Combined Temperature and Salinity Effects on the Passive Sampling of PAHs with an Assessment of Impacts to Petroleum Toxicity

Ibukun Ola[a][*][†], Carsten Drebenstedt[a], Robert M. Burgess[b], Lane Tidwell[c], Kim Anderson[c], Nils Hoth[a] and Christoph Külls[d]

[a]*Institute of Mining and Special Civil Engineering, Technical University Mining Academy, Gustav-Zeuner Street 1A, Freiberg, 09599, Germany*

[b]*U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Measurement and Modeling, Atlantic Coastal Environmental Sciences Division, 27 Tarzwell Drive, Narragansett, Rhode Island 02882, United States*

[c]*Food Safety & Environmental Stewardship Lab Environmental & Molecular Toxicology Oregon State University, United States*

[d]*Labor für Hydrologie und Internationale Wasserwirtschaft, Technische Hochschule Lübeck, Lübeck, 23562, Schleswig-Holstein, Germany*

SUPPORTING INFORMATION

* Corresponding Author: Ibukun Ola (Ibukun.Ola@doktorand.tu-freiberg.de)

Table S1. Salt composition used in the partitioning experiments.

Salt	0‰	18‰	36‰
NaCl	0	10.5	21
Na_2SO_4	0	1.76	3.52
KCl	0	0.31	0.62
KBr	0	0.044	0.088
$Na_2B4O_7 \cdot 10H_2O$	0	0.017	0.034
$MgCl_2.6H_2O$	0	4.75	9.5
$CaCl_2.2H_2O$	0	0.66	1.32
$SrCl_2.6H_2O$	0	0.01	0.02
$NaHCO_3$	0	0.09	0.17
NaN_3	0.05	0.05	0.05
	0.05	18.19	36.32

Table S2. Initial concentrations of test compounds in replicate PE samples.

PAH	Replicate 1	Replicate 2	Replicate 3	Average ± SD
		(µg/PE)		
2-methylnaphthalene	4.88	5.44	5.08	5.13±0.28
Acenaphthene	9.23	9.56	9.42	9.40±0.17
2,6-dimethylnaphthalene	11.6	12.2	11.8	11.9±0.31
Fluorene	9.45	9.65	9.64	9.58±0.11
Phenanthrene	11.7	12.1	11.9	11.9±0.20
1-methylfluorene	18.3	18.7	18.5	18.5±0.20
Fluoranthene	19.4	20.0	19.8	19.7±0.31
Pyrene	22.6	23.4	23.1	23.0±0.40
2-ethylanthracene	35.9	37.0	36.3	36.4±0.56
1-methylpyrene	30.4	32.3	31.0	31.5±1.00
Benzo(a)anthracene	32.5	34.0	34.0	33.6±0.95
Benzo[e]pyrene	39.2	39.0	41.6	39.9±1.45
Benzo(a)pyrene	48.6	48.3	51.0	49.5±1.77
7,12-	34.3	34.1	35.0	34.8±0.9

dimethylbenz[a]anthracene				9
Benzo[ghi]perylene	69.3	66.6	75.2	70.4±4.40

Table S3. Sampling event details including temperature and salinity at Grand Isle, Louisiana (2010-2011). Originally reported by Tidwell et al.[1]

Sampling Event	Time	Deployment period (d)	Average temperature (° C)	Salinity (g/L)
May	May 10 – 13 (2010)	3	27.85	35
June - 1	June 8 – 11 (2010)	4	32.85	35
June - 2	June 11 – July 7 (2010)	28	26.85	35
August	August 5 – September 8 (2010)	34	27.85	35
Sept	September 8 – October 13 (2010)	34	31.85	35
March	February 9 – March 15 (2011)	35	27.85	35
April	March 15 – April 29 (2011)	45	24.85	35
May	April 29 – June 8 (2011)	38	26.85	35

Table S4. Monitored PAHs at Grand Isle, Louisiana (LA) sampling station (from Tidwell et al.[1]).

