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Performance of Passive Samplers for Monitoring Estuarine Water Column Concentrations 1. Contaminants of Concern

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Abstract

Contaminants enter marine and estuarine environments and pose a risk to human and ecological health. Recently, passive sampling devices have been utilized to estimate dissolved concentrations of COCs, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). In the present study, the performance of three common passive samplers was evaluated for sampling PAHs and PCBs at several stations in the temperate estuary Narragansett Bay (Rhode Island, USA). Sampler polymers included polyethylene (PE), polydimethylsiloxane (PDMS) coated solid phase microextraction (SPME) fibers, and polyoxymethylene (POM). Dissolved concentrations of each contaminant were calculated using measured sampler concentrations adjusted for equilibrium conditions with performance reference compounds (PRCs) and chemical-specific partition coefficients derived in the laboratory. Despite differences in PE and POM sampler concentrations, calculated total dissolved concentrations ranged from 14–93 ng/L and 13–465 pg/L for PAHs and PCBs, respectively. Dissolved concentrations of PAHs were approximately three times greater based on POM compared to PE while dissolved concentrations of PCBs based on PE were approximately three times greater than POM. Concentrations in SPME were not reported due to the lack of detectable chemical in the amount of PDMS polymer deployed. Continued research is needed to improve and support PE and POM use for the routine monitoring of COCs. For example, a better understanding of the use of PRCs with POM is critically needed.

Keywords

passive sampler; polychlorinated biphenyls (PCBs); polycyclic aromatic hydrocarbons (PAHs)

INTRODUCTION

A variety of anthropogenic contaminants are present in marine and estuarine environments including industrial contaminants of concern (COC), such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) [1–3]. These COCs represent human

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and ecological health risks if exposures are sufficiently elevated [4–5]. To perform an accurate ecological risk assessment, knowing the dissolved concentration is critical as it is often the best measure of exposure in aquatic systems [6]. For example, the dissolved concentration quantifies the exposure a benthic invertebrate or fish experiences as well as determines the amount of bioavailable contaminant game fish, birds and wildlife may accumulate. However, measuring the dissolved concentrations of COCs accurately in a media like natural estuarine waters is often challenging because these chemicals have relatively limited solubilities resulting in low aqueous concentrations and the tendency to associate with environmental particles which causes sampling artifacts (e.g., not measuring the actual dissolved chemical) [7].

In recent years, several passive sampling methods have been developed for measuring the dissolved concentrations of COCs in natural waters and sediments including semi-permeable membrane devices (SPMDs), polyethylene (PE), polydimethylsiloxane (PDMS), and polyoxymethylene (POM) [e.g., 8–11]. In addition to their ability to estimate freely dissolved concentrations, passive samplers can also avoid some of the artifacts (e.g., presence of colloids and small particles, losses to sampling equipment surfaces) and expenses associated with conventional sampling techniques. This is because these samplers are used in an equilibrium application and therefore the measured dissolved concentrations reflect conditions in which the COC is at equilibrium between all relevant environmental phases (e.g., dissolved and colloidal organic carbon, black carbon, small particles) and the sampler. Furthermore, equilibrium passive sampling is a time-integrated sampling technique rather than the grab or “snap shot” approach used in conventional sampling. A powerful advantage of time-integrated sampling is that it provides the average exposure concentrations in the water column as opposed to infrequent extreme conditions that the grab approach can represent.

Equation 1 was used to calculate the dissolved concentration using passive samplers

$$C_D = \frac{C_{\text{sampler}}}{K_{\text{sampler}}} \quad (1)$$

Here, C_D is the dissolved concentration of a COC ($\mu\text{g/L}$) (e.g., a PCB congener), C_{sampler} is the concentration of the chemical accumulated by the sampler ($\mu\text{g/kg}$) during the deployment period, and K_{sampler} is the passive sampler-water partition coefficient (L/kg). A key underlying assumption of Equation 1 is that the target chemical is at equilibrium between the water and the passive sampler when the sampler is recovered from the deployment.

