APPENDIX F1. PASSIVE SAMPLER CALCULATIONS FOR THE CPAH POREWATER INVESTIGATION

1 Equilibrium Corrections for cPAH Porewater calculations

The clam quality assurance project plan (QAPP) (Windward 2018) described the procedures for calculating the freely dissolved concentrations (C_{free}) of carcinogenic polycyclic aromatic hydrocarbons (cPAH) in porewater. The basis for the equilibrium correction is provided herein. The calculated values, including the equilibrium-corrected concentrations, are provided in Appendix F-2.

The results for the performance reference compounds (PRC) in three replicate time-zero samples are presented in Table F-1. The variance observed is consistent with the expected analytical variance for these compounds (Windward 2018).

Table F-1. PRC results for time-zero samples (n=3)

cPAH PRC	Time Zero Replicate Concentrations (µg/kg)	Mean Concentration (µg/kg)	Coefficient of Variation
[13]C-Phenanthrene	9,540, 9,560, 10,300	9,700	5.5%
Fluoranthene - d10	3,890, 4,490, 5,060	4,480	13%
[13]C-Chrysene	5,220, 4,800, 7,350	5,790	24%
[13]C-Indeno(123cd)pyrene	6,510, 6,140, 8,570	7,073	19%

cPAH – carcinogenic polycyclic aromatic hydrocarbon
PRC – performance reference compound

As expected, the lower-molecular-weight PRC compounds (^{13}C-phenanthrene and fluoranthene -d10) were significantly depleted in all samples after exposure. The higher-molecular-weight PRC compounds (^{13}C-chrysene and ^{13}C-indeno(1,2,3-cd)pyrene) were substantially less depleted (Table F-2). The higher-molecular-weight PRCs are the most influential PRCs for the calculation of cPAH C_{free} in porewater from the polyethylene (PE) passive samplers. Six of the seven target cPAH compounds have K_{ow} values in the range between the K_{ow} values of chrysene and indeno(1,2,3-cd)pyrene.

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Table F-2. Percent depletion in porewater passive samplers

Sample ID	PRC Percent Depletion			
	^{13}C-phenanthrene	fluoranthene-d10	^{13}C-chrysene	^{13}C-indeno (1,2,3-cd)pyrene
LDW18-A01	96.6	88.7	75.3	13.2
LDW18-A02	99.1	96.2	73.2	9.52
LDW18-A04	93.1	79.0	40.6	-1.9[a]
LDW18-A06	94.4	82.3	58.6	20.1
LDW18-A07	92.3	76.3	39.6	4.85
LDW18-A07FD	94.6	86.4	61.3	5.14
LDW18-A08	99.6	97.3	67.5	-6.6[a]
LDW18-A10	93.3	88.8	61.4	-2.92[a]
LDW18-A11	98.0	93.6	71.0	24.4
LDW18-A17	98.0	95.3	75.3	25.4
LDW18-A18	97.9	95.2	77.4	23.5

Orange-shaded rows indicate samples with negative depletion (i.e., increased PRC concentrations). These values were excluded from the first-order kinetic calculations.

Blue-shaded rows indicate samples with percent depletions that are less than the variance associated with the time-zero replicates (19%)

[a]   13C-indeno(1,2,3-cd)pyrene concentrations were as follows: A04 - 7,210 µg/kg dw, A08 - 7,540 µg/kg dw, and A10 - 7,280 µg/kg dw.

ID – identification   PRC – performance reference compound

Three passive samplers (LDW18-A04, LDW18-A08, and LDW18-A10) had a negative percent depletion for ^{13}C-indeno(1,2,3-cd)pyrene, indicating an increase in concentration on the PE passive sampler with time. The percent increases in the indeno(1,2,3-cd)pyrene concentrations for these three samples were within the range of variance of the time-zero samples (Table F-1). The percent depletions of ^{13}C-indeno(1,2,3-cd)pyrene in four samples (LDW18-PWPS-A01, LDW18-PWPS-A02, LDW18-PWPS-A07, and LDW18-PWPS-A07FD) were also less than the observed variance for the time-zero replicates (Table F-2).

Equilibrium corrections for all of the cPAH compounds were made using a first-order kinetics model. The equilibrium corrections for each sample are provided in Appendix F2. The equilibrium corrections were calculated based on a first-order kinetics model rather than the diffusion model specified in the QAPP. Two recent studies have suggested that corrections should be made using first-order kinetics-based methods, rather than diffusion model-based methods like the PRC calculator software (Gschwend et al. 2014) for well-mixed systems (Apell et al. 2018; Sanders et al. 2018). Therefore, a first-order kinetics-based method described by Sanders et al. (2018) was used. This method is based on establishing a linear correlation between the exchange rate of each PRC in each sampler and the K_{ow} of the PRC. The exchange rate can be

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predicted for target cPAH compounds using the correlation line, then used to estimate the fractional equilibrium for each cPAH compound.

