.21 ± 0.13	7.05 ± 0.07	7.05 ± 0.03	6.28 ± 0.36	6.83 ± 0.12	6.9 ± 0.07	6.93 ± 0.13

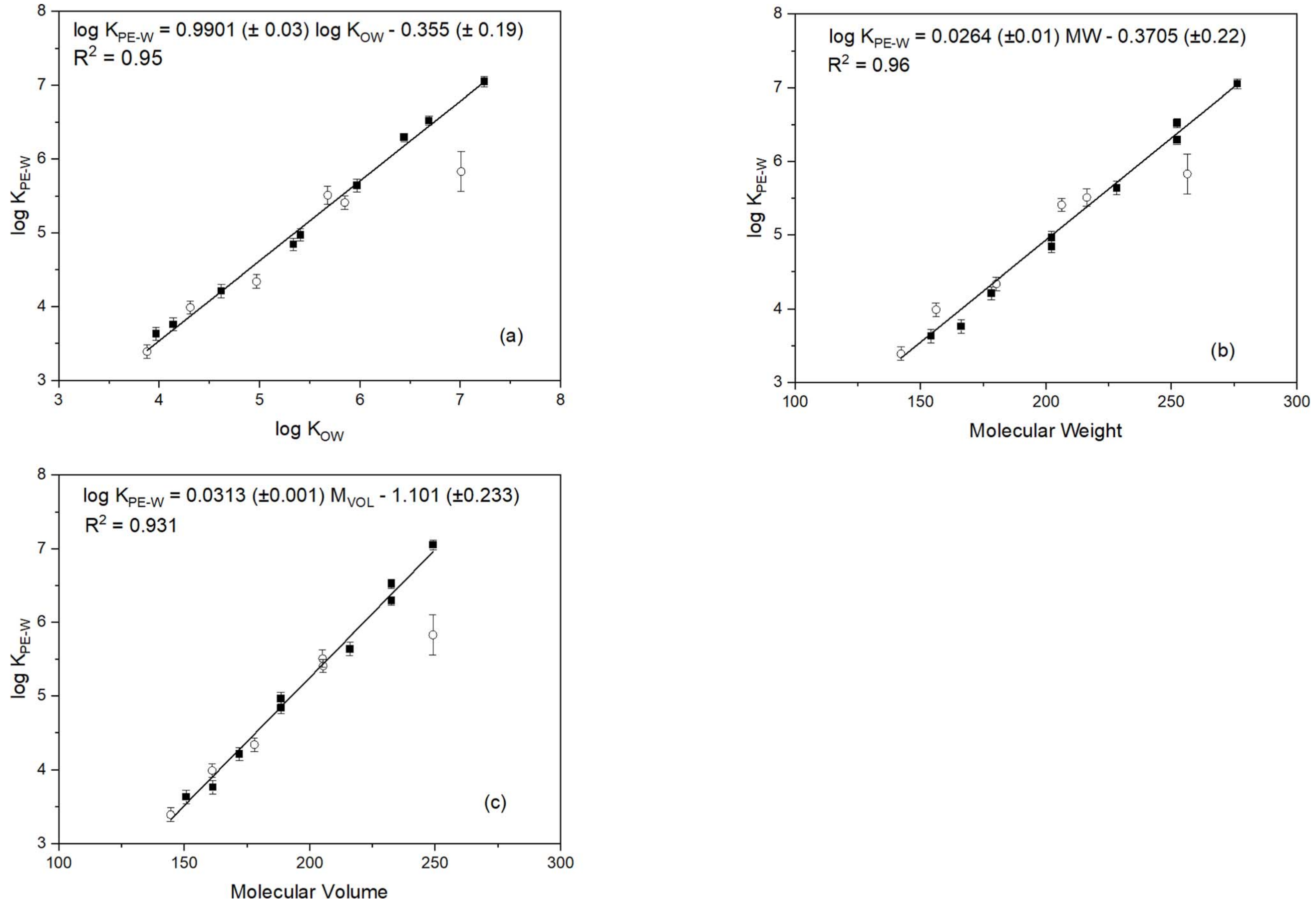

Fig. 1 Relationships between log K_{PE-W} and (a) molecular weight, (b) molecular volume, and (c) log K_{ow} for experimental system under standard conditions (20 °C, freshwater). Solid squares and open circles represent parent- and alkylated-PAHs, respectively, and the solid line represent the regression line. PAH consistently below the regression line (open circle) is 7,12 dimethyl benz[*a*]anthracene.

in previous studies are listed in Table 1 for comparison. It is important to mention, for a fair comparison, only K_{PE-W} values determined at standard conditions were considered. This means K_{PE-W} values for PAHs determined from saline water exposure[20,39,47] or laboratory experiments carried out at lower[20,42] or higher temperatures[16,42,48] were excluded. Also, the suggested best-fit K_{PE-W} values for PAHs from the extensive literature review by Lohmann[41] were excluded because the values were largely derived from pooled K_{PE-W} data that included experimental conditions that were not standard.