Determining if a system is at equilibrium can be challenging. In this context, the COC is being distributed in a system composed of the freely dissolved phase, environmental particles (e.g., colloids, sediment particles), and any other objects that may be present (e.g., organisms). When using POM and PDMS-based passive samplers, like the solid phase microextraction (SPME), it is often assumed the system achieves equilibrium rapidly [9–10], while with PE and SPMD based passive samplers, performance reference compounds (PRCs) are frequently used to estimate equilibrium concentrations under non-equilibrium conditions [8,11]. Huckins et al. [12] first discussed the concept of loading passive samplers with PRCs prior to deployment and now PRCs are widely used [13–15]. During the deployment, as the passive sampler accumulates target contaminants from the environment, the PRCs are released into the surrounding water in order to reach equilibrium. The PRCs, which are often stable isotope labeled (e.g., ^{13}C), should be selected to share common key physicochemical characteristics (e.g., octanol-water partition coefficients (K_{OW})) with the

target chemicals and therefore behave similarly as they transfer from the sampler to the surrounding water. Using the concentrations of remaining PRCs in the sampler following the deployment (C_{PRCf}) relative to the initial concentrations (C_{PRCi}), Equations 2 and 3 are applied to estimate the equilibrium concentration of the target chemical [8,12]:

$$k_e = \ln \left(\frac{C_{PRCi}}{C_{PRCf}} \right) \times \frac{1}{t} \quad (2)$$

where, k_e is a mass transfer coefficient (d^{-1}) and t is the deployment period (d). Next, Equation 3 and k_e are used:

$$C_{Da} = \frac{C_{sampler}}{(1 - e^{-k_e t}) \times K_{sampler}} \quad (3)$$

The adjusted dissolved concentration (C_{Da}) reflects the chemical's dissolved concentration in the water phase at equilibrium based on the remaining PRCs. Unless equilibrium conditions were achieved, not using PRC data will generally result in an underestimation of the chemical's dissolved concentrations in the water.

Despite the progress made with passive sampling (e.g., use of PRCs), many fundamental questions still remain especially with regard to their application for routine monitoring. For example, what kinds of scientific and practical differences exist between the types of passive samplers, what are the differences between partition coefficients (i.e., $K_{sampler}$) for the various passive samplers especially when they are derived in different laboratories, and will these differences result in substantial differences in calculated dissolved concentrations? After all, in principle, if each passive sampler is functioning as dictated by theory, regardless of the polymer and the magnitude of their specific $K_{sampler}$ value, they should estimate the same dissolved concentration. In addition, while using PRCs has the primary advantage of allowing equilibrium concentrations to be determined, they can add expense to performing deployments, require loading time, and their viability with many passive sampling polymers (e.g., POM) has not been explored extensively.

In the present study, the performance of three common passive samplers was evaluated for sampling COCs (i.e., PCBs and PAHs) at several stations in the well-mixed temperate estuary Narragansett Bay (Rhode Island, USA). Sampler polymers included PE, PDMS coated SPME fibers, and POM. Dissolved concentrations of all contaminants were determined based on partitioning calculations using either assumed or PRC-derived equilibrium conditions. This investigation had two specific objectives: (1) compare passive samplers for water column monitoring of selected COCs and (2) derive partition coefficients in one laboratory for the COCs investigated in this study. The overall goal of this research was to provide information to environmental managers for selecting which type(s) of passive sampler to deploy based on the contaminants being monitored, as well as evaluate sampler performance for effectiveness, ease of use, and cost.

MATERIALS AND METHODS

Materials

Chemical stock solutions of PAHs and PCBs were prepared by Ultra Scientific (North Kingstown, RI, USA) in acetone or dichloromethane (DCM). Neat deuterated PAHs and ^{13}C -labeled PCBs in nonane were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Deuterated PAHs in DCM were purchased from Sigma-Aldrich (St.

Louis, MO, USA). Supplemental Data Table S1 provides a list of target chemicals, PRCs, and internal standards.

To ensure that this comparison used polymers commonly employed in monitoring, commercially available passive sampler materials and configurations were evaluated while taking into consideration analytical detection requirements and the logistics of deploying a given polymer. Low-density PE (25 μm thick; Covalence Plastics, Minneapolis, MN, USA) and POM (76 μm ; CS Hyde Company, Lake Villa, IL, USA) were cut into strips of 15 cm $\times$ 40 cm and 6 cm $\times$ 40 cm, respectively. Strips of PE and POM were pre-cleaned by soaking in acetone for 24 h and then in DCM for 24 h. Solid-phase microextraction fibers (200 μm inner silica core with 10 μm outer PDMS; Fiberguide Industries, Stirling, NJ, USA) were cut to 2.5 cm in length and pre-cleaned as described above for PE and POM.

