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Monitoring alkylphenols in water using the polar organic chemical integrative sampler (POCIS): Determining sampling rates via the extraction of PES membranes and Oasis beads



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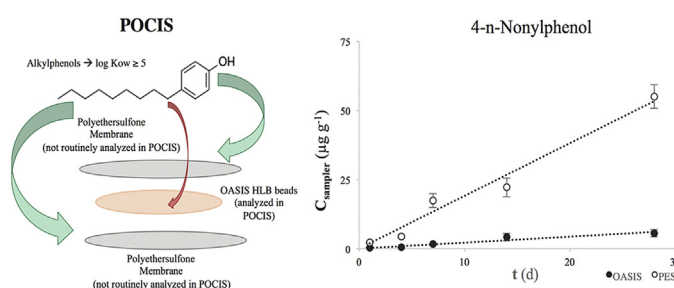
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HIGHLIGHTS

- POCIS was calibrated for APs by extraction of PES membranes and Oasis beads.
- A lag phase was observed over 24 h before uptake in Oasis beads.
- APs were linearly sorbed to PES membranes and Oasis beads over a 28 day period.
- Accumulation in the PES membranes and Oasis beads was a function of hydrophobicity.
- To correctly determine uptake both PES membranes and Oasis beads must be extracted.

GRAPHICAL ABSTRACT



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ABSTRACT

Polar organic chemical integrative samplers (POCIS) have previously been used to monitor alkylphenol (AP) contamination in water and produced water. However, only the sorbent receiving phase of the POCIS (Oasis beads) is traditionally analyzed, thus limiting the use of POCIS for monitoring a range of APs with varying hydrophobicity. Here a "pharmaceutical" POCIS was calibrated in the laboratory using a static renewal setup for APs (from 2-ethylphenol to 4-*n*-nonylphenol) with varying hydrophobicity (log K_{ow} between 2.47 and 5.76). The POCIS sampler was calibrated over its 28 day integrative regime and sampling rates (R_s) were determined. Uptake was shown to be a function of AP hydrophobicity where compounds with log K_{ow} < 4 were preferentially accumulated in Oasis beads, and compounds with log K_{ow} > 5 were preferentially accumulated in the PES membranes. A lag phase (over a 24 h period) before uptake in to the PES membranes occurred was evident. This work demonstrates that the analysis of both POCIS phases is vital in order to correctly determine environmentally relevant concentrations owing to the fact that for APs with log K_{ow} ≤ 4 uptake, to the PES membranes and the Oasis beads, involves

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different processes compared to APs with $\log K_{ow} \geq 4$. The extraction of both the POCIS matrices is thus recommended in order to assess the concentration of hydrophobic APs ($\log K_{ow} \geq 4$), as well as hydrophilic APs, most effectively.

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1. Introduction

Produced water (PW) represents the largest discharge from the oil exploration and gas industry and includes both formation water (seawater or freshwater trapped with oil and gas in a geological reservoir) and injected water (seawater, freshwater and brine water as well as added chemicals that are injected to enhance recovery of oil and gas, and operational safety). It includes components such as dispersed oil, aromatic hydrocarbons including polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs), organic acids, heavy metals, radioactive materials and inorganic salts (Harman et al., 2011; Røe Utvik, 1999). PW is usually treated directly on offshore production units in order to remove a large fraction of the oil before being discharged into the sea (Boitsov et al., 2004). Despite the overall low concentrations of toxic compounds that remain in the treated PW, the large volumes of PW that are discharged lead to large total amounts of toxic compounds being discharged every year (Boitsov et al., 2004; Harman et al., 2011).

APs are also widely present in water due to the alkylphenol polyethoxylates (APEs) degradation, which are largely used as surfactants in industrial and agricultural sector (Ferrara et al., 2005).

Most APs are relatively hydrophilic organic compounds (HpOCs) and as such are soluble and relatively mobile in water. HpOCs are generally characterized by a lower bioaccumulation and lower persistence in the environment than hydrophobic organic compounds (HOCs) (Jones and de Voogt, 1999). Nevertheless, several APs (those that are less hydrophilic) have been demonstrated to accumulate in the aquatic environment, and owing to their endocrine disrupting properties have been observed to cause acute toxicity, chronic abnormalities and considerable reproductive effects in fish (Alvarez et al., 2007; Boitsov et al., 2004; Harman et al., 2008a; Tollefsen et al., 2008). Indeed, octylphenol and nonylphenol are listed as priority substances in the European Water Framework Directive (EU WFD). Monitoring of APs in water, PW discharges to the water column, as well wastewater, is therefore a vital tool in order to assess negative environmental effects.

Passive sampling devices (PSDs) are commonly used for assessing exposure to organic contaminants in the water column (Harman et al., 2011; Røe Utvik, 1999), presenting the unique advantage that very low concentrations, down to the pg L^{-1} range (Cornelissen et al., 2008; Hawthorne et al., 2009), can be detected. They furthermore allow bioavailable water concentrations to be determined, which are most closely related to toxicity to aquatic biota (Hawthorne et al., 2009). PSDs have a role to play in monitoring discharges from the oil and gas industry, where Norwegian regulation requires that they are used to quantify certain compounds in PW (Norwegian Environment Agency, 2015). Thanks to their low cost, reliability and low detection limit, they are seen as fundamental in the progression of oil and gas monitoring (Hale et al., 2016). Several PSDs are suitable for monitoring a wide range of organic contaminants found in PW, with the semipermeable membrane device (SPMD) being the most widely deployed PSD for monitoring PAHs in PW (Harman et al., 2008a, 2009, 2011). SPMDs are integrative passive samplers suitable for monitoring concentrations of HOCs; however, they are not appropriate to

assess concentrations of HpOCs as they are unable to effectively sample compounds with $\log K_{ow} \leq 3-4$ (Alvarez, 2010; Harman et al., 2009, 2011). By contrast, the polar organic chemical integrative sampler (POCIS) is specifically designed to sample polar organic contaminants such as pesticides, pharmaceuticals as well as APs (Harman et al., 2008a, 2009, 2011; Morin et al., 2012, 2013; Vermeirssen et al., 2012).