PAH	Abbreviation
Naphthalene	NAP
Methylnaphthalene	1NAP
Dimethylnaphthalene	2NAP
Acenaphthylene	ACY
Acenaphthene	ACE
Fluorene	FLO
Dibenzothiophene	DBT
Phenanthrene	PHE
Methylphenanthrene	1PHE
Dimethylphenanthrene	2PHE
Anthracene	ANT
Methylanthracene	1ANT
Dimethylanthracene	2ANT
Fluoranthene	FLA
Pyrene	PYR
Methylpyrene	1PYR
Retene	RTN
Benz(a)anthracene	BAA
Chrysene	CHR
Methylchrysene	1CHR
Benzo(b)fluoranthene	BBF

Benzo(k)fluoranthene	BKF
Benzo(e)pyrene	BEP
Benzo(a)pyrene	BAP
Indeno(1,2,3-c,d)pyrene	IPY
Dibenz(a,h)anthracene	DBA
Benzo(ghi)perylene	BPL
Dibenzo(a,l)pyrene	DBP

Table S5. Values of the molecular parameters for selected PAHs used for the correlation plots including log K_{OW}, molecular weight (MW) and molecular volume (M_{vol}).

| PAH	Log K_{ow}	MW	Mvol
			mL/mol
2-methylnaphthalene	3.88[b]	142.2	144.6
Acenaphthene	3.97[b]	154.21	150.8
2,6-dimethylnaphthalene	4.31[a]	156.23	161.16
Fluorene	4.14[b]	166.22	161.41
Phenanthrene	4.62[c]	178.23	172.03
1-methylfluorene	4.97[a]	180.25	177.97
Fluoranthene	5.34[c]	202.26	188.6
Pyrene	5.41[c]	202.26	188.6
2-ethylanthracene	5.85[a]	206.29	205.39
1-methylpyrene	5.68[b]	216.28	205.16
Benzo(a)anthracene	5.97[c]	228.29	216.02
Benzo[e]pyrene	6.44[a]	252.32	232.59
Benzo(a)pyrene	6.69[c]	252.32	232.59
7,12-dimethylbenz[a]anthracene	7.01[b]	256.35	249.14
Benzo[ghi]perylene	7.24[c]	276.34	249.17