Field Site Locations and Deployment

Strips of PE and POM were soaked in a PRC solution (80:20 methanol:water with deuterated PAHs and labeled PCBs) and allowed to equilibrate for at least 28 days on an orbital shaking table. Each PRC jar contained four sampler strips and 900 mL aqueous PRC solution. After soaking, strips of PE and POM were removed from the PRC solution, one strip of each sampler (cut in half for two samples) was taken from each PRC solution jar for measuring pre-deployment PRC concentrations ($C_{\text{PRC}i}$), and the remaining strips were attached to stainless steel wire (diameter = 0.032 in.; Malin, Brookpark, OH, USA). Galvanized extended minnow traps (diameter = 22 cm, length = 30 in.; Tackle Factory, Fillmore, NY, USA) were used to protect samplers from biotic and abiotic threats. Fifteen pre-cut SPME fibers were placed inside a fine copper mesh (TWP, Berkeley, CA, USA) hand-made envelope and the envelope attached to the inside of the trap by stainless steel wire. Three strips of PE and POM were attached inside each trap to maximize their surface area. Three SPME envelopes were also attached to the inside of each trap. Passive sampler traps were deployed during the Summer of 2011 approximately one meter above the sediment surface for 21 days at six site locations in Narragansett Bay (RI, USA) (Supplemental Data, Table S2). Narragansett Bay is a fairly well-mixed estuary of approximately 342 km² with industrial and domestic watershed inputs from Rhode Island and Massachusetts [16]. Four deployments (Greenwich Bay, Bristol Harbor, Mount Hope Bay and Newport Harbor) were from water-based U.S. Coast Guard navigational buoys. Two deployments (U.S. EPA and Providence River) were from docks at site locations. At each site, field blanks were taken out during deployment and retrieval for each sampler.

Partition Coefficient Derivation

Partition coefficients (K_{sampler}) were obtained by plating chemical solutions onto the sides of a 250 mL amber jar before adding 250 mL of Milli-Q water and ~5 mg of a sampler. Sodium azide was added to each jar to prevent COC degradation. For each chemical class, three jars per sampler, were then placed on an orbital shaking table for 56 days at room temperature, which was found to be sufficient for equilibration in prior kinetics studies (data not shown). Jars containing Milli-Q water and samplers were also set-up to serve as blanks. Water and samplers were extracted as described below.

Extraction

Passive samplers were weighed and extracted by soaking sequentially for 24 hours with acetone and DCM on an orbital shaker for light agitation. Supplemental Data, Table S1 indicates the internal standards used for each contaminant class. Samplers retrieved from the field were wiped clean of water and epiphytes before extraction. Acetone and DCM extracts were combined, solvent exchanged to hexane, and volume reduced to 1 mL under a stream of nitrogen gas. Water samples from partition coefficient derivation studies were extracted

twice with pentane. Extracts were combined, treated with sodium sulfate, solvent exchanged to hexane, and volume reduced to 1 ml.

Instrumental Analysis

Analyses of PAHs and PCBs were performed on an Agilent 7890 gas chromatograph equipped with a 5975 mass selective detector (Agilent Technologies, Wilmington, DE, USA) operated in select ion monitoring mode. Analytes and internal standards were separated using an Agilent DB-5MS capillary column (30 m length; 250 μ m diameter; 0.25 μ m thickness) and quantified with a five or six point calibration curve.

Calculation of Dissolved Concentrations

Using Equation 3, dissolved water concentrations were calculated with the chemical-specific partition coefficients (K_{sampler}) described above adjusted for the presence of salt using Setschenow constants [17] with a salt concentration of 0.5 M, measured sampler concentrations (C_{sampler}) minus blank sampler concentrations, and mass transfer coefficients (k_e) obtained from PRC equilibration and Equation 2. Deuterated PAHs and ^{13}C -labeled PCBs were used as PRCs for PAHs and PCBs, respectively (Supplemental Data, Table S1).