The POCIS is an integrative, or kinetic, passive sampler, operating as an infinite sink for analytes during the linear uptake stage (Morin et al., 2012) and it is able to measure time weighted average (TWA) concentrations, and thus capture large fluctuations in discharge concentrations (Harman et al., 2011; Morin et al., 2012). The evaluation of TWA concentrations is particularly useful in the case of PW where discharges are often point source and vary with time. The POCIS consists of three parts: i) a solid sorbent, ii) two polyethersulfone (PES) membranes and iii) two stainless steel rings. The sorbent is sandwiched between the membranes and the rings hold the whole sampler together. The microporous PES membranes function as semipermeable barriers between the effective receiving phase (the solid sorbent) and the surrounding environment (water phase). The pores in the membranes (size 100 nm) exclude the uptake of particulates, colloids and biota with cross-sectional diameters greater than the size of the pores, whilst still allowing the uptake of HpOCs (Morin et al., 2012). There are different POCIS configurations based on the type of solid sorbent that is used, two of which are commercially available and referred to as the “pesticide” POCIS (with a three phase sorbent mixture) and the “pharmaceutical” POCIS (with Oasis[®] HLB as a single sorbent) (Alvarez, 2010).

Traditionally, only the solid sorbent phase of the POCIS is extracted for environmental analysis and therefore the uptake of compounds is assessed solely as uptake in the Oasis[®] HLB beads (Belles et al., 2014; Harman et al., 2008a, 2011). To the best of our knowledge, only Vermeirssen et al. (2012) have additionally studied the accumulation in the PES membranes in order to determine the uptake of a range of compounds (pharmaceuticals, pesticides and biocides) with $\log K_{ow}$ values between -0.07 and 4.5 . Their study concluded that compounds with $\log K_{ow}$ values larger than 5 are taken up very effectively by the PES membranes and that a lag-phase prior to their detection in the solid sorbent occurred.

With regard to monitoring APs in PW, POCIS (solid sorbent phase only) has been successfully calibrated for several hydrophilic APs, however it was reported that the accumulation of hydrophobic APs was less efficient and highly variable (Harman et al., 2008a, 2009). These studies did not consider accumulation in the PES membranes, suggesting that additional investigations are needed in order to assess the full potential of POCIS to monitor APs in PW. More specifically, it is necessary to determine whether POCIS are able to accumulate hydrophobic APs, as if this is the case, POCIS alone could be used for monitoring APs in PW discharges (as opposed to using two PSD with different compound hydrophobicity application domains).

Herein, a pharmaceutical POCIS (with Oasis[®] HLB sorbent, hereafter referred to as Oasis beads, as the receiving phase) was calibrated for the following APs commonly found in PW (Røe Utvik, 1999): Phenol (Phe), 2-Ethylphenol (2-EtPhe), 2-Isopropylphenol

(2-*i*ProPhe), 2-Phenylphenol (2-PhPhe), 4-Tert-Buthyphenol (4-tBuPhe), 2-Tert-Buthyl-4-Methylphenol (2-tBu-4-MePhe), 4-*n*-Heptylphenol (4-HepPhe), 4-*n*-Octylphenol (4-OctPhe) and 4-*n*-Nonylphenol (4-NPhe) using a static renewal laboratory system. POCIS have been calibrated in previous studies for several APs using different experimental set ups: static calibration (Li et al., 2010), continuous flow calibration (Harman et al., 2008a, 2011) and one previous study exists where the POCIS has been calibrated using a static renewal laboratory system, but just for 4-*n*-Octylphenol and 4-*n*-Nonylphenol (Arditsoglou and Voutsas, 2008a). Here the concentrations of APs accumulated in the PES membranes and the Oasis beads were assessed separately, going beyond a simple calibration of the OASIS beads receiving phase. This study is the first to investigate the role of the PES membranes in the uptake of the pollutants by determining the uptake in the POCIS as the combination of Oasis beads and PES membranes, thus the first to calibrate POCIS for APs by separate phase extractions. In addition, this work investigated whether a lag phase in the uptake of APs to the Oasis beads was observable over a short time. This is of relevance when determining suitable deployment times as the sampling time must be longer than the lag-phase in order to assess a TWA concentration as accurately as possible. In this way it is important to understand whether the PES membranes impede the diffusion of the contaminants at the beginning of the uptake process.

2. Materials and methods

2.1. Materials and chemicals

A stock standard solution, ranging in concentration from 840 mg L⁻¹ to 2260 mg L⁻¹, containing a mixture of APs (Phe, 2-EtPhe, 2-*i*ProPhe, 2-PhPhe, 4-tBuPhe, 2-tBu-4-MePhe, 4-HepPhe, 4-OctPhe and 4-NPhe) were prepared in acetone.

