



Polycyclic Aromatic Hydrocarbon Accumulation Performances of Monophasic Butyl Rubber Passive Samplers

O. E. Tureyen¹ · S. D. Yakan¹ · A. Yilmaz² · B. Yetiskin³ · O. Okay³ · O. S. Okay¹

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Abstract

In the present study, polycyclic aromatic hydrocarbon (PAH) accumulation performances of four butyl rubber (BR) monophasic passive samplers with different pore structures were investigated and the results were compared with monophasic polydimethylsiloxane (PDMS) samplers and biphasic semipermeable membrane devices (SPMDs). Stainless steel cages containing passive samplers were deployed in the water column in Istinye Bay, Istanbul Strait, and retrieved after 7 and 28 days. Collected samplers were analyzed using high-performance liquid chromatography (HPLC) to determine their PAH contents. Results showed that BR passive samplers have sampled all PAHs for both short- and long-term sampling periods while SPMD samplers only collected twelve and thirteen PAHs after 7 and 28 days, respectively. PDMS samplers showed the poorest performance, having only sampled seven and ten PAHs after 7 and 28 days, respectively. Among the BR samplers, a monophasic BR sampler with a single pore network (SN10) showed the most feasible performance in terms of PAH sampling and its preparation cost. Results highlighted that the SN10 sampler with a wide absorption range and monophasic structure can be used as an alternative passive sampler for pollution monitoring in marine environments.

Highlights

- Butyl rubber samplers showed the highest accumulation performances for PAHs with high $\log K_{ow}$.
- Butyl rubber passive samplers were found suitable for marine pollution monitoring.
- The most efficient version of butyl rubber samplers for field studies has been determined..

Keywords PAH pollution · Butyl rubber passive sampler · Monophasic passive samplers · SPMD sampler

✉ O. E. Tureyen
tureyen@itu.edu.tr

¹ Department of Shipbuilding and Ocean Engineering, Istanbul Technical University, 34469 Istanbul, Turkey

² Polar Research Institute, TUBITAK Marmara Research Center, 41470 Gebze, Kocaeli, Turkey

³ Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent and hazardous organic compounds consisting of two or more benzene rings, existing in different matrices at the same time like atmosphere, freshwater, marine water, soil, even in ice blocks in Antarctica (Xue et al. 2016). They are generally classified according to their origins such as those based on natural sources, or based on anthropogenic sources including combustion of fossil fuels, vehicle exhaust emissions, pharmaceutical and cosmetic industry, and domestic wastes (Kumar et al. 2016). Adverse effects of PAHs have been addressed for various organisms in the marine ecosystem starting from the lowest trophic level with planktons (Tao and Liu 2019), continuing with mussels (Benali et al. 2017), fish (Li et al. 2019) and cephalopods (Ke et al. 2017), and ending with humans (Rengarajan et al. 2015; Balcioğlu 2016; Ke et al. 2017). Sixteen PAHs are specified as priority pollutants by the European Commission and the US Environmental Protection Agency (EPA) (Xia et al. 2012).

Despite their ubiquitous existence in the water column, biota, and sediments, the detection and monitoring of PAHs in the marine environment is quite challenging due to their strong hydrophobic character. The water solubility of PAHs is known to decrease with increasing $\log K_{ow}$ values, which makes harder to detect their freely dissolved concentrations when the $\log K_{ow}$ value is higher than 5.5. The main method to determine the concentrations of PAHs in the water column is still conventional grab sampling as indicated in the Water Framework Directive (WFD) (European Commission 2009). However, detection of organic pollutants by grab sampling requires a huge amount of water sampling, several pre-treatments and concentration steps to determine the instantaneous concentration of the chemicals in the water column (Allan et al. 2006; Taylor et al. 2021). Moreover, detection of freely dissolved concentrations (C_{Free}) of PAHs, which is the regulating parameter for toxicity of the chemicals, is a laborious and complex process, since the suspended materials are also collected during the batch sampling (Reichenberg and Mayer 2006; Booij et al. 2016).

