

Supplemental Information

Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration and implementation

Upal Ghosh, Susan Kane Driscoll, Robert M. Burgess, Michiel T. O. Jonker, Danny Reible, Frank Gobas, Yongju Choi, Sabine E. Apitz, Keith A. Maruya, William R. Gala, Munro Mortimer and Chris Beegan

CONSENSUS K_{pw} VALUES

Table SI-1. Consensus values for (K_{pw}) for selected PAHs.

Compound	Log	K_{PDMS-w}		K_{PDMS-w}		K_{PE-w}		K_{POM-w}	
	K_{ow}	J-Flex SR-TF		AltelSil Sheet					
	(25C) SPARC	Value	LogError	Value	LogError	Value	LogError	Value	LogError
Naphthalene	3.41	2.9	±0.07	3.03	±0.06	2.81	±0.14	3.05	±0.09
Acenaphthylene	3.71	3.07	±0.08	3.26	±0.06	3.16	±0.14	3.78	±0.06
Acenaphthene	4.06	3.45	±0.06	3.62	±0.05	3.62	±0.12	3.5	±0.04
Fluorene	4.2	3.58	±0.06	3.78	±0.04	3.77	±0.11	3.83	±0.12
Phenanthrene	4.74	3.83	±0.05	4.11	±0.04	4.22	±0.11	4.2	±0.07
Anthracene	4.69	3.91	±0.04	4.21	±0.03	4.33	±0.12	4.31	±0.09
Fluoranthene	5.29	4.29	±0.03	4.62	±0.04	4.93	±0.09	4.54	±0.09
Pyrene	5.25	4.38	±0.04	4.69	±0.06	5.1	±0.07	4.55	±0.09
Chrysene	5.9	4.8	±0.05	5.26	±0.04	5.78	±0.09	5.44	±0.12
Benz[a]anthracene	5.85	4.84	±0.04	5.34	±0.08	5.73	±0.11	5.47	±0.1
Benzo[a]pyrene	6.54	5.22	±0.04	5.71	±0.05	6.75	±0.05	5.96	±0.03
Benzo[b]fluoranthene	6.58							5.8	±0.03
Benzo[k]fluoranthene	6.5	5.26	±0.02	5.75	±0.04	6.66	±0.05	5.94	±0.04
Benzo[ghi]perylene	7.04	5.6	±0.13	6.03	±0.13	7.27	±0.14	6.1	±0.09
Indeno[1,2,3-cd]pyrene	7.09	5.59	±0.19	6.06	±0.18	7.4	±0.17	6.31	±0.1
Dibenz[a,h]anthracene	7.39	5.68	±0.14	6.24	±0.14	7.32	±0.13	6.3	±0.12

K_{PDMS} values are shown for specific sources from Smedes et al. (2009) to illustrate the range of PDMS sorption. The values for PDMS from J-Flex SR-TF are consistent with values for PDMS-coated fibers from Hsieh et al. (2011) and average reported partitioning onto PDMS-coated fibers from manufacturers Polymicro and Supelco (DiFilippo and Eganhouse 2010).

K_{PE} from Smedes et al. (2009).

K_{POM} from Hawthorne et al. (2011).

