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Article

Modeling Compound Loss from Polydimethylsiloxane Passive Samplers

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Abstract: Volatile losses were measured from polydimethylsiloxane (PDMS) passive samplers during determination of contaminant porewater concentrations in sediments. Volatile losses could occur between the time of retrieval and processing of the passive sampler or in intertidal environments where the passive sampler could potentially be exposed above the water surface at low tide. A model was developed to predict losses of absorbed compounds as a function of sorbent geometry and the Henry's Law Coefficient and PDMS-water partition coefficient of the compound of interest. The model suggests that thin layers of PDMS typically used to minimize equilibration times in passive sampling ($\leq$30 μm) may not provide quantitative measurement of naphthalenes or other lighter volatile compounds without special efforts to reduce losses. The results suggest that the samplers should be processed rapidly onsite or kept at low temperatures after retrieval to maximize retention of more volatile compounds or designed with thick PDMS layers. The results also suggest that less volatile compounds, including phenanthrene, and higher molecular weight polynuclear aromatic hydrocarbons (PAHs) exhibit minimal evaporative losses with typical sample processing times.

Keywords: passive sampling; solid phase microextration; polydimethylsiloxane (PDMS); volatile loss

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1. Introduction

The emerging technology of passive sampling to measure contaminant concentrations in sediment porewater has many benefits over conventional sampling techniques including, but not limited to, cost, detection limits, and representativeness [1]. Conventional solvent extraction techniques for sediment samples strip the majority of the compounds from the sediment. While this method is useful for gaining a measure of the total compound mass within the sediment, it does not provide a direct indication of the freely available concentration, which is both mobile and bioavailable [1].

Even with the documented benefits of passive sampling [2–10], it has seen limited acceptance by regulatory agencies for sediment management decisions in part due to the lack of robust quality assurance and quality control (QA/QC) measures [8,9,11]. In order to achieve quantitative measurements of porewater concentration, the passive sampler must achieve a known degree of equilibration during the absorption phase and losses between uptake and extraction into a solvent must be negligible. Polydimethylsiloxane (PDMS) has been extensively used for passive sampling, partly due to relative rapid uptake kinetics compared to polyethylene (PE) and polyoxymethylene (POM), two other commonly used passive sampler materials. PDMS' rapid uptake kinetics, however, also give rise to a potential for loss of more volatile analytes during sampler processing and handling. Any loss would lead to an underestimation of the concentration of the volatile target analyte. In addition, volatile losses of performance reference compounds (PRCs) would lead to an overestimation of the extent of steady state since PRC losses are used to estimate rates of uptake of target compounds [12]. These losses are possible during the processing of the passive sampler between retrieval from the sediment or surface water and extraction into a stable solvent. These may also be important if the sampler is exposed to air during periods of sampling, for example during periods of low tide in samplers deployed into shallow surface water.

Underestimation of porewater concentration may then underestimate toxicity. Narcosis of benthic organisms may be dominated by low molecular weight polynuclear aromatic hydrocarbon (PAH) compounds [13], which are more likely to be subject to volatile losses from a sampler.

This paper seeks to develop a model of the volatile losses as a function of processing time and compound specific properties for *in situ* solid phase microextraction (SPME) PDMS passive samplers. The model allows estimation of sample processing time and conditions that are required to minimize losses and identifies compounds that are not expected to be quantitatively retained under a specific set of processing conditions. An example from a deployment in a marine intertidal environment will also be discussed to highlight the need for a model such as the one developed herein.

2. Methods

2.1. Modeling Loss from a Solid Phase Microextraction (SPME) Polydimethylsiloxane (PDMS) Sorbent Layer

Equation (1) represents the mass balance on a PDMS layer with an initial concentration of a volatile compound resulting from exposure to a sediment porewater or surface water that is exposed to the air during processing before extraction:

$$V_\mathrm{f}\frac{\mathrm{d}C_\mathrm{f}}{\mathrm{d}t} = k_\mathrm{d}A\left(C_\mathrm{g,bulk} - \frac{C_\mathrm{f}H}{K_\mathrm{fw}}\right) \tag{1}$$

where V_f is the volume (m^3) of the passive sampler sorbent layer, C_f is the concentration sorbed to the passive sampler sorbent layer (µg/m^3), $C_\mathrm{g,bulk}$ is the concentration of the compound in the ambient air (µg/m^3), k_d is the desorption rate coefficient (m/day) associated with the air motion around the sampler, A is the surface area of the passive sampler layer (m^2), H is the Henry's Law Constant (dimensionless), and K_fw is the PDMS-water partition coefficient. The model assumes that the primary resistance to evaporation is external to the passive sampler, which is appropriate to assess the initial rate of evaporative losses. The model predicts the air-fiber partition coefficient by assuming equilibrium between air, fiber, and water using the known partition coefficients between the air water and fiber water interfaces. This can be conceptualized as a thin layer of water on the wetted samplers in equilibrium with the surface of the passive sampler and the surrounding air. The concentration of the contaminant of concern in the water is $C_\mathrm{f} / K_\mathrm{fw}$ and the concentration at the air interface is then given by $C_\mathrm{f}\frac{H}{K_\mathrm{fw}}$. K_fw and H have units that are ratios of concentration, e.g., (mg/m^3)$_\mathrm{PDMS}$/(mg/m^3)$_\mathrm{water}$ and (mol/m^3)$_\mathrm{air}$/(mol/m^3)$_\mathrm{water}$, respectively. The ambient air concentration, $C_\mathrm{g,bulk}$, is typically negligible, therefore Equation (1) can be rewritten as:

$$\frac{\mathrm{d}C_\mathrm{f}}{\mathrm{d}t} = -k_\mathrm{d}\left(\frac{H}{LK_\mathrm{fw}}\right)C_\mathrm{f} \tag{2}$$

which when solved using the following initial condition:

$$C_\mathrm{f}\left(t=0\right) = C_\mathrm{o} \tag{3}$$

which leads to Equation (4):

$$C_\mathrm{f} = C_\mathrm{f,o}\mathrm{e}^{\frac{-k_\mathrm{d}H}{LK_\mathrm{fw}}t} \tag{4}$$

The half-life of the compound sorbed to the PDMS layer is equal to:

$$t_{1/2} = \frac{\ln 2}{k_\mathrm{d}H / LK_\mathrm{fw}} \tag{5}$$

Experiments were conducted to assess desorption rates of compounds from a thin layer of PDMS (10–34 µm) during exposure to ambient air. When considering the scenario of loss during processing times, normal processing of SPME PDMS passive samplers involves retrieval of the passive sampler from the medium of exposure (sediment or water), sectioning of the SPME PDMS fiber into individual samples and placement in an extraction solvent that would effectively eliminate any further volatile losses. In the laboratory this can be done on the order of seconds to minutes, but in the field, longer times may be required to transport the sample to a stable work location or to transport it back to the laboratory. In addition to losses during processing time, samplers deployed in the surface water of tidal environments could be exposed for hours during low tide. Experiments evaluating volatile losses over periods of up to 48 h were conducted. The results were used to fit the model to investigate the effects of

PDMS thickness and ambient air temperature on the desorption rate and the model used to evaluate volatization during normal processing and exposure scenarios.

2.2. Estimation of the Desorption Rate Coefficient, k_d

During this study, 60 mL vials were filled with an aqueous solution containing a range of PAHs: naphthalene, fluorene, acenapthene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. These compounds were selected as they are common hydrophobic organic sediment contaminants, common targets of passive sampling, and exhibit a wide range of volatilities. SPME PDMS coated fibers are commercially available and have a PDMS layer is coated onto a glass cylindrical core with a diameter, *d*. The addition of the PDMS coating creates a cylinder or fiber with an outer diameter d_o and an inner diameter d_i. Twenty centimeters of SPME PDMS fiber with approximate outer/inner diameter dimensions of 230/210 µm (10 µm PDMS thickness), 559/486 µm (34 µm PDMS thickness) and 1060/1000 µm (30 µm PDMS thickness) were placed into the vials containing the aqueous solution without headspace and tumbled in a tumbler box for 14 days. The 559/486 µm and 1060/1000 µm SPME PDMS fibers were purchased from Polymicro Technologies (Phoenix, AZ, USA). The 230/210 µm SPME PDMS fibers were purchased from Fiberguide (Stirling, NJ, USA). Preliminary experiments indicated this was sufficient for the PDMS to become equilibrated with the aqueous solution. Three replicates were used for each PDMS thickness and temperature treatment. A blank was prepared containing only deionized water and 20 cm of a specific thickness of SPME PDMS fiber to indicate any uptake during processing from ambient air of the environmental chamber. The vials were transferred into temperature controlled environmental chambers set at 4 °C, 20 °C, and 25 °C. After temperature equilibration, the fibers were removed from the aqueous solution and segmented using a ceramic column cutter into 1 cm lengths. After exposure to the ambient air for the following pre-determined times: 0 min, 0.5 min, 1 min, 1.5 min, 2 min, 3 min, 4 min, 5 min, 7 min, 10 min, 15 min, 20 min, 30 min, 1 h, 2 h, 6 h, 8 h, 12 h, 24 h, and 48 h, the 1 cm fiber lengths were placed in 150 µL of acetonitrile. No attempt was made to control the air motion around the sampler during exposure but instead to simulate evaporative losses during approximately static ambient conditions which would be the desired environment during sectioning of the fiber. Variable air motion during these near-static conditions is likely to lead to greater variability in the results but would also be expected during processing under field conditions. The extracts were analyzed using an Agilent Technologies 1260 Infinity (Santa Clara, CA, USA), high performance liquid chromatography (HPLC) with an ultraviolet-diode array (1260 DAD VL+), and a fluorescence detector (1260 FLD Spectra) based upon EPA standard method 8310 in the SW846 series. The column used was a Phenomenex (Torrance, CA, USA) Luna 5µ C18 column (250 mm × 4.6 mm) maintained at 40 °C. The HPLC was operated under isocratic conditions with a flow rate through the system of 1.0 mL/min with a water to acetonitrile ratio (v:v) of 3:7.

