Contribution of Passive Sampling Devices on the Determination of Hydrophobic Organic Contaminant Bioaccumulation in Marine Organisms

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ABSTRACT
Hydrophobic Organic Contaminants (HOC) are a group of chemicals needed to determine the health of marine ecosystems, and passive sampling devices are promising tools that offer a convenient monitoring opportunity. Traditional biomonitoring studies involved different types of marine organisms, and it appeared that simultaneous deployment of passive samplers with biomonitoring organisms provided the necessary information for the calculation of the aquatic organisms' bioaccumulation factors (BAF). There was not any other parameter than BAF, that could be used to determine the biomagnification and fate of contaminants in the upper trophic levels, which eventually affect all marine and terrestrial ecosystem health. In the light of the essence of BAF, this study applied a modified version of BAF estimation dependent on the contaminant concentrations both in the passive and active samplers. Thus, BAF parameters could be calculated properly without any need of a contaminant concentration in the surrounding water environment. For this purpose, the HOC concentration detected from the anthropogenic settlements in the coastal regions of Turkey were collocated, evaluated, and represented for different HOC groups. It was concluded that the present method is appropriate and applicable for BAF calculations of different groups of HOCs, where there are simultaneous deployments of both active and passive samplers in the process of biomonitoring studies.

Keywords: Passive sampling, HOC, bioaccumulation, BAF, concentration ratio model

INTRODUCTION
Polyaromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and organochloride pesticides all belong to the group of hydrophobic organic contaminants (HOCs). The determination of concentrations of hydrophobic organic contaminants (HOCs) in water samples is difficult because of chemical properties like low water solubility, high lipophilicity, strong adsorption tendency to suspended materials and tendency to accumulate in organisms (David et al., 2010). In order to overcome this obstacle, alternative methods such as biomonitoring and passive sampling have been used for determination of the sources and the fate of HOCs in different matrices of the marine environment (Blasco & Picó, 2009; Bourgeault & Gourlay-Francé, 2013). Bivalve mollusks and Semi-Permeable Membrane Devices (SPMD) are widely used examples of biomonitoring and passive sampling studies for the determination of HOC concentration in a water environment (André Lourenço et al., 2015; Fontenelle, Taniyama, da Silva, & Lourenço, 2019; Lance, Matz, Reeves, & Verbrugge, 2012; Lourenço et al., 2016; Peven, Uhler, & Querzoli, 1996). A wide geographic distribution and the sessile nature of bivalves makes them the preferable organisms in biomonitoring studies, in addition to the accumulation tendency of HOCs in bivalves (Bayne, 1976). On the other hand, passive samplers have the advantage of not being affected
by the poor water quality in contrast to the organisms that need to survive to be used in biomonitoring studies. Thus, a type of passive samplers, SPMDs, have become a popular instrument of detecting HOCs in water bodies (Huckins, J.N.; Petty, J.D.; Booij, 2006; Huckins, J.N.; Tubergen, M.W.; Manuweera, 1990).

Diffusion and partitioning are the main pathways of PAH accumulation in SPMDs, thus freely dissolved contaminants in water can be detected precisely over a specific time interval (Gourlay, Tusseau-Vuillemin, Garric, & Mouchel, 2003; Greenwood, Mills, & Roig, 2007). The deployment of SPMD during a specific time interval has many advantages compared with a spot analysis of water contamination. For example, the decrement of detection limits due to an accumulation tendency of HOCs into the material led eventually to a higher concentration of contaminants accumulated in SPMDs. In addition, the average measurement of a time period instead of a measurement of a moment provides more reliable results of the target zone (Uher, Mirande-Bret, & Gourlay-Francé, 2016). SPMDs are not designed to mimic all metabolic activities of aquatic organisms, but instead to mimic the pathways of diffusion and partitioning in the process of contaminant bioaccumulation through adsorption to the surfaces of the target organism like algae, mussel, fish etc. (Gourlay et al., 2005; Mayer, Philipp; Tolls, Johannes; Hermens, Joop L.M.; Mackay, 2003; Uher et al., 2016). Thus, simultaneous deployment of passive and active sampling devices (for example, SPMDs and bivalves) is promising for more sensitive and reliable measurements as applied in many studies (Amdany et al., 2014; Bourgeault & Gourlay-Francé, 2013; David et al., 2010; Verweij, Booij, Satumalay, Van Der Molen, & Van Der Oost, 2004; Vrana et al., 2014).