Table SI-2. Consensus values for (K_{pw}) for selected PCBs

				K_{PDMS-w}		K_{PDMS-w}		K_{PE-w}		K_{POM-w}	
		Hawker/Connell		J-Flex SR-TF		AltelSil Sheet					
	Congener	Kow		Value	Log Error	Value	Log Error	Value	LogError	Value	LogError
PCB	4	4.65		4.39	±0.09	4.58	±0.09	4.19	±0.12	4.57	±0.10
PCB	10	4.84		4.38	±0.09	4.55	±0.08	4.23	±0.12		
PCB	14	5.28		4.82	±0.06	5.15	±0.03	4.99	±0.11		
PCB	18	5.24		4.99	±0.08	5.24	±0.08	4.9	±0.12	5.12	±0.07
PCB	21	5.51		5.13	±0.07	5.43	±0.06	5.22	±0.11		
PCB	28	5.67		5.23	±0.06	5.54	±0.06	5.4	±0.12	5.68	±0.09
PCB	29	5.6		5.16	±0.04	5.44	±0.04	5.31	±0.07		
PCB	30	5.44		5.06	±0.06	5.25	±0.05	5.13	±0.09		
PCB	31	5.67		5.2	±0.06	5.5	±0.06	5.3	±0.10	5.51	±0.04
PCB	44	5.75		5.52	±0.06	5.82	±0.08	5.48	±0.10	5.65	±0.07
PCB	47	5.85		5.53	±0.06	5.79	±0.08	5.62	±0.10	5.59	±0.2
PCB	49	5.85		5.61	±0.05	5.89	±0.07	5.67	±0.10	5.83	±0.06
PCB	50	5.63		5.51	±0.06	5.71	±0.07	5.52	±0.09		
PCB	52	5.84		5.54	±0.06	5.82	±0.07	5.55	±0.10	5.65	±0.06
PCB	55	6.11		5.65	±0.05	6.01	±0.07	5.82	±0.09		
PCB	56	6.11		5.71	±0.07	6.05	±0.08	5.9	±0.09	6.19	±0.21
PCB	66	6.2		5.69	±0.05	6.05	±0.07	5.95	±0.09	6.08	±0.08
PCB	78	6.35		5.67	±0.06	6.07	±0.06	6.03	±0.08		
PCB	85	6.3		5.93	±0.13	6.26	±0.15	6.14	±0.13	6.07	±0.16
PCB	87	6.29		6.04	±0.07	6.36	±0.09	6.18	±0.09		
PCB	97	6.29		5.93	±0.06	6.22	±0.08	6.1	±0.06	6.23	±0.2
PCB	99	6.39		6.1	±0.06	6.39	±0.06	6.38	±0.06	6.17	±0.04
PCB	101	6.38		6.01	±0.06	6.29	±0.07	6.18	±0.07		
PCB	104	5.81		6.01	±0.07	6.18	±0.08	6.00	±0.08		
PCB	105	6.65		6.07	±0.07	6.44	±0.09	6.44	±0.08	6.38	
PCB	110	6.48		6.02	±0.07	6.32	±0.09	6.16	±0.09	6.2	±0.11
PCB	118	6.74		6.09	±0.06	6.44	±0.07	6.53	±0.06	6.32	±0.14
PCB	128	6.74		6.44	±0.07	6.78	±0.08	6.74	±0.07	6.35	±0.24
PCB	137	6.83		6.54	±0.06	6.83	±0.07	6.93	±0.05		
PCB	138	6.83		6.46	±0.06	6.78	±0.08	6.82	±0.05	6.5	
PCB	141	6.82		6.41	±0.08	6.71	±0.09	6.74	±0.09	6.42	±0.06
PCB	145	6.25		6.48	±0.06	6.66	±0.08	6.52	±0.07		
PCB	149	6.67		6.4	±0.07	6.65	±0.08	6.59	±0.08	6.11	±0.22
PCB	151	6.64		6.38	±0.09	6.59	±0.09	6.55	±0.10	6.25	±0.26
PCB	153	6.92		6.45	±0.08	6.73	±0.09	6.81	±0.08	6.64	±0.19
PCB	155	6.41		6.63	±0.07	6.8	±0.09	6.88	±0.07		
PCB	156	7.18		6.4	±0.10	6.74	±0.11	6.96	±0.10	6.59	
PCB	170	7.27		6.8	±0.15	7.11	±0.16	7.25	±0.14	6.54	
PCB	180	7.36		6.72	±0.17	7	±0.17	7.24	±0.17	6.67	±0.09
PCB	187	7.17		6.66	±0.13	6.89	±0.16	7.01	±0.13	6.44	±0.08
PCB	204	7.3		7.42	±0.33	7.6	±0.35	7.77	±0.33		

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K_{PE} from Smedes et al. (2009).

