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Application of a silicone rubber passive sampling technique for monitoring PAHs and PCBs at three Belgian coastal harbours

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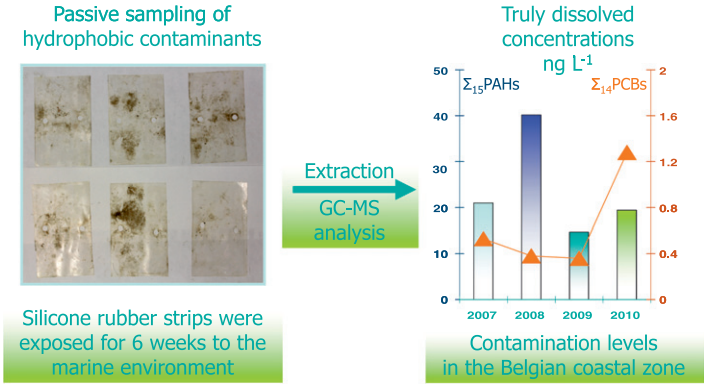
HIGHLIGHTS

- We monitor coastal marine water for four consecutive years.
- We use PDMS passive samplers to measure freely dissolved concentrations.
- We compare sampling rate estimation methods.
- We measure up to 170 ng L^{-1} for sum 15 PAHs and up to 3.1 ng L^{-1} for sum 14 PCBs.

GRAPHICAL ABSTRACT



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ABSTRACT

A 4-year monitoring was performed to study the freely dissolved water concentrations of PAHs and PCBs in three coastal harbours and at an offshore station in the North Sea. The results are part of a more extensive study to provide information on occurrence, distribution and effects of pollutants in the Belgian coastal zone. Several methods for the estimation of freely dissolved water concentrations are reported in the literature. In the present study silicone rubber passive samplers were used. The non-linear least-square (NLS) method proved to be suitable for estimating sampling rates when using the following performance reference compounds: fluorene-d_{10}, phenanthrene-d_{10}, fluoranthene-d_{10}, benzo(e)pyrene-d_{12}, coronene-d_{12}, CB10, CB14, CB50, CB104, CB145 and CB204. The application of two NLS methods for estimating the sampling rate (R_s) resulted in significant differences for freely dissolved concentrations for individual compounds of up to 30% between the two methods. A model that takes into account the decrease of sampling rate for compounds with higher molecular weight should give a more accurate R_s and was the preferred estimation method. R_s varied from 0.9 to 34.8 L d^{-1} for the different target compounds, while estimated freely dissolved concentrations for sum 15 PAHs varied between 3.9 and 170 ng L^{-1} and for sum 14 PCBs between 0.030 and 3.1 ng L^{-1}. The stations located within marinas showed the highest level of contamination, while the offshore station (5 mile from coastline) exhibited the lowest level. The implications of the use of passive samplers for monitoring programs are discussed.

1. Introduction

Monitoring of organic pollutants in the marine environment is costly and time-consuming, but required by international conven-

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tions and legislation such as the Water Frame Directive (WFD, 2000/60/EC) and the Marine Strategy Framework Directive (MSFD, 2008/56/EC). It involves frequent, up to monthly, sample collection with specialised research vessels. Depending on the monitoring program, seawater, sediment or biota samples are required. These samples often pose an analytical challenge because of the low concentrations (ppt-level) of the analytes and the complexity of the matrices that may lead to interferences. Samples taken by spot sampling represent the environment at a specific time and place. However, the marine ecosystem is a complex and dynamic system influenced by tides, currents, river discharges and point sources like harbours, marinas and boat traffic routes. Therefore, analytical measurements of organic micropollutants in marine ecosystems are often not easy to interpret in the context of trend monitoring and environmental risk assessment.

One way to overcome these monitoring problems is the use of passive samplers. Passive samplers consist of a receiving phase into which the organic pollutants diffuse. This diffusion process is driven by the difference in chemical activity of freely dissolved compounds between the environment and the sampler (Reichenberg and Mayer, 2006). The samplers integrate the micropollutants over a given time period (several weeks to months). Episodic pollution, easily missed by spot sampling, can also be detected by the passive sampler. Because the samplers have a good affinity for the target pollutants and accumulate them for the entire period of exposure or until equilibrium is reached, they concentrate the compounds efficiently, enabling the detection of very low concentrations of these compounds. Compared to the classical sampling methods, the cost for analysis of passive samplers is lower due to the relatively simple sample treatment, limited matrix interferences and considerably lower detection limits (Vrana et al., 2005; Greenwood et al., 2007; Allan et al., 2009). As passive samplers represent the freely dissolved fraction of the pollutants in the environment, there is also a clear relation between bioavailability and the measured concentrations (Sijm et al., 2000; Huckins et al., 2006; Reichenberg and Mayer, 2006) and therefore the relation to ecotoxicity of the substances is more straightforward. It was shown by Allan et al. (2009) that the measurements of hydrophobic organic pollutants in the freely dissolved phase in the marine environment is less variable than those in the total water phase, which is strongly influenced by solid particulate matter content. This means that the frequency of sampling could be reduced by the use of passive samplers.

To estimate water concentrations from passive sampling data, compound specific equilibrium constants between the water and the passive sampler phase are required (Huckins et al., 2006; Yates et al., 2007; Smedes et al., 2009; Mills et al., 2011). Equilibrium constants for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are available in literature for hydrophobic samplers, like semi-permeable membrane devices (SPMDs), silicone rubber strips or chemcatcher (Huckins et al., 2006; Yates et al., 2007; Smedes et al., 2009; Mills et al., 2011). For other hydrophobic pollutants, such as brominated flame retardants or non-polar pesticides, more research is needed to produce accurate equilibrium constants (Mills et al., 2011). If the uptake process is still in the linear uptake phase, the sampling rate (R_s) is required for estimating the freely dissolved water concentrations (Huckins et al., 2006; Rusina et al., 2010). For the calculation of R_s, performance reference compounds (PRCs) can be used (Booij et al., 2002; Huckins et al., 2006; Booij and Smedes, 2010). The use of all the PRCs to estimate a more accurate sampling rate by using non-linear least-squares (NLSs) was suggested by Booij and Smedes (2010).

