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Modelling the fate of micropollutants in the marine environment using passive sampling



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ABSTRACT

Polydimethylsiloxane sheets were used to determine freely dissolved concentrations (C_{diss}) of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in the Belgian coastal zone. Equilibrium models were used to predict the whole water concentrations (C_{ww}) of these compounds as well as their concentrations in sediment, suspended particulate matter (SPM) and biota. In general, contaminant concentrations were predicted well for whole water and biota. C_{ww} was increasingly underpredicted as K_{oc} increased, possibly because of the presence of black carbon. Concentrations in biota were overestimated by the equilibrium approach when $\log K_{ow}$ exceeded 6.5, suggesting an increasing role of transformation processes. Concentrations of PAHs and PCBs in sediment and SPM were consistently underpredicted although a good correlation between measured and predicted values was observed. This was potentially due to the use of experimental K_{oc} values which have been found to underestimate partitioning of hydrophobic substances to sediment in field studies.

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1. Introduction

For the environmental and human health risk assessment of chemicals in the aquatic environment, reliable concentration data of chemicals in water, sediment and biota are indispensable. However, the monitoring and analysis of chemicals in these compartments continues to represent a significant challenge. Indeed, using conventional grab samples, a relatively large number of samples is needed for a given sampling area to obtain reliable and meaningful exposure data (Namięśnik et al., 2005; Zabiegała et al., 2010). Such a sampling approach is time consuming and can be very costly (Kot-Wasik et al., 2007) and the chemical analysis often requires difficult extraction and clean-up techniques (Greenwood et al., 2009).

One option to reduce this monitoring effort is to obtain data on freely dissolved concentrations of contaminants. Such data can then be used to predict the partitioning of these compounds to other compartments (e.g. sediment and biota) (Rusina et al., 2007; De Laender et al., 2010a, 2011). However, many nonpolar organic substances such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) readily sorb to

sediments and suspended particulate matter (SPM), causing their dissolved concentrations to be in the low ng L^{-1} to pg L^{-1} range which makes them difficult to quantify (Allan et al., 2009). Moreover, surface water generally also contains dissolved organic carbon (DOC) which is – unlike SPM – not separated from the water sample by the conventional filtration techniques. As hydrophobic compounds (e.g. PAHs and PCBs) bind to DOC, the fraction regarded as “dissolved” concentrations of such compounds in reality still consists of a freely dissolved and a DOC-bound fraction (Hermans et al., 1992).

To measure freely dissolved concentrations of contaminants more directly without interference by the DOC-bound fraction, passive sampling devices can be used (Mayer et al., 2003). Examples of such samplers include the bi-phasic semipermeable membrane devices (SPMDs) which have been used since the 1990s (Huckins et al., 1990). Many single-phase materials such as polydimethylsiloxane (PDMS), low-density polyethylene (LDPE) and polyoxymethylene show a high affinity for hydrophobic compounds as well, are cheaper and easier to use than SPMDs and they have the possibility to be reused (Rusina et al., 2007; Booij et al., 1998; Mayer et al., 2003). Moreover, passive samplers integrate the contaminants over the exposure time which makes it a technique that is much less sensitive to accidental, extreme variations of contaminant concentrations (Namięśnik et al., 2005). In a number of studies, it has already been attempted to compare and

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correlate contaminant concentrations in passive samplers (mostly SPMDs) to those in biota (Axelman et al., 1999; Leslie et al., 2002; Huckins et al., 2004; Verweij et al., 2004; Gourlay et al., 2005; Booij et al., 2006; Ke et al., 2007a,b; David et al., 2010) and to a lesser extent in sediment (Verweij et al., 2004; David et al., 2010). In these studies, uncontaminated biota (often bivalves) were caged and deployed in parallel with the passive samplers.

The goal of this study is to evaluate if dissolved aqueous contaminant concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) derived from passive sampling can be used to obtain reliable estimates of contaminant concentrations in different marine compartments: i.e. the whole water phase, sediment, SPM and biota. The predicted concentrations are compared with analytical data obtained through the conventional chemical analysis of grab samples from the same area where the passive samplers were deployed. The suitability of equilibrium models is discussed for each compartment.