a) 2

b) 3

c) 4
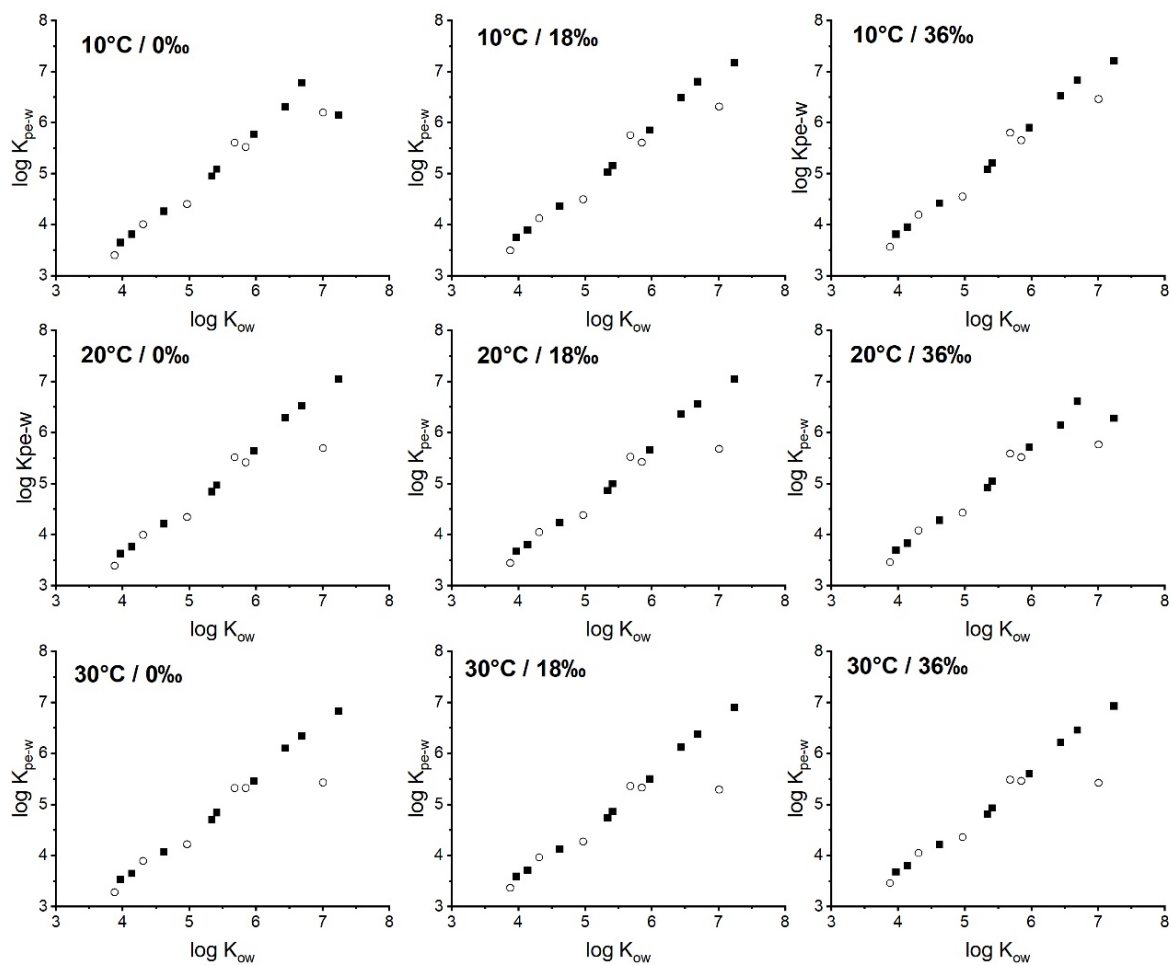
Figure S1. Plots of log K_{PE-W} versus log K_{ow} determined at different treatments (i.e., under combined temperature and salinity regimes). Solid squares and open circles represent parent- and