As seen in Table 1, the log K_{PE-W} values determined here are within the range of those reported in the literature. The log K_{PE-W} values compare best with results from Jonker[25] and Hale *et al.*[49] varying by only ± 0.01 to ± 0.04 log units. Similar minor differences are observed when comparing with data from Smedes *et al.*[21] (±0.01 to ± 0.47 log units), Fernandez *et al.*[50] (±0.14 to ± 0.27 log units), Bao *et al.*[24] (±0.09 to ± 0.62 log units), Reitsma *et al.*[20] (±0.11 to ± 0.68 log units), and Belles *et al.*[14] (±0.03 to ± 0.72 log units). Whereas the majority of our log K_{PE-W} values (particularly the more hydrophobic PAHs) are higher than those from Perron *et al.*[6] (0.03–1.24 log units) and Choi *et al.*[22] (0.08–0.82 log units). In summary, it is evident the log K_{PE-W} values determined under standard conditions in this study compare very well with those reported in the literature.

Temperature effects on K_{PE-W}

Having discussed earlier the uncertainty in the derived K_{PE-W} values of 7,12-dimethylbenz[*a*]anthracene, those data will not be presented relative to temperature and salinity effects. For the other K_{PE-W} values for the remaining PAHs, it is more convenient to visualise the temperature dependency trends by plotting the partitioning data from Table 1 *versus* temperature. These plots are presented in Fig. 2 for selected PAHs.

As expected, the log K_{PE-W} values decrease with increasing temperature, this is consistent with theoretical principles and corroborates with observations from previous studies. As earlier discussed in the Introduction, Adams *et al.* and Booij *et al.* observed similar effects on the partitioning of low molecular weight (LMW) PAHs to PE polymer.[16,42] Also, Jonker *et al.* reported comparable effects on the sorption of several LMW PAHs and PCBs to silicone rubber.[30] The slopes of the plots (Fig. 2) differ an indication that temperature effects are chemical dependent.

Using the slope of the log K_{PE-W} – temperature correlation plots, a numerical quantification of the change in log K_{PE-W} per °C for each individual chemical was determined and is presented in Table S6.† The values range between −0.005 and −0.023 log units per °C (across the three salinities); these values

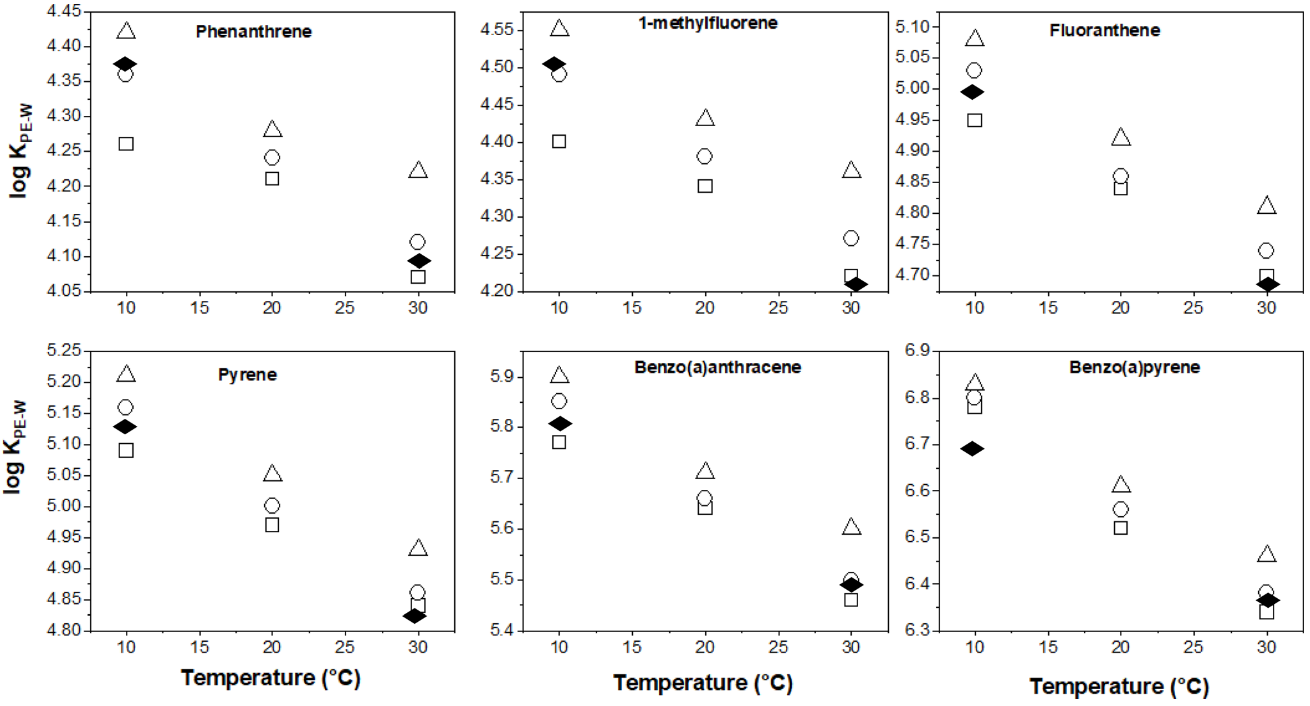

Fig. 2 Log K_{PE-W} *versus* temperature for selected PAHs as a function of salinity:(□) 0‰, (○)18‰, and (△) 36‰ based on this investigation. For comparison, the black diamonds represent adjustments based on corrections reported by Lohmann (2012).