Surrogate standards, 2,4-Dimethylphenol-3,5,6-*d*₃ (2,4-diMePhe-*d*), and 4-(3,6-Dimethyl-3-heptyl)phenol-3,5-*d*₂ (4-diMeHePhe-*d*), were used to check the recovery of the APs; where recovery was considered acceptable if it was between 70% and 130%. Details related to experimental recoveries can be found in the Supporting Information (SI). 3,3',4,4'-Tetrachlorobiphenyl (PCB77) was used as internal standard. In all experiments Millipore water was used from a Direct-Q³ Millipore system (18.2 Ω cm⁻¹, 25 °C). Further information regarding the chemicals used can be found in SI.

The pharmaceutical-POCIS (EWH-Pharm-Hydrophilic Pharmaceutical), consisting of 0.200 g ± 0.004 g of solid sorbent (Oasis[®] HLB sorbent) sandwiched between two PES membranes (thickness approximately 130 μm (Alvarez et al., 2004), pore size ca 100 nm, effective surface area 41 cm² (Tollefsen et al., 2008), 0.200 g), was purchased pre-cleaned and assembled from ExposMeter AB, Sweden; the tests were carried out using the POCIS as received.

2.2. Experimental design

2.2.1. Preliminary degradation experiments

In order to investigate whether degradation of APs occurred under the experimental conditions preliminary degradation experiments were carried out as reported in the Supporting Information.

2.2.2. Lag phase experiments

In order to determine whether a lag phase was evident prior to accumulation of APs in the Oasis beads of the POCIS sampler, a lag phase experiment was carried out over a 24 h period. The tests were carried out in triplicate in 1 L glass beakers containing 1 L of Millipore water spiked with between 4 and 11 μg L⁻¹ of each AP and

one POCIS was added to each beaker. A sub-sample of water (5 mL) was taken after 1, 3, 6, 12 and 24 h and the POCISs were removed from the beakers. The POCISs were disassembled, the Oasis beads and PES membranes were separated and dried overnight and then extracted (as described in 2.3.2.). Sacrificial batches (triplicates) were used in the experiment, all were mixed at 100 rpm on a horizontal shaking table at room temperature (25 °C). Blank replicates were used (without AP spikes) to determine background APs concentration in the PES membranes, Oasis beads and water; no interfering peaks were detected. Sodium azide was added to the sampled water in order to avoid any degradation that could take place in the time before analysis.

2.2.3. POCIS calibration

POCIS calibration was performed to determine uptake rates for the APs. In previous studies, three main methods have been used in order to calibrate the POCIS whilst maintaining constant APs concentrations in the exposure media (water) (Morin et al., 2012): i) a static calibration (Li et al., 2010), ii) a static renewal calibration (Arditsoglou and Voutsas, 2008a) and iii) a continuous flow calibration (Harman et al., 2008b; Morin et al., 2013; Vermeirssen et al., 2012). In this study a static renewal calibration was performed in a closed system (1 L glass beakers) and after 24 h the water was completely refreshed and APs were re-spiked in order to maintain a constant concentration in each beaker. The contaminated water was disposed of after exposure to light for approximately a week which is enough time for photodegradation of APs to occur (Morin et al., 2013).

Calibration tests were performed following the same design describe above. The APs concentration in the water was monitored weekly by extracting the water and checking the spiked concentration of the APs (Harman et al., 2008a; Morin et al., 2013). At preselected times (1, 4, 7, 14, 28 days) the POCISs were removed, disassembled, extracted and analyzed.

2.3. Sample extraction and analysis

2.3.1. Water extraction

Water samples (5 mL) were extracted with 1.25 mL of a mixture of DCM:Ethylacetate (4:1) (Harman et al., 2008a) using a Branson 2210 Sonicator. Surrogate standard (2,4-diMePhe-*d* and 4-diMeHePhe-*d*) were spiked to the water before sonication (1 and 0.5 mg L⁻¹ respectively). After 3 h of sonication the solvent was collected and sodium sulfate was added to remove any remaining water. The solvent was evaporated using a vacuum-concentrator-centrifuge Christ RVC 225 and solvent-switched to toluene. The internal standard (0.5 mg L⁻¹) was added to all samples before analysis via GC-MS (Agilent Technologies).

2.3.2. POCIS extraction

PES membranes and Oasis beads were weighed and placed in amber vials. Both materials were extracted with a mixture of acetone:heptane (4:1; 20 mL of solvent was used to extract 0.1 g of sampler) (Arditsoglou and Voutsas, 2008b). Surrogate standards were spiked before extraction (as reported in 2.3.1.) and then the materials were extracted for 4 days by shaking horizontally at 100 rpm. The solvent was evaporated as described above (section 2.3.1.) and solvent-switched to toluene.

2.3.3. Gas chromatography-mass spectrometry (GC-MS) analysis

A previously described GC-MS method with some slight modifications was followed (Katase et al., 2008). Details can be found in the SI. A 7 points calibration curve was prepared in toluene at concentrations of 0.05, 0.1, 0.5, 1, 2.5, 5, 10 mg L⁻¹.

