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The challenges of using polyethylene passive samplers to determine dissolved concentrations of parent and alkylated PAHs under cold and saline conditions

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23 simulated marine oil spill in the laboratory, PE-based results were within a factor of 2 for the
24 most abundant PAHs compared to conventional sampling results.

25

26

INTRODUCTION

27 The dangers of drilling for oil in the marine environment were recently realized in April
28 2010 when 4.9 billion barrels of oil were released into the Gulf of Mexico. Over a year later, it
29 is thought the majority of the oil has been cleaned up or degraded by bacteria that inhabit the
30 warm waters of the Gulf of Mexico.^{1,2} In contrast, the Exxon Valdez oil spill occurred in 1989,
31 releasing over 11 million gallons of crude oil onto the shores of the Alaskan coastline. It is
32 estimated that 21,000 gallons of oil still persist today, over twenty years after the spill occurred,
33 with contested remaining toxicity.^{3,4} The Arctic is a unique environment and it is still not
34 understood how spilled oil behaves there. As interest in expanding vessel traffic, as well as the
35 exploration of oil and gas reserves in the Arctic increases, so does the need to better understand
36 the impact of oil spills to this unique environment.⁵

37 Passive samplers have been proven to accumulate compounds, such as polycyclic
38 aromatic hydrocarbons (PAHs), in proportion to the truly dissolved concentration of the
39 compound present in the aquatic environment.⁶⁻⁸ In fact, passive samplers actually directly
40 reflect the compounds' chemical activity (which is routinely approximated by its truly dissolved
41 concentration). This can be used, among others, to elegantly measure gradients in the
42 environment, or contribution to mixture toxicity.⁸⁻¹⁰

43 Equilibrium partition coefficients between polyethylene (PE) and water (K_{PEW}) are
44 generally determined in the laboratory under standard conditions (298 K, no salt) and are used to

45 relate the passive sampler concentration (C_{PE}) to the dissolved concentration in the water column
46 (C_w ; equation 1):

$$47 \quad K_{PEw} = \frac{C_{PE}}{C_w} \quad (1)$$

48 K_{PEw} is the ratio of the concentration of the compound in the passive sampler (e.g., ng/ μ L) over
49 the concentration of the compound in the water (e.g., ng/ μ L) under standard conditions.

50 Once the K_{PEw} is known for a compound and a PE is equilibrated in the environment (or
51 corrected for non-equilibrium), the concentration of the compound in water (i.e., truly dissolved)
52 can then be calculated from equation (1). K_{PEw} can be corrected for a temperature other than 298
53 K by using the van't Hoff equation. To account for the effects of dissolved salts on K_{PEw} , the
54 empirical Setschenow constant (K_S) and the molar concentration of salt [*salinity*], present in the
55 water, are used. Both of these equations have been proven reliable at moderate temperatures
56 (30°C to 2°C)⁶ and salinities (0 to 36.7 psu)¹¹.

57 Passive samplers are a useful alternative to conventional direct measurement of
58 environmental phases (i.e. liquid-liquid extraction), such as water and sediment to derive
59 bioaccumulation and bioavailability. Unlike direct measurements, passive samplers only sample
60 the truly dissolved or bioavailable fraction present in the water.⁸ Chemicals sorbed to particles
61 or colloids in the water column are not directly bioavailable (i.e., for passive uptake) and are
62 difficult to separate from the truly dissolved and bioavailable chemicals, such as PAHs.¹² Thus,
63 when water is sampled for PAHs using conventional methods, the dissolved concentrations are
64 often overestimated due to the inclusion of PAHs associated with colloids. Passive samplers are
65 also a preferred method for measuring PAHs for their ease of sampling, lower detection limits in
66 the field, and minimization of contaminated blanks.^{12,13} Conventional methods of water analysis
67 take samples at a discrete point in time, representing the concentration only at that time, while

68 the time averaged concentration determined from passive sampling is a more appropriate
69 reflection of the longer-term exposure in the environment. Passive samplers can often be an
70 inexpensive and reliable option compared to conventional methods.¹²

71 Polyethylene samplers (PEs) are passive samplers that have been proven effective at
72 assessing environmental concentrations of organic pollutants.^{6,7,14} Though passive samplers are
73 an excellent option for assessing dissolved PAH concentrations, their performance has not been
74 tested under the harsh conditions of the Arctic environment. Little is currently known how
75 passive samplers accumulate alkylated PAHs, which could be the majority of compounds
76 released during an oil spill. In this study, we (i) determined the K_{PEW} values of a wide range of
77 alkylated and parent PAHs; (ii) investigated the effect of varying salinities and temperatures on
78 equilibration and partitioning, simulating Arctic conditions; (iii) performed a mock oil spill in the
79 laboratory to evaluate their effectiveness; and (iv) deployed passive samplers in Narragansett
80 Bay, Rhode Island, USA in December 2012 to assess their usefulness in the field.

81

82 MATERIALS & METHODS

83 PAHs

84 Forty-one native PAHs that are commonly present in oil were identified and used to
85 prepare a laboratory standard curve ranging from lower molecular weight components (e.g.,
86 naphthalene) to compounds of higher molecular weight (e.g., chrysene and benzo(a)pyrene)
87 (Table S1). These standards were prepared by from individual PAHs purchased from certified
88 laboratories (Table S2). Twenty-five of these were alkylated PAHs, as they are commonly found
89 in oil, however there is little research available for these compounds. Additionally, three
90 deuterated PAHs (naphthalene-d₈, pyrene-d₁₀, benzo[a]pyrene-d₁₂) were utilized as Performance
91 Reference Compounds (PRCs).

92

93 **PE samplers**

94 For all experiments, 25 μm thick PE, manufactured by a commercial sheeting company
95 (Carlisle Plastics, Inc., Minneapolis, MN, USA), was purchased from a local hardware store.
96 Passive samplers were pre-cleaned in dichloromethane (DCM) twice prior to use. The passive
97 samplers were enriched with PRCs with methods modified from Booij et al (2002) (see SI).¹⁵
98 For the laboratory portion of the study, PEs were cut into small pieces with a mass of
99 approximately 0.09 mg (ca. 1 cm^2). Once samplers were retrieved from the various experiments,
100 they were extracted in DCM and hexane (1:1 v/v), with internal surrogates added at the time of
101 extraction. The extracts were then concentrated under a flow of nitrogen gas. Injection standard
102 (external standard) was added prior to analysis with gas chromatography/mass spectrometry
103 (GC/MS) (Agilent, Santa Clara, CA, USA) (see Supporting Information). To validate the
104 GC/MS analysis, a National Institute of Standards and Technology (NIST) PAH standard 2260a
105 was used to calibrate the in-house PAH standard curve (see Supporting Information).