indicate that every 10 °C rise in temperature would potentially decrease the K_{PE-W}s by a factor of between 0.4 to 1.6. The temperature effects (as quantified by the log K_{PE-W} – temperature correlation plots) do not vary substantially across the different salinities (Table S6†), suggesting temperature influences on K_{PE-W} are independent of the salinity of the experimental systems. Plotting each PAH's temperature effects (*i.e.*, change in log K_{PE-W} per °C derived at different salinities for each individual chemical (Table S6†)) against its respective log K_{OW}, a moderately linear correlation with an r^2 ranging from 0.54 to 0.69 is observed. The changes in log K_{PE-W} per °C values becomes more negative with increasing PAH hydrophobicity (Fig. 3a).

To further understand the effect of temperature on K_{PE-W} of the PAHs, we considered relationships with temperature expressed in van't Hoff form:

$$\ln K_{PE-W} = -\frac{\Delta H_{PE-W}}{RT} + \frac{\Delta S}{R} \tag{4}$$

where ΔH_{PE-W} is the partitioning enthalpy, R is the gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is the temperature (K), and ΔS is the entropy (J K^{-1}). By fitting $\ln K_{PE-W}$ *versus* the reciprocal temperature (K^{-1}), the contributions of enthalpy and entropy to log K_{PE-W} were derived based on the slopes and intercepts of the plots, respectively (Fig. 4). Gibbs free energies were calculated using the fitted parameters. Resulting thermodynamic parameters are provided in Table S7.†

For selected PAHs, the In K_{PE-W} – temperature relationship demonstrated a linear correlation (Fig. 4). The positive slope of the individual chemicals and the negative ΔG values (*i.e.*, ranging from −18.82 to −39.46, (Table S6†)) indicate an exothermic sorption process.[51] Values for ΔH_{PE-W} ranged from −9.5 to 34.7 kJ mol^{-1} (Table S6†) and showed a consistent trend with comparable values for PAHs with the same number of aromatic rings. The entropy term is typically greater than zero (Table S6†) for the individual chemicals. The ΔH_{PE-W} values derived here are similar to those reported by Adams *et al.* (−20 to −30 kJ mol^{-1}) and Booij *et al.* (−20 to −50 kJ mol^{-1}) for PE.[16,42] Muijs & Jonker reported PDMS–water partitioning enthalpy values between −15.7 and −34.7 kJ mol^{-1} for PAHs.[32] Similarly Jonker *et al.* using silicone rubber (SR) observed SR–water partitioning enthalpy values of between −16.9 and −58.0 kJ mol^{-1} for PAHs.[30] Polymers used in the latter two studies (*i.e.*, PDMS and SR) though different from PE yielded comparable results, this suggests the sorption behaviour of PAHs to these polymers (*i.e.*, PE, PDMS and SR) is likely similar thermodynamically.

Salinity effects on K_{PE-W}

To quantify salinity effects, we plotted the log K_{PE-W} – salinity correlation data at the three different experimental temperatures. As seen in Fig. 5, PAH partitioning to PE increased with salinity, this observation agrees with theoretical expectations explained by PAH aqueous solubility being reduced by the salting out effect[41] and corresponds with previous results.[6,16,30]

The changes in log K_{PE-W} per unit salinity (‰) was quantified using the slope of plots in Fig. 5 and the results are presented in Table S8.† The values range from 0.002 to 0.0057 log units indicating that an 18‰ increase in salinity would likely increase K_{PE-W} by a factor of between 0.28 and 0.82. Additionally, the