In this study, polydimethylsiloxane (PDMS) passive samplers were used for monitoring of PAHs and PCBs in the Belgian coastal zone for four consecutive years. For the first time freely dissolved concentrations were determined to study the transfer of established priority compounds via three Belgian coastal harbours to coastal waters. For this purpose, seven sampling sites were chosen in the main harbours of the Belgian coast and one sampling site offshore. As several methods are reported for estimation of R_s in literature (Huckins et al., 2006; Booij and Smedes, 2010; Rusina et al., 2010), two NLS estimation methods for R_s were compared: one taking into account a decline of sampling rates with higher hydrophobicity and another not taking this into account. The use of 11 different PRCs was assessed in this study. The experience, the results and differences in the results of freely dissolved concentrations are discussed in this paper. The utilisation of passive samplers in future regulatory programs is discussed.

2. Materials and methods

2.1. Study area and sampling

A total of seven monitoring stations were located in three major Belgian coastal harbours: Nieuwpoort (NP1, NP2), Oostende (OO1, OO2, OO3) and Zeebrugge (ZB2, ZB3). One station was located approximately 5 miles from the coastline (SEA). The stations NP2, OO2 and ZB2 were located in the marinas of the respective harbours, while OO3 was situated at a docking place for pilot boats. ZB3 was located at a liquefied natural gas terminal. For OO1 a location in the Sluice dock of Oostende, an enclosed, shallow lagoon used for aquaculture activities (oyster and mussel culture), was selected. This lagoon is supplied with water from the inner harbour of Oostende. Finally, NP1 was located at a sluice complex, connecting the harbour and six waterways. The SEA-station was situated off-shore on the Belgian Continental Shelf (BCS), either in the vicinity of Zeebrugge (2007) or near Nieuwpoort (other years of sampling). The deployment sites of the passive sampler cages is illustrated in Fig. 1. All stations were sampled in four consecutive years: 2007, 2008, 2009 and 2010. Typically, samplers were deployed at 1.5–2 m below surface for ca. two months. The periods were corresponding to the available ship time and were: from August till October in 2007, from May till July in 2008, from March till May in 2009 and from mid-July to mid-September in 2010. Exceptions are: station OO1 that could not be sampled in 2009, station SEA that could not be sampled in 2010 and station OO2 where the cage was lost in 2010. In 2007 the sampler cage was not deployed at station OO1 due to logistic reasons, instead it was submerged in an oyster culture bath filled with lagoon water of the site. Water was also spot-sampled for whole water analysis in May 2007, April 2008 and June 2009 at all stations.

2.2. Passive sampling device

PDMS sheets (AlteSil Laboratory Sheet, Altec Products Ltd., Bude, United Kingdom) with a thickness of 0.5 mm were selected as passive samplers based on the properties of the material (Vrana et al., 2005; Rusina et al., 2007). The sheets were cut into sampler strips of 55 mm × 90 mm to obtain a total surface of approximately 100 cm^2 and a mean mass of 3.15 g. In the present study they will be referred to as silicone rubber (SR) strips. Stainless steel sampler cages and holders were used for mounting the SR strips. Pictures of the device are available in Supplementary material. The SR strips were fixed in such a way that they could move freely, as proposed by Smedes (2007). Using this approach, the design does not limit the uptake of the target compounds, whilst it is also reducing the water boundary layer.

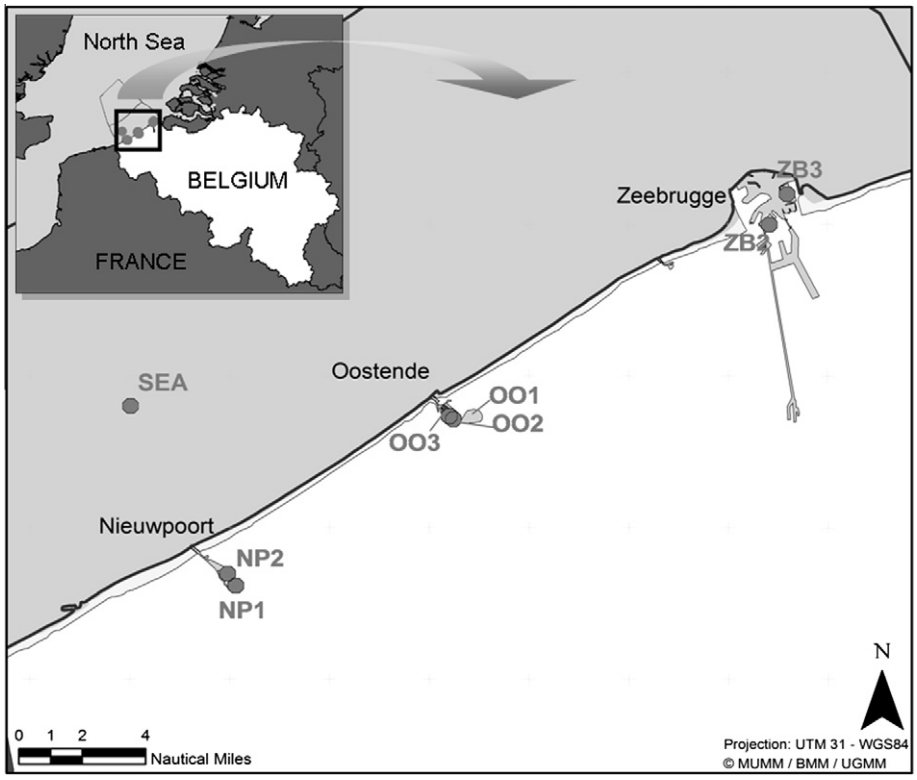

Fig. 1. Sampling area with sampling stations.