106

107 **Polyethylene-water partition coefficients, K_{PEW}**

108 Experimental equilibrium partition coefficients were determined in the laboratory for
109 various PAHs (Table S3). In climate controlled rooms, tests were performed to cover the range
110 of temperatures and salinities commonly found in the marine environment, especially conditions
111 present in the Arctic environment and the brine present within ice (see SI and Table S3).¹⁶ Water
112 samples were prepared at various salinities (245, 100 and 35 psu) by using pure water (18.2 $\text{M}\Omega$
113 cm^{-1} Milli-Q[®] filtered water) and Instant Ocean[®] or Sigma-Aldrich salt mixture, which both
114 mimic the composition of natural seawater. PEs were prepared in triplicate along with a blank

115 and placed in 1 L pre-cleaned amber jars filled with water of the various salinities. The six
116 replicate samples were then spiked with a mixture of the 41 oil components in nonane. To
117 facilitate faster equilibrium times, flasks with PEs were stirred to mimic a very turbulent
118 situation in the natural environment. After spiking with PAH mixture (approximately 10 to 90
119 ng depending on the PAH (Table S1)), each replicate was stirred for approximately 24 hours
120 prior to adding the PE sampler. Experiments were run for various time periods to determine if
121 equilibrium was reached (Table S4).

122 The concentrations of the PAHs in the passive samplers (Table S5) and the water were
123 determined and the K_{PEW} calculated for each compound in each experiment. Experimentally
124 derived K_{PEW} were compared to K_{PEW} found in the literature and corrected for changes in
125 temperature and salinity encountered in all experiments using the van't Hoff and Setschenow
126 correction, respectively.¹⁷

127

128 **Mock oil spill experiment**

129 For the mock oil spill experiment, Statfjord crude oil was employed, the composition of
130 which had been previously studied.^{18,19} The water soluble fraction (WSF) of the oil was
131 prepared utilizing filtered natural seawater (Narragansett Bay) by the methods established by the
132 Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF) proceedings
133 (see SI).^{18,19} To prevent biological alteration of the WSF, sodium azide was added to the sea
134 water to act as a biocide. The PE samplers were then exposed to the oil WSF at a temperature of
135 5°C in an environmental chamber and allowed to reach equilibrium for four weeks. The flasks
136 with PE samplers were stirred on stir plates to facilitate faster equilibrium times. The passive
137 samplers were removed from the water and the PAH concentrations in both PE and water were

138 determined. The experimentally derived K_{PEW} (2°C at 0 psu) were adjusted for the effects of
139 salinity and used to calculate the freely dissolved PAH concentration of the oil WSF and
140 compared to the liquid-liquid extraction results. In a follow-up experiment, triplicate dissolved
141 organic carbon (DOC) samples were collected weekly over 3 weeks. They were filtered
142 (Millipore type RA, 1.2 μm), acidified to pH 2 and refrigerated until analysis on a Shimadzu
143 TOC-V CPH total organic carbon analyzer.

144

145 **Sampling of Narragansett Bay Water for PAHs**

146

147 PE samplers were field tested in December 2012 over 3 weeks in a tank in the Aquarium
148 Building at the University of Rhode Island's Graduate School of Oceanography (URI-GSO).
149 Tanks were fed Narragansett Bay water pumped through an intake pipe originating under the
150 URI-GSO dock and passed through a sand filter to reduce particles. An in-tank chiller
151 maintained water temperature at 9°C in the tank (outside temperature was $12-13^{\circ}\text{C}$). The tank
152 measured 1.2 m Dia x 0.6 m deep with a water level maintained at 0.3 m. The water was pumped
153 into the tank at a rate of 2.4 L/min. The tank was sampled for DOC daily at the same time each
154 day to track changes over the tidal cycle.

155 Polyethylene samplers measuring ca. 0.1 m x 0.40 m x 51 μm (ca. 2 g each) were
156 prepared as a single batch by first cleaning (24 hours in acetone and hexane each) and then
157 impregnating with performance reference compounds, as above. The samplers were each strung
158 on a stainless steel wire and wrapped individually in muffled aluminum foil until deployed. PE
159 samplers were suspended in the water on ropes in 3 groups of 3. One group of PEs was collected
160 at one week intervals for 3 weeks, rewrapped in the aluminum foil and stored in a freezer (-20
161 $^{\circ}\text{C}$) until analyzed.

162 Conventional sampling for PAHs consisted of pumping approximately 15-L at 1 L/min
163 through a glass fiber filter (Watman GF/F) and then through tandem polyurethane foam (PUF)
164 plugs.^{14,20,21} This was completed once to per day at the same time each day to track changes in
165 PAH concentrations throughout the tidal cycle. Filters and PUFs were changed weekly in
166 conjunction with collection of the PE strips and stored at -20 °C until analyzed. PUF plugs and
167 PE samplers were then analyzed for PAHs (see SI).

168
169

170

RESULTS & DISCUSSION

171 The experimental $\log K_{PEW}$ results determined at 20 °C at 0 psu were plotted against the
172 PAHs' octanol-water partition coefficient (K_{ow}) (Figure 1, Table S3). As expected, the
173 experimentally determined $\log K_{PEW}$ values increased with increasing molecular weight and \log
174 K_{ow} , except for acenaphthylene ($\log K_{PEW} = 3.17$; $\log K_{ow} = 4.2$). Above $\log K_{ow}$ of 5.5,
175 measured K_{PEW} values of PAHs often exceeded their respective $\log K_{ow}$ values. In general,
176 measured values were within a factor of two (average 71%) of $\log K_{ow}$ values (Table S3).
177 Exceptions were several alkylated PAHs that were greater than 2-times below their respective
178 K_{ow} values (e.g., 2-isopropyl-naphthalene, 9-ethylfluorene, 2-methylfluorene, and 1,2-
179 dimethyldibenzothiophene), while the few compounds greater than 2-times above K_{ow} were
180 mostly higher molecular weight parent PAHs (2,6-diisopropyl-naphthalene, 2,4,7-
181 trimethyldibenzothiophene, benzo(b)fluoranthene, benzo(h)fluoranthene and benzo[a]pyrene).
182 In the case of the alkylated PAHs, appropriate K_{ow} literature values were difficult to find;
183 calculations had at times to rely on relationships developed for parent PAHs (e.g., Ma et al.,
184 2010)²². The deuterated PAHs used as PRCs (naphthalene-d₈, pyrene-d₁₀, benzo[a]pyrene-d₁₂),

185 showed good agreement with the non-deuterated PAHs, indicating equilibrium had been reached
186 in the 20 °C at 0 psu experiments (Table S3).

187 To further validate the experimental $\log K_{PEW}$ values determined in this study, they were
188 compared to other published results (Table S6). The greatest difference between the published
189 results and the results reached in this study was evident for naphthalene, where other
190 publications determined an average $\log K_{PEW}$ of 2.8, 3 and 3.23 and this study $\log K_{PEW}$ of 3.7.
191 The remainder of values determined in this study compared well with previous results, varying
192 only 0.1 to 0.2 log units for most compounds. For some of the HMW PAHs, there was a large
193 spread in the $\log K_{PEW}$, with the results from this study within the published range. K_{PEW} agreed
194 best with results from Smedes et al. (2009)²³. Fernandez et al. (2009)²⁴ included four alkylated
195 PAHs, three of which were similar to ones incorporated in this study, specifically 2-
196 methylphenanthrene (1-methylphenanthrene in this study), 3,6-dimethylphenanthrene, and 2-
197 methylanthracene (9-methylanthracene in this study). Log K_{PEW} values derived from the two
198 studies showed excellent agreement with 4.7 and 4.92 for methylphenanthrene, 5.2 and 5.36 for
199 3,6-dimethylphenanthrene, and 5.0 and 4.92 for methylanthracene, respectively. Choi et al.
200 (2013) included a suite of alkylated PAHs in their study, 12 of which were similar to those in this
201 study.²⁵ The best agreement between the K_{PEW} s in both studies was for 9-methylanthracene,
202 with only 0.12 log units difference, 2-methylphenanthrene (1-methylphenanthrene in this study),
203 with 0.25 log units difference and 1-methylphenanthrene and 2-methylanthracene (9-
204 methylanthracene in this study), both 0.27 log units difference. The largest difference (0.58 log
205 units) between the alkylated K_{PEW} of these studies was 6-methylchrysene (1-methylchrysene in
206 this study). The remainder of the alkylated K_{PEW} values were separated by 0.3 to 0.42 log units.