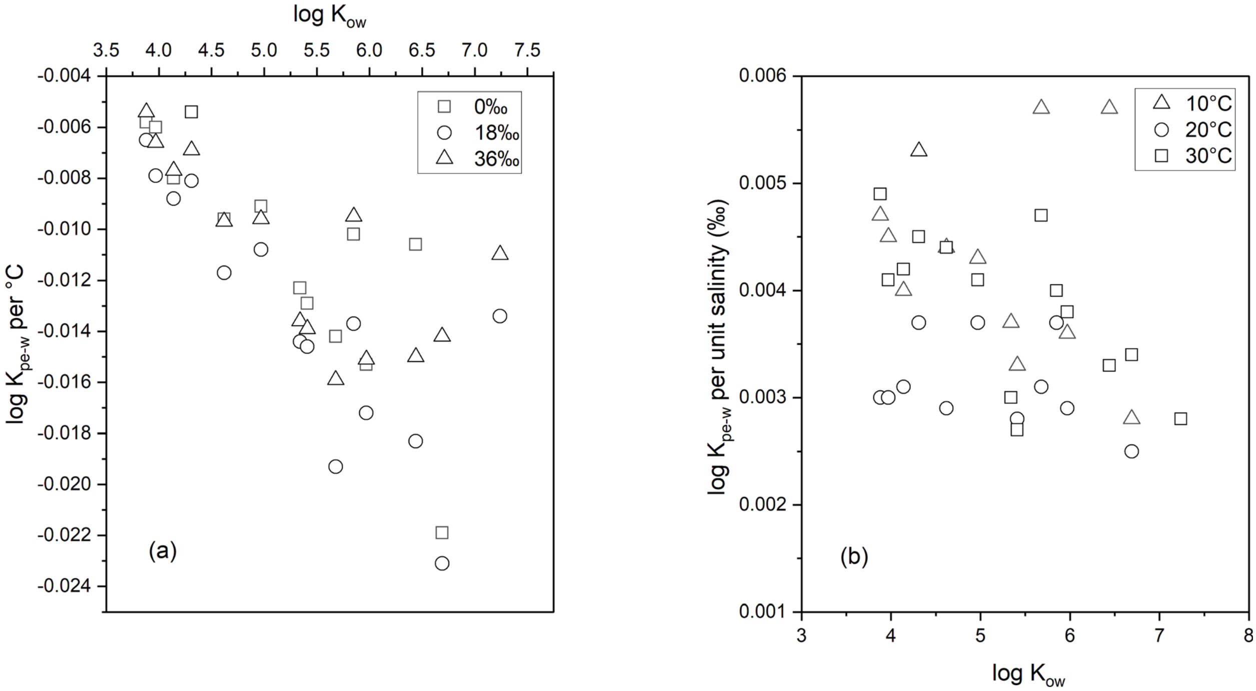

Fig. 3 Temperature effects (determined by the change in log K_{PE-W} per °C) *versus* log K_{OW} (a) and the salinity effects (determined by the change in log K_{PE-W} per unit salinity (‰)) *versus* log K_{OW} (b). The regression equation for temperature effects in the absence of salt (*i.e.*, 0‰) = −0.0041 log K_{OW} + 0.010 (r^2 = 0.69).

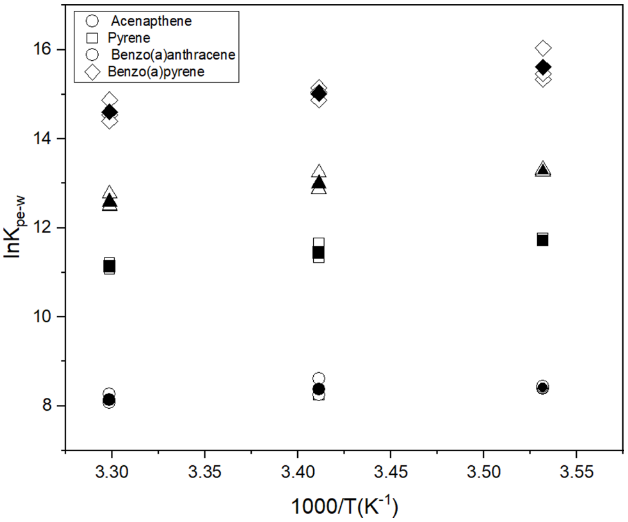

Fig. 4 Temperature effects for selected PAHs in van't Hoff equation form. Solid symbols represent the average value at a given temperature while open symbols are the results of experimental triplicates.

data in Table S7† show salinity effects are similar across the three temperatures (observable but small), suggesting salinity effects on K_{PE-W} is independent of temperature of the aqueous systems. A plot of the salinity effect as measured by the change in log K_{PE-W} per unit salinity (‰) for individual PAHs determined at different temperature against their respective log K_{OW} show appreciable scatter with no clear relationship between the two variables (Fig. 3b).

Combined effects of temperature and salinity on K_{PE-W}

As discussed above, the effects of both temperature and salinity on K_{PE-W} are independent and non-interrelated (*i.e.*, temperature effects are similar at different salinities and salinity effects are similar at different temperatures), consequently, it is possible to assess the joint effects of both parameters and derive chemical-specific compensation equations involving the impacts of both environmental variables. A single equation of the following form, first developed by Jonker *et al.*[30] may be used for this purpose:

$$\log K_{PE-W}(T,S) = \log K_{PE-W}(20,0) + \beta \times (T - 20) + \alpha \times (S) \quad (5)$$

T represents temperature in °C, S stands for salinity in ‰, while β and α represent the temperature and salinity effect factors, respectively. Eqn (5) was used for all the test chemicals except 7,12-dimethylbenz[*a*]anthracene (Table S8†). Potentially, the equation could also be used to calculate chemical-specific compensation equation K_{PE-W} values for other PAHs not included in this study. To achieve this, the log K_{PE-W} (20,0), β and α first need to be estimated based on the PAH's log K_{OW} values using the relationships presented in Fig. 1a and 3a.