2.3. Sampler preparation and processing

Before deployment the SR strips were pre-cleaned by Soxhlet extraction for 100 h with ethylacetate. Subsequently the SR strips were air-dried and spiked with PRCs in batches, applying the method described in Booij et al. (2002) with a 80/20 methanol–water mixture (*v*/*v*). The following set of PRCs were used: fluorene-d_{10}, phenanthrene-d_{10}, benzo(e)pyrene-d_{12}, coronene-d_{12}, CB10, CB50, CB104, CB145 and CB204 with a final concentration of at least 100 μg g^{-1} of each PRC per SR sheet. In 2009 and 2010 also fluoranthene-d_{10} and CB14 were added as PRCs. The SR strips were stored in the spiking solution in a closed dark glass container until deployment. At each station 10 SR strips were deployed of which 5 were kept as a back-up in case the analysis had to be repeated. Additional spiked and non-spiked SR strips were used as laboratory blanks and field blanks, the latter being exposed to the air during deployment and retrieval at the station and brought back to the laboratory.

After the sampling period, the loaded sampler holders were carefully dismantled and the strips were transferred in pre-cleaned closed glass container and transported to the laboratory on ice, where they were stored at −20 °C. Before analysis the strips were gently cleaned with soft tissue and deionised water in order to remove any bio-fouling. Internal standards (deuterated analogues of parent PAH compounds and CB155) were added and the SR strips were extracted for 6 h with a Soxhlet extractor using a 1:3 acetone–hexane (*v*/*v*) solution. The extract was concentrated to 1 mL using an evaporative solvent reduction apparatus (Zymark TurboVap II; Zymark, Hopkinton, MA, USA). Co-extracted material was removed by adsorption chromatography over 2 g of alumina and eluated with 30 mL of hexane. Recovery standards (chrysene-d_{12}, CB29 and CB129) were added and the eluate was further concentrated to 1 mL. All solvents used were of purity suitable for organic residue analysis.

2.4. Spot-sampling method and processing

A 10 L Niskin bottle was used for sampling. An aliquot of 1 L was used for the analysis of naphthalene, an aliquot of 5 L was used for all other analytes. PAHs and PCBs were extracted using solid-phase extraction with Bakerbond Speedisk C18 extraction cartridges (Mallinckrodt Baker, Deventer, The Netherlands). Internal standards (deuterated analogues of parent PAH compounds and CB155) were added before extraction and recovery standards (chrysene-d_{12}, CB29 and CB129) prior to concentration of the extract to 1 mL. The method for PAH analysis was optimised and validated to meet the analytical requirements of the Water Frame Directive (WFD) (Directive 2002/45/EC). QA-data and validation parameters of the analytical method are described in the Supplementary material.

2.5. GC–MS analysis for PAHs and PCBs

The extract was divided to perform the GC-analysis of PAHs and PCBs separately. The programmable temperature vaporizer (PTV) large volume method was optimised per compound group, with injection volumes of 15 μL for PAHs and 70 μL for PCBs. For that purpose, a glass-sintered liner was used combined with a BEST PTV Injector (Thermo Electron Corporation, Austin, TX, USA). The analytical system consisted of a Trace GC fitted with a Combipal autosampler (CTC Analytics, Switserland). Separation of compounds for PAHs was done on a 30 m RTX-5 SIL-MS (Restek) fused silica capillary column (0.25 mm ID and 0.25 μm film thickness), while detection was done on a mass spectrometric (MS) single quadrupole detector operated in the single ion monitoring election-impact (EI) ionisation mode. PCBs were separated on a 50 m Thermo TR-PCB 8MS column with 0.25 mm ID and 0.25 μm film thickness. The detection of PCBs was done with an ion-trap MS (ThermoFinnigan, Austin, USA) in EI-MS–MS mode. 22 PAHs and

14 PCBs were quantified with internal calibration. The target PAHs were the PAH EPA 16. The target PCBs were CB-18, 28, 31, 44, 52, 101, 105, 118, 138, 153, 156, 170, 180 and 187, which includes the ICES 7 indicator PCBs. Quantification limits were 2.5 ng mL^{-1} for PAHs and 5.0 ng mL^{-1} for PCBs in the final extract. Details on the analytical procedures and QA are available in the Supplementary material.

2.6. Data processing

The measured concentration of indiviual PAHs and PCBs in the SR strips (C_s in ng g^{-1}) was calculated to water concentrations (C_w in ng L^{-1}) using the diffusion and kinetic models of Huckins et al. (2006) and Rusina et al. (2010). Concentrations of PRCs were expressed as ratio's, N_t/N_0 where N_t and N_0 are the PRC amounts at the end and at the beginning of the exposure. Sampling rate R_s (L d^{-1}) was calculated taking all available PRC-data into account. A 'common' R_s was calculated with a NLSs method, considering N_t/N_0 as a continuous function of K_{sw}, with R_s as an adjustable parameter (Booij and Smedes, 2010):

$$\frac{N_t}{N_0} = e^{\left(-\frac{R_s \cdot t}{m_s \cdot K_{sw}}\right)} \quad (1)$$

where m_s is the mass of the SR sheet and K_{sw} the sampler-water partition coefficient, in the remainder referred to as 'common' R_s. According to Booij and Smedes (2010) the application of the NLS method reduces the uncertainty of R_s and the overall uncertainty of C_w. Also a second method was used to calculate a 'variable' R_s, where R_s varies according to $MW^{-0.47}$, where MW is molecular weight and as proposed by Rusina et al. (2010) in:

$$R_s = F \cdot A \cdot MW^{-0.47} \quad (2)$$

where A is the surface area of the sampler and factor F is a proportionally constant depending on flow rate, sampler geometry and other factors that are required to fit the unit. The model takes into account that uptake controlled by diffusion is expected to decrease with molecular weight. The NLSs method was used, by considering N_t/N_0 as a continuous function of K_{sw}, with $F \cdot A$ as an adjustable parameter.