2.3. Deployment of Polydimethylsiloxane (PDMS) Passive Samplers in a Marine Intertidal Environment

Porewater and marine surface water samples were collected via SPME PDMS methods in November/December 2013 at 13 shallow subsurface or surface water sampling locations within the East Harbor Operable Unit (OU-1) of the Wyckoff/Eagle Harbor Superfund Site (Bainbridge Island, WA, USA). The project area encompasses 11 acres of intertidal portions of the East Beach and North Shoal areas that are affected by known or suspected historical contamination of NAPL products that could potentially pose an exposure risk to human and ecological receptors. The SPME PDMS sampling effort was completed in support of a focused feasibility study (FSS) being conducted by the USEPA. Nine shallow subsurface porewater samplers and four marine surface water samplers were deployed on 13 November 2013 and retrieved on 5 December 2013. Based upon previous deployment of PDMS samplers in Eagle Harbor, the deployment period was long enough to ensure between 50% and 90% of equilibrium of target PAHs was achieved. The nine shallow subsurface porewater samplers were deployed along three transects, while the four marine water column samplers were deployed at four deep intertidal to shallow subtidal zone locations. Based on the high and low tides during the deployment period, the surface water sampler of one of the transects would be exposed above tidal waters a maximum of 8 h per day and remain submerged and fully wetted 16 h per day. The three remaining surface water samplers would be exposed above tidal waters up to 4 h per day and remain submerged and fully wetted up to 20 h per day. The volatile losses during the period of exposure were evaluated. The surface water samplers had a PDMS coating with an outer/inner diameter of 1060/1000 μm.

Fluoranthene-d10, chrysene-d12, benzo(b)fluoranthene-d12, and dibenz(a,h)anthracene-d14 were selected as PRCs to evaluate the kinetics of uptake of the target PAHs in the environment. The SPME PDMS fibers were pre-loaded with these four deuterated PAHs prior to deployment at the site as described in [14]. The PRC depletion and uptake of the target analytes were analyzed as described in [15]. The developed model was used to evaluate evaporative losses of both PRCs and to evaluate uptake and loss of the target analytes.

3. Results and Discussion

3.1. Model Calibration

Analysis of the concentration gradients over time during the laboratory processing of the passive samplers revealed that the most hydrophobic compounds under investigation had very little to no desorption from the PDMS sorbent layer of the SPME PDMS fibers. For the 559/486 μm and 1060/1000 SPME PDMS fiber, no measurable desorption was observed for compounds with a $\log K_{ow}$ ($\log K_{ow}$ values for PAHs (SPARC estimates) [15]) of 4.7 or higher, 5.29 or higher, 6.58 or higher, for ambient temperatures of 4 °C, 20 °C, and 25 °C, respectively. For the 230/210 μm SPME PDMS fiber, there was substantial change from the initial concentration sorbed to the PDMS layer over the duration of the experiment for all three temperature treatments. Generally, the PAHs of potential concern for substantial loss from the SPME PDMS fibers included naphthalene ($\log K_{ow} = 3.41$), acenaphthene ($\log K_{ow} = 4.06$), fluorene ($\log K_{ow} = 4.2$), anthracene ($\log K_{ow} = 4.69$), and phenanthrene ($\log K_{ow} = 4.74$). The concentration *versus* time behavior for these compounds suggests a relatively rapid (exponential) loss initially followed by a slowing of evaporation after a long time, likely associated with increasing importance of internal mass transfer resistances on evaporation. Our goal is to model losses to ensure that any such losses are small (e.g., less than 10%) for a sampling event either due to sample processing times or environmental factors like tides. Thus the model and the analysis was focused on the initial exponential loss phase.

Vapor pressure, Henry's Law Coefficient, and temperature relationships were available for the PAHs of most concern in this study and dimensionless Henry's Law Coefficients ((mol/m^3)$_{air}$/(mol/m^3)$_{water}$) at ambient temperatures of 4 °C, 20 °C, and 25 °C are compiled in Table 1 [16]. The estimated logk_d (in m/day) consistent with the observed loss over time for these five compounds averaged approximately 2 ± 0.2 (average ± 95% confidence interval on the mean) with no significant dependence upon compound, sampler thickness or temperature as shown in Figure 1. This is for the relatively static environment in a lab or protected area in the field likely to be used for sample processing and the variability likely represents variations associated with air motion in the static but uncontrolled environment. Naphthalene and the thinnest PDMS layer k_d values were more variable due to the relatively rapid loss of this compound making measurements difficult and the greater influence of internal mass transfer resistances.