alkylated-PAHs, respectively. PAH (open circle) consistently below the other molecules is 7,12 dimethyl benz[a]anthracene.
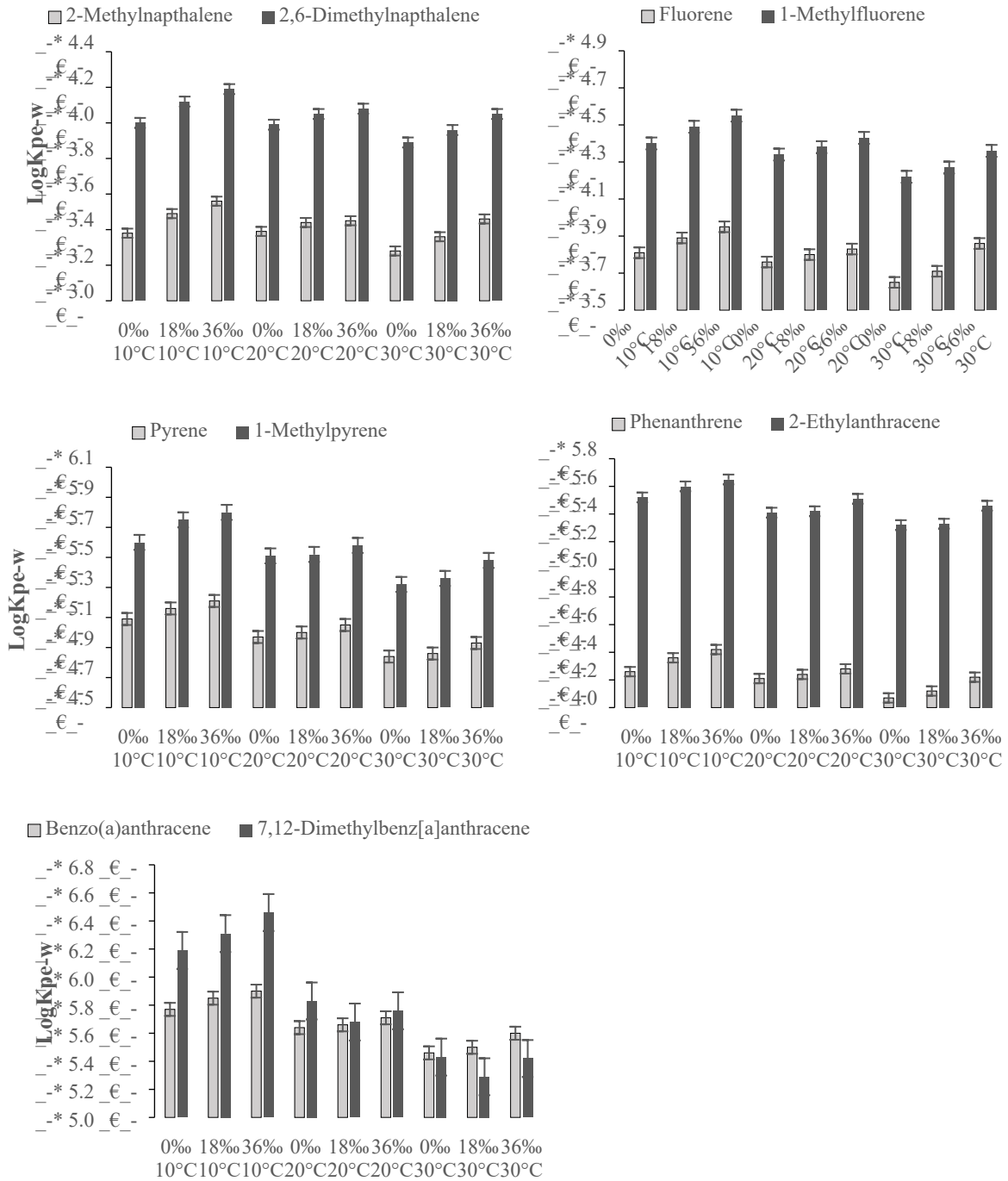
Figure S2. Influence of the addition of a methyl group on log K_{PE-W} values of selected PAHs.