$$\frac{N_t}{N_0} = e^{\left(\frac{-F \cdot A \cdot MW^{-0.47} \cdot t}{m_s \cdot K_{sw}}\right)} \quad (3)$$

This formula allows extrapolation of analyte uptake rates at higher $\log K_{ow}$ range and allows a more accurate calculation of C_w for the more hydrophobic compounds.

In order to reduce uncertainties regarding the K_{sw}, the K_{sw} determined with the co-solvent method were used as proposed by Smedes et al. (2009). Finally, C_w (ng L^{-1}) was calculated using a general formula:

$$C_w = \frac{C_s}{m_s . K_{sw} \cdot (1 - e^{-k_e})} \quad (4)$$

with k_e being the exchange rate constant (d^{-1}) defined by:

$$k_e = \frac{R_s}{m_s \cdot K_{sw}} \quad (5)$$

and C_s (ng g^{-1}) the concentrations of target compound measured in the SR strips. PRC dissipation rates were expressed as time to dissipate completely from the SR strips, τ (d), or time to dissipate for 50% from the SR strips, so called half-life time or $t_{1/2}$ (d) and were calculated using the following formula:

$$\tau = \frac{1}{k_e} \quad (6)$$

or

$$t_{1/2} = \frac{\ln 2}{k_e} \quad (7)$$

3. Results and discussion

3.1. Method development using PRCs

3.1.1. Use of PRCs

The SR strips were spiked with 11 PRCs, covering a $\log K_{ow}$ range from 2.8 to 7.6. After the exposure period the percentage of fluoranthene-d_{10} ($\log K_{ow}$ 5.18) and CB10 ($\log K_{ow}$ 4.84) retained on the SR strips ranged between 30% and 80%. The PRCs with $\log K_{ow} < 4.2$, fluorene-d_{10} and phenanthrene-d_{10}, dissipated for more than 80%, while the PRCs with $\log K_{ow} > 5.2$ dissipated for less than 20% from the SR strips. Dissipation of PRCs of more than 80% or less than 20% leads to difficulties to measure the ratio of PRCs added in the beginning and at the end of the exposure accurately. In this study, fluoranthene-d_{10} ($\log K_{ow}$ 5.18) and CB10 would have been suitable for calculation of R_s according to the method proposed by Huckins et al. (2006). The average half-life time for fluoranthene-d_{10} and CB10 was 44 d, meaning that 50% of the compound was dissipated from the SR strips after approximately 6 weeks. This confirms the observation that the transition between equilibrium and linear uptake generally takes place for PRCs with $\log K_{ow}$ 4.5–5.2 for exposure times of several weeks (Huckins et al., 2006; Allan et al., 2009). The percentage recovery of spiked PRCs in the SR strips at the end of the exposure period, dissipation rate k_e (d^{-1}) and time to dissipate completely from the SR strips (d) are detailed in Table 1. Similar dissipation rates were found in other studies using passive sampling devices for monitoring hydrophobic compounds (Gourlay-Francé et al., 2008; Allan et al., 2009).

Table 1
Of each PRC, sampler-water partition coefficient ($\log K_{sw}$), % remaining in the SR strips after exposure, exchange rate (k_e in d^{-1}) and time to dissipate completely from the SR strips (τ in d).

PRC	$\log K_{sw}$	% remaining		k_e (d^{-1})	τ (d)	
Fluorene-d_{10}	3.65	5.6	(0.1–29)	1.4 E−01	7.0	(1–31)
Phenanthrene-d_{10}	4.06	13	(0.8–55)	5.4 E−02	19	(4–83)
Fluoranthene-d_{10}	4.57	63	(30–88)	1.6 E−02	64	(13–290)
CB10	4.55	60	(28–80)	1.6 E−02	64	(13–290)
CB14	5.13	84	(72–98)	4.1 E−03	240	(50–1100)
Benzo(e)pyrene-d_{12}	5.59	87	(73–110)	1.3 E−03	750	(150–3300)
CB50	5.70	95	(71–110)	9.7 E−04	1000	(210–4600)
CB104	6.17	97	(79–110)	3.1 E−04	3200	(660–14000)
Coronene-d_{12}	6.39	88	(78–99)	2.0 E−04	5100	(1100–23000)
CB145	6.65	104	(88–130)	9.9 E−05	10000	(2100–45000)
CB204	7.59	98	(84–110)	1.0 E−05	96000	(20000–420000)

Mean (min–max) values.