207 The good agreement between parent and alkylated K_{PEW} values from this and other studies
208 corroborates the log K_{PEW} values determined in this study.

209 A recent review article combined the log K_{PEW} values (at 20 °C and 0 psu) of various
210 PAHs (n=65) from independent research studies and correlated them against their respective log
211 K_{ow} values²⁶:

$$212 \quad \text{Log}K_{PEW} = 1.22(\pm 0.046)\text{log}K_{ow} - 1.22(\pm 0.24) \quad (r^2=0.92, SE=0.27, n=65) \quad (2)$$

213 with a high R^2 of 0.92 and low standard error (SE) of 0.27.²⁶ Focusing only on the parent PAHs,
214 including those from this study, and utilizing log K_{ow} values from²², the strong linear agreement
215 remains:

$$216 \quad \text{Log}K_{PEW} = 1.18(\pm 0.04)\text{log}K_{ow} - 1.06(\pm 0.20) \quad (r^2=0.92, SE=0.31, n=83) \quad (3)$$

217 To include the alkylated PAHs studied in this data set, log K_{ow} values had to be determined.

218 Building upon the parent log K_{ow} values, values were added for each methyl group of the
219 alkylated compounds.²⁷ All the PAHs included in this study were then incorporated in the data
220 set, resulting in (Figure 1):

$$221 \quad \text{Log}K_{PEW} = 1.14(\pm 0.04)\text{log}K_{ow} - 0.95(\pm 0.21) \quad (r^2=0.89, SE=0.34, n=109) \quad (4)$$

222 Incorporating all of the data from this study slightly decreases the correlation, with slightly
223 higher scatter. Overall, from both the plot and the regression line, it is clear that the log K_{PEW}
224 values determined in this study are similar to other researchers in the field.

225 The understudied alkylated PAHs were the particular interest to this study, as they could
226 be important contributors to the toxicity of oil.^{28,29} In a recent atmospheric field study, Khairy
227 and Lohmann (2012) reported that tri and tetra-alkylated PAHs partitioned differently into PEs
228 than predicted based on correlations with parent PAHs.³⁰ It was unclear at the time whether this

229 reflected inherent physico-chemical partitioning, was due to sampling bias or a higher reactivity
230 of the higher alkylated PAHs.

231 In this study, the $\log K_{PEW}$ of C₁-alkylated PAHs increased by an average of 0.38 log units
232 compared to the $\log K_{PEW}$ of the parent PAH. As the number of alkylated carbons increased, so
233 did the difference from the parent (Table 1). With 2 alkylated carbons, the $\log K_{PEW}$ values
234 increased by an average of 0.67 log units, while with 4 alkylated carbons the difference grew to
235 an average of 1.57 log units. Overall, this suggests that for each additional alkylated carbon, the
236 $\log K_{PEW}$ increases by an average of 0.40 (± 0.20) log units relative to the unsubstituted parent
237 PAH (n=25). For parent PAHs, the average contribution of each aromatic carbon was 0.33 (\pm
238 0.02) log units (n=20). In recent work, Choi et al. (2013) reported the carbon contribution
239 towards $\log K_{PEW}$ as 0.313 (aromatic) and 0.461 (aliphatic), very similar to the results obtained
240 here.²⁵ Our values are also in good agreement with the atom/fragment addition method
241 developed by Meyland and Howard (1995), who reported an increase of 0.49 (-CH₂) and 0.55
242 log units (-CH₃) for alkylated carbon and 0.29 for aromatic carbon in predicting $\log K_{ow}$ values.²⁷
243 This further supports the similarity of partitioning of nonpolar fragments between octanol and
244 polyethylene, as manifested in roughly similar $\log K_{ow}$ and $\log K_{PEW}$ values.²⁶

245 We compared how well the estimated atom contribution method was able to explain
246 measured values. The agreement was satisfactory; the atom addition method explained 91% of
247 the variance in the data, with a slope and intercept not significantly different from 1 and 0,
248 respectively:

249
$$\text{Log}K_{PEW, \text{pred}} = 0.95(\pm 0.05)\text{log}K_{PEW, \text{meas}} + 0.30(\pm 0.25) \quad (r^2=0.91, \text{SE}=0.40, n=41) \quad (5)$$

250

251 Other approaches have been developed to correlate and predict passive sampler partitioning
252 values that go beyond an atom or fragment contribution approach, most notably the poly-
253 parameter linear free energy relationships (pp-LFER). These are essential for understanding and
254 predicting the partitioning of (a)polar compounds with complex polymers (those with
255 interactions beyond van-der-Waals interactions). Yet in the case of PE, we note that the vast
256 majority of partitioning data has been reported for apolar or weakly polar molecules. This
257 renders pp-LFER approaches for PE difficult to derive. As PE can only interact via van-der-
258 Waals interactions, we deem the above simple carbon addition model appropriate for the task of
259 predicting $\log K_{PEw}$ for (unknown) alkylated PAHs.

260

261 **Equilibration of PAHs in experiments**

262 Initial analysis of all of the experiments revealed $\log K_{PEw}$ of the lower molecular weight
263 (LMW) PAHs increased with increasing $\log K_{ow}$, while compounds with $\log K_{ow}$ values above
264 4.5, depending on the experimental temperature and salinity, tended to level off and not continue
265 to increase as expected (Table S3 & S7). Since neither DOC nor solubility (Table S8) could
266 explain these results, we hypothesized that the higher MW (HMW) PAHs did not reach
267 equilibrium in these experiments. To verify this, the apparent PE-water distributions (K_{PEw} ,
268 apparent) of the PRCs and native PAHs were compared (Figure 2). The observed % equilibrium
269 was determined as:

$$270 \quad \text{PE-w \% equilibrium (obs)} = 10 \frac{[\log K_{PEw, \text{apparent}}(\text{native}) - \log K_{PEw, \text{apparent}}(\text{deuterated})]}{2} \times 100 \quad (6)$$

271 Naphthalene was equilibrated in all experiments (as evidenced by similar $\log K_{PEw}$ values
272 between the native and deuterated compound) regardless of temperature and salinity (Table S3).