The main advantage of simultaneous deployment of active and passive sampling methods is to be able to determine the bioaccumulation tendency of HOCs in selected marine organisms without any need of ambient water concentration data (Booij, Smedes, Van Weerlee, & Honkoop, 2006). The similar uptake processes of HOCs in both bivalves and passive samplers enable researchers to obtain the bioaccumulation data by means of a comparison of accumulated HOC concentrations in both organisms and samplers (Harman, Brooks, Sundt, Meier, & Grung, 2011). The assessment of HOCs in different matrices of the marine environment was performed using this approach in several studies (e.g. Bourgeault & Gourlay-Francé, 2013; David et al., 2010). This study aimed to determine the bioaccumulation factors in marine organisms using the concentrations of HOCs detected in the western and north-western regions of Turkey by means of this simultaneous monitoring type of approach. Within the scope of this study, bioaccumulation of HOCs in selected marine organisms were determined without the necessity of additional HOCs data, like its presence and concentration in the surrounding water environment. Consequently, the results of the simultaneous deployment of the Mediterranean mussel species, Mytilus galloprovincialis, and SPMDs were evaluated using a published concentration ratio model (Booij et al., 2006) that was taken as the basis of a BAF determination, and adapted for evaluation of HOCs in determining bioaccumulation factors of selected marine organisms for PAH, PCB and OCP.

**MATERIALS AND METHODS**

The concentration data of HOCs (PAHs, PCBs and OCPs) in mussels and SPMDs were collocated from three previously published papers (Karacik, Okay, Henkelmann, Pfister, & Schramm, 2013; O. S. Okay et al., 2014; Oya S. Okay et al., 2017). The data in the referenced papers was reorganized into Excel sheets and used as inputs for the present study. The field studies in the papers were accomplished in total at 13 different stations: four stations along the Istanbul Strait with a deployment time of seven and 21 days; and nine stations in anthropogenic settlements like shipyards and marinas with a deployment time of 30 and 60 days, which are located in the west and north-west coast of Turkey (three marinas in the west, three shipyards and three marinas in the north-west coast of the country). Because the detailed locations of sampling stations were given in the referenced papers (Karacik et al., 2013; O. S. Okay et al., 2014; O.S. Okay et al., 2017) and the choice of sampling stations were out of the scope of the present study, the sampling stations are only shown in general as seen in Figure 1.

The variety of stations enhanced the results of this study. For example, sampling stations at the north-west coast of the country are in the most populated city of the country (Istanbul) with about 17 million inhabitants. Marinas and shipyards in this region are on different sides of the city. The east part of the south entrance of the Istanbul Strait is filled with marinas while the east border of the city is filled with several shipyard companies consisting of a higher number of workers. On the other hand, sampling stations at the west coast of the country are located in a less populated area which is popular with summer tourism. As mentioned in the referenced papers, the Mediterranean mussel, Mytilus galloprovincialis, was used as the selected mussel species, and simultaneously deployed with a commercial type of passive sampler, SPMD. The data from these two different types of samplers, named as active and passive samplers, was used as inputs in the present study in order to determine the bioaccumulation potential of HOCs.
The analyzed results of HOCs in mussels and SPMDs were used in the slightly modified version of the mussel/SPMD concentration ratio model (Booij et al., 2006). The modification included the parameter of initial contaminant concentration in transplanted mussels, which is not a zero value naturally, at the time of deployment. The fitting of field data was implemented using the NonlinearModelFit method in Mathematica (Wolfram Research, version 10.0). The kinetic rate constants were matched with the results of mussel and SPMD analysis. Not all the results were used in the NonlinearModelFit method because of the detection limitations of some HOCs. Among all HOCs, the data of 14 PAHs and 11 PCBs were used for the implementation of the NMF method. Regression equations presented in the referenced publication were used for determination of the SPMD-water partitioning coefficient ($K_{spmd}$, L kg$^{-1}$) and elimination rate constant of the SPMD ($k_e$, d$^{-1}$) (Booij et al., 2006). The bioaccumulation factors (BAF, L kg$^{-1}$) were obtained by replacing the determined coefficients and constants in Equation (1).