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Temperature, salinity, and pressure correction of K_{pw}

A factor that may affect the determination of C_{free} is temperature, which influences the equilibrium distribution of chemicals between all phases (e.g., sediment and colloidal particles, water, organisms, passive sampler) in the sampled medium (Muijs and Jonker 2011; Booij et al. 2003; Adams et al. 2007). Thus, ex-situ exposures performed in the laboratory at room temperature may not exactly reflect C_{free} in the field at other temperatures (e.g., 4 °C). Similarly, using K_{pw} determined at room temperature to derive C_{free} during field exposures may result in biased data. Schwarzenbach et al. (2003) discuss mathematic approaches for adjusting K_{pw} for the effects of temperature. As an example, Figure SI-2a presents the modeled effects of various temperatures on the magnitude of K_{pw} . Theoretically, C_{free} decrease as temperature decreases, due to increased sorption to sediment and other environmental phases, but because uptake in organisms also increases with decreasing temperature (Muijs and Jonker 2009), the overall effect (actual bioaccumulation) may be represented acceptably by ex-situ exposures in the laboratory at room temperature. Therefore, as long as extreme conditions are not expected at the field site, the error introduced by performing ex-situ exposures at room temperature is expected to be relatively small compared to other causes of uncertainty and may be well within limits acceptable for regulatory purposes (e.g., a factor of two). The same is true for the effects of salinity, a principal factor that also affects the equilibrium distribution of HOCs between environmental phases (Adams et al. 2007; Jonker and Muijs 2010; Ni and Yalkowsky 2003). If pure water serves as the reference phase for C_{free} used in bioavailability assessment, then salinity correction is not needed. When using C_{free} for purposes such as advective transport assessment, salinity correction may be necessary. As with temperature, Schwarzenbach et al. (2003) discuss mathematical approaches for adjusting K_{pw} for the effects of ionic strength (salinity). Figure SI-2b illustrates the modeled effects of different salinities on the magnitude of K_{pw} . Correction for or adjustment of the salinity (and temperature) of laboratory ex-situ exposures to the salinity (or temperature) relevant to field conditions is relatively easily performed and can be used to improve the environmental relevance and data quality of laboratory (ex-situ) determinations of C_{free} when necessary (Diflippo and Eganhouse 2010; Jonker and Muijs 2010). Thus, adjustments for temperature and salinity can be performed when it is necessary and viable to validate the data and assess the accuracy of the adjustments. To ensure transparency whenever C_{free} results are presented it should be clearly stated if and how corrections for temperature and salinity have been performed. It should be noted however that the model calculations assume universal behavior of all sorption phases (here, passive sampling materials), which, although theoretically plausible, may not be true. The effect of temperature and salinity has for instance been observed to differ between different polymers (unpublished results). More research in this area therefore is needed.

While C_{free} is also expected to be impacted by water pressure, especially for deep sea, fjord, or lake environments, there is little experimental work on pressure effects on K_{pw} at this time.

Jonker MTO, Muijs B. 2010. Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals. *Chemosphere* **80**:223-227.

Muijs B, Jonker MTO. 2011. Temperature-Dependent Bioaccumulation of Polycyclic Aromatic Hydrocarbons. *Environ. Sci. Technol.* **43**:4517-4523.

Ni N, Yalkowsky SH. 2003. Prediction of Setschenow constants. *Int J Pharm* **254**:167-172.