Passive samplers are devices used to overcome the mentioned drawbacks of the conventional batch sampling method. Unlike conventional water sampling, they provide time-averaged concentrations of the chemicals and their freely dissolved concentrations (C_{Free}) instead of the total ones (C_{Total}) (Booij et al. 2016). Being mentioned as a complementary method by WFD, passive sampling of chemicals in the water column is also encouraged by both EPA (Fernandez et al. 2012) and the Oslo-Paris Convention for the protection of the marine environment of the North-East Atlantic (OSPAR) (Commission 2013). Since the 1990s, several passive samplers have been developed to detect pollutants in marine environments. Different types of samplers were used not only for organic pollutants (Maruya et al. 2015; Belles et al. 2017), but also for heavy metals (Bailon et al. 2019), micropollutants (Mutzner et al. 2020), and biotoxins (Zendong et al. 2016). Although several passive samplers are used to monitor organic pollutants in the marine environment such as polydimethylsiloxane (PDMS) (Jonker et al. 2015), polyoxymethylene (POM) (Josefsson et al. 2015), low-density polyethylene (LDPE) (Estoppey et al. 2016), and butyl rubber (BR) (Tureyen et al. 2021), only semipermeable membrane devices (SPMDs) are standardized and commercially available (Booij and Smedes 2010).

Molecular weights of PAHs and their octanol/water partition coefficients (K_{ow}) are positively correlated. Besides, the time required to reach the equilibrium phase in samplers becomes longer as the $\log K_{ow}$ values of PAHs increase. For example, in a study conducted

by Luellen and Shea (2002), the linear uptake phase was reached after 30 days for PAHs with $\log K_{ow} > 4.5$ whereas, the required time was found 15 days for PAHs with $\log K_{ow} < 4.5$ (Luellen and Shea 2002). In some other studies, it was also shown that lower molecular weight (2- and 3-rings) PAHs needed approximately 30 days for equilibrium, while for higher molecular weight (4- and 5-rings) PAHs, a longer time was needed such as 60 days (Booij et al. 1998; Vinturella et al. 2004). Therefore, there is a research gap regarding the efficient sampling of the PAHs with high $\log K_{ow}$ values.

Butyl rubber (BR) sorbents were introduced into the literature to collect petroleum products from oil spills in marine environments and to remove PAHs from aqueous solutions (Ceylan et al. 2009). Although they were prepared with one standard pore morphology at the beginning, alternative versions with different pore structures and porosities were developed to increase their PAH sampling performance for all $\log K_{ow}$ values. For this purpose, BR sorbents with double-network (DN) and triple-network (TN) pore structures were developed along with the single network (SN) rubbers with different butyl rubber concentrations (SN5 and SN10). Basically, the DN sorbents have two different sizes of pores, and the TN sorbents have three different sizes of pores while SN sorbents have a standard uniform pore structure. The purpose of synthesizing monophasic BR sorbents with different pore sizes was to obtain an efficient absorption performance of the PAHs with all $\log K_{ow}$ values. These BR sorbents with tunable pore morphologies showed extraordinary mechanical properties, and high sorption rates and capacities for PAHs (Yetiskin et al. 2019; Tureyen et al. 2021).

In this study, all types of BR sorbents were used in a field study to compare their performances for the accumulation of PAHs. Biphasic SPMDs and monophasic PDMS samplers were also deployed along with the BR sorbents for comparison. Those samplers were selected because, at present, biphasic SPMDs are the only standardized and commercially available passive samplers for hydrophobic compounds; on the other hand, PDMSs are monophasic samplers similar to BR samplers. The use of both SPMDs and PDMSs for many years in laboratory and field studies produced numerous data in the literature (ter Laak et al. 2008; O'Brien et al. 2012; Page et al. 2014; Taylor et al. 2021). However, even though the SPMDs are the only commercialized passive samplers, they have several drawbacks which are mentioned in detail in the literature (Smedes et al. 2010). The most common problem with the SPMDs is the leakage of the triolein during the field or laboratory processes which poses a contamination risk and all sampling activities should be repeated in such cases. Moreover, due to its biphasic structure, both the preparation and the extraction processes require a relatively long time and higher amounts of extraction solvents than the monophasic samplers. However, recently, there is no standardized commercial monophasic product available. Therefore, there is a need for a standardized, easy-to-produce, monophasic sampler for pollution monitoring; it is expected that the use of monophasic samplers will be favored over the use of SPMDs. The PAH accumulation performances and the spectrum of PAHs accumulated in the BR sorbents in this field study conducted in Istinye Bay, Istanbul Strait, highlighted the fact that the potential use of monophasic macroporous rubber sorbents in marine pollution studies is encouraging.