Results presented in Table S9† show the overall effect of temperature and salinity increasing with hydrophobicity and are largest for the more hydrophobic chemicals. For example, at freezing temperatures (*i.e.*, 0 °C) and 36‰, a corrected log K_{PE-W} value for benzo(*a*)pyrene would exceed its corresponding values determined at standard conditions by 0.63 log units (a factor of 5.4) while for a less hydrophobic chemical, like fluorene, the difference is smaller at 0.2 log units (a factor of 1.7). A visual

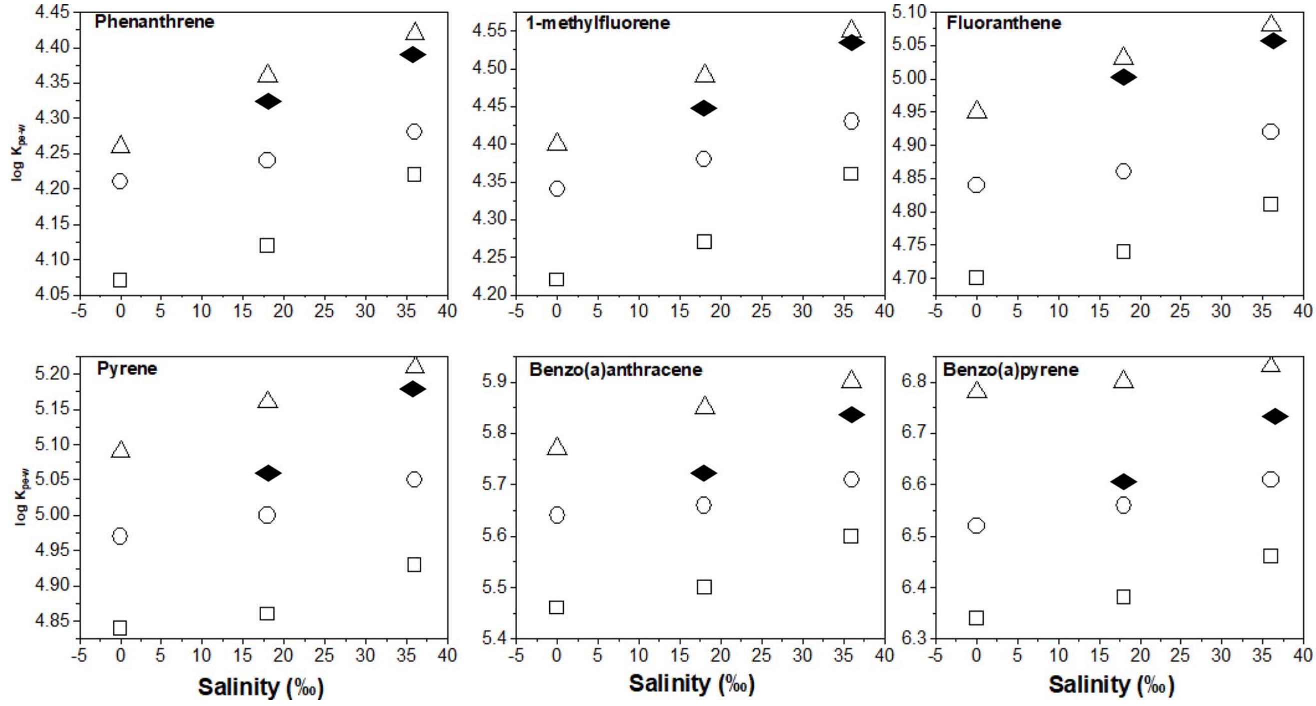

Fig. 5 Log K_{PE-W} – salinity correlation plots for selected PAHs as a function of temperature: (△) 10 °C, (○) 20 °C and (□) 30 °C based on this investigation. For comparison, the black diamonds represent adjustments based on corrections reported by Lohmann (2012).

representation of the combined effect of temperature and salinity on the log K_{PE-W} of benzo(*a*)pyrene is presented in Fig. S3.† The plot shows that relative to log K_{PE-W} values determined under standard conditions (benzo(*a*)pyrene: 6.52 ± 0.06), low temperatures combined with high salinities result in increased log K_{PE-W} values ranging between 0.4 to 0.76 log units. However, high temperatures combined with the low salinities also reduces the log K_{PE-W} by about 0.12 to 0.22 log units.