2. Methodology

2.1. Conventional sampling and chemical analysis

Detailed information on the sampling methods and the subsequent chemical analysis can be found in Monteyne et al. (2013) and Claessens et al. (2012). Briefly, water, sediment, suspended particulate matter (SPM), shrimp (*Crangon crangon*) and flatfish (*Limanda limanda*, muscle tissue and liver separately) were sampled at 6 offshore locations on the Belgian Continental Shelf. Additional water and sediment samples were taken at different locations in three Belgian coastal harbours. All sampling stations are represented in Fig. 1. Full sampling campaigns were conducted in 2007, 2008 and 2009.

Water samples were extracted using solid-phase extraction. Sediment samples were centrifuged with a flow-through centrifuge (Biofuge Stratos Heraeus, Kendro Laboratory Products, Hanau, Germany) to obtain the clay fraction (<63 µm), biota samples were homogenized with a dispersion tool (IKA Ultra-Turrax® T25 Basic, Staufen, Germany). All solid material samples were then freeze dried with a Christ LMC-2 (Osterode, Germany), milled and homogenized with a Fritsch Pulverisette (Idar-Oberstein, Germany) and subsequently extracted using pressurised liquid extraction. Extracts were cleaned up by adsorption chromatography on alumina with AlOx and compounds were eluted with hexane. All extracts were analysed for PAHs with GC/MS (Thermoquest, Rodano, Milan, Italy) and for PCBs by GC/MS/MS (ThermoFinnigan, Austin, Texas, USA). A full list of the analysed substances including physicochemical characteristics is available in the Supporting Information (SI).

The dissolved organic carbon (DOC) content of the water samples was determined as described by Heining et al. (2002). The sample was automatically injected and pumped through a Skalar continuous flow chain (Skalar Analytical, Breda, The Netherlands). A known ratio of potassium hydroxide and disodiumtetraborate were added after which the sample was led through a Quartz tube coiled around a UV-lamp followed by the addition of sulphuric acid and heating to 97 °C. The acid was subsequently neutralized by the addition sodium hydroxide in the presence of ascorbic acid to neutralize chlorine. A known ratio of molybdate and ascorbic acid were added to a sample of the resulting solution and heated to 40 °C, causing colour formation. Finally, the extinction of the sample was measured at 880 and 1010 nm with a matrix photometer. Organic carbon contents of sediment and SPM were determined with a flash element analyzer (Thermoquest, Milano, Italy), using the principle of catalytic oxidation followed by gas chromatography (Heining et al., 2002). The carbon in the samples is transformed into carbon dioxide in the presence of pure oxygen and tungstenoxide. Subsequently, water is

removed from the CO₂-gas by passing it through a magnesium perchlorate column. The CO₂-gas is then separated from nitrogen gas on a packed GC column and detected with a thermal conductivity detector. Glycine was used as a standard.

To determine the lipid contents of the organisms, the lipid weight was measured by pressurised liquid extraction followed by a drying step. Freeze dried biota was extracted using an Accelerated Solvent Extractor (ASE) (Dionex, California, USA). The ASE was used with 100% of dichloromethane with purity for organic residue analysis as solvent. Extraction cells of 11 mL containing 1 g of biota were filled with solvent and heated within 5 min to 100 °C. The materials were extracted with 2 static cycles of 5 min. Between each static cycle 60% of the solvent was renewed. At the end of the extraction, the cells were rinsed with solvent and purged with nitrogen. The extract was collected in a pre-weighed vial and then dried in an oven at 50 °C until constant weight was attained. Based on the final weight of the vial, the lipid content was calculated and expressed as a percentage of the dry weight.