2 Materials and Methods

2.1 Materials

SPMDs of $91.4 \text{ cm} \times 2.5 \text{ cm} \times 70\text{--}95 \text{ }\mu\text{m}$ in dimensions were obtained from Exposmeter (Sweden). The samplers contain 1 mL triolein spiked with Performance Reference Compounds (PRCs) of phenanthrene-d10, acenaphthene-d10, chrysene-d12, and fluorene-d10, benzo(e)pyrene-d12 ($2 \text{ }\mu\text{g} / \text{SPMD}$). Another commercial passive sampler PDMS (kSil GP60), used as a reference, was supplied from Silicone Engineering Ltd. (Blackburn, UK). Soxhlet extraction was used to clean PDMS samplers with ethyl acetate for 5 days. Both PDMS and BR samplers were prepared at size of 2 cm width and 20 cm length.

BR passive samplers with a single network (SN5 and SN10), double network (DN), and triple network (TN) structures were fabricated as detailed before (Muslumova et al. 2019). Briefly, to prepare SN5 and SN10 passive samplers, 5 and 10 g purified BR was first dissolved in 100 mL benzene at room temperature overnight, to obtain 5 and 10 w/v% BR solutions, respectively. Then, S_2Cl_2 (6 v/w% with respect to BR) was added to homogeneous BR solutions as a crosslinker and the solutions were then stirred for about 2 min. After pouring the reaction solutions into several sealed trays, they were exposed to $-18 \text{ }^\circ\text{C}$ for 24 h for the cryogenic vulcanization (cryogelation) of the BR, which endows to passive samplers their macroporous architectures.

DN and TN passive samplers were prepared via successive cryogelation reactions conducted within the pores of the previous ones. Thus, in order to prepare DN passive samplers, a dried SN5 passive sampler in sheet geometry was immersed in a 10 w/v% BR solution containing S_2Cl_2 crosslinker until swelling equilibrium. Then SN5 passive sampler sheets, whose pores were filled with this BR solution, were put at $-18 \text{ }^\circ\text{C}$ for 24 h to conduct the cryogelation reactions of the second network within the pores of the first network. TN pas-

Fig. 1 Map of the sampling location, Istinye Bay in Istanbul Strait



sive samplers were prepared with the same approach, i.e., via the cryogelation of the third network within the pores of the second network after immersing of a dried DN passive sampler sheet in the same BR solution (10 w/v%).

2.2 Study Area and Sampling Process

Istinye Bay in the Istanbul Strait (coordinates of 41° 06' 49.0" and N 29° 03' 16.5" E) was chosen as the study area. The selected area has busy marine and city traffic, high domestic waste discharge through the Istinye Stream, and also hosted a high functioning shipyard for decades, making the area having a high potential for PAH pollution. Previous studies conducted in the same area investigated the PAH content in the marine sediments and water column, and therefore, the PAH level history is well known (Karacik et al. 2009, 2013; Barut et al. 2016; Yılmaz et al. 2019). The map of the study area is given in Fig. 1.

All passive samplers were placed in special stainless-steel cages and were deployed in a water column of 2 m depth and 5 m above the seabed. They were collected after 7 and 28 days. Deployment and collection of the cages were conducted with field blanks for each type of passive samplers to detect any possible contamination in the processes. All samples were immediately transferred to the laboratory after retrieval in ice bags and stored at -20 °C until further analysis.

2.3 PAHs Content Analysis of the Samplers

To determine the PAH contents, samplers were placed into glass vials, and PAHs were extracted with 120 mL of n-hexane/acetone mixture (3:1 v/v) in a horizontal shaker at 120 rpm for 24 h. That process was repeated three times. The extracts were then collected in flasks and concentrated to a volume of 5 mL using a rotary evaporator.

The concentrated extracts were purified with column chromatography using 10 g silica gel and 25 mL n-hexane/dichloromethane (3:2, v/v) as the elution mixture. The eluants were then re-concentrated to 5 mL using a rotary evaporator. The concentrated extracts were transferred to HPLC vials for solvent exchange to acetonitrile under gentle nitrogen flow. PAH contents of the extracts were analyzed with high-performance liquid chromatography (Agilent Technologies 1260 Infinity HPLC). The chromatography conditions were set at an injection volume of 10 µL, column temperature of 25 °C, a flow rate of 0.850 mL/min, and excitation wavelength of 260 nm. Water:acetonitrile (%/%) mobile phase gradient was as follows: 60:40 (0–17 min), 0:100 (17–25 min), and 60:40 (27–30 min).