Table 1. logK_{fw}, (log(µg/L)$_{PDMS}$/(µ/L)$_{water}$), log$H$ (log (mol/m^3)$_{air}$/(mol/m^3)$_{water}$), and logH/K_{fw} values for select polynuclear aromatic hydrocarbons (PAHs) at the temperatures of interest.

Compound	logK_{fw} [1]	log$H$ (277 K)	logH/K_{fw} (277 K)	log$H$ (293 K)	logH/K_{fw} (293 K)	log$H$ (298 K)	logH/K_{fw} (298 K)
Naphthalene	2.95	−2.38 [2]	−5.3	1.86 [3]	−4.8	−1.76 [3]	−4.7
Acenaphthene	3.42	−2.81 [4]	−6.2	−2.35 [4]	−5.8	−2.28 [4]	−5.7
Fluorene	3.52	−3.05 [4]	−6.6	−2.61 [4]	−6.1	−2.39 [4]	−5.9
Anthracene	3.77	−3.26 [4]	−7.1	−2.84 [4]	−6.7	−2.63 [4]	−6.5
Phenanthrene	3.79	−3.39 [4]	−7.3	−2.96 [4]	−6.9	−2.75 [4]	−6.7

[1] K_{fw} values from Ghosh *et al.* (2014) [8]; [2] Henry's Law Constant values from Alaee *et al.*, (1996) [17]; [3] Henry's Law Constant values (Pa·m^3/mol) from Bamford *et al.* (1999) [18].

Defining $\frac{k_d H}{L K_{fw}} = k_d^*$ suggests a linear relationship between k_d^* and H if k_d is constant (Figure 2). The slope of $\log(k_d^*)$ and log(H) is approximately one, which lends support to the model. High H compounds will evaporate more rapidly and H can be minimized by reducing the temperature. The variability seen in Figures 1 and 2 could be attributed to the different air flow conditions of the temperature controlled environmental chambers, as indicated previously. Keeping the samplers at a lower temperature, and thereby reducing the Henry's constant, reduces evaporation. Based upon the experimental results, the half-life of naphthalene on a 230/210 µm SPME PDMS fiber can be increased tenfold to 0.2 h by storing the sampler at 4 °C rather than 25 °C.

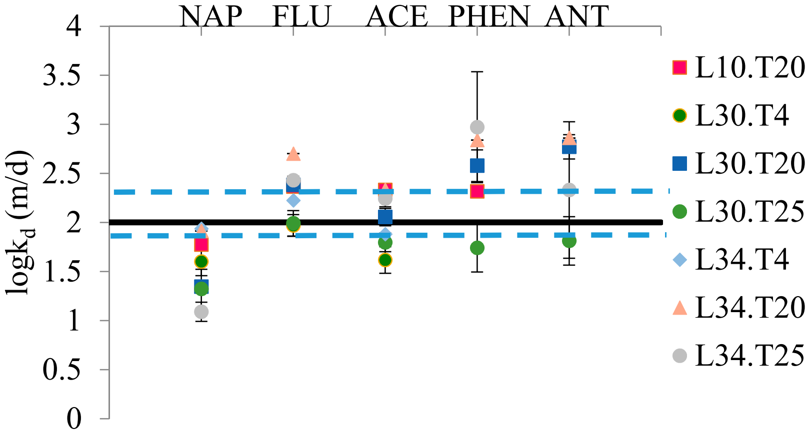


Figure 1. Experimentally determined log (k_d) values for the compounds that showed the most rapid desorption for all experimental treatments. L refers to volume to area ratio of sampler and T is temperature, °C. k_d is the desorption rate coefficient (m/day) associated with the air motion around the sampler. $\log k_d$ is a constant equal to 2 ± 0.2 (average ± 95% confidence interval on mean, n = 31). Solid line represents average and broken line represents confidence interval on mean. NAP: naphthalene; FLU: fluorene; ACE: acenaphthene; PHEN: phenanthrene; ANT: anthracene.