2.2. Passive sampling

Full details on the passive sampling methodology can be found in Monteyne et al. (2013). Briefly, polydimethylsiloxane sheets (AlteSil Laboratory Sheet, Altec Products Ltd, Bude, United Kingdom) measuring 0.5 × 55 × 99 mm³ were used as passive samplers. The samplers were precleaned by soxhlet extraction with ethylacetate and subsequently spiked with performance reference compounds (PRCs) according to the method described by Booij et al. (2002). From 2007 to 2009, passive samplers were deployed annually as part of the integrated sampling campaigns. In addition, passive samplers were deployed in parallel with caged mussels as part of 2 biomarker experiments conducted in 2008 and 2009 (Claessens et al., 2012). The tissue of the mussels used in these experiments were analyzed for PAHs and PCBs according to the procedures described above. For each passive sampling campaign, samplers were deployed at 4 to 7 stations for six to eleven weeks in a stainless steel cage. All stations used for passive sampling are represented in Fig. 1. After retrieval, the samplers were cleaned to remove biofouling and subsequently extracted by soxhlet extraction using a 1:3 acetone-hexane (v/v) solution. Extracts were analyzed for PAHs and PCBs by GC/MS. Freely dissolved water concentrations of PAHs and PCBs (C_{diss} expressed in µg L⁻¹) were calculated using the sampling rate R_s (L d⁻¹) according to the non-linear least squares method described by Booij and Smedes (2010). The latter was derived from dissipation rates of the PRCs following the methodology of Rusina et al. (2010). More details on the derivation of C_{diss} can be found in Monteyne et al. (2013).

2.3. Modelling

The freely dissolved water concentration data of PAHs and PCBs obtained with passive sampling was used as input in a simple equilibrium model to predict the concentrations of these compounds in sediment, SPM and biota as well as their whole water concentrations (C_{ww}). In order to calculate C_{ww} , the following formula was used:

$$C_{ww} = C_{diss}(1 + K_{oc} \cdot [DOC] + K_{oc} \cdot [POC]) \quad (1)$$

where C_{diss} is the freely dissolved concentration in seawater as derived from passive sampling (µg L⁻¹), K_{oc} is the organic carbon-water partition coefficient in L kg⁻¹, and [DOC] and [POC] are the concentrations of DOC and POC in seawater (kg L⁻¹), respectively.

Concentrations in sediment and SPM were calculated as:

$$C_{sol} = C_{diss} \cdot K_{oc} \cdot f_{oc,sol} \quad (2)$$

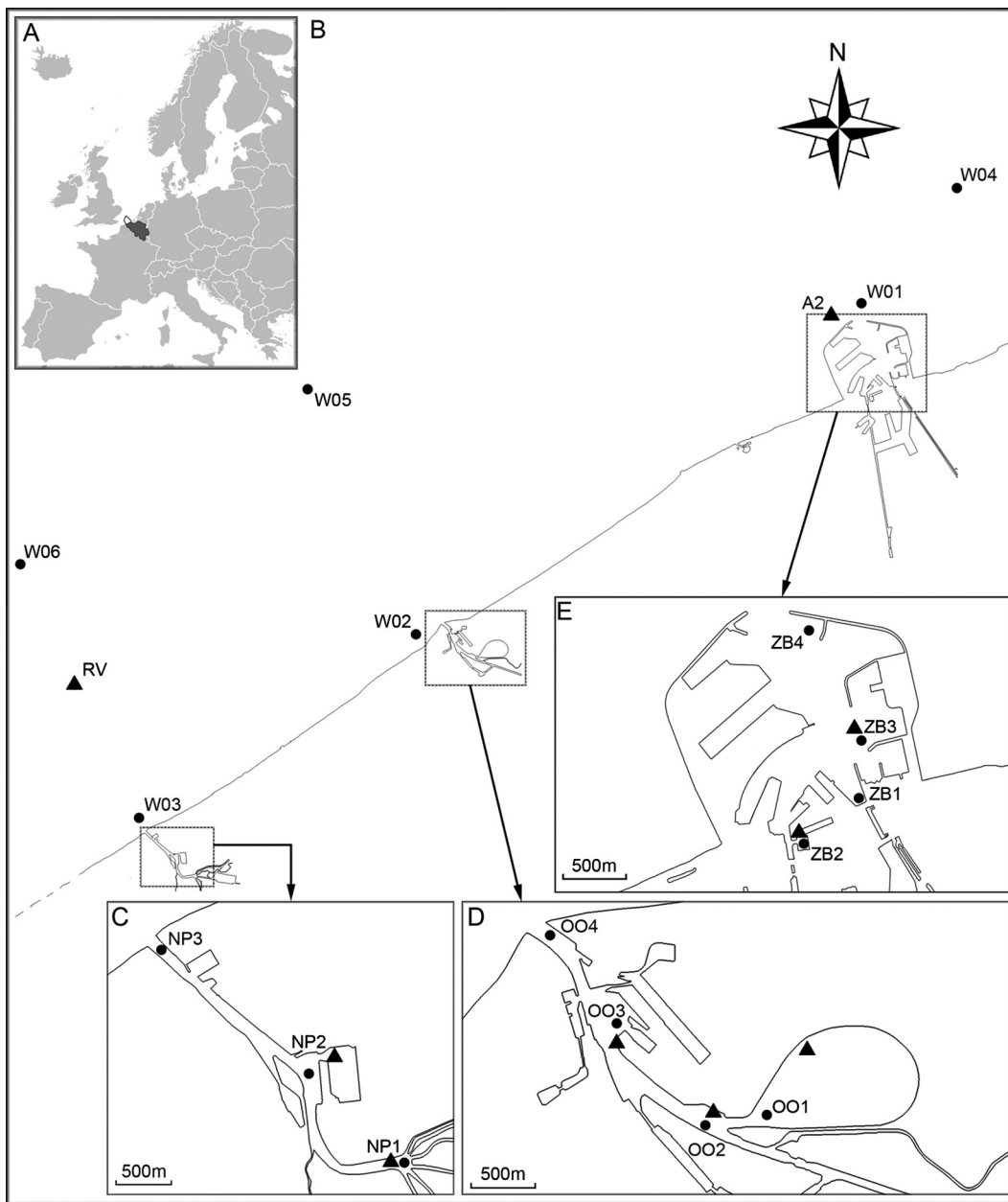


Fig. 1. The study area; (A) Location of Belgium in Europe; (B) Overview of the Belgian coastal zone showing eight sampling stations (including 2 passive sampling stations) on the Belgian Continental Shelf; (C) Three sampling stations in the harbour of Nieuwpoort; (D) Four sampling stations in the harbour of Oostende; (E) Four sampling stations in the harbour of Zeebrugge. ●: station included in the integrated sampling campaigns; ▲: station where passive samplers were deployed.

where C_{sol} is the concentration of pollutants in solids (either sediment or SPM, $\mu\text{g kg}^{-1}$) and $f_{oc,sol}$ is the fraction of organic carbon in the solids.

Concentrations in biota were calculated as:

$$C_{biota} = C_{diss} \cdot K_{ow} \tag{3}$$

where C_{biota} is the concentration in biota (either shrimps, mussels, flatfish liver or flatfish muscle tissue, $\mu\text{g kg lipid}^{-1}$) and K_{ow} is the octanol–water partition coefficient (L kg^{-1}). A list of the used values for K_{oc} and K_{ow} is available in the SI.

To investigate the performance of the models for each compartment, the model bias (MB) was calculated as:

$$MB = 10^{\frac{\sum_{i=1}^n \log \frac{\text{Predicted}(i)}{\text{Observed}(i)}}{n}} \tag{4}$$

where $\text{Predicted}(i)$ is the concentration predicted by the model in the respective compartment at a given location and time, $\text{Observed}(i)$ is the corresponding measured concentration and n is the number of observations. Additionally, the accuracy of the model predictions was assessed by calculating the percentage of predicted data falling within a certain factor of the observed data. When a compound was not detected by conventional monitoring in a certain compartment, its concentrations was set at half the detection limit. It is important to note that while in the harbours the passive sampling stations are in close proximity of the stations used for the conventional sampling campaigns, this is not the case for the offshore stations. Indeed, as passive sampling station RV is situated roughly halfway in between stations W03 and W06 (Fig. 1), there is no conventional sampling station available for direct comparison. For this reason, median measured values from the offshore stations

were used for comparison with the predicted data from stations A2 and RV. As the open sea can be considered as a more homogeneous mass than the water bodies within the strongly enclosed harbours, this approach was not expected to generate any additional mismatches.