2.4. Calculation of sampling rate

Diffusion drives compounds accumulation from the sampled media (water in this study) to the receiving phases of the POCIS (Morin et al., 2012). The accumulation of compounds in the POCIS follows a three sequential regimes: an integrative (or linear), a curvilinear and an equilibrium regime (Alvarez et al., 2007; Morin et al., 2012). The calibration of the POCIS must be carried out in the integrative regime (Morin et al., 2012), where the POCIS is considered to operate as an infinitive sink for contaminants and they are accumulated linearly within this time period. The evaluation of the amount of compounds in the POCIS is based on a TWA concentration in the sampled media (Alvarez et al., 2004, 2007).

POCIS was herein calibrated under laboratory conditions; the calibration allows the sampling rate (R_s) value for each compound to be determined. The R_s is a function of the temperature, flow rate and compound properties and can be affected by biofouling (Morin et al., 2012). However, it is independent of the analyte concentration in the sampled media (Alvarez et al., 2004). R_s ($L d^{-1}$) was calculated according to Equation (1):

$$C_s = \frac{C_w R_s t}{M_s} \quad (1)$$

Where C_s and C_w are respectively the analyte concentration in the POCIS ($\mu g g^{-1}$) and in the water ($\mu g L^{-1}$, calculated from the spiked APs concentration), M_s is the mass of the POCIS (g), and t is the sampling time (d).

Several authors have determined the sampler concentration, C_s , by extracting the analytes in the Oasis beads alone (Alvarez et al., 2004; Belles et al., 2014; Harman et al., 2008a, 2009, 2011; Vallejo et al., 2013). In this study the PES membranes and the Oasis beads sorbent were extracted separately and then the APs concentration in the POCIS (C_s) was calculated adding the concentration of APs in the PES membranes and Oasis beads (Equation (2)):

$$C_s = \frac{m_o + m_p}{M_o + M_p} \quad (2)$$

where m_o and m_p are the μg of APs in the Oasis beads and in the PES membranes, while M_o and M_p are the grams of the Oasis and the PES. Equation (1) was then used to calculate R_s for each AP and C_w was determined weekly during the kinetic tests based upon the spiked water concentration. Both Equations (1) and (2) pass across 0,0 coordinates due to blank analysis: no APs peaks were detected in the water either in the POCIS (see Supporting Information).

3. Results and discussion

3.1. Preliminary degradation experiments

The preliminary experiments showed that there was no degradation of APs, on the other hand possible analytical issues can be observed for 2-EtPhe water extraction at low concentration; further discussion and results can be found in the Supporting Information and in Fig. S1.

3.2. Lag phase experiments

The results from the lag phase experiments for select APs (2-PhPhe, 4-tBuPhe, 2-tBu-4-MePhe and 4-HepPhe) are shown in Fig. 1. These compounds are shown as examples in order to span a large range of hydrophobicity ($3.09 \leq \log K_{ow} \leq 5.01$) but all APs displayed the same lag phenomenon. Results for all other

compounds (excluding 2-EtPhe and 2-iProPhe due to low recoveries for sampling time points ≤ 6 h) can be found in Fig. S2 in the Supporting Information. Delay in uptake was previously observed for more hydrophobic compounds with POCIS (Morin et al., 2013; Vermeirssen et al., 2012), while Challis et al. (2016) recently demonstrated the active role of PES membrane in diffusive gradients in thin films sampler for polar organics (o-DGT). The present study is the first experiment of its kind to investigate whether a lag phase exists prior to integrative uptake of the selected APs in the Oasis beads. Fig. 1 shows that there is a delay before compounds diffuse through the PES membranes and reach the Oasis beads. The uptake of APs to the Oasis beads likely occurs via a three phase process whereby APs diffuse through the sampled media to the PES membrane, are sorbed and then diffuse through the PES membrane, and are then accumulated by the Oasis beads (Smedes et al., 2013). The membranes initially impede APs diffusion from the water to the Oasis beads, causing a non-linear accumulation within 24 h. APs reached the Oasis beads relatively quickly, possibly due to diffusion through water-filled membrane pores, whilst other APs reached the sorbent more slowly due to the uptake in the PES membrane itself. It appears that the time to reach the sorbent increases with increasing compound hydrophobicity possibly due to an increase in the interactions between the APs and the PES membranes. However, the lag phase tests do not allow an assessment of the exact amount of time for which the lag phase lasted, but rather provides evidence for the occurrence of a lag phase over a 24 h period. It is therefore advocated that to effectively assess the concentration of APs in the field, sampling times greater than 24 h must be used (as explained in section 4.) in order that the linear regime is reached. Sampling times less than 24 h are not in the integrative sampling regime but inside the lag phase, further explanation of this issues can be found below (section 3.3.2.) and in SI (Table S3).

3.3. POCIS calibration

3.3.1. APs accumulation into the PES membranes and Oasis beads

The uptake of 2-iProPhe, 2-PhPhe, 2-tBu-4-MePhe, 4-HepPhe, 4-OctPhe and 4-NPhe in the PES membranes and in the Oasis beads is shown in Fig. 2a–f. APs were linearly accumulated in the Oasis beads over 28 days, agreeing with previous studies for several other HpOCs (Harman et al., 2008a, 2009). The uptake of all APs in the PES membranes over the 28 days was also linear (see also Supporting Information, Fig. S3). For 2-EtPhe, 2-iProPhe, 4-tBuPhe, 2-tBu-4-MePhe and 2-PhPhe ($2.5 \leq \log K_{ow} \leq 4$), the Oasis beads accumulated a greater amount than the PES membranes. The more hydrophobic APs 4-HepPhe, 4-OctPhe and 4-NPhe ($K_{ow} \geq 5$) showed the opposite trend as these compounds were accumulated to a greater extent in the PES membranes. These opposing trends likely result from the difference in ability of the two sampling phases to accumulate compounds with varying hydrophobicity.