Table S6. Log K_{PE-W} values determined under standard conditions (20°C, deionized water) in the present study as compared to values reported in the literature. Move to SI?

Source	(Cornelissen et al. 2008)	(Fernandez et al. 2009)	Reitsma et al. (2013)	Perron et al. (2013)	(Choi et al. 2013b)	(Smedes et al. 2009)	(Hale et al. 2010)	(Bao et al. 2012)	(Belles et al. 2016)	(Lei et al. 2020)	(Jonker 2022)	This study
Polymer thickness (µm)	100	25	25	25	51	70	26	50	100	nd	25	70
Equilibration period (weeks)	nd	nd	3	8	11	8.7	2	52	12	nd	12	11
PAH	Log K_{PE-W}											
2-methylnaphthalene	nd	nd	3.66±0.08	nd	3.31±0.05	nd	nd	nd	nd	nd	nd	3.39±0.09
Acenaphthene	nd	nd	3.74±0.02	3.60±0.04	3.53±0.03	3.16 ±0.14	nd	4.25±0.12	3.60 ± 0.07	nd	nd	3.63±0.09
2,6-dimethylnaphthalene	nd	nd	nd	4.01±0.01	3.85±0.04	nd	nd	nd	nd	nd	nd	3.99±0.09
Fluorene	3.78± 0.04	nd	3.75±0.05	3.92±0.02	3.67±0.04	3.77 ±0.11	nd	4.51±0.12	3.70 ± 0.10	nd	nd	3.76±0.09
Phenanthrene	4.14±0.02	4.3±0.1	4.39±0.03	4.08±0.07	4.04±0.03	4.22 ±0.11	4.17±0.05	4.78±0.12	4.11±0.14	4.45±0.01	4.18±0.01	4.21±0.09
1-methylfluorene	nd	nd	nd	nd	4.15±0.05	nd	nd	nd	nd	nd	nd	4.34±0.09
Fluoranthene	4.85±0.02	4.9±0.1	5.09±0.04	4.85±0.06	4.75±0.03	4.93 ±0.09	nd	4.93±0.14	5.00±0.07	4.89±0.01	4.83±0.00	4.84±0.08
Pyrene	5.02±0.03	4.7±0.1	5.22±0.02	5.00±0.08	4.89±0.03	5.10 ±0.07	5.01±0.12	5.07±0.14	5.25±0.21	5.10±0.01	4.97±0.00	4.97±0.08
2-ethylanthracene	nd	nd	nd	nd	5.25±0.02	nd	nd	nd	nd	nd	nd	5.41±0.09
1-methylpyrene	nd	nd	5.74±0.05	nd	5.41±0.04	nd	nd	nd	nd		nd	5.51±0.12
Benzo(a)anthracene	5.62±0.02	5.5±0.1	5.91±0.03	5.46±0.19	5.43±0.04	5.73 ±0.11	nd	5.79±0.15	6.22±0.25	5.67±0.02	5.65±0.01	5.64±0.09
Benzo[e]pyrene	6.27±0.09	nd	nd	5.43±0.29	6.04±0.05	6.41±0.05	nd	nd	nd	nd	6.31±0.01	6.29±0.06
Benzo(a)pyrene	6.22±0.12	6.4±0.1	6.81±0.03	5.75±0.31	6.14±0.06	6.75 ±0.05	nd	nd	7.24±0.21	6.02±0.02	6.52±0.01	6.52±0.06
7,12-dimethylbenz[a]anthracene	nd	nd	6.55±0.05	nd	6.23±0.03	nd	nd	nd	nd	nd	nd	-
Benzo[ghi]perylene	5.81±0.07	nd	6.37±0.04	5.81±0.84	6.23±0.08	7.27 ±0.14	nd	7.36±0.04	6.83±0.17	6.17±0.02	7.09±0.02	7.05±0.07

nd   Not determined or reported; -   Value not included due to anomalous behaviour of 7,12-dimethylbenz[a]anthracene with polymer.

Table S7. Change in log K_{PE-W} value per °C for individual PAH derived using the slope of the log K_{PE-W} – temperature correlation plots given in Figure 2 (main text).

PAH	0‰	18‰	36‰
2-Methylnaphthalene	-0.0058±0.0014	-0.0065±0.0056	-0.0054±0.0015
Acenaphthene	-0.006±0.0019	-0.0079±0.0036	-0.0066±0.0012
2,6-Dimethylnaphthalene	-0.0054±0.0022	-0.0081±0.0053	-0.0069±0.0014
Fluorene	-0.008±0.0022	-0.0088±0.0042	-0.0077±0.0009
Phenanthrene	-0.0096±0.0025	-0.0117±0.0039	-0.0097±0.0008
1-Methylfluorene	-0.0091±0.0019	-0.0108±0.0043	-0.0096±0.0006
Fluoranthene	-0.0123±0.0018	-0.0144±0.0065	-0.0136±0.0003
Pyrene	-0.0129±0.0019	-0.0146±0.0063	-0.0139±0.0005
2-Ethylanthracene	-0.0102±0.0046	-0.0137±0.0056	-0.0095±0.0032
1-Methylpyrene	-0.0142±0.0025	-0.0193±0.0029	-0.0159±0.0017
Benzo(a)anthracene	-0.0153±0.003	-0.0172±0.0036	-0.0151±0.0026
Benzo[e]pyrene	-0.0106±0.0054	-0.0183±0.0066	-0.015±0.0029
Benzo(a)pyrene	-0.0219±0.0101	-0.0231±0.0064	-0.0142±0.0031
7,12-Dimethylbenz[a]anthracene	-	-	-
Benzo[ghi]perylene	-[2]	-0.0134±0.0173	-0.011±0.0123