Estimating PAH C_{free} under field conditions

In this section, we illustrate the practical implications of compensating for temperature and salinity effects on K_{PE-W} using a case study. The case study draws from the PE-derived Deepwater Horizon spill monitoring data collected from the Grand Isle, Louisiana (USA) station in the Gulf of Mexico. As previously discussed, the original monitoring results, which encompassed the dissolved concentrations of several parent and alkylated PAHs, were presented in the study conducted by Tidwell *et al.*[44] The raw data (*i.e.*, amount of PAHs accumulated in the PE (N_{PE}) and PRC release data (DEQ), and actual recorded temperatures of the water while sampling) underlying this study were used to recalculate C_{free} under different theoretical temperature scenarios for Grand Isle, Louisiana station (*i.e.*, 10 °C and 30 °C) over the duration of the monitoring. Details on the calculations can be found in the ESI section.†

For one sampling event (April 2011) at the Grand Isle station, Fig. 6 evaluates the influence of adjustments in K_{PE-W} due to variations in temperature (10 °C, 24.85 °C (actual field temperature), and 30 °C) and salinity (a constant salinity of 35 ppt is maintained to align with field conditions reported by Tidwell *et al.*[44]) on the estimated sum PAH of C_{free}. As temperature increases from actual conditions to a hypothetical 30 °C, there is a consistent rise in sum PAH of C_{free}. This indicates that the adjustments to K_{PE-W} for higher temperatures lead to higher estimated PAH concentrations, highlighting the temperature–concentration relationship inherent in the adjusted partitioning behavior. Conversely, sum PAH of C_{free} decreases relative to the actual conditions when adjusted for 10 °C (Fig. 6). PAHs with higher log K_{ow} values (>5.5) tend to exhibit a reduced sensitivity to the adjustments. Fig. 7 presents the sum PAH of C_{free} for each of the eight sampling events applying the adjusted K_{PE-W} values. Fig. 7b, indicates the relative change in sum PAH of C_{free} compared to the actual field conditions. Overall, increasing the temperature to 30 °C resulted in an average 5.73 ± 2.52% increase in the C_{free} while reducing the temperature to 10 °C affected a mean 29.9 ± 5.90% decrease in sum PAH of C_{free}. It is important to note that the temperature correction does not directly affect the actual C_{free} values but does influence the deviation in estimating C_{free}. The direct inference from Fig. 7 is that the utilization of adjusted K_{PE-W} values correlates with substantial increases or decreases in sum PAH of C_{free} as temperatures adjusted up or down relative to actual conditions. This trend is consistently observed across the eight distinct sampling events. Even in cases such as June-1 and September sampling events, where field temperatures exceeded 30 °C, the use of adjusted K_{PE-W} values led to an increase in C_{free}.

To assess the impact of K_{PE-W} adjustments on estimates of toxicity to aquatic life, an analysis was conducted across the eight distinct sampling events. Specifically, the sum PAH toxic units (TU) were estimated for each event (Fig. 8). The TU for an individual PAH is calculated by dividing its C_{free} value (μg L^{-1})