In order to investigate the correlation between APs accumulation and hydrophobicity, the ratios between AP accumulated in the PES membranes and the Oasis beads were calculated for each R_s and the average value across all times (C_{PES}/C_{OASIS}) were plotted against $\log K_{ow}$ ($\log K_{ow}$ values can be found in Table 1), as shown in Fig. S4 in the Supporting Information. C_{PES}/C_{OASIS} is generally constant for APs with $\log K_{ow}$ up to around 4. C_{PES}/C_{OASIS} of 2-EtPhe, 2-iProPhe, 4-tBuPhe and 2-tBu-4-MePhe (with $\log K_{ow}$ values of 2.47–3.97) was on average 0.27 ± 0.045 , however 2-PhPhe represented an exception. Despite having a $\log K_{ow}$ of 3.09 2-PhPhe was accumulated in the PES membranes (C_{PES}/C_{OASIS} is 1.4). At $\log K_{ow}$ around 4, C_{PES}/C_{OASIS} increased sharply with

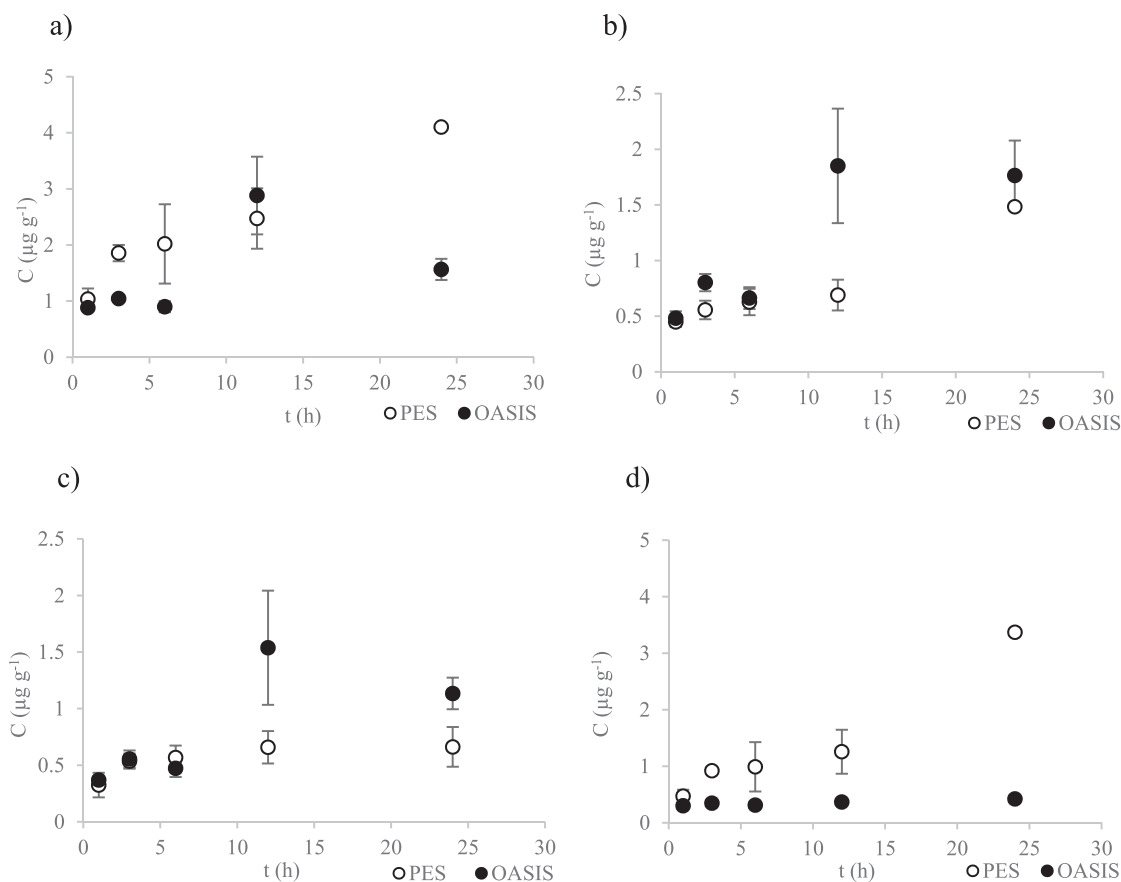


Fig. 1. Lag phase tests. APs accumulated in the PES membranes and in the Oasis beads over 24 h, for a) 2-PhPhe, b) 4-tBuPhe, c) 2-tBu-4-MePhe, d) 4-HepPhe. Error bar = standard deviation of three measurements; relative standard deviation $\leq 30\%$.

compound hydrophobicity and it was on average 9.6 ± 1.0 for 4-HepPhe, 4-OctPhe and 4-NPhe ($5.01 \leq \log K_{ow} \leq 5.76$). Thus as compound hydrophobicity increases, accumulation in the PES membranes exceeds that of the Oasis beads and diffusion through the membranes is retarded. The same behavior was observed by Vermeirssen et al. (2012) for pesticides, biocides and pharmaceuticals, C_{PES}/C_{OASIS} increased with an increase in $\log K_{ow}$. This phenomenon could be explained in three ways: i) decreasing affinity of the Oasis beads for APs with increasing hydrophobicity, ii) steric occlusion effects and iii) uptake delay effects (all discussed below).

