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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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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Abstract

Passive samplers can be useful tools to determine truly dissolved concentrations of organic contaminants in the water. Polyethylene (PE) samplers were validated for measuring polycyclic aromatic hydrocarbons (PAHs), with a focus on alkylated PAHs that can dominate in an oil spill. Equilibrium partition coefficients ($K_{PEw}$) between water and PE passive samplers were measured for 41 PAHs both at ambient conditions (20 °C, no salt), down to -15 °C and 245 psu present in ice brine. For each additional alkylated carbon, $\log K_{PEw}$ increased by an average of 0.40 (± 0.20) log units, close to predictions. The increase per aromatic carbon was only 0.33 (± 0.02) log units. Apparent PE-water distributions of pyrene and deuterated pyrene (performance reference compound) were within 0.1 log unit for all experiments at 20 and 2 °C, but started to diverge by 0.8 log units (-4 °C, 100 psu) and 3.1 log units (-15 °C, 245 psu). The delay in equilibrating PAHs in these experiments was dominated by increases in the water’s viscosity, which in turn affected both the PAHs’ aqueous diffusivity and the thickness of the water boundary layer.
simulated marine oil spill in the laboratory, PE-based results were within a factor of 2 for the 
most abundant PAHs compared to conventional sampling results.

INTRODUCTION

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

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

Equilibrium partition coefficients between polyethylene (PE) and water ($K_{PEw}$) are 
generally determined in the laboratory under standard conditions (298 K, no salt) and are used to
relate the passive sampler concentration ($C_{PE}$) to the dissolved concentration in the water column ($C_W$; equation 1):

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

$K_{PEw}$ is the ratio of the concentration of the compound in the passive sampler (e.g., ng/µL) over the concentration of the compound in the water (e.g., ng/µL) under standard conditions. Once the $K_{PEw}$ is known for a compound and a PE is equilibrated in the environment (or corrected for non-equilibrium), the concentration of the compound in water (i.e., truly dissolved) can then be calculated from equation (1). $K_{PEw}$ can be corrected for a temperature other than 298 K by using the van’t Hoff equation. To account for the effects of dissolved salts on $K_{PEw}$, the empirical Setschenow constant ($K_S$) and the molar concentration of salt [salinity], present in the water, are used. Both of these equations have been proven reliable at moderate temperatures (30°C to 2°C) and salinities (0 to 36.7 psu).

Passive samplers are a useful alternative to conventional direct measurement of environmental phases (i.e. liquid-liquid extraction), such as water and sediment to derive bioaccumulation and bioavailability. Unlike direct measurements, passive samplers only sample the truly dissolved or bioavailable fraction present in the water. Chemicals sorbed to particles or colloids in the water column are not directly bioavailable (i.e., for passive uptake) and are difficult to separate from the truly dissolved and bioavailable chemicals, such as PAHs. Thus, when water is sampled for PAHs using conventional methods, the dissolved concentrations are often overestimated due to the inclusion of PAHs associated with colloids. Passive samplers are also a preferred method for measuring PAHs for their ease of sampling, lower detection limits in the field, and minimization of contaminated blanks. Conventional methods of water analysis take samples at a discrete point in time, representing the concentration only at that time, while
the time averaged concentration determined from passive sampling is a more appropriate
reflection of the longer-term exposure in the environment. Passive samplers can often be an
inexpensive and reliable option compared to conventional methods.\textsuperscript{12}

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

\textbf{MATERIALS & METHODS}

\textbf{PAHs}

Forty-one native PAHs that are commonly present in oil were identified and used to
prepare a laboratory standard curve ranging from lower molecular weight components (e.g.,
naphthalene) to compounds of higher molecular weight (e.g., chrysene and benzo(a)pyrene)
(Table S1). These standards were prepared by from individual PAHs purchased from certified
laboratories (Table S2). Twenty-five of these were alkylated PAHs, as they are commonly found
in oil, however there is little research available for these compounds. Additionally, three
deuterated PAHs (naphthalene-d$_8$, pyrene-d$_{10}$, benzo[a]pyrene-d$_{12}$) were utilized as Performance
Reference Compounds (PRCs).
PE samplers