273 Deuterated and native pyrene were in equilibrium for all experiments at 20 and 2 °C, but started
274 to diverge to 0.8 log units (-4 °C, 100 psu) and 3.1 log units (-15 °C, 245 psu) under colder and
275 saltier conditions (Figure 2 and S1). Benzo(a)pyrene was in equilibrium at the 20 °C
276 experiments, while it did not reach equilibrium in colder and higher salinity experiments. The
277 difference between native and deuterated benzo(a)pyrene reached more than 4 orders of
278 magnitudes at the coldest experiment. This served as evidence that the HMW PAHs, such as
279 pyrene and benzo(a)pyrene, had not reached equilibrium (Figure 2). Lower temperature
280 experiments were analyzed at time intervals one week apart. Overall, the % equilibrium of
281 pyrene and benzo(a)pyrene gently increased with increasing length of the experiments, but the
282 increase was not significant. For example, at the -4 °C experiment, the % equilibrium for pyrene
283 increased from 16% (21 days) via 18% (28 days) to 19% (35 days). For benzo(a)pyrene, the
284 increase was from 5.6% via 6.7% to 8.4% after 35 days.

285 Both decreasing temperature and increasing salinity affect water viscosity. Assuming that
286 the equilibration of PAHs was limited by the aqueous boundary layer, increasing the water's
287 viscosity should delay equilibration of PAHs, as they have to diffuse across a thicker layer. The
288 experimental set-up allowed us to observe both the effects of salinity and temperature on
289 kinetics, and assess their relative importance. The effect of temperature is clearly visible in
290 comparing the + 2 °C and -4 °C experiments, both performed at 100 psu. The 6 °C temperature
291 decrease slowed down equilibration of pyrene from 100% to 40%, and that of benzo(a)pyrene
292 from 11% to 1% (SI Figure S1). Increasing salinity (e.g., at 20 °C from 0 to 35 psu) slowed
293 down partitioning such that benzo(a)pyrene was only 72% equilibrated at the higher salinity.
294 Likewise, increasing the salinity from 0 to 100 psu at 2 °C reduced the equilibration of
295 benzo(a)pyrene from 56% to 11% (Figure 2).

296 We established a simple model to better understand the reasons for the slowed down
 297 equilibration of PAHs at lower temperature and increasing salinity. The model is similar to
 298 equation (22) in²⁶:

$$299 \quad \frac{1}{k_e} = \frac{1}{K_{PE-w} \times \delta_{PE}} \times \frac{1}{\frac{\delta_w}{D_w} + \frac{\delta_{PE} \times K_{PEw}}{D_{PE}}} \quad (7),$$

300 where

301 k_e is the *in situ* exchange rate constant (1/day),

302 δ_{PE} and δ_w are the thicknesses of the 1/2 PE sheet, and the water boundary layer (m), and

303 D_{PE} and D_w are the PAH's diffusivities in PE and water respectively (m²/s)

304 The predicted state of equilibrium was calculated as

$$305 \quad \% \text{ equilibrium (pred)} = (1 - e^{-k_e t}) \quad (8),$$

306 with time t in days

307

308 Our experiments were agitated with a stir bar, but as discussed elsewhere, this is not

309 necessarily sufficient to prevent diffusive control by an aqueous boundary layer.²⁶ We initially

310 assumed $\delta_w = 10 \mu\text{m}$ (δ_{PE} was $12.8 \mu\text{m}$) as an approximation of the boundary layer thickness in a

311 well stirred experiment (see Lohmann, 2012).²⁶ Values of D_{PE} were taken from²⁶ and K_{PE} from

312 this study. D_w was calculated based on the PAHs' molar volume, V_m , (from Fuller, in cm³/mol)

313 and the water's dynamic viscosity η (in centipoise)¹⁷:

$$314 \quad D_w = \frac{1.326 \times 10^{-4}}{V_m^{0.589} \times \eta^{1.14}} \quad (9)$$

315 The effect of temperature and salinity on η was calculated from equations (22) and (23) by

316 Sharqawy et al. (2010) for all experiments.³¹

317 The value of $\delta_w = 10 \mu\text{m}$ was a good choice for the experiments conducted at 20 °C at 0 psu, 20
318 °C at 35 psu and 2 °C at 0 psu, resulting in < 20 % difference between measured and predicted %
319 equilibrium (Figure 2 & Table S9). We predicted the water boundary layer thickness would
320 increase as the inverse of increasing dynamic viscosity. The D_{PE} values were left constant
321 throughout these model scenarios, as their temperature-dependency are currently unknown. The
322 glass transition temperature of polyethylene is around -125 °C³²; this should not affect the D_{PE}
323 values of the PAHs in the temperature range considered here. For our different experimental
324 conditions, we predicted δ_w to increase from an estimated 10 μm at 25 °C and 0 psu to over 64
325 μm at -15 °C and 245 psu (Table S9). Overall, this resulted in a decent agreement between
326 measurements and predictions, particularly for the experiments at 20 °C, 2 °C and -15 °C,
327 whereas the results obtained from the -4 °C experiments differed strongly from the predicted
328 results (Figure 2). At 25 °C (both 0 and 100 psu), and 2 °C (0 psu), model and measurements
329 agreed with < 20%. At 2 °C and 100 psu, pyrene was still well predicted, but benzo(a)pyrene
330 was predicted to be 43% equilibrated, while the experiments yielded 11%. At -4 °C, the model
331 overpredicted equilibration of benzo(a) pyrene by approximately 10-fold, and 5-fold for pyrene.
332 Fairly good agreement was again observed for the final experiments at -15 °C at 245 psu, where
333 the model (over) predicted equilibrium within a factor of 2 (benzo(a)pyrene) and 4 (pyrene) of
334 measured results.

335 These results suggest that changes in aqueous viscosity were the main driver slowing
336 down equilibrations in our experiments. We used equation (9) to assess the sensitivity of PAHs'
337 equilibration towards changes in their diffusivity in polyethylene. At 2 °C and below, the PAH's
338 diffusivity in polyethylene needed to decrease by 10^3 to 10^4 fold to significantly reduce
339 equilibration (i.e., outcompete limitation by δ_w). This suggests that the delay in equilibrating

340 PAHs in our experiments was entirely driven by changes in the water's viscosity, which in turn
341 affects both the PAHs' aqueous diffusivity and the thickness of the water boundary layer. The
342 PAH's diffusivity in the PE almost certainly decreased in the experiments (though it is unknown
343 by how much), but it was most likely not the rate-limiting step. We thus predict that PE
344 deployments in cold, saline water will have to deal with much increased equilibration times, and
345 that these are dictated by the properties of the water, much more so than by the PE properties
346 themselves. Lastly, we note that our experiments were stirred constantly, likely achieving fluid
347 movements well above those found in the oceans, suggesting that our equilibration times are
348 faster than can be observed in the field.

349

350 **Effects of Salinity and temperature on Equilibrium Partition coefficients**

351 Initially, we had performed these equilibration experiments to assess the effects of
352 temperature and salinity on equilibrium partition coefficients. Yet as detailed above, our results
353 highlighted the effect of water properties and severely impeded equilibrium in our experiments.
354 The corrections necessary to obtain equilibrium partition coefficients rendered any influences of
355 salinity and temperature difficult to tease out correctly.,

356 More work is needed to confirm whether there is an effect of size on K_s values, as
357 postulated by Ni and Yalkowski (2003)³³, but not observed by Jonker and Muijs (2010).³⁴
358 Similarly, it is unclear whether K_{PEW} values always increase with colder temperatures, as reported
359 by Adams et al. (2007). At least Booij et al. (2003) observed a decrease in K_{PEW} at lower
360 temperatures for HMW PAHs.