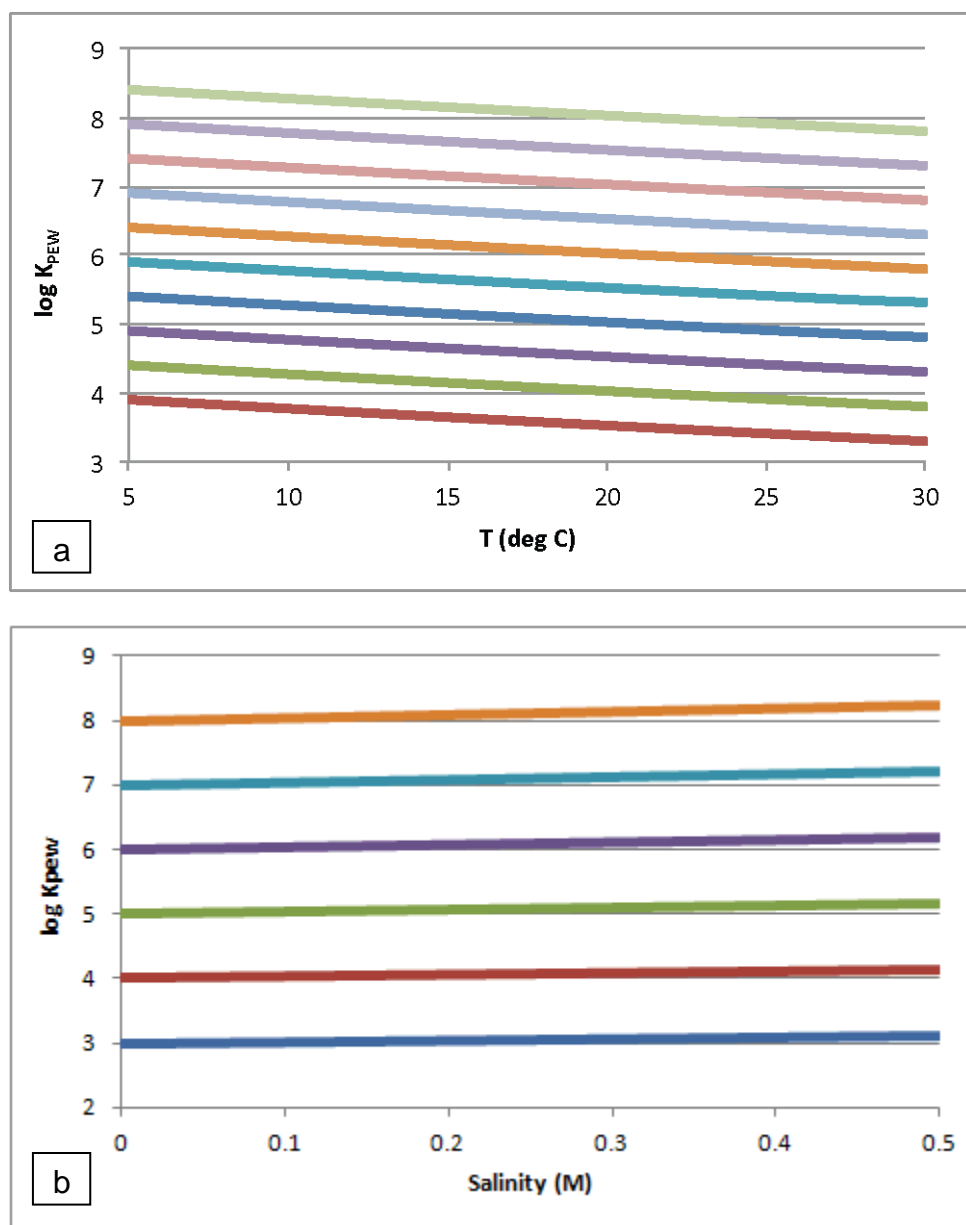


Figure SI-1. $\log K_{PEW}$ versus (a) temperature, calculated following Lohmann (2012) for compounds with an excess enthalpy of solution in water of 39 kJ mol^{-1} . The assumed excess enthalpy of solution is the average of 13 compounds (4 PAHs, 6 PCBs, and 3 DDTs), derived from data compiled by Mackay et al. (2006); and (b) salinity, calculated following Lohmann (2012), using $\log K_{OW}$ -dependent Setschenow constants, as described by Ni and Yalkowsky (2003).