For all experiments, 25 µm thick PE, manufactured by a commercial sheeting company (Carlisle Plastics, Inc., Minneapolis, MN, USA), was purchased from a local hardware store. Passive samplers were pre-cleaned in dichloromethane (DCM) twice prior to use. The passive samplers were enriched with PRCs with methods modified from Booij et al (2002) (see SI). For the laboratory portion of the study, PEs were cut into small pieces with a mass of approximately 0.09 mg (ca. 1 cm²). Once samplers were retrieved from the various experiments, they were extracted in DCM and hexane (1:1 v/v), with internal surrogates added at the time of extraction. The extracts were then concentrated under a flow of nitrogen gas. Injection standard (external standard) was added prior to analysis with gas chromatography/mass spectrometry (GC/MS) (Agilent, Santa Clara, CA, USA) (see Supporting Information). To validate the GC/MS analysis, a National Institute of Standards and Technology (NIST) PAH standard 2260a was used to calibrate the in-house PAH standard curve (see Supporting Information).

Polyethylene-water partition coefficients, \( K_{PEw} \)

Experimental equilibrium partition coefficients were determined in the laboratory for various PAHs (Table S3). In climate controlled rooms, tests were performed to cover the range of temperatures and salinities commonly found in the marine environment, especially conditions present in the Arctic environment and the brine present within ice (see SI and Table S3). Water samples were prepared at various salinities (245, 100 and 35 psu) by using pure water (18.2 MΩ cm⁻¹ Milli-Q® filtered water) and Instant Ocean® or Sigma-Aldrich salt mixture, which both mimic the composition of natural seawater. PEs were prepared in triplicate along with a blank.
and placed in 1 L pre-cleaned amber jars filled with water of the various salinities. The six replicate samples were then spiked with a mixture of the 41 oil components in nonane. To facilitate faster equilibrium times, flasks with PEs were stirred to mimic a very turbulent situation in the natural environment. After spiking with PAH mixture (approximately 10 to 90 ng depending on the PAH (Table S1)), each replicate was stirred for approximately 24 hours prior to adding the PE sampler. Experiments were run for various time periods to determine if equilibrium was reached (Table S4).

The concentrations of the PAHs in the passive samplers (Table S5) and the water were determined and the $K_{PEw}$ calculated for each compound in each experiment. Experimentally derived $K_{PEw}$ were compared to $K_{PEw}$ found in the literature and corrected for changes in temperature and salinity encountered in all experiments using the van’t Hoff and Setschenow correction, respectively.\textsuperscript{17}

Mock oil spill experiment

For the mock oil spill experiment, Statfjord crude oil was employed, the composition of which had been previously studied.\textsuperscript{18,19} The water soluble fraction (WSF) of the oil was prepared utilizing filtered natural seawater (Narragansett Bay) by the methods established by the Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF) proceedings (see SI).\textsuperscript{18,19} To prevent biological alteration of the WSF, sodium azide was added to the sea water to act as a biocide. The PE samplers were then exposed to the oil WSF at a temperature of 5°C in an environmental chamber and allowed to reach equilibrium for four weeks. The flasks with PE samplers were stirred on stir plates to facilitate faster equilibrium times. The passive samplers were removed from the water and the PAH concentrations in both PE and water were
determined. The experimentally derived $K_{PEw}$ (2°C at 0 psu) were adjusted for the effects of salinity and used to calculate the freely dissolved PAH concentration of the oil WSF and compared to the liquid-liquid extraction results. In a follow-up experiment, triplicate dissolved organic carbon (DOC) samples were collected weekly over 3 weeks. They were filtered (Millipore type RA, 1.2 µm), acidified to pH 2 and refrigerated until analysis on a Shimadzu TOC-V CPH total organic carbon analyzer.

**Sampling of Narragansett Bay Water for PAHs**

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

Polyethylene samplers measuring ca. 0.1 m x 0.40 m x 51 µm (ca. 2 g each) were prepared as a single batch by first cleaning (24 hours in acetone and hexane each) and then impregnating with performance reference compounds, as above. The samplers were each strung on a stainless steel wire and wrapped individually in muffled aluminum foil until deployed. PE samplers were suspended in the water on ropes in 3 groups of 3. One group of PEs was collected at one week intervals for 3 weeks, rewrapped in the aluminum foil and stored in a freezer (-20 °C) until analyzed.
Conventional sampling for PAHs consisted of pumping approximately 15-L at 1 L/min through a glass fiber filter (Watman GF/F) and then through tandem polyurethane foam (PUF) plugs. This was completed once to per day at the same time each day to track changes in PAH concentrations throughout the tidal cycle. Filters and PUFs were changed weekly in conjunction with collection of the PE strips and stored at -20 °C until analyzed. PUF plugs and PE samplers were then analyzed for PAHs (see SI).