361

362 **Mock Oil Spill Experiment**

363 After 4 weeks of stirring, the PEs had approached equilibrium (94% for d-pyrene, 75%
364 for d-benzo(a)pyrene); no further correction was performed. The WSF for Statfjord crude oil was
365 composed mainly of LMW compounds, such as phenolic compounds, naphthalenes and
366 methylated-naphthalenes, which were similar to reports from previous studies (Table S10).¹⁹
367 Overall, 36 of the 41 compounds investigated in this study were detected. Naphthalene, methyl-
368 naphthalenes and biphenyl were present in concentrations in the single to tens of µg/L range.
369 Phenanthrene, methylphenanthrene and fluorene were just below 1 µg/L. Very few HMW
370 compounds (>200 g/mol) were present in significant concentrations in the WSF of the Statfjord
371 crude oil, confirming previous results (Table S10).¹⁹ In contrast to other WSF studies, PAH
372 concentrations in our study were not above their subcooled-liquid solubilities in seawater at 5
373 °C.³⁵

374 Overall, there was good agreement for total PAH concentrations between the two
375 methods. Liquid-liquid extraction yielded 85 µg/L of total PAHs, while PE-based concentrations
376 were 66 µg/L. The difference was mostly due to naphthalene results between the two
377 approaches. A closer look at the results revealed an increasing underestimation of passive
378 sampler results with increasing MW of the PAHs (Figure 3; Figure S2). We used filtered
379 seawater, in which DOC was present at 5 mg/L in the experiments. The partitioning of PAHs to
380 DOC is defined as:

381
$$K_{DOCw} = \frac{C_{DOC}}{C_w} \quad (10),$$

382 where K_{DOCw} is the equilibrium partitioning constant for PAHs between DOC and water,
383 and C_{DOC} is the DOC-bound PAH concentration. We corrected for this third phase effect by

384 assuming average partitioning of PAHs to DOC ($\log K_{\text{DOC}} = 1.18 \log K_{\text{ow}} - 1.56$)³⁶ according to
385 equation (11)

$$386 \quad C_{w,\text{corr}} = \frac{C_{w,\text{app}}}{1 + [\text{DOC}]K_{\text{DOC}w}} \quad (11),$$

387 in which [DOC] is in kg/L, and

388 $C_{w,\text{corr}}$ is the DOC-corrected apparent dissolved PAH concentration ($C_{w,\text{app}}$).

389 For PAHs with a $\log K_{\text{ow}} \leq 5$, both conventional sampling and PE sampling agreed mostly within
390 a factor of 2 (Figure SI 4). For almost all PAHs with a $\log K_{\text{ow}} > 5$ (or MW > 200), PE-based
391 results accounted for less than 50% of liquid-liquid results. While the DOC correction improved
392 the comparison, it was not sufficient to align results for PAHs with higher MW (SI Figure S2).

393 Results in Figure 3 could imply that the estuarine DOC in our seawater displayed a
394 significant higher affinity for PAHs than the mostly freshwater DOCs included in Burkhard's
395 (2000) review.³⁶ A similar conclusion was previously reached by Friedman et al. (2011) who
396 reported that polychlorinated biphenyls (PCBs) in the New Bedford Harbor estuary sorbed 5 – 20
397 times stronger to DOC than predicted.³⁷ We included results for the DOC-correction of apparent
398 dissolved PAH concentrations from liquid-liquid extraction assuming that DOC sorbed PAHs 5 –
399 times stronger than predicted by Burkhard³⁶, resulting in better agreement between higher MW
400 PAHs from both methods.

401 Overall there was good agreement between the PE samplers and the (DOC-corrected)
402 extracted water concentrations for the most abundant PAHs (Figure 3), mostly within a factor of
403 2. Our experiments highlighted once more the challenge of having other phases, such as DOC
404 present, which greatly exaggerate apparent dissolved concentrations from liquid-liquid
405 extractions.

406

407 **Winter deployment in Narragansett Bay water, RI (USA)**

408 PE field deployments were carried out under quiescent water flow conditions in a tank
409 with flowing seawater to be able to easily sample the water on a daily basis. Unfortunately, this
410 resulted in much reduced sampling rates (R_s) compared to previous deployments in Narragansett
411 Bay (Table S11). The R_s was determined by evaluating the loss rate of the PRCs. Based on loss
412 of d_{12} -pyrene, R_s ranged from 3 – 7 L/day, while they were around 20 L/day (for pyrene) in
413 previous field deployments in Narragansett Bay.¹⁴ These low sampling rates effectively
414 prevented us from observing a significant loss of d_{12} -benzo(a)pyrene. The predicted loss of
415 benzo(a)pyrene based on a sampling rate of 3 – 7 L/day is only around 1% after 3 weeks, or
416 much smaller than our analytical uncertainty.

417 Results from active sampling implied that apparently dissolved concentrations increased
418 after the first sampling week but remained fairly constant in weeks 2 and 3 (Table S12). Typical
419 concentrations were at or below 1 ng/L for fluorene, phenanthrene, and methyl-pyrene, 2 ng/L
420 for fluoranthrene and around 6 ng/L for pyrene (Figure 4), in line with previous results for
421 Narragansett Bay water.¹⁴

422 Truly dissolved PAH concentrations calculated from PE-deployments decreased over
423 time, with increasing certainties of results (Table S13). For the three week deployments, we
424 deduced concentrations of below 1 ng/L for fluorene, phenanthrene and methyl-pyrene, 2.5 ng/L
425 for fluoranthrene and 8.6 ng/L for pyrene. For these 5 representative PAHs, the agreement
426 between active and passive sampling increased from a 30-fold difference (week 1) to 1.4 times
427 (week 2) to within a factor of 1.1. Clearly, deployment times of 2 weeks or more were needed
428 under these quiescent flow conditions to arrive at satisfactory results for the passive samplers.

429 Within a 3-week deployment window, though, very good agreement was observed between both
430 approaches.

431

432 **Implications**

433 Our results imply that PE samplers can be used to detect both the parent PAHs, as
434 observed in previous studies, but also a wide range of alkylated PAHs. K_{PEW} for unknown
435 alkylated PAHs can be approximated by adding 0.40 (± 0.24) log units per alkylated carbon to
436 the log K_{PEW} of the parent PAH. Our experiments were aimed at verifying the use of passive
437 samplers in ice brine, but our results suggest that equilibration in brines below 0 °C is extremely
438 slow. We investigated these results with a diffusion model. The results suggest that the
439 equilibration is limited by a decrease of the kinematic viscosity, rather than changes of the
440 PAHs' diffusivity in the PE itself. This in turn implies that it will probably affect all passive
441 samplers and most compounds of interest. In open ocean deployments, a decrease of the
442 kinematic viscosity will also lead to a marked slowing down of equilibrations. Including PRCs in
443 PE samplers prior to deployments proved essential for our laboratory work to determine the lack
444 of equilibration, and will be equally important to correct for non-equilibrium under field
445 conditions. The pre-loading of PRCs, as reported by Booij et al. (2002) works well in that regard.
446 ¹⁵ Extra matrix and field blanks then serve to determine initial PRC concentrations, which are
447 used to fit a 1-dimensional loss model to the field data. Lastly, we validate the use of PE
448 samplers both for a mock oil spill in the laboratory and under field conditions. Our results
449 suggest that PE samplers are a valuable asset when studying areas without known PAH
450 contamination sources, representing low background concentrations, and can determine the PAH
451 concentrations present in the water column under unique conditions.