All modelling was performed using the free software R (R Development Core Team, 2011).

3. Results and discussion

3.1. Whole water concentrations

The equilibrium model predicted 66% and 79% of the measured data within a factor of 5 and within an order of magnitude, respectively (Fig. 2A). When interpreting these data, it is important to realise that the water concentrations measured using conventional methods only represent a single point estimate and therefore show a much higher degree of variability than the time-weighted average (TWA) concentrations obtained by passive sampling. This variability is, in a short time frame, due to tidal action and causes differences in contaminant concentrations of up to a factor of 16 (Boyden et al., 1979; Pane et al., 2005). On a longer term, variability may also be due to other factors like weather conditions (e.g. heavy rainfall) and temporal differences in emissions of the contaminants.

Further analysis of model-data deviations (Fig. 2B) revealed that the whole water concentrations were increasingly underpredicted as the K_{oc} value of the compounds increased. Different factors may explain this trend. Firstly, to model partitioning of compounds to DOC and POC specific partition coefficients (i.e. K_{DOC} and K_{POC} , respectively) are often used instead of K_{oc} from which they differ (e.g. Lüers and ten Hulscher, 1996; Burkhard, 2000). Thus, an attempt to eliminate the model bias was made by using K_{DOC} and K_{POC} values to model partitioning of PAHs and PCBs to DOC and POC, respectively (see SI). In a regression analysis $\log K_{DOC}$ and $\log K_{POC}$ showed significant linear relations with $\log K_{oc}$, with slopes of 1.19 and 1.11, respectively (see SI). As such, using K_{DOC} and K_{POC} as refined estimates of K_{oc} should improve the model's accuracy with increasing $\log K_{oc}$. Indeed, the use of these parameters made this bias less pronounced (see SI) but the resulting model bias of 0.29 indicated a stronger overall underprediction. Monteyne et al. (2013) – who performed a similar, less extensive modelling

exercise on the data used in this study – suggested that the presence of black carbon (BC) in the water column may be responsible for the underprediction of whole water concentrations. As data on BC concentrations were not available in this study, the fraction of compounds sorbed to BC could not be taken into account. Similar as for $\log K_{DOC}$ and $\log K_{POC}$, the BC-water partition coefficient $\log K_{BC}$ exhibits a slope of 1.10 in relation with $\log K_{oc}$ (see SI) and inclusion of BC in the equilibrium model may as such contribute to reduce the observed trend in the model bias. While the fraction of BC in SPM is in general more than a factor of 10 lower than the fraction of OC (Zhou et al., 1999), K_{BC} is on average a factor of 37.4 ± 27.4 higher than K_{oc} for the substances in this study. As such, BC should be included in any future modelling efforts of this kind.

3.2. Concentrations in sediment and SPM

The equilibrium model performed poorly for sediment and SPM. The model bias (MB) indicated that the model generally underestimated both the concentrations in sediment and SPM by a factor of 50. Only about 10% of the predicted values was accurate within an order of magnitude for both matrices (Table 1). Fig. 3A and B confirm this bias graphically but nevertheless also indicate a relatively strong relationship between the observed and predicted data. Indeed, statistical analysis of the data yielded Pearson correlation coefficients of 0.66 ($N=322$, $p < 0.001$) and 0.73 ($N=48$, $p < 0.001$) between the measured and predicted data for sediment and SPM, respectively. The slopes of the regression lines were 0.86 ± 0.06 and 0.70 ± 0.10 for sediment and SPM, respectively (Fig. 3). While at first it may seem interesting to look at factors like salinity and temperature – which both affect partition coefficients (DiFilippo and Eganhouse, 2010) – as a potential explanation for this underestimation, these factors are unlikely to have a significant effect on the predictions made in this study. First of all, any effect they have on (in this case) K_{oc} is highly unlikely to be sufficient to explain the underestimation of the PAH and PCB concentrations in sediment and SPM. For instance, the increase of K_{oc} with decreasing temperature has been found to be in the range of 60% per 10 °C for PAHs (Delle Site, 2001), which is not large enough to explain the observed underestimation. Secondly, it is important to realise that not only K_{oc} would have to be corrected, but K_{sw} (the passive sampler-water partition coefficient) as well (Muijs and Jonker, 2009). This would have the opposite effect on