RESULTS & DISCUSSION

The experimental log $K_{ PEw }$ results determined at 20 °C at 0 psu were plotted against the PAHs’ octanol-water partition coefficient ($K_{ ow }$) (Figure 1, Table S3). As expected, the experimentally determined log $K_{ PEw }$ values increased with increasing molecular weight and log $K_{ ow }$, except for acenaphylene (log $K_{ PEw } = 3.17$; log $K_{ ow } = 4.2$). Above log $K_{ ow }$ of 5.5, measured $K_{ PEw }$ values of PAHs often exceeded their respective log $K_{ ow }$ values. In general, measured values were within a factor of two (average 71%) of log $K_{ ow }$ values (Table S3). Exceptions were several alkylated PAHs that were greater than 2-times below their respective $K_{ ow }$ values (e.g., 2-isopropynaphthalene, 9-ethylfluorene, 2-methylfluorene, and 1,2-dimethyldibenzothiophene), while the few compounds greater than 2-times above $K_{ ow }$ were mostly higher molecular weight parent PAHs (2,6-diisopropynaphthalene, 2,4,7-trimethyldibenzothiophene, benzo(b)fluoranthene, benzo(h)fluoranthene and benzo[a]pyrene). In the case of the alkylated PAHs, appropriate $K_{ ow }$ literature values were difficult to find; calculations had at times to rely on relationships developed for parent PAHs (e.g., Ma et al., 2010). The deuterated PAHs used as PRCs (naphthalene-$d_8$, pyrene-$d_{10}$, benzo[a]pyrene-$d_{12}$),
showed good agreement with the non-deuterated PAHs, indicating equilibrium had been reached in the 20 °C at 0 psu experiments (Table S3).

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

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

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

with a high $R^2$ of 0.92 and low standard error (SE) of 0.27. Focusing only on the parent PAHs, including those from this study, and utilizing log $K_{ow}$ values from, the strong linear agreement remains:

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

To include the alkylated PAHs studied in this data set, log $K_{ow}$ values had to be determined. Building upon the parent log $K_{ow}$ values, values were added for each methyl group of the alkylated compounds. All the PAHs included in this study were then incorporated in the data set, resulting in (Figure 1):

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

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

The understudied alkylated PAHs were the particular interest to this study, as they could be important contributors to the toxicity of oil. In a recent atmospheric field study, Khairy and Lohmann (2012) reported that tri and tetra-alkylated PAHs partitioned differently into PEs than predicted based on correlations with parent PAHs. It was unclear at the time whether this
reflected inherent physico-chemical partitioning, was due to sampling bias or a higher reactivity
of the higher alkylated PAHs.

In this study, the log $K_{PEw}$ of C$_1$-alkylated PAHs increased by an average of 0.38 log units
compared to the log $K_{PEw}$ of the parent PAH. As the number of alkylated carbons increased, so
did the difference from the parent (Table 1). With 2 alkylated carbons, the log $K_{PEw}$ values
increased by an average of 0.67 log units, while with 4 alkylated carbons the difference grew to
an average of 1.57 log units. Overall, this suggests that for each additional alkylated carbon, the
log $K_{PEw}$ increases by an average of 0.40 ($\pm$ 0.20) log units relative to the unsubstituted parent
PAH (n=25). For parent PAHs, the average contribution of each aromatic carbon was 0.33 ($\pm$
0.02) log units (n=20). In recent work, Choi et al. (2013) reported the carbon contribution
towards log $K_{PEw}$ as 0.313 (aromatic) and 0.461 (aliphatic), very similar to the results obtained
here. Our values are also in good agreement with the atom/fragment addition method
developed by Meyland and Howard (1995), who reported an increase of 0.49 (-CH$_2$) and 0.55
log units (-CH$_3$) for alkylated carbon and 0.29 for aromatic carbon in predicting log $K_{ow}$ values. This further supports the similarity of partitioning of nonpolar fragments between octanol and
polyethylene, as manifested in roughly similar log $K_{ow}$ and log $K_{PEw}$ values.