The POCIS (specifically with Oasis beads functioning as the solid sorbent) was developed with the aim of sampling HpOCs ($\log K_{ow} \leq 3$) but has also been demonstrated to effectively accumulate some hydrophobic compounds ($\log K_{ow}$ 3 to 4) (Morin et al., 2012). This may explain why 4-HepPhe, 4-OctPhe and 4-NPhe ($\log K_{ow} \geq 5$) are not accumulated to a great extent in the Oasis beads. The second explanation may lie in the fact that with increasing compound $\log K_{ow}$ and concurrent increase in compound dimensions, the PES membranes become a barrier for the diffusion of the APs to the Oasis beads. However, taking the largest AP, 4-NPhe and the length of a single C–C bond (being the longest of C=C and C–C) of 1.54 (Weast, 1984), a very rough estimate of the size of 4-NPhe is 20 Å. Comparing this to the size of the PES membrane pores which are 1000 Å, steric occlusion effects are unlikely. The final explanation may lie in the delayed uptake of APs in the Oasis beads, which is connected to the high affinity that some of the APs have for the PES membranes. APs can be sorbed to

the outer pores of the PES membranes and this leads to a retarded diffusion through the PES membranes. As noted in a previous study (Smedes et al., 2013), diffusion of organic compounds through PES membranes is extremely slow. PES was intended as a nano-filtration glassy membrane for small molecules, and thus larger organic compounds can be sorbed in the membrane. This hypothesis is strengthened comparing the lag phase data of 2-PhPhe over 24 h with its accumulation in the PES membranes and in the Oasis beads over 28 days (Figs. 1a and 2b). The accumulation of 2-PhPhe in the PES membranes is higher than in the Oasis beads over 24 h (Fig. 1a), but the opposite is observed after 28 days (Fig. 2b). It appears that initially a bottle neck exists in the diffusion of 2-PhPhe through the PES membranes, which is overcome with time, thus pointing towards a delayed uptake effect. This can be explained by the chemical interactions occurring between the AP and the PES membranes. The occurrence of π - π interactions between aromatic rings is well documented (Tsuzuki et al., 2002) and it may be extended to the aromatic rings of the PES and the aromatic rings of the APs. This could explain why although 2-PhPhe has a lower $\log K_{ow}$ than 4-tBuPhe and 2-tBu-4-MePhe, its uptake in the PES membranes is comparatively high. The occurrence of π - π interactions between the two aromatic rings of 2-PhPhe as opposed to the single ring in both 4-tBuPhe and 2-tBu-4-MePhe, with the aromatic ring in the PES membrane, could explain the greater delayed uptake effect. This theory could also corroborate the occurrence of the observed delay in uptake over short sampling times and for more hydrophobic APs ($\log K_{ow} \geq 4$ -5).