452

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459 and ice cores'

460

461 **Supporting Information Available**

462 Additional information on results comparison, figures, and tables were included in the
463 Supporting Information section. This information is available free of charge via the Internet at
464 <http://pubs.acs.org/>.

465

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571
572

Table 1: Log K_{PEW} (L/kg) of parent and alkylated PAHs (determined at 20 °C at 0 psu), number of aromatic and alkylated carbon, calculated individual aromatic and alkyl atom contribution to the log K_{PEW} values

PAHs	Log $K_{PEW, meas}$	N ^o C _{arom}	N ^o C _{alkyl}	C _{arom}	C _{alkyl}
Naphthalene	3.67	10		0.37	
Biphenyl	3.72	10		0.37	
Acenaphthylene	3.17	12		0.33	
Dibenzothiophene	4.27	13		0.33	
Phenanthrene	4.39	14		0.31	
Anthracene	4.43	14		0.32	
Fluoranthene	5.09	16		0.32	
Pyrene	5.22	16		0.33	
Chrysene	5.91	18		0.33	
Benz(a)anthracene	5.91	18		0.33	
Benzo(b)fluoranthene	6.36	18		0.35	
Benzo(h)fluoranthene	6.56	18		0.36	
Benzo[a]pyrene	6.81	20		0.34	
Perylene	6.71	20		0.34	
Indeno(1,2,3-c,d)pyrene	6.47	22		0.29	
Dibenzo(a,h)anthracene	6.76	22		0.31	
Benzo(g,h,i)perylene	6.37	22		0.29	
2-Methyl naphthalene	3.66	10	1		-0.01
acenaphthene	3.74	10	1		0.07
4,5-Methylene phenanthrene	4.70	14	1		0.31
Fluorene	3.75	12	1		0.08
2-Methyl dibenzothiophene	4.74	13	1		0.47
1-Methyl phenanthrene	4.92	14	1		0.53
9-Methyl anthracene	4.92	14	1		0.49
2-Methyl fluorene	4.53	13	1		0.77
1-Methyl pyrene	5.74	16	1		0.51
1-Methyl chrysene	6.52	18	1		0.61
1,5-Dimethyl naphthalene	4.17	10	2		0.25
3,6-Dimethyl phenanthrene	5.36	14	2		0.49
1,2-Dimethyl dibenzothiophene	4.93	13	2		0.33
7,12-Dimethyl benz(a)anthracene	6.55	18	2		0.32
2,3,5-Trimethyl naphthalene	4.61	10	3		0.31
2-isopropyl naphthalene	4.32	10	3		0.22
9-Ethyl fluorene	4.33	12	3		0.29
1,2,5/1,2,7-Trimethyl phenanthrene	6.36	14	3		0.65
2,4,7-Trimethyl dibenzothiophene	6.57	13	3		0.76
1,4,6,7-Tetramethyl naphthalene	5.01	10	4		0.34
1,2,5,6-Tetramethyl naphthalene	4.98	10	4		0.33
9-n-Propyl fluorene	5.23	12	4		0.49
Retene	6.46	14	4		0.52
2,6-Diisopropyl naphthalene	6.04	10	6		0.40

Figure 1: $\log K_{PEW}$ (L/kg) versus $\log K_{ow}$ of selected PAHs from the literature^{6,7,23,24,38} and those measured in this study at 20 °C, 0 psu for 28 days.