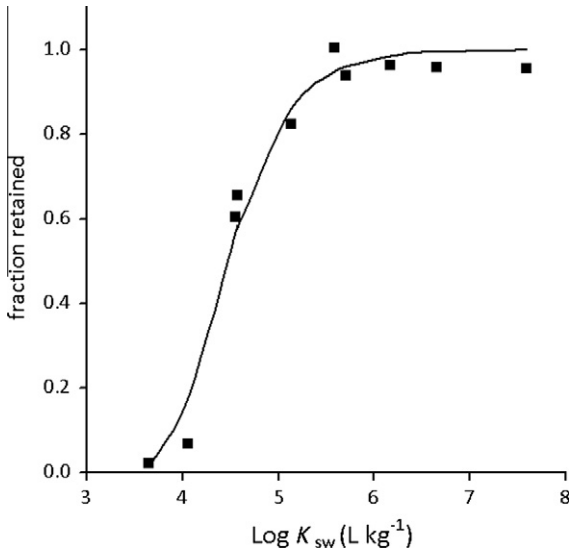

Fig. 2. Example of retained PRC fractions and model fit for station OO3 sampled in 2009. The drawn line represents the best NLS fit.

Deuterated PAHs and PCBs were used together as PRCs to calculate the sampling rate R_s with Eq. (1), subsequently Eq. (3). An example of applying NLS to PRC data at station OO3 in 2009 is shown in Fig. 2. In all cases a good fit was achieved. The average deviation of PRC ratio's from the best NLS fit was less than 3%, except for CB10 and benz(e)pyrene-*d10*, that both showed an average deviation of 10%. The estimation of a meaningful R_s without a PRC situated in the range of logK_{ow} 4.2 and 5.2 was still possible, the latter being the transition range between equilibrium and linear uptake. However, the absence of a PRC in that transition range results in deviations for R_s of more than 40%. Exclusion of an arbitrary PRC not in the range of 4.2 and 5.2, gave minor (<10%) deviations for R_s in 96% of the cases. The R_s estimation method of Booij and Smedes (2010) with NLS guarantees the estimation of sampling rates from the PRC dissipation data, but our research shows that the method is more robust when at least one PRC in the transition range between equilibrium and linear uptake is used. Uncertainties calculated with the R language for statistical computing using the method described in Booij and Smedes (2010) gave standard deviations for R_s between 9% and 14% when all 11 PRCs were included. However, without a PRC in the transition range, uncertainties were often higher than 25%.

3.1.2. Sampling rates

Sampling rates R_s were all normalised to 10 g SR strips. 'Common' R_s estimated with Eq. (1) varied between 1.4 and 25 L d^{-1}. The 'variable' R_s calculated with Eq. (3), varied depending on the target analyte between 0.9 and 34.8 L d^{-1}. For the target analyte benzo(a)anthracene (logK_{sw} 5.3), sampling rates varied from 1.2 to 27 L d^{-1}. Fig. 3 shows the measured 'variable' and 'common' R_s for all sampling events. Common R_s will be used to discuss the measured sampling rates. R_s in the harbours varied within half an order of magnitude. Because of the low hydrodynamics in the enclosed oyster culture bath, the lowest value of R_s (1.4 L d^{-1}) was measured in 2007 at station OO1. In 2008 and 2010 an R_s of 2.9 L d^{-1} was measured in the lagoon itself. In the harbour stations R_s varied between 2.3 and 5.5. These values were not significantly different, nor between stations, nor between years (ANOVA respectively Friedman test, $P < 0.05$). At SEA station, significantly higher R_s were measured (ANOVA, $P < 0.05$), ranging from 16 to 26 L d^{-1}. The higher R_s found at open sea can be explained by the highly dynamic water masses at sea compared to the sheltered harbours. The sampling rates in this study are in good agreement with other studies using SR strips in the marine aquatic environment (Allan et al., 2009; O'Hara, 2009). For SPMDs variable sampling rates of target PAHs ranging from 8 to 43 L d^{-1} after 6 d of exposure in wastewater have been reported (Gourlay-Francé et al., 2008) and from 4.1 to 14.8 L d^{-1} after 6 weeks of exposure in the Norwegian North Sea (Harman et al., 2009).

3.2. Monitoring results

3.2.1. Estimation method of freely dissolved concentrations

As concentrations of naphthalene on the field blanks were in most cases higher than 30% of the concentrations measured on the deployed samplers, naphthalene concentrations are not reported in this study. Probably, due to the high fugacity of naphthalene, the exchange rate between the air and the SR strips is too high to ensure uncontaminated blanks. Also, it cannot be guaran-

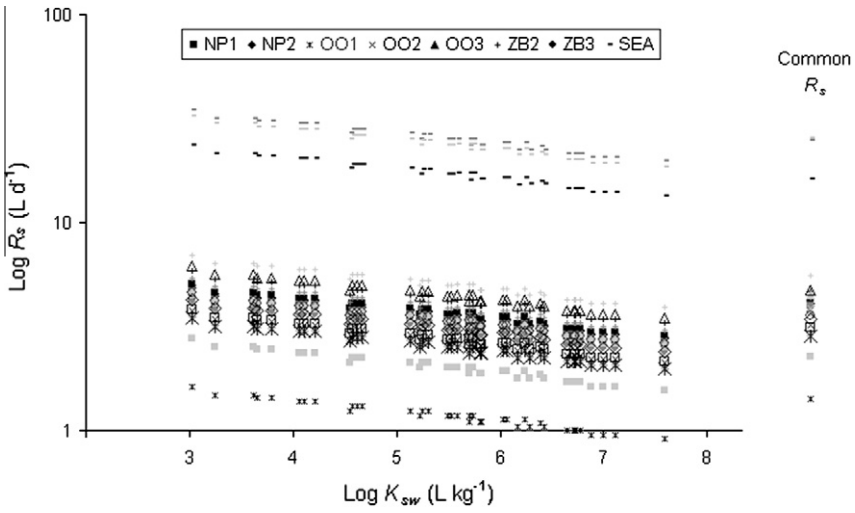

Fig. 3. For all sampling stations, estimated variable R_s (L d^{-1}) as a function of log K_{sw} and common R_s (L d^{-1}). Stations sampled in 2007 are depicted in full black, 2008 in grey, 2009 in light grey and 2010 in unfilled symbols.

teed that no significant loss of naphthalene will occur during deployment or retrieval of the SR strips, caused by handling and/or transport. Because this kind of loss is difficult to control, more research is needed to measure the more volatile PAHs on SR strips.