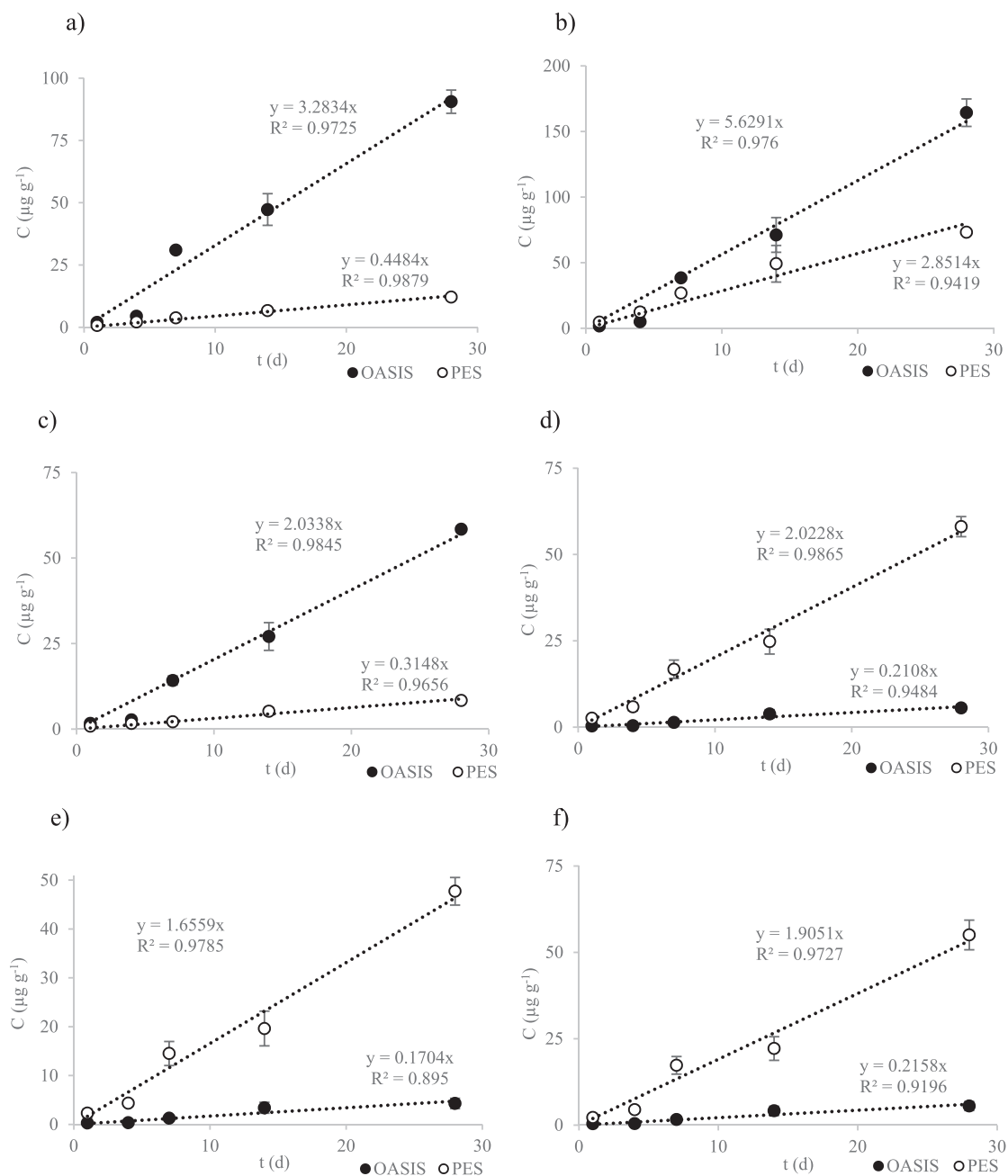


Fig. 2. POCIS calibration experiments. APs concentration in the PES membranes ($\mu\text{g g}_{\text{PES}}^{-1}$) and in the Oasis beads ($\mu\text{g g}_{\text{OASIS}}^{-1}$) over 28 days, for a) 2-iProPhe, b) 2-PhPhe, c) 2-tBu-4-MePhe, d) 4-HepPhe, e) 4-OctPhe, f) 4-NPhe. Error bar = standard deviation of three measurements; relative standard deviation $\leq 30\%$.

3.3.2. APs accumulation into the POCIS and sampling rate calculation

The accumulation of 2-PhPhe, 4-tBuMePhe, 4-HepPhe and 4-OctPhe in the POCIS (calculated as the sum of uptake in the PES membranes and Oasis beads) is shown in Fig. 3. The fitting has been forced through 0,0 due to the blank analysis as explained above. However we also performed a similar analysis without forcing through 0,0 according to Vermeirssen et al. (2012). The results were very similar and information can be found in Table S4 in SI.

Results for all other compounds are shown in Fig. S5 in the Supporting Information. The uptake of the APs within 28 days was

linear. The POCIS is therefore functioning as a kinetic passive sampler and linear accumulation confirms an integrative uptake regime during 28 days (R^2 0.97–0.99).

Uptake curves were fitted using a linear model fitted to all time points and then sampling rates R_s were calculated according to Equations (1) And (2). All time points were used following a close analysis of the data in order to determine whether sampling times occurring in the lag phase should be included. A discussion of this along with the results are shown in the SI (Table S3). Sampling rates for the POCIS ($R_{s, \text{POCIS}}$), for Oasis beads ($R_{s, \text{Oasis}}$) and for PES membranes ($R_{s, \text{PES}}$), ranged respectively from 0.0895 to 0.288 L d^{-1} , from 0.0105 to 0.110 L d^{-1} and from 0.0218 to 0.279 L d^{-1} , are shown in

Table 1
Sampling rate values (R_s , $L d^{-1}$) for the selected APs calculated from the accumulated amount in the POCIS ($R_{s,POCIS}$), in the Oasis beads ($R_{s,Oasis}$) and in the PES membranes ($R_{s,PES}$) with comparison to literature values. Coefficients of determination, respectively for the POCIS (R^2_{POCIS}), the Oasis beads (R^2_{Oasis}) and the PES membranes (R^2_{PES}) for the sampling rates, are obtained from linear regression analysis of curve fittings.

APs	log K_{ow}	$R_{s,POCIS}$ this study	R^2_{POCIS}	$R_{s,Oasis}$ this study	$R_{s,Oasis}$, literature values	R^2_{Oasis}	$R_{s,PES}$, this study	R^2_{PES}	Calibration method
2-EtPhe	2.47 ^a	0.122 ± 0.0137	0.969	0.0837		0.949	0.0275	0.961	Static renewal
2-iProPhe	2.88 ^b	0.132 ± 0.0145	0.981	0.0933		0.973	0.0293	0.988	Static renewal
2-PhPhe	3.09 ^a	0.238 ± 0.0321	0.991	0.105		0.976	0.123	0.942	Static renewal
4-tBuPhe	3.31 ^a	0.150 ± 0.0182	0.983	0.110		0.975	0.0281	0.984	Static renewal
					0.120 ^d				Continuous flow
					0.170 ^{e,i}				Continuous flow
					0.09 ^{f,i}				Continuous flow
					0.12 ^{f,i,j,k}				Continuous flow
2-tBu-4-MePhe	3.97 ^c	0.0895 ± 0.0125	0.993	0.0612		0.984	0.0218	0.966	Static renewal
					0.218 ^{e,i}				Continuous flow
					0.08 ^{f,i}				Continuous flow
					0.11 ^{f,i,j,k}				Continuous flow
4-HepPhe	5.01 ^c	0.288 ± 0.0516	0.988	0.0126		0.948	0.279	0.986	Static renewal
4-OctPhe	5.50 ^c	0.276 ± 0.0607	0.981	0.0120		0.895	0.268	0.979	Static renewal
					0.0100 ^g				Static renewal
					0.0062 ^{g,k}				Static renewal
4-Nphe	5.76 ^a	0.222 ± 0.0311	0.976	0.0105		0.920	0.214	0.973	Static renewal
					0.1167 ^g				Static renewal
					2.459 ^h				Static
					1.654 ^{h,l}				Static
					1.199 ^{h,m}				Static
					0.923 ^{h,n}				Static
					0.105 ^{g,k}				Static renewal