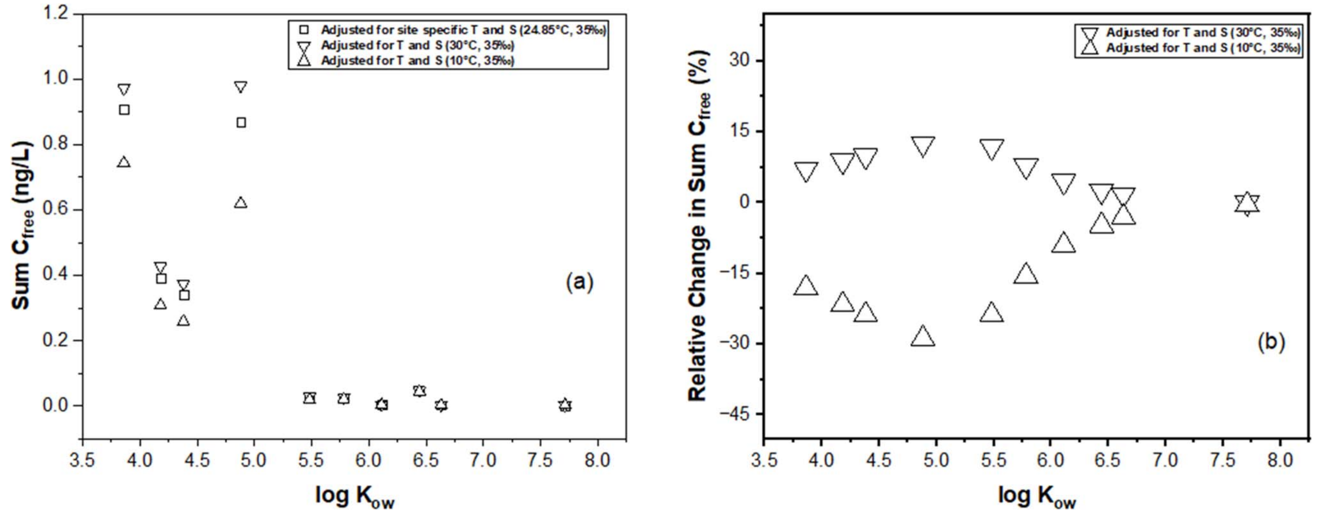

Fig. 6 Passive sampling-based estimates of freely dissolved concentrations of selected PAHs at the Grand Isle (LA, USA) station monitored during the 2010 Deepwater Horizon oil spill. One 45 days deployment (March 15–April 29 2011) was selected for this example. (a) Treatments include the C_{free} adjusted for site specific temperature salinity, the C_{free} at an elevated temperature of 30 °C, and the C_{free} at a reduced temperature of 10 °C. (b) The relative change in PAH C_{free} at 30 °C and 10 °C compared to the actual station conditions.

by the corresponding narcosis secondary chronic value (SCV) based on Di Toro *et al.*[3] and Burgess *et al.*[52] To obtain the sum PAH TU for a given event, the individual PAH TU values were summed. The estimated TU values for these events ranged from 0.001 to 0.045. A sum PAH TU exceeding 1 is typically indicative of potential sublethal toxicity to aquatic life.[52] However, these findings indicate the TU values remain well below this threshold, implying a very low likelihood of toxicity resulting from the presence of PAHs from the Deepwater Horizon spill at these stations at the time of the passive sampler deployments.

Adjustments to the K_{PE-W} values were found to have a minimal impact on the TU calculations. A comparison of TU values before and after the adjustments showed changes within a small range (0.001 to 0.003 units), indicating that while the adjustments refine the accuracy of the partitioning coefficients, they do not significantly alter the overall toxicity estimates. The TU calculations included 31 PAH compounds (Table S4†), selected for their prevalence and toxicological relevance in the context of the Deepwater Horizon spill. While it is acknowledged that petroleum spills contain thousands of compounds contributing to narcotic toxicity through additive effects, the selected PAHs serve as representative indicators. Therefore, despite the potential presence of additional unmeasured compounds, the low TU values observed for the analyzed PAHs indicate a relatively low risk of sublethal toxicity under the conditions and timeframe of this study.

This exercise demonstrates the power of having K_{PE-W}s that allow these temperature adjustments to be accurately

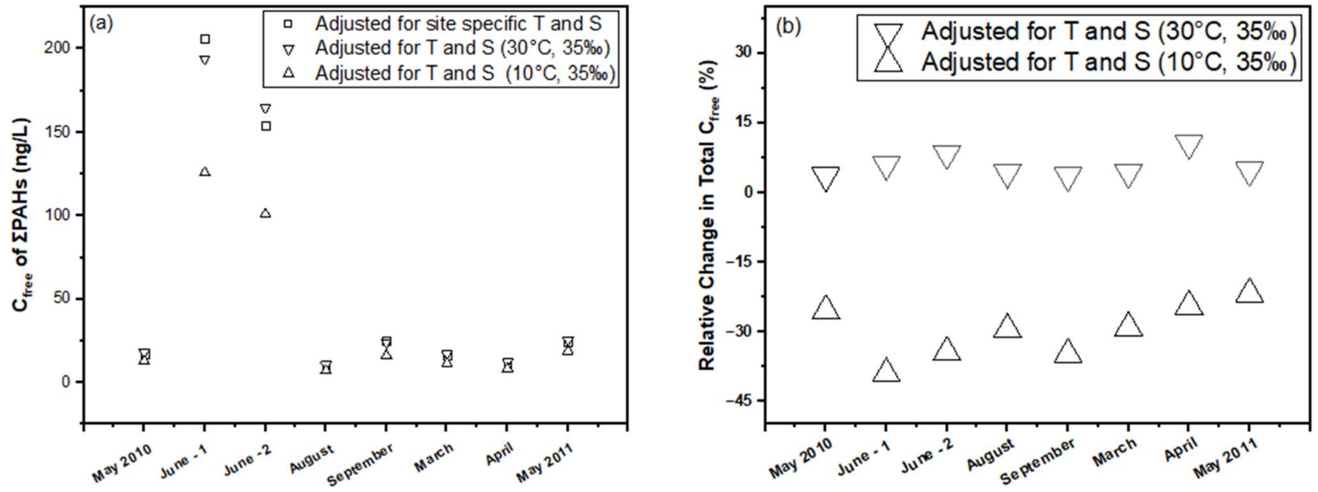

Fig. 7 Sum PAH of C_{free} for eight sampling events. (a) Treatments include the C_{free} adjusted for site specific temperature and salinity, the C_{free} at an elevated temperature of 30 °C, and the C_{free} at a reduced temperature of 10 °C. (b) The relative change in PAH C_{free} at 30 °C and 10 °C compared to the actual station conditions.