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

$$\log K_{PEw, pred} = 0.95(\pm 0.05) \log K_{PEw, meas} + 0.30(\pm 0.25) \left( r^2=0.91, SE=0.40, n=41 \right) (5)$$
Other approaches have been developed to correlate and predict passive sampler partitioning values that go beyond an atom or fragment contribution approach, most notably the poly-parameter linear free energy relationships (pp-LFER). These are essential for understanding and predicting the partitioning of (a)polar compounds with complex polymers (those with interactions beyond van-der-Waals interactions). Yet in the case of PE, we note that the vast majority of partitioning data has been reported for apolar or weakly polar molecules. This renders pp-LFER approaches for PE difficult to derive. As PE can only interact via van-der-Waals interactions, we deem the above simple carbon addition model appropriate for the task of predicting $\log K_{PEw}$ for (unknown) alkylated PAHs.

Equilibration of PAHs in experiments

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

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

Naphthalene was equilibrated in all experiments (as evidenced by similar $\log K_{PEw}$ values between the native and deuterated compound) regardless of temperature and salinity (Table S3).
Deuterated and native pyrene were in equilibrium for all experiments at 20 and 2 °C, but started to diverge to 0.8 log units (-4 °C, 100 psu) and 3.1 log units (-15 °C, 245 psu) under colder and saltier conditions (Figure 2 and S1). Benzo(a)pyrene was in equilibrium at the 20 °C experiments, while it did not reach equilibrium in colder and higher salinity experiments. The difference between native and deuterated benzo(a)pyrene reached more than 4 orders of magnitudes at the coldest experiment. This served as evidence that the HMW PAHs, such as pyrene and benzo(a)pyrene, had not reached equilibrium (Figure 2). Lower temperature experiments were analyzed at time intervals one week apart. Overall, the % equilibrium of pyrene and benzo(a)pyrene gently increased with increasing length of the experiments, but the increase was not significant. For example, at the -4 °C experiment, the % equilibrium for pyrene increased from 16% (21 days) via 18% (28 days) to 19% (35 days). For benzo(a)pyrene, the increase was from 5.6% via 6.7% to 8.4% after 35 days.

Both decreasing temperature and increasing salinity affect water viscosity. Assuming that the equilibration of PAHs was limited by the aqueous boundary layer, increasing the water’s viscosity should delay equilibration of PAHs, as they have to diffuse across a thicker layer. The experimental set-up allowed us to observe both the effects of salinity and temperature on kinetics, and assess their relative importance. The effect of temperature is clearly visible in comparing the + 2 °C and -4 °C experiments, both performed at 100 psu. The 6 °C temperature decrease slowed down equilibration of pyrene from 100% to 40%, and that of benzo(a)pyrene from 11% to 1% (SI Figure S1). Increasing salinity (e.g., at 20 °C from 0 to 35 psu) slowed down partitioning such that benzo(a)pyrene was only 72% equilibrated at the higher salinity. Likewise, increasing the salinity from 0 to 100 psu at 2 °C reduced the equilibration of benzo(a)pyrene from 56% to 11% (Figure 2).
We established a simple model to better understand the reasons for the slowed down equilibration of PAHs at lower temperature and increasing salinity. The model is similar to equation (22) in:

\[
\frac{1}{k_e} = \frac{1}{K_{PE-w} \times \delta_{PE}} \times \frac{1}{\frac{\delta_{w} \times \delta_{PE} \times K_{PEw}}{D_{w}} + \delta_{w} \times K_{PEw}}
\]  

(7),

where

- \( k_e \) is the *in situ* exchange rate constant (1/day),
- \( \delta_{PE} \) and \( \delta_{w} \) are the thicknesses of the \( \frac{1}{2} \) PE sheet, and the water boundary layer (m), and
- \( D_{PE} \) and \( D_{w} \) are the PAH’s diffusivities in PE and water respectively (m\(^2\)/s)

The predicted state of equilibrium was calculated as

\[
\% \text{ equilibrium (pred)} = (1 - e^{-k_e t})
\]  