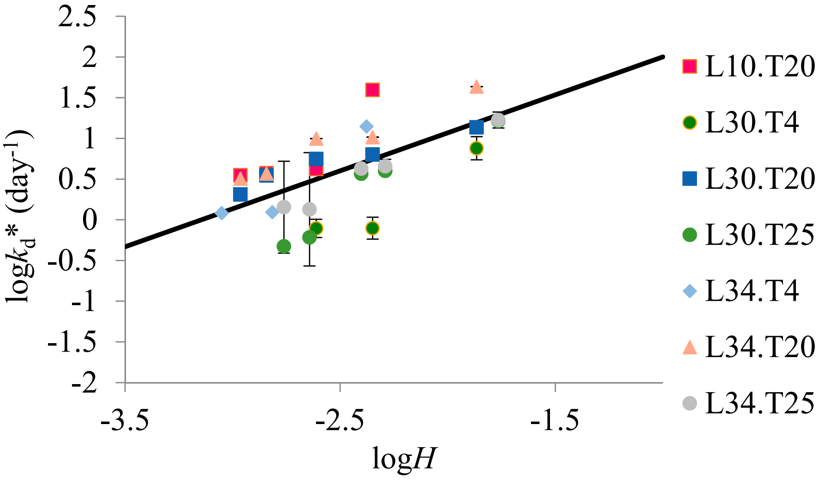


Figure 2. $\log H$ (H is dimensionless) *versus* $\log k_d^*$ for all solid phase microextraction (SPME) polydimethylsiloxane (PDMS) thickness (L10, L30, or L34) and temperature treatments (T4, T20, or T25) for naphthalene, fluorene, acenaphthalene, and anthracene. L10, L30, and L34 refer to the PDMS thickness of the 230/210 μm, 1060/1000 μm, and the 559/486 μm SPME PDMS fibers used in this experiment, respectively. T4, T20, and T25 refer to the temperatures of 4 °C, 20 °C, and 25 °C used in this experiment, respectively. $\frac{k_d H}{L K_{fw}} = k_d^*$, where k_d is the desorption rate coefficient (m/day) associated with the air motion around the sampler, H is the dimensionless Henry's constant, L is the PDMS sorbent thickness, and K_{fw} is the PDMS-water partition coefficient. The solid black line represents the relationship between $\log H$ and $\log k_d^*$, where $\log k_d^* = 1(\pm 0.2)\log H + 3(\pm 0.5)$, $r^2 = 0.53$. The error bars represent the standard deviation associated with each measurement.

The model also suggests that the sorbent dimensions will influence evaporation half-life through L, the sampler's volume to area ratio or essentially the sorbent thickness. There was found to be little difference in half-lives between the 1060/1000 µm and 559/486 µm SPME PDMS fibers for the three temperatures of this study due to their PDMS thicknesses being similar (~30 µm). In general, there is a decrease in the desorption half-life of the compounds for all temperatures when using the 230/210 µm SPME PDMS fiber *versus* the 1060/1000 µm and 559/486 µm SPME PDMS fiber. For example, naphthalene, the most volatile PAH in this study, has a half-life of 0.2 h when initially sorbed to a 1060/1000 µm or 559/486 µm SPME PDMS fiber and exposed to an ambient air temperature of 25 °C compared to a half-life of 0.02 h when sorbed to a 230/210 µm SPME PDMS fiber (10 µm thick PDMS layer) at the same temperature. The very fast desorption time onto the thinner fibers suggests that naphthalene is not a viable target compound of the thinner PDMS fiber in the field. Evaporation of naphthalene and fluorene from the 230/210 fiber was generally too rapid to be accurately measured and these were excluded from subsequent analysis.

The half-life results suggest that when using SPME PDMS fibers with dimensions of 559/486 µm or 1060/1000 µm, compounds with $\frac{H}{K_{\mathrm{fw}}} > 10^{-5}$ are stable ($C_{\mathrm{f}}/C_{\mathrm{f,o}} \geq 0.9$) for 20 min exposure periods at an ambient air temperatures of 25 °C. Compounds with $\frac{H}{K_{\mathrm{fw}}} > 10^{-6}$ are stable for 20 min exposure periods sorbed to a 230/210 µm SPME PDMS fiber, with an approximate 10 µm thickness of PDMS, and exposed to an ambient air temperatures of 20 °C. In general, the results suggest if rapid processing is not possible, thicker sorbent layers or lower processing temperatures should be used for volatile compounds such as naphthalene. Figure 3 depicts the predicted *versus* observed half-life times in days for the different SPME PDMS fiber thicknesses. The predicted values were calculated using k_{d}^{*} values predicted from the relationship between $\log H$ and $\log k_{\mathrm{d}}^{*}$ and Equation (5).

Figure 4 shows the modelled $C_{\mathrm{f}}/C_{\mathrm{f,o}}$ (from Equation (4)) *versus* time curves for a 10 µm or 30 µm sorbent layer thickness of PDMS for sampling hydrophobic organic contaminants, exposed to air at 4 °C or 20 °C. Table 2 provides estimates of the sampling time required to ensure 90% concentration retention of naphthalene using PDMS passive sampling sorbent of various thicknesses at 20 °C and 4 °C, respectively. If samplers are retrieved and immediately stored at low temperatures, there is an increase in the maximum time for which the fibers can be exposed without losing more than 10% of the sorbed analyte. For example, when using a 30 µm PDMS sorbent layer, the sample processing time required to minimize losses to less than 10% of the analyte sorbed to PDMS increases from approximately 2 min to 7 min. Using thicker sorbent layers is an option for increasing the retention time of the compounds sorbed to the polymer, but using thicker sorbent layers also increases the time necessary to reach equilibrium between the polymer and the sediment porewater or surface water. For example, a 1.4 cm thickness of PDMS would retain 90% of naphthalene sorbed to it for a 24 h period exposed to ambient air at 293 K, but would require lengthy absorbing time (centuries) to achieve 90% of equilibrium for porewater concentration measurement of highly hydrophobic five and six ring PAHs.