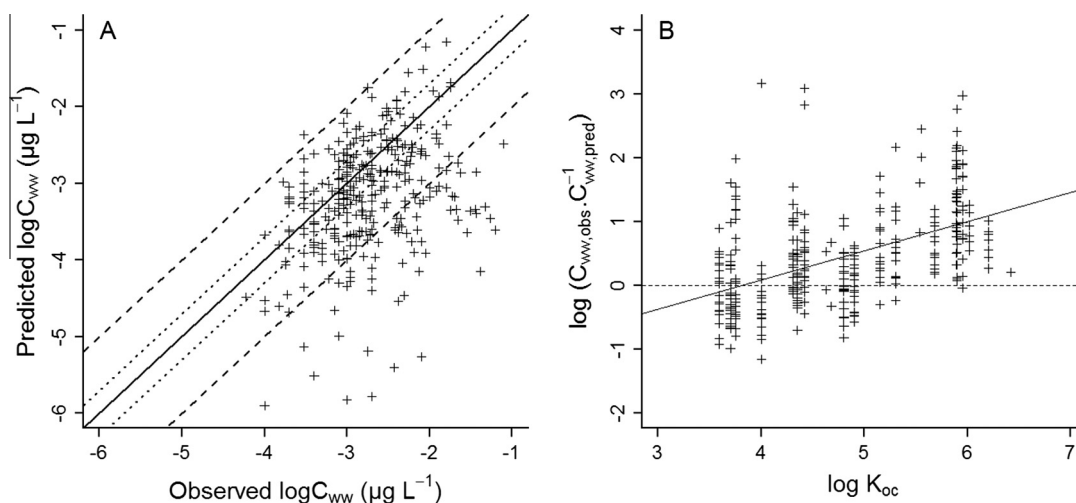


Fig. 2. Equilibrium model results for the prediction of whole water concentrations of PAHs and PCBs based on freely dissolved concentrations of these compounds as derived from passive sampling. (A) Measured versus predicted whole water concentrations of PAHs and PCBs. (B) The logarithm of the ratio of observed and predicted concentration data in water vs. $\log K_{oc}$. The solid line represents the regression line ($\log(C_{ww,obs} \cdot C_{ww,pred}^{-1}) = 0.46 \log K_{oc} - 1.74$, $N = 324$, $R^2 = 0.243$). Where $\log(C_{ww,obs} \cdot C_{ww,pred}^{-1})$ equals zero (dashed line), observed and predicted data are equal.

Table 1

Percentage of modelled PAH and PCB concentrations in sediment and SPM that fall within a specific factor (as given in the first column) of the measured data. The last row represents the model bias. N: number of data points; MB: model bias.

	Sediment (N = 322)	SPM (N = 48)
Factor 2	0.9	0
Factor 5	3.7	2.1
Factor 10	9	12.5
Factor 100	67.1	68.8
Factor 1000	96.3	96.3
MB	0.02	0.02

the predicted compound concentrations in sediment, as a higher K_{sw} leads to lower values for C_{ww} . A possible cause of the observed consistent underestimation is the tendency of literature values of K_{oc} to be an underestimate of field K_{oc} values. This was for example observed by Hawthorne et al. (2006), who found that field K_{oc} values were typically up to two orders of magnitude higher than literature values. In their review on the sorption of organic compounds to different carbon types in sediments and soils, Cornelissen et al. (2005) confirm this phenomenon for many different aquatic environments and multiple compound classes (including PAHs and PCBs). This was also observed in laboratory measurements of K_{oc} of PAHs and PCBs in which solid phase microextraction (SPME) was used to monitor freely dissolved concentrations of the organic chemicals (Durjava et al., 2007). The observed discrepancy between the literature and measured K_{oc} values was explained as an artifact due to the difficulties with measuring free concentrations of highly hydrophobic substances in other studies (Durjava et al., 2007). Indeed, any overestimation of freely dissolved concentrations would cause an underestimation of the true K_{oc} values (Burkhard, 2000). In order to perform a similar comparison between field- and lab-derived K_{oc} values, we calculated $\log K_{oc,field}$ from our data as follows:

$$\log K_{oc,field} = \log \left(\frac{C_{sol} \cdot f_{oc}}{C_{diss}} \right) \quad (5)$$