Toxic Unit Calculations

To determine if there were sufficient concentrations of dissolved PAHs and PCBs to cause sublethal toxicity to aquatic organisms, toxic units were calculated. If total TU was less than or equal to 1, then it is unlikely that the chemical will cause chronic toxicity to sensitive organisms. Conversely, if the total TU exceeds 1, then chronic toxicity may occur due to the chemical [18]. Toxic units (TU) were calculated for each PAH and PCB by dividing the calculated dissolved concentrations by the appropriate final chronic values (FCV). For PAHs, FCVs were obtained from U.S. EPA [18]. For PCBs, FCVs were calculated using narcosis theory following Equation 4 based on the octanol-water partition coefficients (K_{OW}) for narcotic chemicals taking into consideration the effects of chlorination [19]:

$$\log \text{FCV} = 0.597 - 0.945 \log K_{\text{OW}} \quad (4)$$

For this exercise, the narcotic toxicity of the PAHs and PCBs was considered additive, which allows for the addition of TU together for a given class of contaminants (e.g., PAHs). Since only 20 PAHs were measured in the present study, rather than the 34 considered as “total PAHs”, the total TU for PAHs was multiplied by an uncertainty factor of 4.14 to achieve a level of 95% confidence [18]. No similar uncertainty factor exists for PCBs. The Aroclor mixture detected at the highest concentrations and throughout Narragansett Bay is Aroclor 1254 [20] and the PCBs measured in the present study comprise 55.6% of the PCBs found in that Aroclor [21]. Therefore, the total TU for PCBs was calculated by multiplying the total TU for PCBs by 1.8, which is the inverse of 0.556.

RESULTS AND DISCUSSION

Partition coefficients

Partition coefficients for PE, POM, and SPME were obtained for 18 PAHs and 26 PCBs. Chemical-specific K_{sampler} values are listed in the supporting information (Supplemental Data, Table S3). For each passive sampler, K_{sampler} values have been plotted against $\log K_{\text{OW}}$ values by chemical class and are shown in Figure 1.

For PE, a good correlation between chemical-specific PE partition coefficients (K_{PE}) and K_{OW} was observed for both compound classes (Figure 1a). The $K_{\text{PE}}\text{-}K_{\text{OW}}$ relationship was

linear for all PAHs (Pearson correlation coefficient (r) = 0.95; $\log K_{PE} = 0.792 \log K_{OW} + 0.719$). Several studies have derived K_{PE} values for subsets of the PAHs measured in this study [14,22–26]. These literature values were found to be similar to the values obtained in this study (Table 1). For PCBs, a good correlation between K_{PE} and K_{OW} was also observed up to a $\log K_{OW}$ value of ~ 6.7 ($r = 0.97$; $\log K_{PE} = 0.903 \log K_{OW} + 0.102$). Partition coefficients for PCB congeners with $\log K_{OW}$ values above this appeared to plateau and were approximately the same. This observed plateau has also been reported by others and is attributed to differences in Gibbs free energies for cavity formation in the passive sampler polymer and octanol, such that the energy needed for cavity formation in the passive samplers becomes much higher for larger chemicals while the amount of energy needed for cavity formation in octanol changes little for the same chemicals [27]. Other explanations are also possible for the occurrence of the plateau by the high molecular compounds including disequilibria in the experimental system and/or incomplete extraction from the sampler polymer. As with PAHs, several studies have derived K_{PE} values for subsets of the PCBs measured in this study [22,24–26] and these values were in the same range as those obtained here (Table 1).

A distinct curvilinear relationship was observed between chemical-specific POM partition coefficients (K_{POM}) and K_{OW} for the PAHs (Figure 1b). In contrast, the relationship between chemical-specific POM partition coefficients (K_{POM}) and K_{OW} for the PCBs demonstrated a plateau similar to the PCB values with PE polymer (Figure 1a). The peak of the curvilinear relationship for the PAHs occurred at a $\log K_{OW}$ of ~ 5.5 while the plateau observed for the PCBs started at a $\log K_{OW}$ value of ~ 7.0 . Above we discussed possible reasons for the plateau in these types of relationships but it is less certain as to the cause of the curvilinear relationship between K_{POM} and K_{OW} . One explanation may be the incomplete dissolution of the PAHs into solution during the equilibration period resulting in the water extractions incorporating crystalline PAH. However, this behavior was not observed in either the PE or SPME treatments which contradicts what would be expected if this issue were a common experimental artifact. Good correlation was observed for PAHs ($r = 0.89$; $\log K_{POM} = 0.809 \log K_{OW} + 0.524$) and PCBs ($r = 0.99$; $\log K_{POM} = 1.12 \log K_{OW} - 0.947$) before the peak and plateau, respectively. Partition coefficients for PAHs with POM have been derived for thicknesses ranging from 55–500 μm [23,28–30]. Since the POM used in this study was $\sim 76 \mu\text{m}$, literature values for thinner POM were comparable to the values obtained in this study. Partition coefficients for POM have been derived for subsets of the PCBs measured in this study using 50–76 μm POM [28–31] and produced $\log K_{POM}$ values similar to those obtained in the present study (Table 1).