2.4 Quality Control and Data Handling

In order to secure the data precision, sampling activities were conducted with 2 replicates for each passive sampler and averaged results with standard deviations are presented in the graphs. The extraction and purification processes of the samples were examined in terms of the recovery rate with 9,10-Dimethylanthracene as the surrogate standard. PAH concentrations of the samplers were calculated by taking the site and laboratory contamination into account with field blank and laboratory blank samplers. The comparison of the passive sampler performances was conducted with recovery and weight corrections, and the results were given per unit gram of sampler.

3 Results and Discussion

Individual and total concentrations of PAHs in the six different passive samplers for 7 and 28 days are presented in Table 1; Fig. 2, respectively. Only results for 14 PAHs out of 16 could be measured due to analytical problems.

The dominant PAHs in the area are the low molecular weight PAHs (acenaphthene (AC), fluorene (FL), phenanthrene (PHE), anthracene (AN), fluoranthene (FA), and pyrene (PY)) for both 7 and 28 days. As was expected, the total PAH concentrations accumulated in 7 days were lower than the levels accumulated in 28 days (Fig. 2). When total amounts of PAHs in the samplers were considered, SPMD and SN5 samplers had the highest performances and showed similar performances. However, the accumulated amounts of the individual compounds may be diverse depending on the characteristics of the chemicals, and the total amounts may not reflect the true performances of the samplers. Thus, the individual amounts of the PAHs in the samplers should be considered separately.

When the individual PAH levels in the samplers (Table 1) were investigated, it is seen that the AC levels in PDMS and TN samplers after 28 days are lower compared to 7-day values. This behavior was observed only for the smallest PAH in the samplers; thus, this may be due to the escape of the accumulated AC from the samplers in time. On the other hand, for these mentioned dominant PAHs, SPMD samplers showed almost the highest performances for both 7 and 28 days. While all BR sorbents accumulated all the fourteen PAHs, only seven PAHs with the lowest log K_{ow} values were detected in PDMS samplers after 7 days and ten PAHs after 28 days. When this comparison was made for the SPMD,

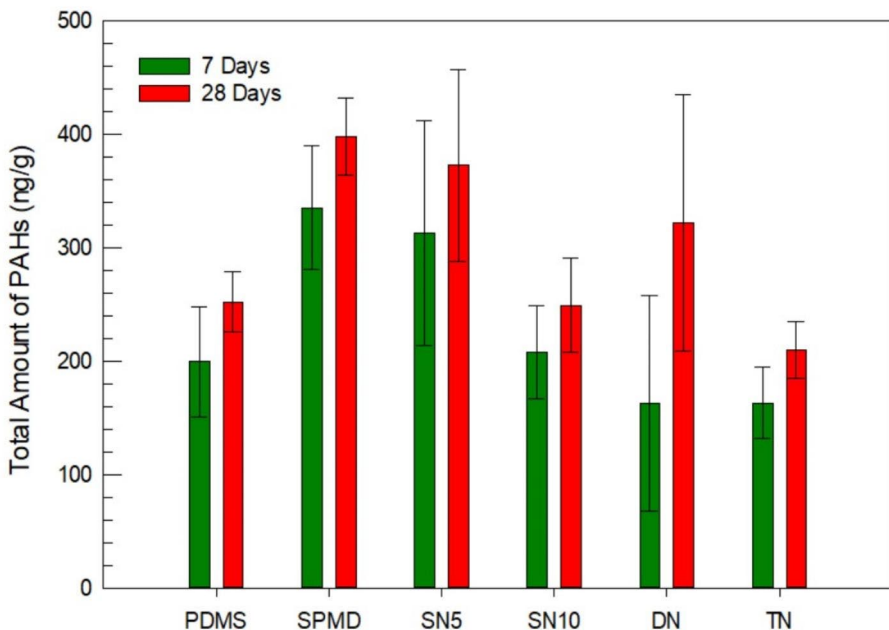


Fig. 2 The total amount of sampled PAHs in the samplers

it can be seen that the detected numbers of PAHs were twelve and thirteen after 7 and 28 days, respectively.

Benzo(a)anthracene (BaA), chrysene (CHR), and benzo(b)fluoranthene (BbFA) were accumulated at the highest concentrations by SMPDs for both sampling days. However, this accumulation behavior changed for the PAHs with $\log K_{ow}$ values higher than 6.0. For example, for benzo(k)fluoranthene (BkFA), SN10 and DN sampled the highest amount for 7 and 28 days, respectively. Moreover, for benzo(a)pyrene (BaP) which exhibits the most carcinogenic and mutagenic effects on the organisms (Lee and Shim 2007), the highest amounts were detected by SPMD after 7 days and by DN after 28 days.