-     Values not included in the table due to anomalous behaviour of 7,12-dimethylbenz[a]anthracene with PE.

-[2]   Value not included in the table because K_{PE-W} value at 30°C > than value at 10°C.

Table S8. Derived thermodynamic parameters explaining the partitioning of PAHs to PE at 293K.

PAH	ΔH_{PE-W} (kJ/mol)	$T\Delta S$ (kJ/mol)	ΔG (kJ/mol)
2-Methylnaphthalene	-9.63±0.86	9.18±0.83	-18.82±0.12
Acenaphthene	-9.8±2.9	10.5±2.8	-20.34±0.09
2,6-Dimethylnaphthalene	-8.9±3.4	13.4±3.5	-22.21±0.12
Fluorene	-13.1±3.5	7.9±3.5	-20.96±0.14
Phenanthrene	-15.6±4.0	7.8±3.9	-23.44±0.08
1-Methylfluorene	-14.9±2.9	9.3±3.0	-24.21±0.16
Fluoranthene	-20.2±2.8	6.9±2.7	-27.09±0.12
Pyrene	-21.1±3.0	6.7±2.9	-27.85±0.12
2-Ethylanthracene	-16.8±7.5	13.6±7.4	-30.38±0.18
1-Methylpyrene	-23.1±3.8	7.6±3.7	-30.71±0.15
Benzo(a)anthracene	-25.2±4.8	6.4±4.9	-31.55±0.17
Benzo[e]pyrene	-22.3±1.9	12.6±2.1	-34.9±0.18
Benzo(a)pyrene	-36±17	0.74±16.27	-36.72±0.38
7,12-Dimethylbenz[a]anthracene	-	-	-
Benzo[ghi]perylene	-22±29	18±28	-39.46±0.32

- Values not included in the table due to anomalous behaviour of chemical with PE.

Table S9. Change in log K_{pe-w} values per unit salinity (*‰*) for individual chemical derived using the slope of the log K_{pe-w} – salinity correlation plots given in Figure 5 (main text).

PAH	10°C	20°C	30°C
2-Methylnaphthalene	0.0047±0.001	0.003±0	0.0049±0.0007
Acenaphthene	0.0045±0.0007	0.003±0.0006	0.0041±0.0013
2,6-Dimethylnaphthalene	0.0053±0.001	0.0037±0.0001	0.0045±0.0019
Fluorene	0.004±0.0005	0.0031±0.0008	0.0042±0.0012
Phenanthrene	0.0044±0.0003	0.0029±0.0002	0.0044±0.0007
1-Methylfluorene	0.0043±0.0004	0.0037±0.0009	0.0041±0.0011
Fluoranthene	0.0037±0.0007	0.003±0.0007	0.003±0.0005
Pyrene	0.0033±0.0008	0.0028±0.0008	0.0027±0.0005
2-Ethylanthracene	0.0037±0.0016	0.0037±0.0011	0.004±0.0007
1-Methylpyrene	0.0057±0.0011	0.0031±0.0006	0.0047±0.0013
Benzo(a)anthracene	0.0036±0.0012	0.0029±0.0004	0.0038±0.0016
Benzo[e]pyrene	0.0057±0.0013	-[2]	0.0033±0.0022
Benzo(a)pyrene	0.0028±0.0006	0.0025±0.0006	0.0034±0.0021
7,12-Dimethylbenz[a]anthracene	-	-	-
Benzo[ghi]perylene	-[3]	-[2]	0.0028±0.0017

- Values not included in the table due to anomalous behaviour of 7,12-Dimethylbenz[a]anthracene with PE.