In this study, the analytical sensitivity in combination with the sampling rates were suitable for the estimation of freely dissolved concentrations of the target compounds. As R_s is directly proportional to m_s, higher sampling rates could have been achieved when more SR strips would have been taken into analysis. Sampling cages are designed to hold more than 30 SR strips, so the only restraint for a larger intake of SR sheet for the analysis would be the size of a Soxhlet extraction tube, as SR strips are currently extracted in one tube in order to lower the work load and solvent usage.

The freely dissolved concentration C_w (ng L^{-1}) was estimated both using Eq. (4) in combination with the 'common' R_s from Eq. (1) and the 'variable' R_s from Eq. (3), resulting in two different aqueous concentrations, called $C_{w,common}$ and $C_{w,variable}$. For individual target compounds, these differed maximum 31% for PAHs and 40% for PCBs from each other. $C_{w,variable}$. was generally higher than $C_{w,common}$ for compounds with $\log K_{ow} > 4.6$., while for those that were in equilibrium ($\log K_{ow} < 4.6$) the difference was less than 5% (information about how close to equilibrium each reported compound was, can be found in Supplementary material). Differences were proportional to the $\log K_{ow}$, with higher differences for compounds with higher $\log K_{ow}$ following Eq. (2). Also Σ_{15}PAHs and Σ_{14}PCBs differed significantly between both calculation methods (Wilcoxon matched-pairs test, $P = 0.05$). For Σ_{15}PAHs differences varied between 8.3% and 0.022%, for Σ_{14}PCBs between 33% and 3.1%. Taking into account an analytical uncertainty of 30%, these differences are not significant for Σ_{15}PAHs, however, for Σ_{14}-PCBs these differences were significant in 14% of the cases. This implies that the use of a 'common' R_s could be responsible for underestimation of more than 30% of freely dissolved concentrations.

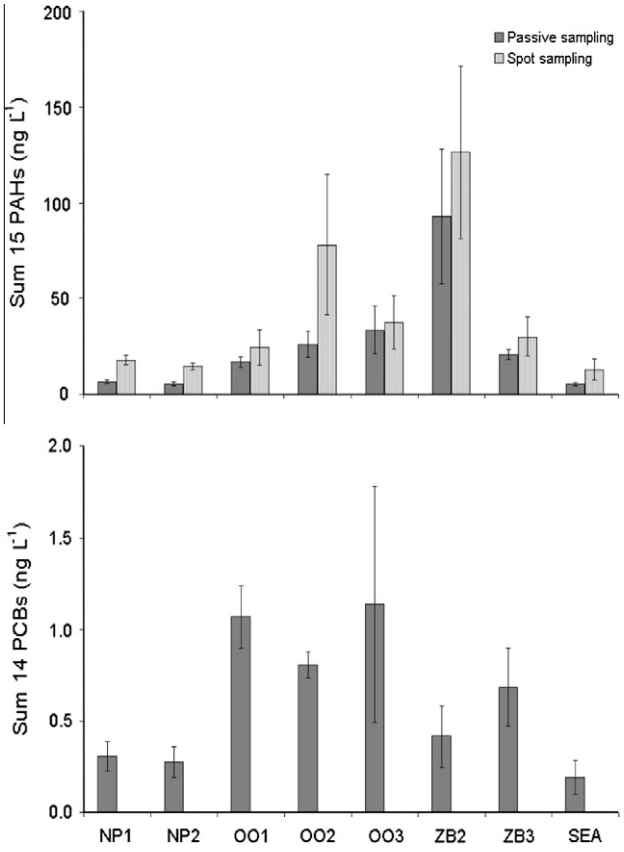

Fig. 4. Σ_{15}PAHs (upper graphic) and Σ_{14}PCBs (lower graphic) expressed in ng L^{-1} for passive sampling resulting in freely dissolved concentrations compared to spot sampling of Σ_{15}PAHs or whole water concentrations. Whole water concentrations for Σ_{14}PCBs are not presented as more than 98% of the concentrations was below LOQ (1.0 ng L^{-1}).

3.2.2. Levels of freely dissolved concentrations in Belgian harbours

Freely dissolved concentrations were estimated using Eq. (4) combined with variable R_s of Eq. (3). Freely dissolved concentrations of Σ_{15}PAHs ranged from 3.9 to 170 ng L^{-1}, while Σ_{14}PCBs varied from 0.030 to 3.1 ng L^{-1} (Fig. 4). In general, stations in marinas showed highest levels and the sea stations lowest. ZB2 showed the highest PAH-levels compared to other stations. This was also reflected by the whole water analysis of PAHs as shown in Fig. 4. In 2008 at ZB2, freely dissolved concentrations of Σ_{15}PAHs summed up to 170 ng L^{-1}, while the whole water spot sampling analysis in April 2008 totalled 120 ng L^{-1} (data are available in the Supplementary material). These higher PAH concentrations are possibly related to dredging activities executed in the same period. Sediment relocation can cause a release of dissolved PAHs and to a lesser extend PCBs as was shown by Cornelissen et al. (2008). The other spot sampling data and passive sampling data showed no correlation for Σ_{15} PAHs (the 2008 record was excluded for this test) ($r^2 = 0.29$ with $P = 0.01$). For Σ_{14}PCBs a correlation test was not possible, because whole water concentrations were below the quantification limit (LOQ of 1.0 ng L^{-1}) in almost all cases (>98%). Whole water concentrations obtained by spot sampling in coastal areas were highly variable, because of the interaction between constant discharges upstream and flushing by seawater. To obtain a real time weighted concentration by spot sampling, the required number of samples would be unrealistically high. Therefore, the concentration levels in whole water spot samples are considered as indicative for the levels found with the integrative passive samplers. If fugacity-based environmental equilibrium partitioning is assumed, significantly higher freely dissolved concentrations are an indication that other compartments in the ecosystem are contaminated.