The difference between $\log K_{oc,field}$ and $\log K_{oc}$ was on average 1.76 ± 0.63 for sediment and 1.78 ± 0.62 for SPM (see SI for a graphical representation), which is similar to the findings of Hawthorne et al. (2006). As such, differences between field- and lab-derived K_{oc} values are a likely explanation for the poor performance of the equilibrium model for sediment and SPM.

Also, like for the whole water concentrations, the underestimation of PAH and PCB concentrations in solids may be due to the presence of BC. However, it is questionable whether the inclusion of BC could eliminate the observed underestimation by the equilibrium model for solids. Indeed, as mentioned above K_{BC} is on average a factor of 37 higher than K_{oc} . Given that BC generally represents only a small fraction of the total organic carbon content of solids (e.g. the total organic carbon in marine sediments can contain between 15 and 30% of BC (Middelburg et al., 1999)), including BC would not be sufficient to resolve the underestimation of PAH and PCB concentrations in sediments and SPM.

3.3. Concentrations in biota

The equilibrium approach explored in this paper performed better for biota than for sediment and SPM. Between 68% (fish liver) and 90% (fish muscle tissue) of the predicted data was accurate within an order of magnitude of the measured values, and between 47% (fish liver) and 73% (shrimp) were accurate within a factor of 5 (Table 2). The MB indicated a general tendency of the equilibrium model to overestimate the data with a factor of up to 3.65, which was also apparent when assessing the model fit (see SI for details). When further exploring the data, it becomes apparent that this bias is mainly caused by compounds with a $\log K_{ow} \geq 6.5$, and that this bias becomes stronger as $\log K_{ow}$ further increases (Fig. 4). To a certain extent this was unexpected, as it is generally acknowledged that assimilation of contaminants via uptake of contaminated food becomes an increasingly important contributor to the body burden, at least for the higher trophic levels (Borga et al., 2004; De Laender et al., 2010b). As such, one would expect a modelling approach entirely based on equilibrium partitioning theory to underestimate rather than overestimate body burdens as hydrophobicity increases. Possibly, this seemingly contradictory observation can be explained by (1) the relatively low trophic level of the species considered here, (2) biotransformation, or (3) the loss of a linear relationship between $\log K_{ow}$ and uptake of contaminants in organisms. The latter has been described in literature extensively (Veith and Kosian, 1983; Bintein et al., 1993; Meylan et al., 1999; Gobas and Morrison, 2000; Borga et al., 2004). While there is no scientific consensus on the cause, this phenomenon has for example been attributed to lower bioavailability and a higher significance of the elimination via faeces of very hydrophobic compounds (Thomann et al., 1992; Gobas and Morrison, 2000). Other scientists claim it to be an artifact arising from so-called