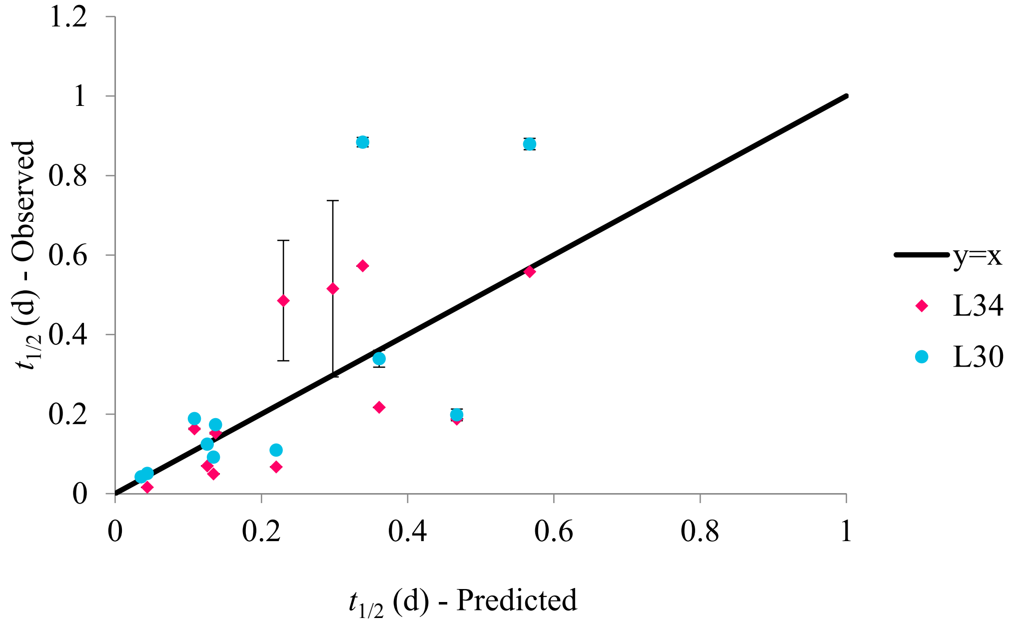


Figure 3. Observed half-life ($t_{1/2}$-Observed) values *versus* predicted half-life ($t_{1/2}$-Predicted) values for naphthalene, fluorene, acenaphthene, phenanthrene, and anthracene desorption from SPME PDMS fibers. L30 and L34 refer to the PDMS thickness of the 1060/1000 µm, and the 559/486 µm SPME PDMS fibers used in this experiment, respectively. The observed half-lives were calculated using measured k_d values in Equation (5). The predicted half-lives were calculated using the relationship determined between log(k_d^*) and log$H$ (logk_d^* = 1(±0.2)log$H$ + 3(±0.5), r^2 = 0.53) and Equation (5). The black solid line represents a one-to-one relationship.

3.2. Modeling the Effect of Intertidal Drying

The model was applied to estimate losses during intertidal exposure of the surface water PDMS passive samplers in a field study. The average air temperature during the period of deployment was 7 °C and the PDMS water samplers were exposed to ambient air for up to 4 h or 8 h per day depending upon sampler location. During exposure, loss of the volatile target contaminants would limit the ability to quantify their concentration in the water. In addition, any loss of the PRCs during the exposure period would limit the ability to assess the extent of equilibrium uptake. The model developed previously was used to estimate the evaporative losses of the sixteen PAHs and the four PRCs used in the study. Figure 5 shows the estimated loss of the most volatile compounds and each of the PRCs from the PDMS layer during the exposure period of 4 h or 8 h. For both scenarios, naphthalene, the least hydrophobic compound of interest for this study, exhibits substantial losses. The model predicts for both scenarios losses less than 10% of the mass sorbed to the PDMS for phenanthrene and other PAHs with greater hydrophobicity. Additionally, the loss of PRCs when exposed from the surface water is negligible (<10%) and therefore kinetic uptake estimates will not be influenced. Moreover the kinetics of loss of the PRCs of different hydrophobicity were consistent as per the analysis of [15]. If evaporative loss of the PRCs were of concern, the lighter PRCs would show greater losses than expected.