$$C_M = \frac{C_{SPMD} \cdot k_{BAF} \cdot (1-e^{-kt_{SPMD}}) + C_{M0} \cdot e^{-kt_{M0}}}{K_{SW} \cdot (1-e^{-kt_{M0}})} \quad (1)$$

In Equation (1), $C_M$ (ng g$^{-1}$), $C_{SPMD}$ (ng g$^{-1}$), $C_{M0}$ (ng g$^{-1}$ triolein), $t_{SPMD}$ (g mL$^{-1}$) represents the mussel concentration at any day, the mussel concentration at the initial day (day 0), the SPMD concentration and its density, respectively. Because the initial concentrations of mussels are not always zero, Equation (1) consists of an additional term compared with the original equation in reference (Booij et al., 2006). After fitting Equation (1), the parameters of BAF were evaluated with respect to their octanol-water partition coefficient ($K_{ow}$) dependency. Thus, BAFs (L kg$^{-1}$) of mussels for a series of HOCs were obtained without any need of ambient water concentration.

RESULTS AND DISCUSSION

Log $K_{ow}$ values for a series of HOCs range within 3.37 and 7.41; specifically, between 3.37 – 6.9 for PAHs, 5.66 – 7.41 for PCBs and 3.7 – 7.13 for OCPs. This variation brought about inherently different patterns of accumulation. It was seen that Log $K_{ow}$ values positively correlate with the accumulation of PAH and OCP both in the passive and active samplers. On the contrary, the accumulation of PCBs followed a different trend. This difference was probably the result of having comparatively higher Log $K_{ow}$ values. The different nature of HOCs reflected their accumulation patterns.

The activities that originated from human actions were the main source of PAHs. The field monitoring results in the areas of the marina and shipyard were evidence of this fact (O. S. Okay et al., 2014; Oya S. Okay et al., 2017; Yılmaz et al., 2014). In addition, the products of industrial waste were the sources of PCBs (Cardelicchio et al., 2007; Cetin et al., 2017; Helou, Harmouche-Karaki, Karake, & Narbonne, 2019; Hong, Yim, Shim, Li, & Oh, 2006), and this was seen clearly in the comparison between the shipyard and marina zones. The machinery and equipment used in the construction, maintenance, and repair of ships in shipyards seemed to directly affect this pattern difference. The main source of OCPs are the products related to agriculture (Ahmad, Salem, & Estatieh, 2010; Fenik, Tankiewicz, & Biziuk, 2011; Helou et al., 2019), thus they are generally detected at low rates.

The results of HOCs were grouped into two groups, depending on their deployment times. The reason for this grouping was to help in the evaluation of different features at the sampling stations. The first group deployment time was 7 and 21 days, and the second group was 30 and 60 days. Therefore, NonlinearModelFit function was run separately for the two groups, and the output was represented as separate figures. Figures 2 and 3 are results of the first group while Figure 5 represents the output of the second group.