As was mentioned, the main difference related to PAH accumulation performances between butyl rubber and other samplers was observed for the PAHs having higher $\log K_{ow}$ values. To highlight these performance differences of the samplers, the sampled amounts of dibenzo (a,h)anthracene (DBahA), benzo(g,h,i)perylene (BghiP), and indeno(1,2,3-c,d)pyrene (IP) by the passive samples were compared in Fig. 3. DBahA was not collected at all by PDMS and SPMD samplers for both sampling periods. Although BghiP was sampled by PDMS sampler in both periods, it could only be detected by SPMDs after 28 days. IP, on the other hand, was sampled by SPMDs for both periods, but it was not collected by the PDMS sampler. Moreover, even when these three PAHs were sampled by PDMS and SPMD samplers, the sampled amounts were too low when compared with the BR samplers.

These performance differences between samplers can be explained by various factors. Firstly, when the performance of the PDMS sampler is investigated, their lack of ability to collect PAHs with high molecular weight can be explained by their sampling rates and capacity. Previous laboratory studies have shown that for the PAHs with low $\log K_{ow}$ values, namely naphthalene, phenanthrene, fluoranthene and pyrene, BR sorbents reached equilibrium more rapidly than PDMS sampler; in addition, the absorbed amounts of these PAHs were much higher in BR sorbents. For example, amounts of naphthalene in the equilibrium phase by 1 g of samplers were 12 mg and 28 mg for PDMS and BR sorbent, respectively, which indicates a lower absorption capacity for the PDMS sampler (Tureyen et al. 2021). The difference between PDMS and BR sorbents can be explained with the same phenomena with laboratory studies, which shows that PDMS samplers become repleted with low molecular weight PAHs rapidly and are not able to sample high molecular weight PAHs. BR sorbents, on the other hand, do not become repleted because of their high surface area to volume ratios and high absorption capacities, and they are able to collect all PAHs.

When the performances of the SPMDs and BR sorbents are compared, the difference can be explained by their biphasic and monophasic structures, respectively. In the literature, it was indicated numerous times that SPMDs reach equilibrium for high molecular weight PAHs slowly and the required times can reach more than 60 days (Booij et al. 1998; Virturella et al. 2004) as mentioned before, and in the presented study, sampling periods were 7 and 28 days, which can be insufficient for SPMDs to sample PAHs with high $\log K_{ow}$ values. This behavior is attributed to its biphasic structure because for PAHs with high $\log K_{ow}$ values, diffusion through the membrane walls is challenging. On the other hand, BR sorbents have a monophasic structure and PAHs can be absorbed directly into the pores of the sampler. The same difference in performance between BR sorbents and SPMD sorbents for high molecular weight PAHs was also reported in a previous study (Yilmaz et al. 2014). In that study, it was indicated that the ratio of PAH concentrations in SPMD and BR sam-

Table 1 Individual PAH concentrations in passive samplers (ng/g) used in Istinye Bay

	log K _{ow}	PDMS-7	PDMS-28	SPMD-7	SPMD-28	SN5-7	SN5-28	SN10-7	SN10-28	DN-7	DN-28	TN-7	TN-28
AC	3.92	19.2	7.7	40.6	44.8	22.8	27.4	15.4	15.5	15.8	23.2	18.3	14.6
FL	4.18	27.4	28.6	22.5	27.6	17.7	20.1	11.8	15.6	16.2	15.9	9.6	14.9
PHE	4.57	26.4	90.6	33.9	102.4	39.0	82.8	27.7	50.3	25.5	60.5	28.7	46.7
AN	4.54	0.2	1.5	5.0	5.8	0.9	1.7	4.2	4.0	1.7	4.2	2.3	2.4
FA	5.22	7.3	25.5	15.1	57.2	14.1	32.8	12.7	18.8	8.5	31.7	9.2	14.6
PY	5.18	6.8	43.4	17.3	77.0	14.3	51.1	11.0	26.9	8.1	40.5	7.8	20.6
BaA	5.91	bdl*	bdl	19.6	19.7	3.9	2.1	7.5	7.2	3.8	11.4	3.6	3.8
CHR	5.86	0.4	0.6	11.9	12.3	4.6	8.8	7.8	8.4	3.8	8.0	3.3	5.0
BbFA	5.8	bdl	0.5	15.5	18.0	4.7	7.7	6.9	7.2	4.0	17.1	3.4	4.9
BkFA	6	bdl	bdl	5.7	5.7	2.2	2.3	6.0	5.8	3.4	7.4	2.8	3.3
BaP	6.04	bdl	0.4	9.0	10.0	4.2	5.8	6.8	6.3	5.2	13.5	3.7	12.0
DBahA	6.75	bdl	bdl	bdl	bdl	6.0	3.4	5.4	4.3	6.9	1.5	3.1	3.0
BghiP	6.5	0.1	1.2	bdl	0.9	6.9	12.9	6.6	7.1	8.2	14.1	4.1	2.1
IP	6.58	bdl	bdl	0.7	1.9	3.5	4.6	5.1	5.2	4.9	13.8	3.5	3.3

