Marine Pollution Bulletin xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

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

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ARTICLE INFO

Article history:
Received 9 August 2014
Revised 12 May 2015
Accepted 13 May 2015
Available online xxxx

Keywords:
Passive sampling
Marine environment
Equilibrium modelling
Environmental fate

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.

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 (Namieśnik et al., 2005; Zabiegala 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 (Namieśnik et al., 2005). In a number of studies, it has already been attempted to compare and

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http://dx.doi.org/10.1016/j.marpolbul.2015.05.040
0025-326X/

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 Heininger 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 (Heininger 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 CO_2-gas by passing it through a magnesium perchlorate column. The CO_2-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 $0.5 \times 55 \times 99\ mm^3$ 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 $\mu g\ L^{-1}$) 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:

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

where C_{diss} is the freely dissolved concentration in seawater as derived from passive sampling ($\mu g\ L^{-1}$), 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:

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