Calculation of the mass of polymer required to achieve a known detection limit.

The mass of polymer needed depends on the detection limit of the chosen analytical method (regular GC-ECD, HPLC, or GC-MS versus HR-GC/HR-MS), anticipated C_{free} (more needed for

low concentrations), and K_{pw} . The following equation provides an estimate of polymer mass required to achieve a lower limit target concentration of C_{free} .

$$M_P = DL / (C_W * K_{pw})$$

where M_P is the mass of polymer in kg, DL is the mass detection limit for the analytical method chosen (ng), C_W is the freely dissolved concentration target lower limit in ng/L; and K_{pw} is the polymer-water partition coefficient in L/kg.

Example of the use of PSMs in support of site assessment and management.

This section provides a theoretical example of the use of C_{free} to develop a site-specific exposure-response relationship in support of site assessment and management. Although the example provided is for PAHs, it illustrates an approach that can be used to evaluate the acceptability of a mixture of sediment-associated organic chemicals within the framework of the U.S. EPA (2012) approach (illustrated in Figure 5).

In this example, a site assessment was conducted to determine whether contaminated sediments adjacent to a former manufactured gas plant (MPG) site posed a risk to the community of benthic invertebrates. Concentrations of total PAHs (based on a list of 34 parent and alkylated PAHs) in sediment samples at the site ranged from 41 to 5,795 mg/kg dw and were elevated in comparison to ambient upstream areas beyond the influence of the manufactured gas plant site (5 to 8 mg/kg dw). Sediment organic carbon normalized concentrations of 34 individual parent and alkylated PAHs were divided by corresponding ESBs to calculate toxic units (U.S. EPA 2003). The sum of toxic units (Sum-TU) for site samples ranged from 1.0 to 123, indicating that sensitive benthic organisms could be unacceptably affected by PAHs.

Since ESBs can be under- or over-protective in the presence of strongly sorbing phases such as black carbon in sediment (U.S. EPA 2012), Sum-TU were also calculated from direct measurement of C_{free} based on the commercially available SPME extraction method (ASTM 2007). For this assessment, 28-day sediment toxicity tests with the freshwater amphipod *Hyalella azteca* were also conducted to assess the toxicity of these field sediments. Despite high concentrations of PAHs in bulk sediment (Figure S2a) and a corresponding ESB-based Sum-TU greater than 1.0 in all site samples (Figure SI-2b), only four of the 19 site samples were significantly more toxic than the reference site samples. These results indicate that PAHs in the site sediments are less bioavailable than expected based on generic EqP assumptions, and predictions based on organic carbon-normalized concentrations of PAHs overestimated potential toxicity to *H. azteca*. Sum-TU calculated from concentrations of PAHs in pore water measured directly were in much closer agreement with sediment toxicity test results. Four of the 10 site samples with Sum-TUs greater than 1.0 were significantly more toxic than the reference sites (Figure SI-2c).

Six of the 10 site samples with Sum-TUs greater than 1.0 were not significantly more toxic than the reference site, and none of the site samples with Sum-TU less than 1.0 were toxic, indicating that an ESB-based Sum-TU of 1.0 is a conservative predictor of potential toxicity at this site. Note, however, that the ESBs used in this example (i.e., U.S. EPA 2003) are based on the 5th

percentile of the species sensitivity distribution. ESBs based specifically on data for *H. azteca*, the organisms used in these toxicity tests, would likely be less conservative and in closer agreement with observed results. A preliminary remediation goal for the protection of benthic invertebrates (based on a C_{free} measurements and a $\text{Sum-TU} = 1.0$) corresponds to a bulk sediment concentration of 520 mg/kg dw total PAH. Thus, in this example, C_{free} measurements were used to develop refined predictions of toxicity and support the development of risk-based clean-up goals.