(8),

with time \( t \) in days

Our experiments were agitated with a stir bar, but as discussed elsewhere, this is not necessarily sufficient to prevent diffusive control by an aqueous boundary layer. We initially assumed \( \delta_{w} = 10 \) µm (\( \delta_{PE} \) was 12.8 µm) as an approximation of the boundary layer thickness in a well stirred experiment (see Lohmann, 2012). Values of \( D_{PE} \) were taken from and \( K_{PE} \) from this study. \( D_{w} \) was calculated based on the PAHs’ molar volume, \( V_m \), (from Fuller, in cm\(^3\)/mol) and the water’s dynamic viscosity \( \eta \) (in centipoise):

\[
D_w = \frac{1.326 \times 10^{-4}}{V_m^{0.589} \times \eta^{1.14}}
\]  

(9)

The effect of temperature and salinity on \( \eta \) was calculated from equations (22) and (23) by Sharqawy et al. (2010) for all experiments.
The value of $\delta_w = 10 \, \mu m$ was a good choice for the experiments conducted at 20 °C at 0 psu, 20 °C at 35 psu and 2 °C at 0 psu, resulting in < 20% difference between measured and predicted % equilibrium (Figure 2 & Table S9). We predicted the water boundary layer thickness would increase as the inverse of increasing dynamic viscosity. The $D_{PE}$ values were left constant throughout these model scenarios, as their temperature-dependency are currently unknown. The glass transition temperature of polyethylene is around -125 °C; this should not affect the $D_{PE}$ values of the PAHs in the temperature range considered here. For our different experimental conditions, we predicted $\delta_w$ to increase from an estimated 10 µm at 25 °C and 0 psu to over 64 µm at -15 °C and 245 psu (Table S9). Overall, this resulted in a decent agreement between measurements and predictions, particularly for the experiments at 20 °C, 2 °C and –15 °C, whereas the results obtained from the -4 °C experiments differed strongly from the predicted results (Figure 2). At 25 °C (both 0 and 100 psu), and 2 °C (0 psu), model and measurements agreed with < 20%. At 2 °C and 100 psu, pyrene was still well predicted, but benzo(a)pyrene was predicted to be 43% equilibrated, while the experiments yielded 11%. At -4 °C, the model overpredicted equilibration of benzo(a)pyrene by approximately 10-fold, and 5-fold for pyrene. Fairly good agreement was again observed for the final experiments at -15 °C at 245 psu, where the model (over) predicted equilibration within a factor of 2 (benzo(a)pyrene) and 4 (pyrene) of measured results.

These results suggest that changes in aqueous viscosity were the main driver slowing down equilibrations in our experiments. We used equation (9) to assess the sensitivity of PAHs’ equilibration towards changes in their diffusivity in polyethylene. At 2 °C and below, the PAH’s diffusivity in polyethylene needed to decrease by $10^3$ to $10^4$ fold to significantly reduce equilibration (i.e., outcompete limitation by $\delta_w$). This suggests that the delay in equilibrating
PAHs in our experiments was entirely driven by changes in the water’s viscosity, which in turn affects both the PAHs’ aqueous diffusivity and the thickness of the water boundary layer. The PAH’s diffusivity in the PE almost certainly decreased in the experiments (though it is unknown by how much), but it was most likely not the rate-limiting step. We thus predict that PE deployments in cold, saline water will have to deal with much increased equilibration times, and that these are dictated by the properties of the water, much more so than by the PE properties themselves. Lastly, we note that our experiments were stirred constantly, likely achieving fluid movements well above those found in the oceans, suggesting that our equilibration times are faster than can be observed in the field.

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

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

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

**Mock Oil Spill Experiment**
After 4 weeks of stirring, the PEs had approached equilibrium (94% for d-pyrene, 75% for d-benzo(a)pyrene); no further correction was performed. The WSF for Statfjord crude oil was composed mainly of LMW compounds, such as phenolic compounds, naphthalenes and methylated-naphthalenes, which were similar to reports from previous studies (Table S10). Overall, 36 of the 41 compounds investigated in this study were detected. Naphthalene, methyl-naphthalenes and biphenyl were present in concentrations in the single to tens of µg/L range. Phenanthrene, methylphenanthrene and fluorene were just below 1 µg/L. Very few HMW compounds (>200 g/mol) were present in significant concentrations in the WSF of the Statfjord crude oil, confirming previous results (Table S10). In contrast to other WSF studies, PAH concentrations in our study were not above their subcooled-liquid solubilities in seawater at 5°C. Overall, there was good agreement for total PAH concentrations between the two methods. Liquid-liquid extraction yielded 85 µg/L of total PAHs, while PE-based concentrations were 66 µg/L. The difference was mostly due to naphthalene results between the two approaches. A closer look at the results revealed an increasing underestimation of passive sampler results with increasing MW of the PAHs (Figure 3; Figure S2). We used filtered seawater, in which DOC was present at 5 mg/L in the experiments. The partitioning of PAHs to DOC is defined as:

\[ K_{DOCw} = \frac{C_{DOC}}{C_w} \] (10),

where \( K_{DOCw} \) is the equilibrium partitioning constant for PAHs between DOC and water, and \( C_{DOC} \) is the DOC-bound PAH concentration. We corrected for this third phase effect by
assuming average partitioning of PAHs to DOC \((\log K_{DOC} = 1.18 \log K_{ow} - 1.56)\) \(^{36}\) according to equation (11)

\[
C_{w,corr} = \frac{C_{w,app}}{1 + [DOC]K_{DOCw}}
\]

\(^{(11)}\),

in which \([DOC]\) is in kg/L, and

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

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

Results in Figure 3 could imply that the estuarine DOC in our seawater displayed a significant higher affinity for PAHs than the mostly freshwater DOCs included in Burkhard’s (2000) review.\(^{36}\) A similar conclusion was previously reached by Friedman et al. (2011) who reported that polychlorinated biphenyls (PCBs) in the New Bedford Harbor estuary sorbed 5 – 20 times stronger to DOC than predicted.\(^{37}\) We included results for the DOC-correction of apparent dissolved PAH concentrations from liquid-liquid extraction assuming that DOC sorbed PAHs 5 – 10 times stronger than predicted by Burkhard\(^ {36}\), resulting in better agreement between higher MW PAHs from both methods.

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

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

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

Truly dissolved PAH concentrations calculated from PE-deployments decreased over time, with increasing certainties of results (Table S13). For the three week deployments, we deduced concentrations of below 1 ng/L for fluorene, phenanthrene and methyl-pyrene, 2.5 ng/L for fluoranthrene and 8.6 ng/L for pyrene. For these 5 representative PAHs, the agreement between active and passive sampling increased from a 30-fold difference (week 1) to 1.4 times (week 2) to within a factor of 1.1. Clearly, deployment times of 2 weeks or more were needed under these quiescent flow conditions to arrive at satisfactory results for the passive samplers.
Within a 3-week deployment window, though, very good agreement was observed between both approaches.

**Implications**

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

This work could not have been accomplished without the help of the following individuals: Eric Morgan, Victoria Dekany, Julia Sullivan, Carey Friedman, Matthew Lambert, Victoria Dekany, Lin Zhang, and Victoria Sacks (all GSO). This project was funded by a grant from NOAA/UNH Coastal Response Research Center. NOAA Grant Number(s): NA04NOS4190063. Project Number: 08-102 ‘Detecting dissolved PAHs from oil spills using passive samplers in cold water and ice cores’

Supporting Information Available

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

REFERENCES


(34) Jonker, M. T. O.; Muijs, B. Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals Chemosphere 2010, 80, 223-227.


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Figure 1: $\log K_{PEw}$ (L/kg) versus $\log K_{ow}$ of selected PAHs from the literature 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.

[Graph showing predicted and measured % equilibrium for pyrene and benzo(a)pyrene at various conditions of temperature and salinity.]
Figure 3: Comparison of PAH concentrations from a mock oil spill (5 °C, 30 psu): PE-based results versus apparent and DOC-corrected PAH concentrations from liquid-liquid extraction.
Figure 4: Concentrations of selected PAHs (ng/L) in Narragansett Bay water (December 2012) from PE-deployments versus weekly active sampling: (a) fluorene; (b) phenanthrene; (c) pyrene; (d) fluoranthene
log $K_{PEw}$s of PAHs at -15 °C & 245 psu after 5 weeks of stirring

![Graph showing log $K_{PEw}$ vs log $K_{OW}$](image)

- Green diamonds: Initial log $K_{PEw}$
- Red squares: Adjusted log $K_{PEw}$
- Dashed line: 1:1 Line