A correlation between chemical-specific SPME partition coefficients (K_{SPME}) and K_{OW} was observed for all PAHs ($r = 0.84$; $\log K_{SPME} = 0.451 \log K_{OW} + 2.87$) and PCBs ($r = 0.94$; $\log K_{SPME} = 0.541 \log K_{OW} + 2.51$) (Figure 1c). However, the K_{SPME} and K_{OW} relationship for the PAHs did demonstrate a level of scatter that was not observed for the PCBs. For PAHs, several studies have derived $\log K_{SPME}$ values [23,32,33]. Overall, values obtained in this study were slightly greater in magnitude as compared to the literature values. Similarly for PCBs, derived K_{SPME} values [34–36] were comparable to values obtained in this study especially when similar PDMS coating thickness was used (Table 1). A possible explanation for the modest disagreements in the literature partition coefficient values and those values presented here are differences in the sources of the PDMS used in the manufacturing of the SPME. Different PDMS sources may be expected to have a range of partition coefficients.

PRC Behavior

To account for disequilibrium, PRCs were loaded into the PE and POM samplers and measured before and after deployment. These initial and post-deployment PRC

concentrations were used to calculate k_e for each PRC using Equation 2. By plotting this against a physicochemical property, such as K_{OW} or molar volume, for each class of PRCs (i.e., deuterated PAHs, ^{13}C -labeled PCBs), a linear relationship is observed and can be used to obtain an equation to estimate percent equilibration for each target chemical of interest. For PE, this linear relationship was observed at all sites for both classes of PRCs with r^2 values of 0.8 or higher. Alternatively, weak or non-linear relationships were observed with POM, especially with ^{13}C -labeled PCBs.

Application of PRCs with POM is not as commonly practiced as with PE and typically equilibrium is assumed for calculating dissolved concentrations using POM. For example, in their work with PCBs and PAHs using POM, Hawthorne et al. [30,31] did not use PRCs but concluded based on time series analysis that 28 days was sufficient to achieve equilibrium conditions in contaminated sediment-water slurries. In contrast, Oen et al. [37] used five rare PCB congeners as PRCs with POM for in situ sediment deployments at a contaminated mudflat in San Francisco Bay (CA, USA). Working in a sediment system with limited exchange dynamics between the sampler and interstitial water, their deployments went to 154 days and found PRC depletions ranged from 80 to 20% for tri- to heptachlorinated congeners. The only concern noted with PRC performance was that uptake of target PCBs by the POM was greater than the release of PRC PCBs by the POM. Oen et al. [37] suspected this observation had more to do with differences in mass transfer conditions between the polymer and sediment phases than unexpected interactions between the PRCs and the polymer structure.

The cause of the PRC behavior with POM in the present study is unknown, but could be attributed to the structure of the polymer. Specifically, the structure of POM contains a repeating oxygen-containing group (i.e., ether), while PE is entirely comprised of carbon and hydrogen. For nonionic organic chemicals like PCBs and PAHs, ordinarily their intermolecular interactions with the polymers would be dominated by van der Waals dispersive forces [17]. These forces affect the strength of the affinity of the COCs for the polymer as well as the ability of the COCs to diffuse into, within and out of the polymer matrix. The presence of the oxygen in the POM suggests that other molecular interactions with the COCs may be occurring in that polymer and consequently affecting the rate of PRC release from the polymer. For example, electron donor-acceptor interactions [17] between the PAHs (and PCBs) and oxygen groups (i.e., ether group) would be stronger than van der Waals dispersive forces and could retard the diffusion and accumulation of these contaminants in POM. This explanation may help clarify the behavior of the PRCs with the POM as discussed above. At this point, this explanation is speculation, but it highlights the need to better understand what is occurring in and around the POM and represents a critical area of future research for the use of PRCs with this passive sampler.