![Figure 2. The ratio of contaminant concentrations in SPMD ($C_{SPMD}$) and transplanted mussel ($C_M$) versus octanol-water coefficients ($Log K_{ow}$) of related contaminants is shown. Each contaminant group is represented with a different color: PAH in green, PCB in red and OCP in blue for the deployment durations of 7 and 21 days, formed with open and closed symbols, respectively. Fitting models of each contaminant group are shown in their assigned colors in addition to the combined PAH-PCB-OCP data in grey color.](image-url)

The relationship between the ratios of SPMD and mussel concentrations ($C_{SPMD}/C_M$) and Log $K_{ow}$ values are shown in Figure 2 for the first group. An inverse trend was observed for the group of PAHs. The accumulation of PAHs decreased with the increase of Log $K_{ow}$ values. In contrast, the group of PCBs, which have higher $K_{ow}$ values, show the opposite trend. The trend of the data is represented with Equation (1) for PAH (in green), PCB (in red) and OCP (in blue) separately, as shown in Figure 2. The combined evaluation of PAH, PCB and OCP data (black spline in Figure 2) shows a plateau, which could be explained by the steric hindrance of higher molecular weight HOCs of Log $K_{ow}$ > 5.0, especially during the accumulation of PAHs through the pores of SPMDs (Luellen & Shea, 2002). This fact of uptake restriction due to the morphology was also mentioned in several observations (Huckins et al., 1999; Luellen & Shea, 2002).

Bioaccumulation factors (BAFs) were evaluated versus Log $K_{ow}$ values of contaminants. The data are matched separately and together for the groups of PAHs, PCBs and OCPs, as shown in Figure 3. Separate PAH and PCB data were matched well with linear regressions. Although the data of OCPs were scattered, they were also matched and represented with linear regression. Moreover, the combined data of PAH, PCB and OCP were fitted by a hyperbolic function. The characteristics of a fitted hyperbol-
ic function was not affected by the scattered data of OCPs. However, the data of PCBs was the main factor affecting the characteristics of the fitted function due to its decreasing trend with the increasing Log $K_{OW}$ values. This fact can also be considered as a probable inhibition of high Log $K_{OW}$ valued PCB accumulation (Baskaran, Armitage, & Wania, 2019; Qiu, Qiu, Zhang, & Li, 2019).

In Figure 4, y-scale of Log $C_S/CM$ enabled researchers to observe the different accumulation trends of the active and passive samplers, and the black line at Log 10 indicates the equality of their concentrations. The upper part of the black line signifies that the metabolism of HOCs in the selected marine organism is higher, whereas the lower part of the black line indicates that the contaminants in the particular phase were higher than their dissolved forms, as a reminder that the dissolved phase of contaminants accumulated in the passive sampler (Bourgeault & Gourlay-Francé, 2013; Gourlay-Francé, Lor-
deployment duration, the necessity and importance of the exposure time is a minimum of five days for SPMDs as stated in previous studies (Luellen & Shea, 2002). The outputs represented in Figure 6, range from seven days to an unlimited period of time. The results of different deployment times (7, 21, 30, 60, 360 and unlimited days), as shown in Figure 6, could be used for the evaluation and estimation of an efficient deployment time for prospective field monitoring studies. The importance of deployment time should not be undervalued for the design of field studies in an effort to reduce expenses such as disposables and chemicals used both in the field and laboratory and the addition of travel and transportation expenses in distance sampling.

![Figure 6. Predictions of deployment time, for different periods of time, ranging from seven days to infinity.](image)

**CONCLUSION**

The deployment of passive sampling devices in coordination with the field studies of marine organisms is a promising tool for the determination of bioaccumulation factors. The simultaneous usage of both active and passive sampling devices is increasing worldwide for the monitoring of hydrophobic organic contaminants in coastal zones. This study points out an additional feature of this simultaneous deployment: Determination of bioaccumulation factors in marine organisms without any need of HOC concentration data from the surrounding water environment. For this purpose, the concentration ratio model was modified successfully in the implementation of field data for Turkish coastal zones. Additionally, this same model equation was used for the comparison of different periods of deployment time, that could be a guide for an efficient planning of field studies with fewer expenses in consumables and transportation.

**Conflict of interests:** The author declares no financial, commercial and legal conflict of interest.

**Ethics committee approval:** In this study, the mathematical evaluation of a number of biomonitoring studies has been performed. Thus, the author declares that it does not need any ethics committee approval.

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**Disclosure:** -

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