-[2] K_{PE_W} values at 36‰ < values at 0‰.

-[3] Value not included because K_{PE-W} determined at 10°C,0‰ is significantly different from those determined at 10°C, 18‰ and 10°C, 36‰.

Table S10. Chemical-specific correct equations for the combined effects of temperature and salinity on K_{PE-W} values.

PAH	Equation
2-Methylnaphthalene	$\log K_{pe-w}(T,S) = 3.39 - 0.0058 * (T-20) + 0.003 * S$
Acenaphthene	$\log K_{pe-w}(T,S) = 3.63 - 0.006 * (T-20) + 0.003 * S$
2,6-Dimethylnaphthalene	$\log K_{pe-w}(T,S) = 3.99 - 0.0054 * (T-20) + 0.003 * S$
Fluorene	$\log K_{pe-w}(T,S) = 3.76 - 0.008 * (T-20) + 0.003 * S$
Phenanthrene	$\log K_{pe-w}(T,S) = 4.21 - 0.0096 * (T-20) + 0.003 * S$
1-Methylfluorene	$\log K_{pe-w}(T,S) = 4.34 - 0.0091 * (T-20) + 0.003 * S$
Fluoranthene	$\log K_{pe-w}(T,S) = 4.84 - 0.0123 * (T-20) + 0.003 * S$
Pyrene	$\log K_{pe-w}(T,S) = 4.97 - 0.0129 * (T-20) + 0.003 * S$
2-Ethylanthracene	$\log K_{pe-w}(T,S) = 5.41 - 0.0102 * (T-20) + 0.003 * S$
1-Methylpyrene	$\log K_{pe-w}(T,S) = 5.51 - 0.0142 * (T-20) + 0.003 * S$
Benzo(a)anthracene	$\log K_{pe-w}(T,S) = 5.64 - 0.0153 * (T-20) + 0.003 * S$
Benzo[e]pyrene	$\log K_{pe-w}(T,S) = 6.29 - 0.0106 * (T-20) + 0.003 * S$
Benzo(a)pyrene	$\log K_{pe-w}(T,S) = 6.52 - 0.0219 * (T-20) + 0.003 * S$
7,12-Dimethylbenz[a]anthracene	-
Benzo[ghi]perylene	$\log K_{pe-w}(T,S) = 7.05 - 0.0134 * (T-20) + 0.003 * S$