Acenaphthene: AC; Fluorene: FL; Phenanthrene: PHE; Anthracene: AN; Fluoranthene: FA; Pyrene: PY; Benzo(a)anthracene: BaA; Chrysene: CHR; Benzo(b)fluoranthene, BbFA; Benzo(k)fluoranthene: BkFA; Benzo(a)pyrene: BaP; Dibenzo (a,h)anthracene: DBahA; Benzo(g,h,i)perylene: BghiP; Indeno(1,2,3-c,d)pyrene: IP; *bdl: below detection limits

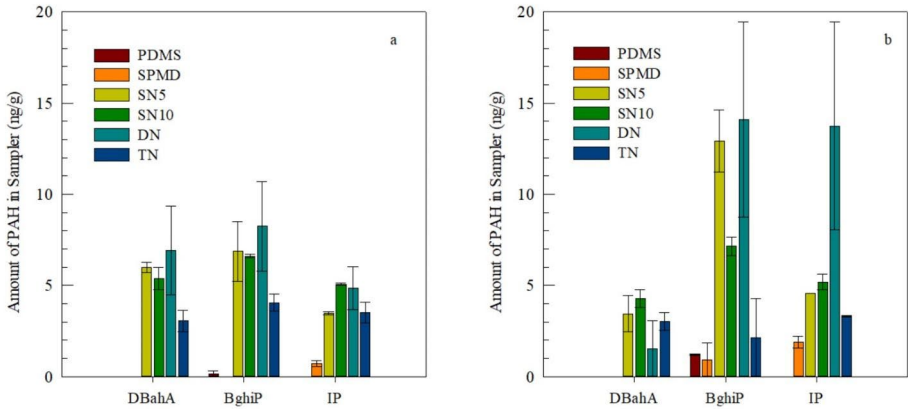


Fig. 3 The sampled amounts of PAHs with log K_{ow} values higher than 6.0: (a) for 7-day sampling period; (b) for 28-day sampling period

plers decreased with an increase in the value of the octanol-water partition coefficients of the PAHs.

When the performances of BR samplers are compared only among them, although the sampled amounts of PAHs are different, all of them were able to collect all PAHs. However,