Calculated Dissolved Concentrations of PAHs

Sources of PAHs, which are ubiquitous throughout Narragansett Bay, are pyrogenic and petrogenic in nature. Pyrogenic inputs are from combustion processes, such as coal burning power plants and automobile and boat engine exhaust. Petrogenic PAHs enter the bay through direct spills, municipal wastewater treatment plants, runoff and industrial effluents [38]. Annual PAH input into Narragansett Bay has been estimated to be about 1000 kg/year [39]. Riverine inputs derived from atmospheric deposition and petroleum inputs have been identified as the dominant supply of PAHs to the bay. Additional contributions of PAHs are attributed to wastewater/industrial effluents and direct atmospheric deposition [39]. Sediments act as sinks for many nonionic organic contaminants, such as PAHs, and accumulate contaminants over time. As a result, sediments can also act as a source of PAHs into the water column [40].

Calculated total dissolved PAH concentrations are presented in Figure 2. Results are only shown for PE and POM because contaminants were not detectable in SPME samples. The lack of detectable chemicals in the SPME replicates clearly indicates that not enough PDMS polymer was deployed (~1.25 mg PDMS vs. ~1.5 and ~3 g of PE and POM, respectively). As a result of a tropical storm-damaged cage, POM replicates were lost at the Bristol Harbor site and no data are shown. Dissolved PAH concentrations calculated using measured sampler concentrations (Supplemental Data, Figure S1) and PRC adjustments ranged from 14–93 ng/L. Total dissolved PAH concentrations calculated using PRC adjusted POM were approximately 1.5–4 times higher than those obtained using PRC adjusted PE. Assuming equilibrium with POM, as others have [30,31], would result in decreased total dissolved PAH concentrations ranging from 15.6–51.3 ng/L corresponding to a 26–63% decrease from concentrations calculated using PRC adjustments. Interestingly, these non-PRC adjusted dissolved PAH concentrations were more similar to those calculated using PE.

The highest concentrations of total dissolved PAHs were calculated for Providence River and Newport Harbor, the two sites with the highest boat traffic in Narragansett Bay. Total TU for total dissolved PAHs ranged from 0.009 to 0.032 for PE and 0.013 to 0.13 for POM indicating dissolved PAH concentrations were unlikely to result in chronic toxicity at any sites with total TU below 1. When taking a closer look at individual PAH compounds at each site, calculated water concentrations were found to be of the same magnitude for PE and POM. For example, data for individual PAHs are shown for the Providence River site (Figure 3). For both samplers, the highest concentrations were observed for phenanthrene, fluoranthene, pyrene, and acenaphthene. On an individual basis, dissolved water concentrations calculated using POM were higher than those obtained using PE for all PAH compounds (median $\approx$ 3 times higher).

Calculated Dissolved Concentrations of PCBs

Historical industrial activity in Narragansett Bay contributed large amounts of PCBs into the bay [41]. Since the ban on their production and use in the 1970s, PCBs have still been detected in coastal waters and sediments in Narragansett Bay due to sediment resuspension, runoff and volatilization [42]. Consequently, particulate bound PCBs from rivers, as well as sporadic input from wastewater treatment plants, comprise the main sources of PCBs into the estuary [41].

Calculated total dissolved PCB concentrations are presented in Figure 4. As noted with PAHs, contaminants were not detectable in SPME and POM replicates were lost at the Bristol Harbor site therefore no data are shown. Calculated total dissolved PCB concentrations using measured sampler concentrations (Supplemental Data, Figure S2) and PRC adjustments ranged from about 38–465 pg/L. Total dissolved PCB concentrations calculated using PRC adjusted POM were approximately 2–3 times lower than those obtained using PE. Assuming equilibrium with POM would result in decreased total dissolved PCB concentrations ranging from 13.4–115 pg/L corresponding to a 55.4–66.2% decrease from PRC adjusted concentrations. In contrast to PAHs, these non-PRC adjusted dissolved PCB concentrations are more dissimilar to those calculated using PE.