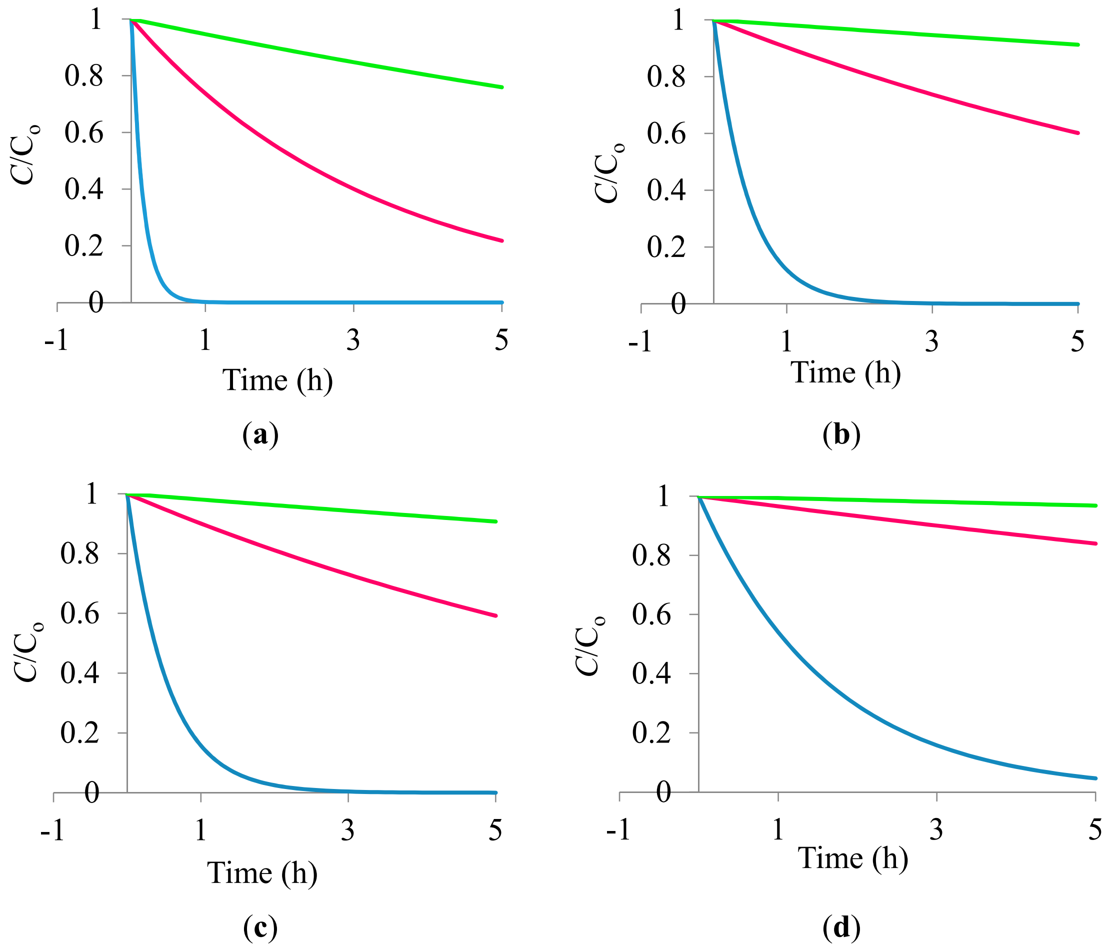
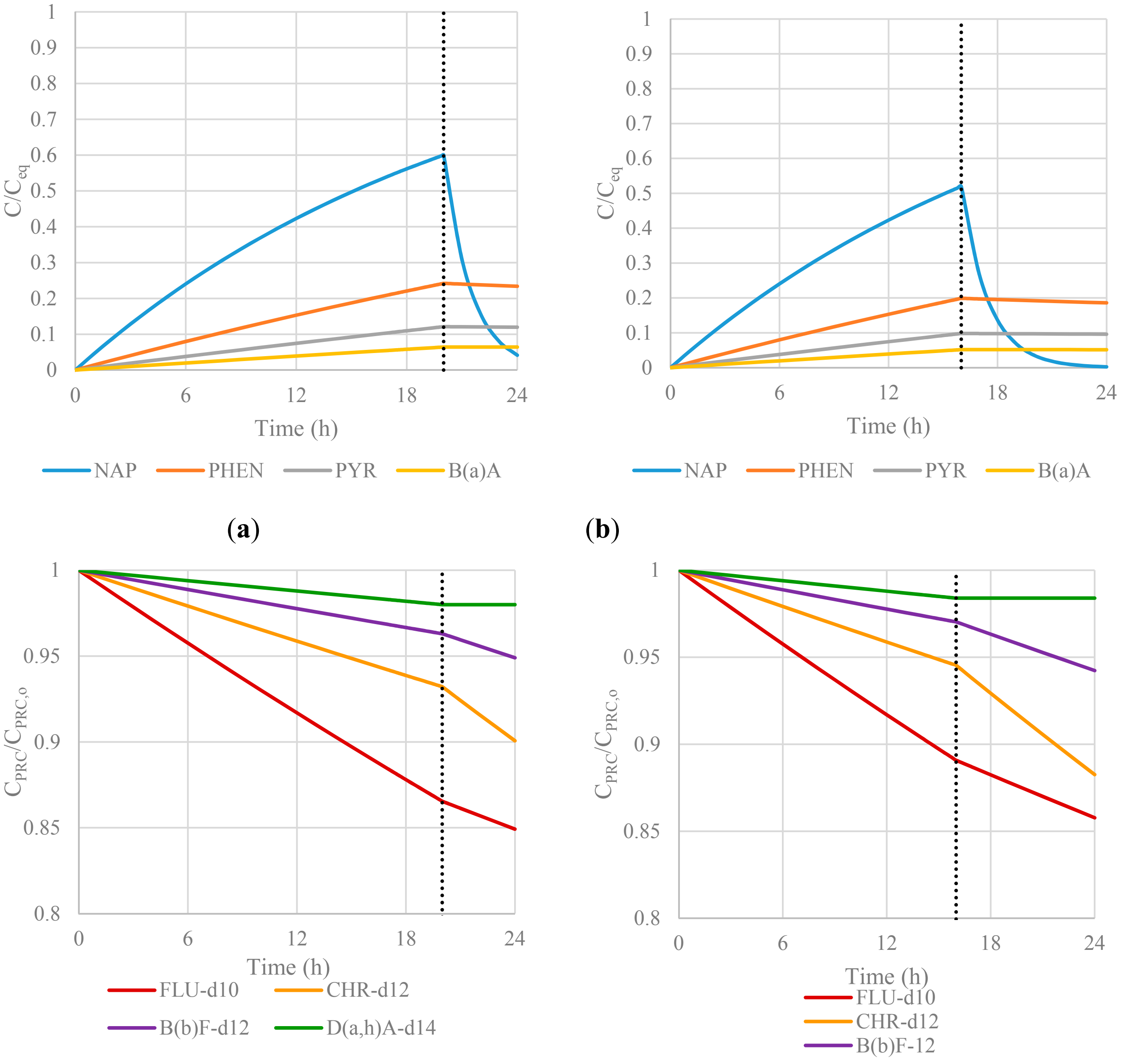