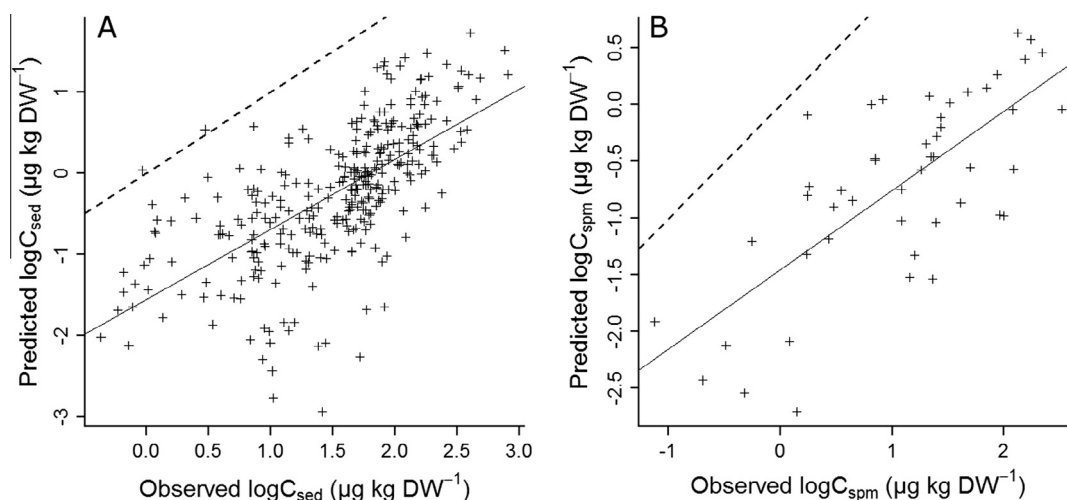


Fig. 3. Predicted vs. observed concentrations of PAHs and PCBs in (A) sediment and (B) SPM. The solid line represents correlation between the measured and predicted concentrations, the dashed line represents the 1:1 relationship.

Table 2

Percentage of modelled PAH and PCB concentrations in shrimp, mussel tissue, fish liver and fish muscle that fall within a specific factor (as given in the first column) of the measured data. The last row represents the model bias. *N*: number of data points; MB: model bias.

	Shrimp (<i>N</i> = 15)	Mussel tissue (<i>N</i> = 101)	Fish liver (<i>N</i> = 34)	Fish muscle (<i>N</i> = 10)
Factor 2	20	30.7	26.5	30
Factor 5	73.3	68.3	47.1	70
Factor 10	73.3	82.2	67.6	90
Factor 100	100	100	97.1	100
MB	3.65	2.66	2.08	1.30

third phase effects and nonequilibrium conditions occurring during laboratory bioconcentration measurements (Jonker and van der Heijden, 2007). While the real reason for the deviation observed in this study cannot be deduced from our data, a few comments can be made. As the concentration data derived from passive sampling represent the freely dissolved and thus by definition the bioavailable fractions of the contaminants, a reduced bioavailability cannot be the reason for the discrepancy we observe for biota. What remains is the possibility of a lower uptake rate combined with growth dilution and/or a higher excretion rate of the highly hydrophobic contaminants, thereby causing a divergence from equilibrium conditions. This may be further explored by using more advanced modelling techniques (e.g. the use of food web models) rather than using a simple equilibrium model.

3.4. Concluding remarks

Our study shows that a passive sampling approach combined with a simple equilibrium partitioning model can function as a baseline or 'null' model to predict contaminant concentrations in different environmental matrices. Deviations between these predictions and observations can be used to hypothesize which processes contribute to the environmental behaviour of these chemicals. When extended with these processes, e.g. using more advanced modelling approaches such as pharmacokinetic models or foodweb models, passive samplers can be a cost-effective way to estimate true integrated exposure profiles to organic pollutants in the marine environment.

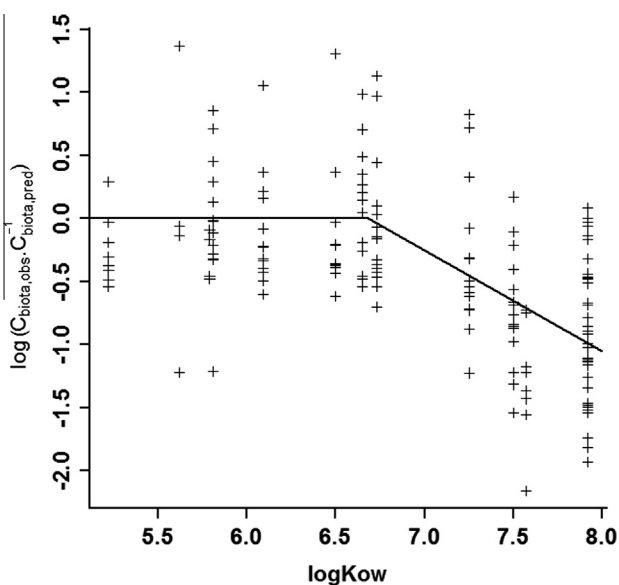


Fig. 4. The logarithm of the ratio of observed and predicted concentration data in biota vs. $\log K_{ow}$.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.marpolbul.2015.05.040>.

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