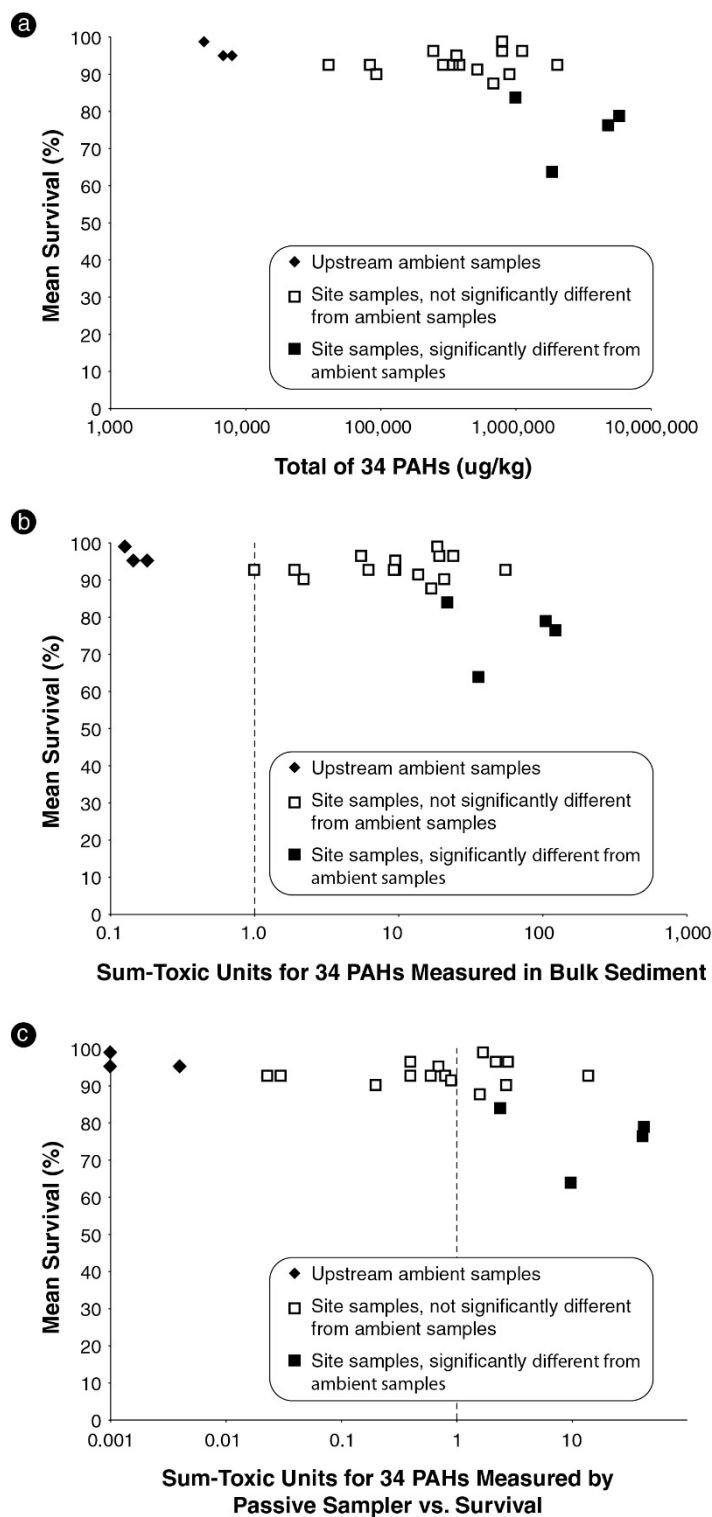


Figure SI-2. Amphipod survival in a 28-day sediment toxicity test versus (a) concentration of total PAH in bulk sediment; (b) ESB-based Sum-TU for PAHs in bulk sediment, and (c) Sum-TU for PAHs based on C_{free} measurements.