Figure 4. Modeled $C_f/C_{f,o}$ values for 10 µm and 30 µm thick PDMS passive sampling materials for NAP-blue, FLU-red, and PHEN-green exposed to ambient air at 4 °C (277 K) and 20 °C (293 K): (**a**) L = 10 µm, T = 293 K; (**b**) L = 30 µm, T = 293 K; (**c**) L = 10 µm, T = 277 K; (**d**) L = 30 µm, T = 277 K.

Table 2. Estimates of the time (min) at which $C_f/C_{f,o}$ = 0.9 for NAP for different thicknesses of PDMS, exposed at 277 K and 293 K using model parameters tabulated above. Estimates based on k_d model fit of 10^2 m/d.

PDMS layer thickness	**NAP $C_f/C_{f,o}$ = 0.9 at time (min)**	
	T = 277 K	T = 293 K
30 µm	10	3
100 µm	34	10



(**a**) (**b**)

(**c**) (**d**)

Figure 5. (**a**) Model of sorption and desorption of four select COCs from the 1060/1000 SPME PDMS fiber during a low tide event lasting 4 h (t_{sw} = 20 h); (**b**) model of sorption and desorption of four select COCs from SPME PDMS fiber during a low tide event lasting 8 h (t_{sw} = 16 h); (**c**) desorption of the four PRCs from the SPME PDMS fiber during submersion in surface water (t_{sw} = 20 h) and during exposure to air during a 4 h low tide event; and (**d**) desorption of the four PRCs from the SPME PDMS fiber during submersion in surface water (t_{sw} = 16 h) and during exposure to air during an 8 h low tide event. Average air temperature estimated to be 7 °C during air exposure period. C/C$_{eq}$ represents the fraction of steady state achieved between the porewater and the SPME PDMS fiber. $C_{PRC}/C_{PRC,o}$ represents the fraction lost of PRCs from the initial concentration spiked into the SPME PDMS fiber.

4. Significance and Implications

One of the concerns when completing field sampling events with passive sampling methods is the accuracy of the reported concentrations, especially for low molecular weight compounds that can be more volatile. The experiments, using SPME PDMS fibers of different thicknesses exposed to various ambient air temperatures for different times, indicated that the key parameters for estimating evaporative losses during ambient processing of samples are the compound's Henry Law Coefficient, sorbent-water partitioning coefficient and the geometry (thickness) of the sorbing fiber. To maximize retention of volatile compounds such as naphthalene during sample processing, either thick PDMS layers (≥30 µm), rapid processing (≤5 min) or low processing temperatures (4 °C) are necessary. Phenanthrene and less volatile PAHs can also be lost during processing, but were much less sensitive to PDMS thickness or processing conditions. In general, passive samplers that provide the best performance (rapid uptake) for highly hydrophobic compounds are not optimum for monitoring less hydrophobic, more volatile compounds, and vice versa. The selection of a passive sampler must be based upon the sampling objectives and the selection of the optimum sampler thickness, material, and exposure and processing conditions to achieve the desired uptake and ensure sample integrity during processing.

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Author Contributions

Courtney L. Thomas and Danny D. Reible conceived and designed the experiments. Courtney L. Thomas performed the experiments, analyzed the data, and wrote the article. Danny D. Reible provided oversight during data analysis and writing of the article.

Conflicts of Interest

The authors declare no conflict of interest.

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