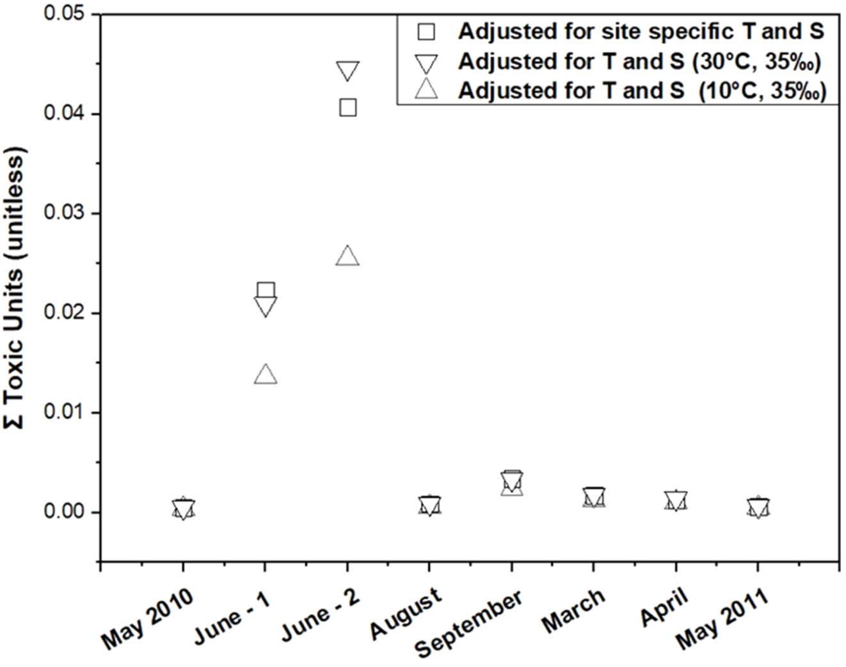

Fig. 8 Estimated toxic units for total PAHs under various sampling events with different treatment conditions.

performed. The continuing effects of climate change increasing oceanic water temperatures along with our on-going reliance on fossil fuels, and consequently, the occasional petroleum spill, provide a 'real world' application for this type of exercise. For example, modelling projected effects onsum PAH of C_{free} under different future seawater temperatures and various spill volume magnitudes would be very useful for assessing petroleum exploration, transport and usage risks especially in sensitive habitats.

Conclusions

It is vital to understand the degree of potential bias using $K_{\text{PE–W}}$ values determined at standard conditions may introduce to C_{free} values for passive samplers deployed under environmental conditions. Understanding this bias allows for a more accurate estimation and assessment of toxicity, bioaccumulation, and potential transfer of contaminants to the food web.

Partition coefficients for PAHs were reliably determined at varying temperatures and salinities, the resulting data allowed for the direct quantification of individual and combined effects of both parameters on $K_{\text{PE–W}}$ values. Individual influences of both parameters on PAH $K_{\text{PE–W}}$ values were substantial: a factor of 0.4 to 1.6 decrease for a 10 °C increase in temperature and a factor between 0.28 to 0.82 increase per every 18‰. Observed temperature effects were chemical-specific, moderately dependent on hydrophobicity and independent of salinity, whereas salinity effects were independent of temperature and hydrophobicity. Furthermore, when combining both temperature and salinity effects, an increasing trend with respect to chemical hydrophobicity for $K_{\text{PE–W}}$ was observed. As shown in the current study, correcting PE-based monitoring data for site-specific environmental conditions (temperature and salinity) using the Deepwater Horizon oil spill dataset substantially influenced the final C_{free}s. Notably, this correction led to a decrease in sum PAH of C_{free} of about 30% when adjusted to 10 °C and an increase in C_{free} of about 6% when adjusted to 30 °C.

This study benefits the application of passive sampling technology in a number of ways including: (1) a new set of reliable experimentally determined $K_{\text{PE–W}}$ for PAHs and (2) data on the direct quantification of temperature and salinity effects on PAH partitioning to PE demonstrates the greatest impacts particularly at low temperature and elevated salinities (*i.e.*, 10 °C, 18‰ and 36‰). Normally, these trends and behavior are difficult to tease out due to non-equilibration issues with experimental systems. Finally, tools for determining the effects of temperature and salinity on PAH partitioning into PE are available herein and shown in Tables S5 and S7† while combined effects may be corrected for using the chemical specific equations given in Table S8.† Use of these chemical specific correction equations maybe extended to PAHs not specifically covered in this study if they are within the log K_{OW} range used here (*i.e.*, 3.88 to 7.24).

Disclaimer

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

Ibukun Ola: conceptualization, data curation, project administration, writing – original draft, writing – review & editing. Carsten Drebenstedt: supervision, project administration. Robert M. Burgess: conceptualization, writing – original draft, writing – review & editing. Lane Tidwell: data curation, writing – review & editing. Kim Anderson: data curation, writing – review & editing. Nils Hoth: supervision, project administration. Christoph Külls: supervision, project administration.

Conflicts of interest

The authors declare no conflicts of interest. The authors were not compensated for their contributions to this work.

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