To apply the first-order kinetics-based model, regression lines were established for each sample using data from the four individual PRCs (^{13}C-phenanthrene, and fluoranthene-d10 ,[13]C-chrysene, ^{13}C-indeno(1,2,3-cd)pyrene) (Figure F-1). The ^{13}C-indeno(1,2,3-cd)pyrene results for three samples (LDW18-PWPS-A04, LDW18-PWPS-A08, and LDW18-PWPS-A10) were excluded, because of the negative depletion. For these three samples, the regression lines were established using the PRCs ^{13}C-chrysene, ^{13}C-phenanthrene, and fluoranthene-d[10]. The resulting regression lines for these three samples had slopes and intercepts similar to those of the other eight samples (Figure F-1). This similarity supports the assertion that both sets of correlations (i.e., with and without the use of ^{13}C-indeno(1,2,3-cd)pyrene) are appropriate for the calculation of porewater cPAH concentrations; no additional data qualification is required.
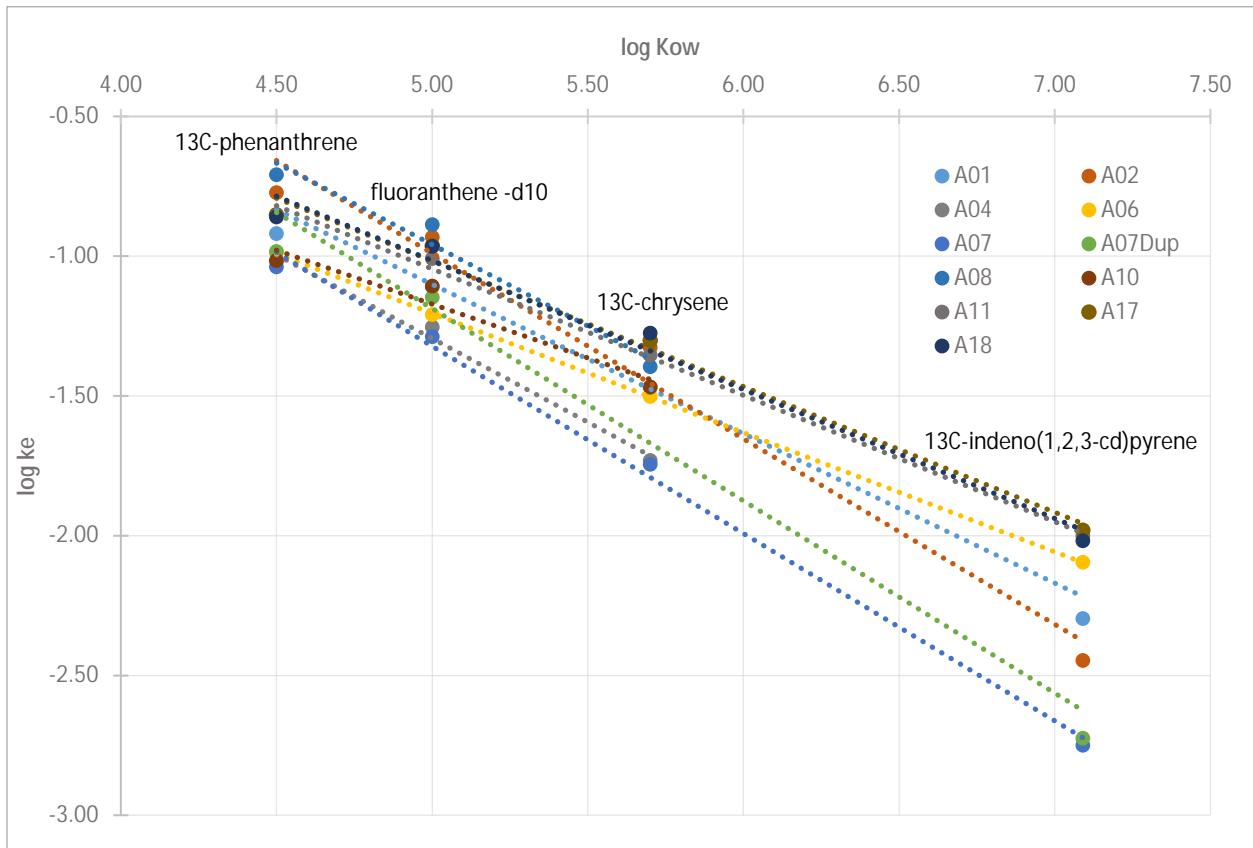

Figure F-1. Regression lines for PRC log K_{ow} vs exchange rate (log ke) (excluding indeno(1,2,3-cd)pyrene for three samples)

2   References

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