The northern portion of Narragansett Bay (i.e., Providence River) is more industrial than the rest of the bay. This may explain the higher concentrations of dissolved PCBs calculated for the northern stations. Total TU for total dissolved PCBs were well below 1, (1.18×10^{-4} to 6.10×10^{-4} for PE and 5.32×10^{-5} to 1.83×10^{-4} for POM), which again indicates total dissolved PCB concentrations are unlikely to cause toxic effects. When taking a look at individual PCB congeners, calculated water concentrations from PE and POM were found to be of the same magnitude. For example, data for individual PCB congeners is shown for the Providence River site (Figure 5). Individual dissolved water concentrations of PCBs

calculated using POM were lower than those obtained using PE for all congeners except CB8 (median $\approx$ 2.5 times lower).

CONCLUSIONS

Each sampler has its own advantages and disadvantages for water column deployments. Both PE and POM are relatively inexpensive polymers (i.e., less than \$1 per sampler) that can be deployed for extensive amounts of time due to their durable nature. They are easy to cut into desired sizes and simple to deploy in large masses to achieve higher analytical sensitivity. Conversely, due to its flexibility, PE can fold on itself making it difficult to clean after deployments. The rigidity of POM, on the other hand, makes it easier to clean, but causes it to be susceptible to ripping off the wire during deployments. Additionally, as discussed earlier, there are issues with using PRCs with POM that may be due to the chemical structure of the polymer and the resulting intermolecular forces. At this point, there are insufficient data to make firm recommendations as how to address these issues. However, there are two provisional strategies: (1) assume POM has achieved equilibrium based on previous deployments where equilibrium was demonstrated or (2) apply PRCs, as with PE, to adjust POM data for non-equilibrium conditions. As discussed, the first strategy is frequently used by POM practitioners, but requires an assumption of equilibrium in systems that may not be comparable to the system in which the original equilibrium time frame was established for POM. This could introduce uncertainty around any estimated freely dissolved contaminant concentrations. As illustrated in the current study, the second strategy runs the risk of the PRCs not actually operating in a predictable fashion in the POM matrix. As with the first strategy, this situation generates uncertainty with any estimates of freely dissolved contaminant concentrations. Clearly, one critical research question is to better understand the interactions of PRCs and POM or to demonstrate that there is no need to use PRCs with POM at all. The use of SPME as a passive sampler for water column deployments may be problematic. Although it is believed they achieve equilibrium quicker than PE and POM, as seen in the present study, large masses of SPME are needed in order to achieve analytical sensitivity comparable to PE and POM when COC levels are relatively low like in Narragansett Bay. Additionally, SPME fibers are fragile and small so they can be difficult to handle. In future water column deployments, the use of PDMS in a film configuration, which can be used in much larger masses and surface areas than the SPME configuration, is likely to be more successful.

Both PE and POM were effective sampling devices for monitoring COCs in the water column, but, as noted, continued research is needed to improve and support their use for routine monitoring programs. Further demonstration and validation of passive samplers for effectively measuring dissolved COCs is needed to enhance acceptance of their use. For example, comparing passive sampler results for low to moderately hydrophobic chemicals to measurements obtained through conventional water sampling methods can verify their accuracy and endorse their use for monitoring programs. Further, there are questions regarding the use of the current suite of passive samplers (i.e., PE, POM, SPME) with emerging contaminants as compared to the more common practices of working with COCs. Additionally, passive sampler research needs to focus on the optimization of PRC loading techniques. Currently, loading techniques are time-consuming and organic-solvent intensive, which increases the cost of using passive samplers. Investigations into PRC selection and loading are needed to continue developing methods that are cost-effective and useful scientifically. Finally, the dissolved concentration and resulting toxic units suggest chronic toxic effects of PAHs and PCBs in Narragansett Bay are unlikely. However, the presence of these dissolved concentrations indicates these COCs will continue to be bioavailable, bioaccumulated by aquatic organisms, and potentially trophically transferred up the food web.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Sampler-water partition coefficients (L/kg) for PE (a), POM (b), and SPME (c) plotted against octanol-water partition coefficients (L/kg) for polycyclic aromatic hydrocarbons (PAHs, ●) and polychlorinated biphenyls (PCBs, □). The mean and one standard deviation are shown.

Figure 2.