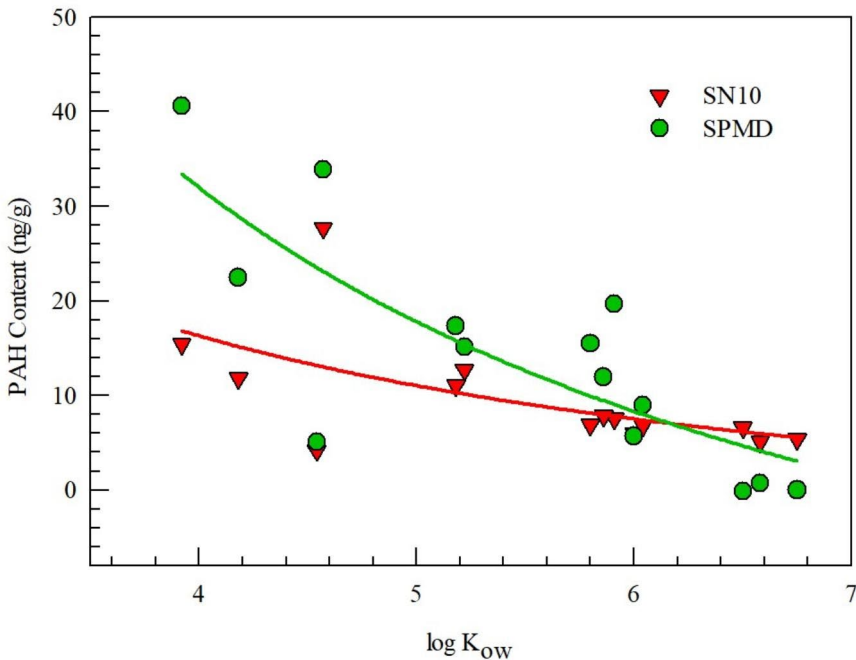


Fig. 4 Comparison of SN10 and SPMD sampler performances for different log K_{ow} values

it is worth mentioning that some analytical problems have been encountered with the SN5 sampler. Since the SN5 sampler has a high surface roughness, it is likely that the suspended materials in the water column were adsorbed to the sampler surfaces. Even though their surfaces, like all other samplers, were gently cleaned after their retrieval, it is considered that this phenomenon may have affected the results and the use of SN5 sorbents is not suggested by the authors for field studies. Other BR samplers have smoother surfaces which makes it hard for suspended materials to adsorb, and hence, no significant amounts of these materials were observed in the sampling processes. Moreover, double- and triple-network samplers have macroporous structures with different sizes of pores due to the multiple cryogelation processes, which make their production more complex and costlier; however, their overall PAH sampling performances are not improved as was expected by the authors, when compared with the single network BR samplers. In light of these facts, for field studies, the SN10 BR sampler can be considered as the most feasible option among BR samplers and DN samplers can be the second-best choice. In Fig. 4, the sampling performances of the SN10 sampler and the SPMD sampler for the PAHs with different $\log K_{ow}$ values are presented for clearer comparison.

As it can be seen from Fig. 4, even though the SPMD sampled higher amounts than the SN10 sampler for the PAHs with low $\log K_{ow}$ values, its performance decreases dramatically for PAHs with higher hydrophobicity. In fact, in this study, as mentioned earlier, they were not able to sample certain chemicals from the water column. On the other hand, SN10 samplers show consistent sampling performances for all $\log K_{ow}$ values and are able to sample all PAHs. Moreover, the ability to sample all pollutants from water to detect their existence in the water column is more critical and significant than the sampled amounts due to the fact that after certain amounts of sampling, the sampled amount is irrelevant for calculating the water concentrations of the chemicals. The significant parameters for back-calculating water concentrations of the pollutants are the sampling rates and partition coefficients rather than the “sampled amounts”.

4 Conclusions

The performance of the BR sorbent as an alternative passive sampler was determined via laboratory studies, and absorption rates and capacities of the different types of BR sorbents were compared with PDMS sampler for four PAHs, namely naphthalene, phenanthrene, fluoranthene and pyrene (Yetiskin et al. 2019; Tureyen et al. 2021). The results of these laboratory studies showed that BR sorbents have higher absorption rates and capacities for all four PAHs and encouraged future field studies for all 16 PAHs because those results indicated that the use of BR samplers is feasible and promising.

The PAH sampling ability of a series of BR sorbents was examined in field studies in Istinye Bay, Istanbul Strait. Four different types of BR sorbents were placed in the water column for 7 and 28 days along with the commercial samplers, SPMD, and PDMS. The collected amounts of PAHs in the samplers were determined in the laboratory, and the results showed that BR samplers have the ability to collect all fourteen PAHs regardless of their $\log K_{ow}$ values for both sampling periods. However, PDMS samplers only sampled seven and ten PAHs after 7 and 28 days, respectively, and SPMDs were only able to collect twelve and thirteen PAHs after 7 and 28 days, respectively. When compared with the biphasic structure

of the SPMD samplers, the monophasic BR samplers also provide more undemanding and effortless analytical procedures in field studies.

Moreover, the present study also indicates that BR samplers with a single network structure, like SN10 sampler, have the ability to sample all PAHs for both short- and long-term periods, and should be selected for monitoring studies. It should be noted that only the accumulated amounts of PAHs in the samplers were measured in this study, and the water concentrations of chemicals were not calculated. Further studies to determine partition coefficients of the BR samplers should be conducted primarily to back-calculate the water concentrations.

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Author contributions All authors contributed to the study's conception and design. Material preparation, data collection and analysis were performed also by all authors. The first draft of the manuscript was written by Oktay Eren Tureyen and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data Availability The datasets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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