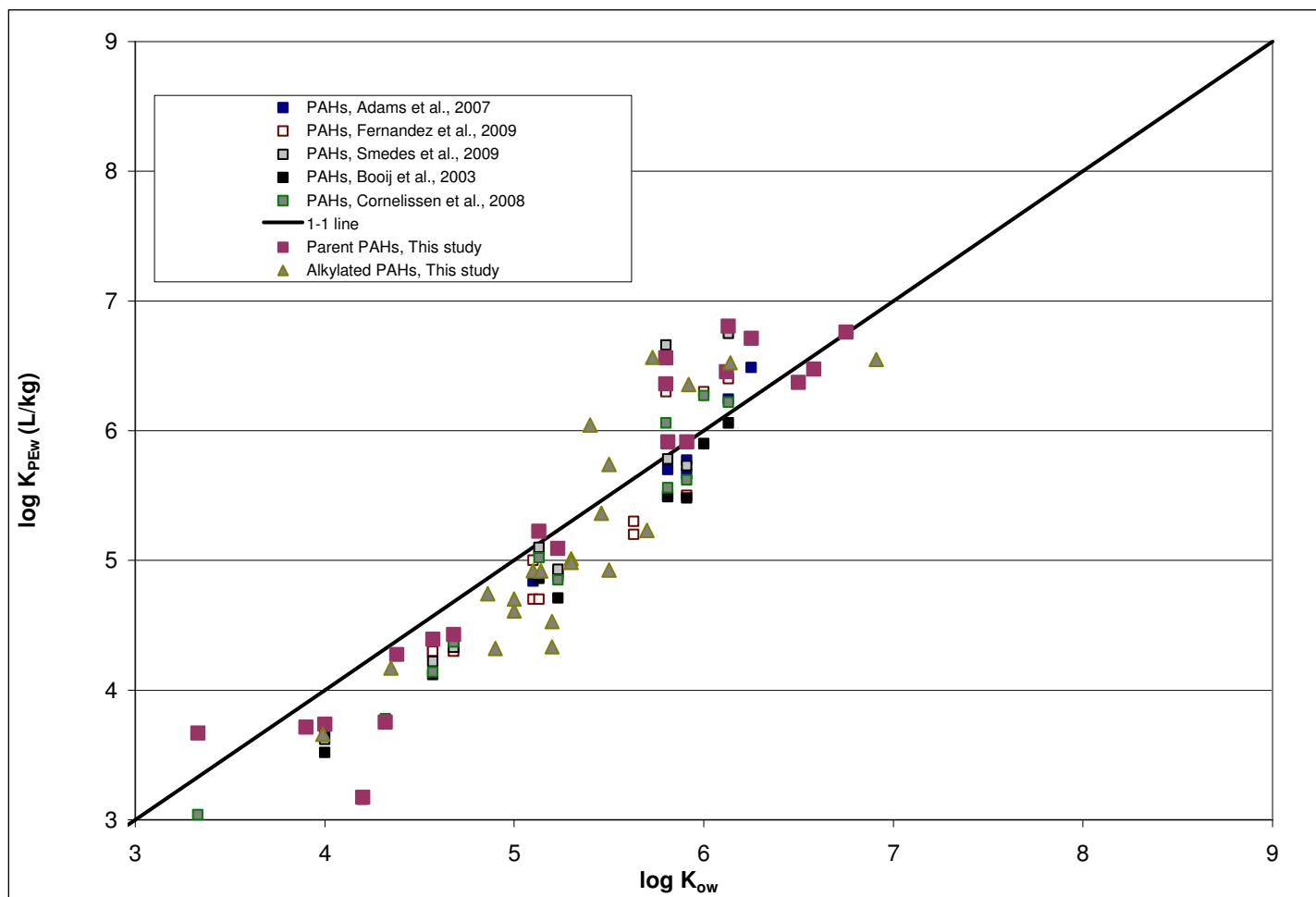
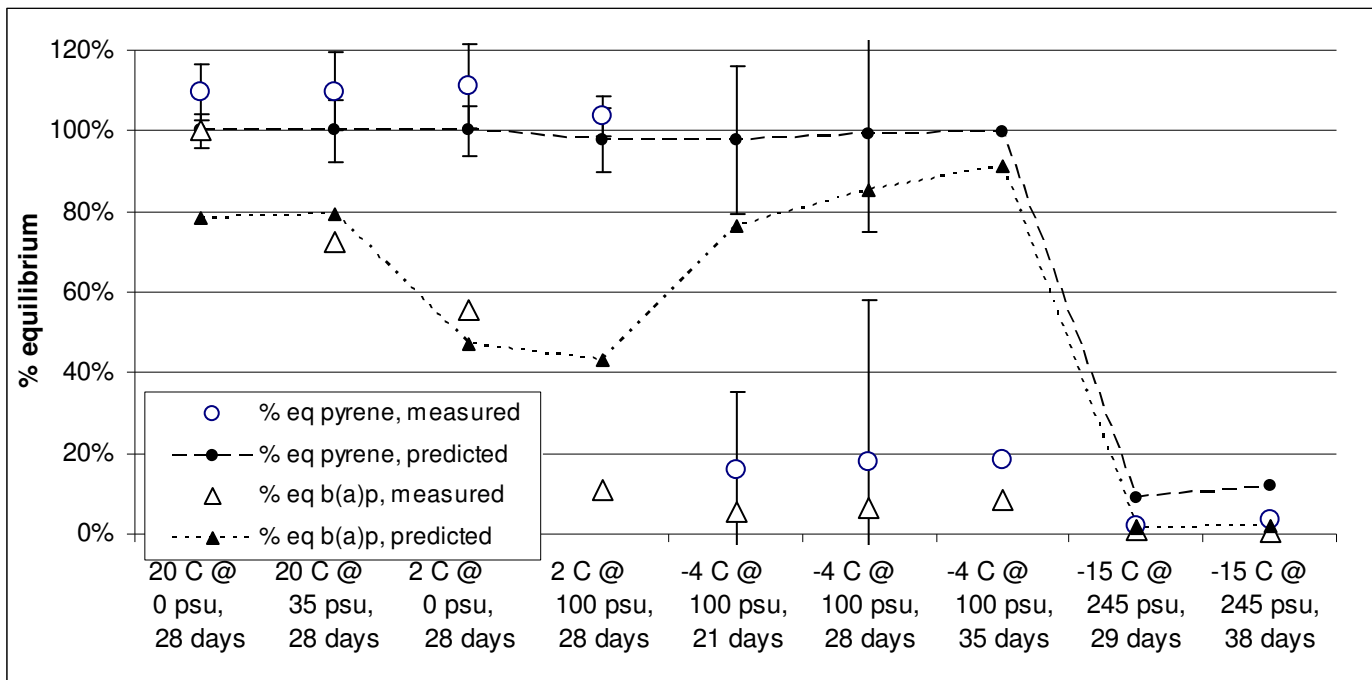
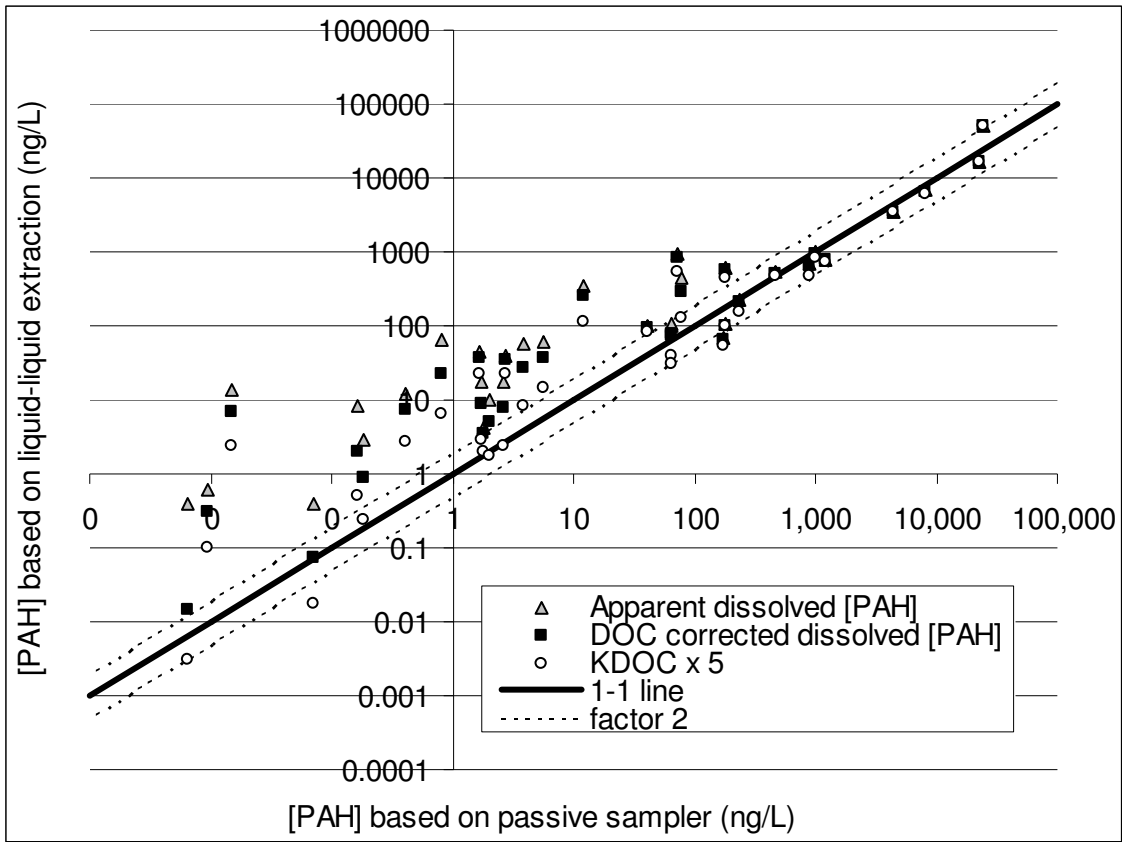


Figure 2: Predicted versus measured (difference between native and deuterated) % equilibrium for pyrene and benzo(a)pyrene during PE experiments at decreasing temperature and increasing salinity