Calculated dissolved concentrations (ng/L) of total polycyclic aromatic hydrocarbons (PAHs) derived from measured contaminant concentrations in polyethylene (PE) and polyoxymethylene (POM) at the six study sites in Narragansett Bay, RI. Concentrations derived from PE adjusted with performance reference compounds (PRCs) (black bars), PRC- adjusted POM (white bars), and non-PRC adjusted POM (hashed bars) are presented. ND denotes no data for the Bristol Harbor site where POM replicates were lost due to a tropical storm.

Figure 3.

Calculated dissolved concentrations (ng/L) of individual polycyclic aromatic hydrocarbons (PAHs) at the Providence River site derived from measured concentrations and performance reference compounds (PRCs) in polyethylene (PE, grey bars) and polyoxymethylene (POM, white bars). Mean and one standard deviation are presented.

Figure 4.

Calculated dissolved concentrations (pg/L) of total polychlorinated biphenyls (PCBs) derived from measured contaminant concentrations in polyethylene (PE) and polyoxymethylene (POM) at the six study sites in Narragansett Bay, RI. Concentrations derived from PE adjusted with performance reference compounds (PRCs) (black bars), PRC- adjusted POM (white bars), and non-PRC adjusted POM (hashed bars) are presented. ND denotes no data for the Bristol Harbor site where POM replicates were lost due to a tropical storm.

Figure 5.

Calculated dissolved concentrations (ng/L) of individual polychlorinated biphenyls (PCBs) at the Providence River site derived from measured concentrations and performance reference compounds (PRCs) in polyethylene (PE, grey bars) and polyoxymethylene (POM, white bars). Mean and one standard deviation are presented.

Log passive sampler-water partition coefficient values (K_{sampler} ; L/kg) from the present study and the literature for selected polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyl (PCBs) for polyethylene (PE), polyoxymethylene (POM), and solid phase microextraction (SPME) fibers with polydimethylsiloxane (PDMS) coating. For the present study, mean and one standard deviation are presented. All K_{sampler} values are reported in Supplemental Data, Table S3.

Table 1

	Present Study	Literature Values ^c	References
<i>PE</i>			
anthracene	4.20 ± 0.04	4.25, 4.3, 4.33, 4.6	[23, 24, 25, 26 ^d]
fluoranthene	4.85 ± 0.06	4.9, 4.99, 4.73, 4.9, 4.93, 4.86	[14, 22 ^{ab} , 23, 24, 25, 26 ^d]
pyrene	5.00 ± 0.08	5.0, 5.15, 4.9, 4.7, 5.1	[14, 22 ^{ab} , 23, 24, 25]
PCB 28	5.28 ± 0.14	5.4, 5.4, 5.89	[24, 25, 26 ^d]
PCB 52	5.42 ± 0.13	5.73, 5.5, 5.55, 5.54	[22 ^{ab} , 24, 25, 26 ^d]
PCB 118	6.03 ± 0.19	5.9, 6.4, 6.53	[22 ^{ab} , 24, 25]
<i>POM</i>			
anthracene	4.14 ± 0.01	3.3, 3.47, 3.68, 4.3	[23 ^a , 28, 29 ^a , 30]
chrysene	4.71 ± 0.05	4.15, 4.51, 4.39, 5.43	[23 ^a , 28, 29 ^a , 30]
benzo[e]pyrene	4.73 ± 0.06	4.37, 4.73, 4.75, 5.67	[23 ^a , 28, 29 ^a , 30]
PCB 52	5.57 ± 0.04	4.44, 5.4, 5.66, 5.65	[28, 29 ^a , 30, 31]
PCB 70	5.93 ± 0.02	5.75, 5.98	[29 ^a , 31]
PCB 110	6.18 ± 0.01	5.81, 6.2	[29 ^a , 31]
<i>SPME</i>			
fluoranthene	4.99 ± 0.04	4.48, 4.26, 4.16	[23 ^a , 32, 33]
pyrene	4.62 ± 0.24	4.49, 4.32, 4.25	[23 ^a , 32, 33]
benzo[g,h,i]perylene	5.60 ± 0.55	4.9, 5.5, 5.52	[23 ^a , 32, 33]
PCB 77	5.85 ± 0.57	5.68, 5.61	[35 ^a , 36]
PCB 118	6.13 ± 0.76	5.87, 5.55, 6.1	[34, 35 ^a , 36]

^c Sampler thicknesses may vary between studies