- Values not included in the table due to anomalous behaviour of 7,12-Dimethylbenz[a]anthracene with PE.
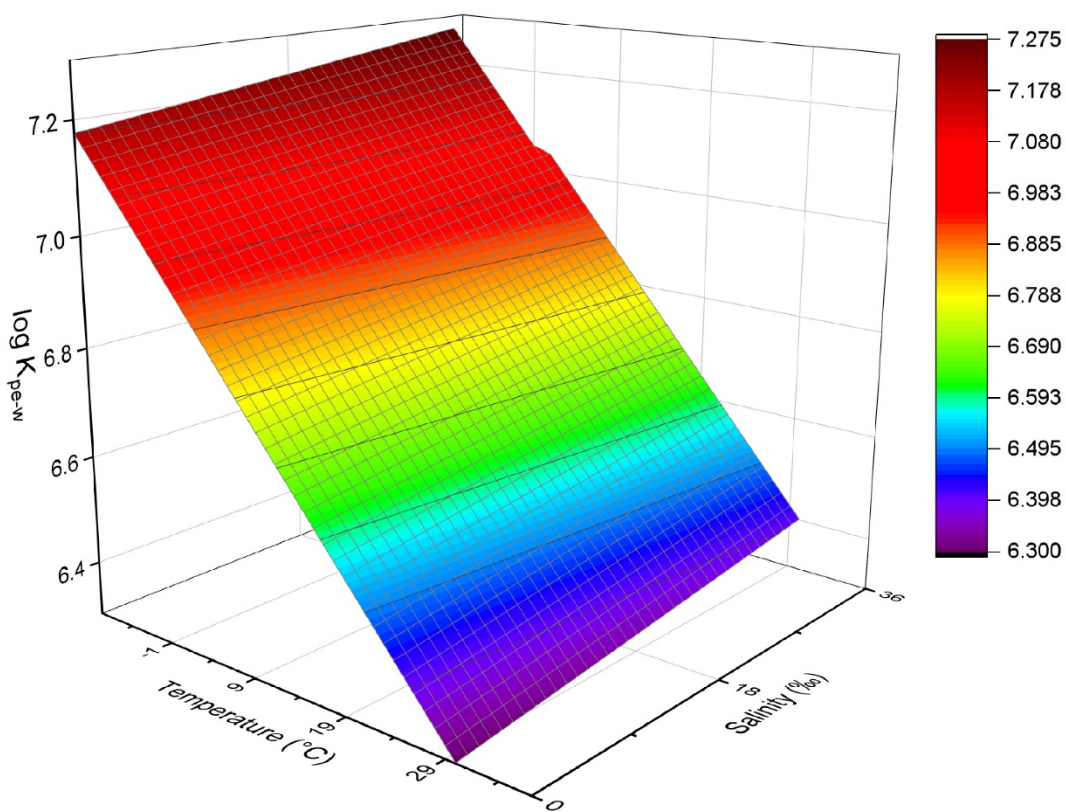
Figure S3. Surface plot of temperature and salinity effects on the log $K_{PE\text{-}W}$ of benzo(a)pyrene.

Details on the calculation of freely dissolved concentrations from the Deepwater Horizon oil spill

The freely dissolved aqueous concentration (C_{free}) of the monitored PAHs were estimated using the model (Equation 1) from Huckins *et al.* [5] and Smedes & Booij [6]

$$C_{free} = \frac{N_{PE}}{m_p * K_{PE-W} * DEQ}$$

[1]

where C_{free} is in units of µg L^{-1}, N_{PE} is the target PAH amounts accumulated in the PE (µg) and m_p represents PE mass (g) while K_{PE-W} and DEQ are the PE-water partition coefficient (L kg^{-1}) and the degree of equilibrium (unitless) reached during exposure (based on the PRCs), respectively. The DEQ term is used to account for non-equilibrium condition and was derived for all target PAHs using the mass transfer model (Equation 2) from Smedes and Booij [6]:

$$DEQ = 1 - \exp\left(\frac{R_s * t}{m_p * K_{PE-W}}\right)$$

[2]

where R_s is the (equivalent) water sampling rate and t represents exposure period (d).

The K_{PE-W} values used here were estimated from an empirical relationship derived from our previous study (*In preparation*, Table S2). R_s values were estimated using a mechanistic model (Equation 3) derived by Rusina *et al.* [7]:

$$R_s = \frac{B}{MW^{0.47}}$$

[3]

where B is an exposure specific term that accounts for the effect of flow on uptake rate while MW is the molecular weight of the target analyte. The factor $MW^{0.47}$ accounts for the effect of molecular size on R_s. B is derived using nonlinear least-squares (NLS) method [8] by fitting the PRC fraction retained (f_{ret}) as a function of $K_{PE-W} M^{0.47}$.

The entire calculation procedure was initially conducted using K_{PE-W} values determined under the standard conditions (i.e. 20°C, 0‰). Subsequently, to account for location-specific variations, the calculations were repeated with K_{PE-W} values adjusted for

temperature and salinity. These adjusted values were obtained by applying Equation 11(Main text). By comparing the results obtained from the two sets of calculations, the extent to which adjusting the $K_{PE\text{-}W}$ values for temperature and salinity influences the final data could be quantified.

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