Hydrophobic contaminants in water can be expressed as (1) as freely dissolved (estimated by passive sampling), (2) as dissolved (by filtration of water, thus removing the PAHs associated with suspended matter and colloidal material) or (3) in 'whole' water (dissolved + particulate). It is recognised that colloidal-bound hydrophobic compounds are not fully retained by a filter (Evers and Smedes, 1994), but filtration is used to simulate the separation of the dissolved and suspended phase. In Table 2 a comparison is made between whole water, dissolved and freely dissolved concentrations for the sum of PAHs in the marine coastal environment. Concentrations observed in our study were generally in accordance with those of other studies (Fernandez et al., 1997; Hellou et al., 2005; Sabin et al., 2010; Schaanning et al., 2011). Some studies report higher levels of PAHs than those measured in our study (factor 5–10), for both dissolved and whole water measurements (Law et al., 1997; Mzoughi and Chouba, 2011). Harman et al., (2009) found background levels for freely dissolved Σ_{16}EPA PAHs (minus naphthalene) for the North Sea of ±2 ng L^{-1}, while Josefsson et al. (2011) measured background levels of an average of ±2 pg L^{-1} for freely dissolved Σ_7PCBs in a coastal area of the Baltic sea. The background level for ΣPAHs was exceeded by a factor 2 (open sea station) to 85 (harbour stations) in our study, whilst for ΣPCBs the background level was exceeded by a factor 15 (open sea station) to 1500 (harbour stations), indicating a flux of freely dissolved organic pollutants from coastal harbours to the open sea.

Table 2
Comparison of concentrations for whole water concentrations (W), filtered dissolved (D) and freely dissolved (PS) water concentrations in coastal urban areas in ng L^{-1}.

Location	No. congeners	Phase	Mean (ng L^{-1}) ± Stdev (ng L^{-1})	No. samples	Reference
Tunisia, Gulf of Tunis	Σ_{24}PAHs	W	360 ± 89	12	Mzoughi and Chouba (2011)
England and Wales, estuaries	Σ_{14}PAHs	W	180 ± 120	8	Law et al. (1997)
Belgium, coastal harbours	Σ_{15}PAHs	W	41 ± 18	21	Present study
England and Wales, estuaries	Σ_{14}PAHs	D	140 ± 130	8	Law et al. (1997)
Southern California, coastal embayments	Σ_{28}PAHs	D	36 ± 17	7	Sabin et al. (2010)
Canada, Halifax harbour	Σ_{29}PAHs	D	30 ± 17	27	Hellou et al. (2005)
France, Seine estuary	Σ_{12}PAHs	D	20 ± 13	6	Fernandez et al., 1997
Norway, inner Oslofjord	Σ_{16}PAHs	PS	6.0 ± 3.3	24	Schaanning et al. (2011)
Ireland, Galway and Dublin bay	Σ_{16}PAHs	PS	42 ± 36	2	O'Hara (2009)
Belgium, coastal harbours	Σ_{15}PAHs	PS	27 ± 18	25	Present study
Ireland, Galway bay	Σ_{7}PCBs	PS	0.021	1	O'Hara (2009)
Ireland, Dublin bay	Σ_{7}PCBs	PS	0.15	1	O'Hara (2009)
Australia, Sydney harbour	Σ_{12}PCBs	PS	0.028 ± 0.005	4	Roach et al. (2009)
Australia, Sydney harbour	Σ_{12}PCBs	PS	0.23 ± 0.21	4	Roach et al. (2009)
Belgium, coastal harbours	Σ_{14}PCBs	PS	0.65 ± 0.60	26	Present study

Due to the low solubility, PCB concentrations in water are usually extremely low and hence difficult to detect. In most cases, concentrations are lower than 1 ng L^{-1} (OSPAR, 2000), explaining why only sum of PCBs measurements with passive samplers were reported in Table 2. Freely dissolved PCB concentrations at coastal Belgian harbours from this study seemed to be higher (factor 3–30) compared with other coastal marine sites (Table 2). It should be noted that the concentrations reported by Roach et al. (2009) are probably an underestimation, because they only reported the sum of dioxinlike PCBs.

3.2.3. Variation and patterns of freely dissolved concentrations in Belgian harbours

The average sum of concentrations per year of PAHs and PCBs over 4 years varied from 18% to 113%. For Σ_{15}PAHs some years were significantly different from other years (2007 from 2008, $P < 0.05$; 2008 from 2009, $P < 0.01$; 2009 from 2010, $P < 0.05$). The other years were not significantly different for Σ_{15}PAHs ($P > 0.05$) (Tukey–Kramer multiple comparison test). An *F*-test showed that the stations were significantly correlated for Σ_{15}PAHs ($P < 0.01$) and Σ_{14}PCBs ($P < 0.0001$), therefore the stations were paired in the statistical tests. For Σ_{14}PCBs, 2010 differed significantly from all other years with a *P* value <0.001 (ANOVA). The summer of 2010 was a remarkably wet season which could explain a larger influx of PCBs into the harbours during the summer of 2010, resulting in the higher freely dissolved PCB concentrations measured in the SR strips. From 2007 to 2009 the average Σ_{14}PCBs in harbour stations varied less than 30%, which indicates a relatively constant freely dissolved PCB concentration, influenced by riverine input e.g. through land-fill run-off. This corroborates the findings of OSPAR (2009), whom states that despite the regulatory phase-out, the release of PCBs to water still continues due to land-fill run-off.