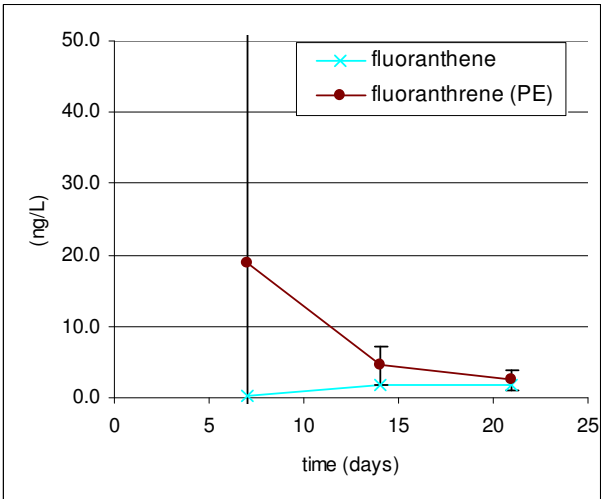
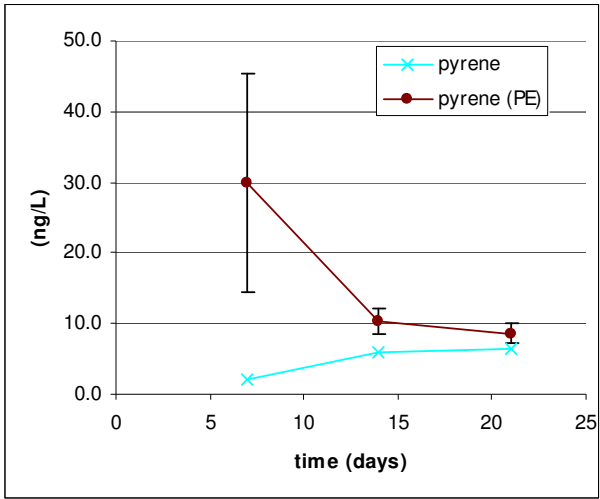
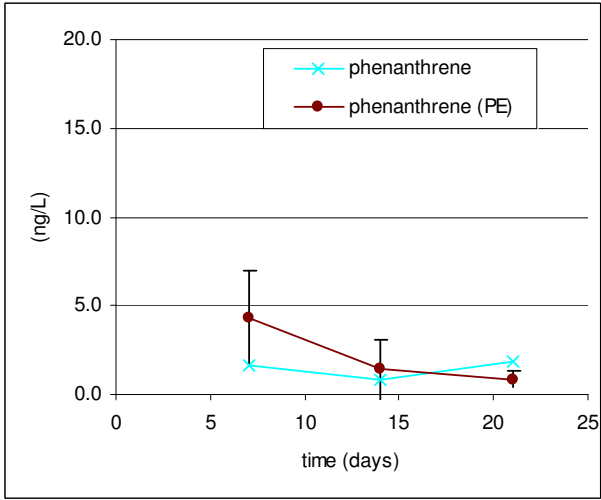
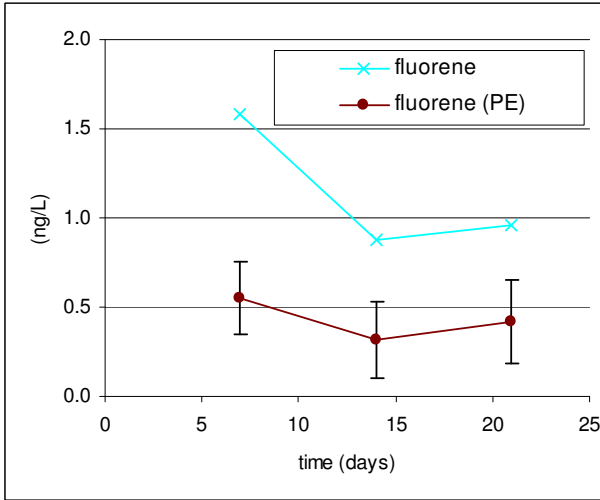


1 **Figure 3: Comparison of PAH concentrations from a mock oil spill (5 °C, 30 psu): PE-**
2 **based results versus apparent and DOC-corrected PAH concentrations from liquid-liquid**
3 **extraction.**
4



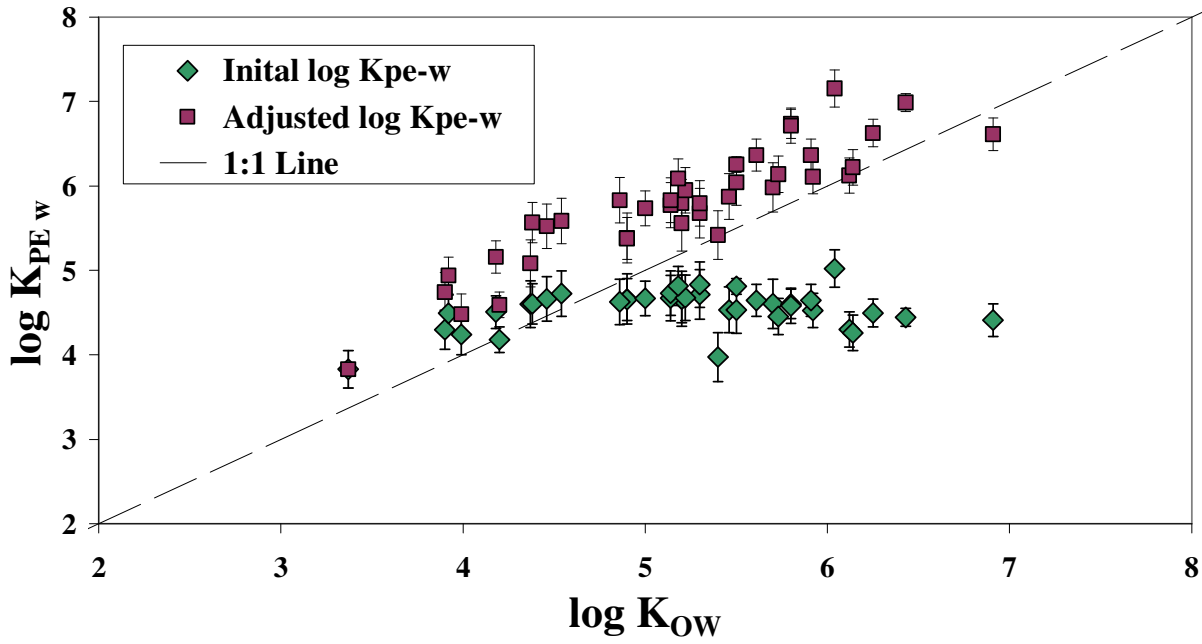
5

6 **Figure 4: Concentrations of selected PAHs (ng/L) in Narragansett Bay water (December**
 7 **2012) from PE-deployments versus weekly active sampling: (a) fluorene; (b) phenanthrene;**
 8 **(c) pyrene; (d) fluoranthene**
 9



10
 11
 12

**log K_{PEW} s of PAHs at -15 °C & 245 psu after
5 weeks of stirring**



14

15