Highest concentrations were found for PAH compounds acenaphtene, fluoranthene and pyrene and for PCB congeners CB52, CB101 and CB153. Different PAH patterns could be observed over the years in the three harbours, indicating different sources of contamination for each harbour. The PCB patterns, however, were not always consistent (e.g. in 2009 at station NP02 and ZB03 and in 2010 at ZB03) and reflected small-scale variation in congener composition within the harbours. This is consistent with the findings of Roach et al. (2009), who also reports that the levels of freely dissolved PCBs in various areas of the Sydney harbour results not only from downstream transport, but is also the result of local equilibria established by a slow enough water movement and reflecting contributions from local sources. Refer to Supplementary material for the corresponding graphs.

3.3. Future regulatory use of passive sampling data

Current international environmental standards such as environmental assessment criteria (EAC) of OSPAR and environmental quality standards (EQSs) of the Water Framework Directive do not relate directly to passive sampling data. The EAC of OSPAR are expressed as concentration levels in sediment and/or biota, while EQS of the WFD are expressed as water concentrations. Freely dissolved water concentrations measured with passive samplers can be converted to whole water concentrations taking into account sorption to dissolved and particulate organic carbon (DOC and POC) in the water column. This can be done using formula A.1 (Supplementary material) previously described by Allan et al. (2009), Dueri et al. (2008) and ter Laak et al. (2006). The PAH concentrations with passive sampling obtained in this study in 2007, 2008 and 2009 were converted to whole water concentrations with formula A.1. DOC and POC measurements were made during the sampling of the freely dissolved concentrations once per sampling event. Table 3 compares the converted whole water PAH concentrations with the spot sampling concentrations from this study. Comparison to the Annual Average – Environmental Quality Standard (AA-EQS) of the WFD shows that the frequency of exceedance is higher for spot sampling than for passive sampling data (Table 3). An underestimation of the PAH concentration by sorption to soot, unaccounted for in the computation, could be a possible explanation (Dueri et al., 2008). Also, the sampling period of the spot samples (early in the year for 2007 and 2008) may partly explain the higher observed spot sample concentrations. Finally, it should be taken into account that for compounds that are still in the linear uptake phase, passive samplers integrate the concentrations of over a period of 6–8 weeks. This concentration is then averaged using a daily sampling rate, resulting in a relative small deviation of the actual average concentration in case of limited and periodic environmental fluctuations (Gourlay-Francé et al., 2008).

Concentrations of contaminants measured by passive samplers allows the estimation of the bio-available fraction (Vrana et al., 2005; Reichenberg and Mayer, 2006) and this concentration can be a proxy for the pollution pressure on the aquatic ecosystem. As it is most likely that eco-toxicity is mainly caused by contaminants in the freely dissolved water phase, a passive sampler constitutes a direct link between toxicity and integrated environmental monitoring. Current work related to OSPAR's EAC and to the EU's EQS of the WFD could greatly benefit from this approach to contaminant pressure. Translating EAC or EQS to the freely dissolved phase would constitute a major step in environmental status assessment. Not only is measuring hydrophobic organic pollutants

Table 3
Ranges of whole water concentrations measured by spot sampling or calculated from freely dissolved TWA concentrations taking into account sorption to dissolved and particulate organic carbon (DOC, POC) and frequency of exceedance of the AA-EQS for PAHs (Daughter directive of WFD, 2008/105/EC).

Analyte	AA-EQS (ng L^{-1})	Passive sampling whole water (n = 23)			Spot sampling whole water (n = 24)[a]		
		Min–max (ng L^{-1})	Median (ng L^{-1})	Exceed AA-EQS (n)	Min–max (ng L^{-1})	Median (ng L^{-1})	Exceed AA-EQS (n)
Anthracene	100	0.01–3.0	0.34	0	<0.50–7.7	0.70	0
Fluoranthene	100	0.65–66	3.2	0	0.71–24	3.1	0
Benzo(a)pyrene	50	0.001–1.3	0.14	0	<0.50–10	1.1	0
$\sum$ (Benzo(b)fluoranthene, benzo(k)fluoranthene)	30	0.11–3.0	0.71	0	<0.50–21	2.9	0
$\sum$ (Benzo(g,h,i)perylene, Indeno(1,2,4-cd)pyrene)	2	0.10–5.3	0.96	6	<0.50–20	3.0	15

[a] If value <0.50, 0.25 was used for calculations.

in matrices like water, sediment or biota analytically challenging (Vrana et al., 2005; Allan et al., 2009), but often difficulties arise during inter-comparison of pollution pressure between different geographic areas or during temporal trend monitoring (Booij et al., 2006).

Monitoring and ecotoxicity assessment of organic substances such as PAHs, PCBs or new emerging substances could be improved by a more independent measurement unit, such as the concentration integrated by a passive sampler phase in a defined period of time. All these substances move from one compartment to another through the dissolved phase. The driving force is the physico-chemical partitioning between the phases. The latter however needs to be further studied and confirmed. Data generated during this project will be used to study the applicability of a simple equilibrium model – using the R statistical package – to model average environmental concentrations of micropollutants in SPM, sediment and biota based on freely dissolved concentrations derived from passive samplers.

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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.chemosphere.2012.11.074.

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