^a Leo and Hoekman 1995, ^b Mackay et al. 2006, ^c EPA 2000, ^d Harman et al. 2008b, ^e Harman et al. 2008, ^f Harman et al. 2009, ^g Ardisoglou and Voutsas 2008a, ^h Li et al. 2010, ⁱ salted water, ^j fouled POCIS, ^k pesticide-POCIS, ^l T = 15 °C, ^m T ≤ 10 °C, ⁿ unstirred conditions Standard deviations of three measurements.

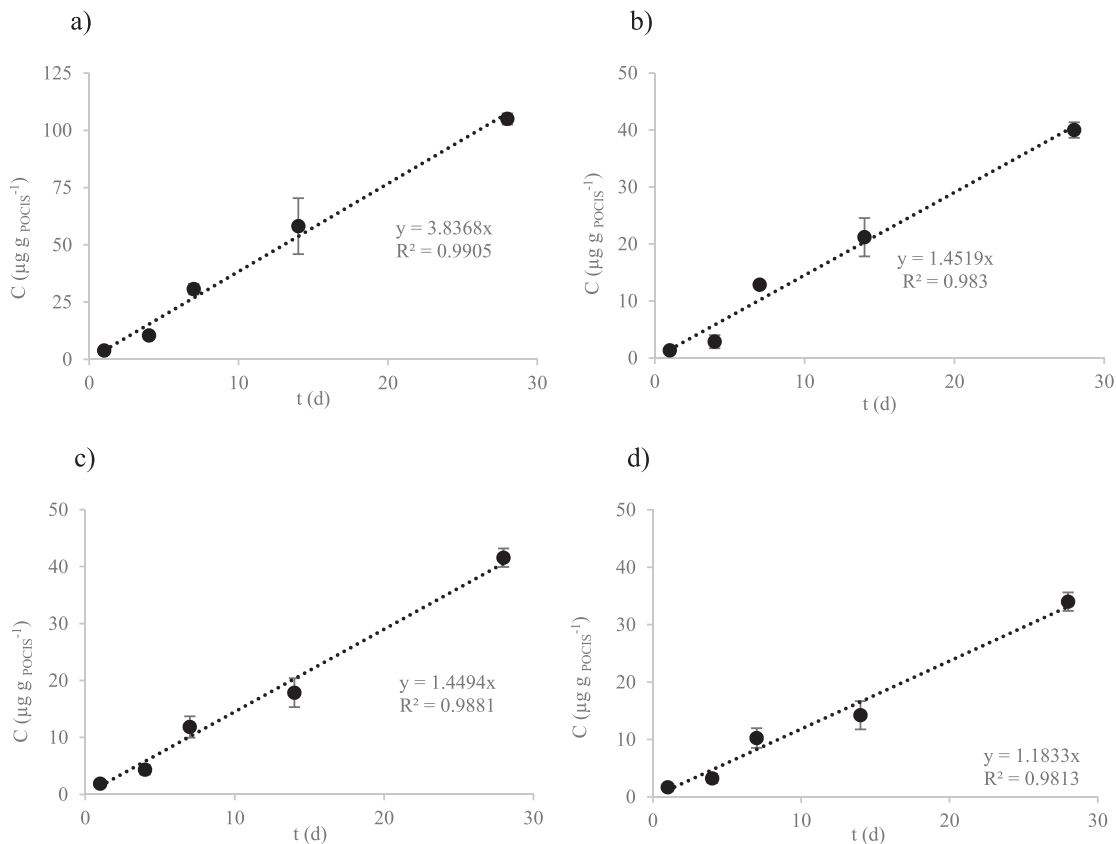


Fig. 3. POCIS calibration experiments. APs concentration in the POCIS over 28 days, respectively a) 2-PhPhe, b) 4-tBuPhe, c) 4-HepPhe, d) 4-OctPhe. Error bar = standard deviation of three measurements; relative standard deviation ≤ 30%.

Table 1. The POCIS was able to efficiently accumulate APs with log K_{ow} up to 5.8, provided that the AP accumulation was assessed in both the Oasis beads and the PES membranes. Sampling rates for a wide range of compounds including bactericide, repellent, insecticides, pharmaceuticals and plasticizer are available in the literature (Morin et al., 2012), but studies for APs are quite scarce. Table 1 shows all previously reported literature values for the APs used in this study assessed by determining uptake to the Oasis beads ($R_{s,Oasis}$). A comparison of those values with the values determined here is difficult due to differences in sampling systems and POCIS configuration. However, a comparison with the sampling rates calculated by Harman et al. (2008a, 2008b, 2009) and Arditoglou and Voutsas 2008a, was carried out for 4-tBuPhe, 2-tBu-4-MePhe and 4-OctPhe. The values agreed around 20% of those determined here.

3.3.3. Correlation between sampling rate R_s and compound log K_{ow}

Several authors have investigated the correlation between sampling rate R_s and log K_{ow} reporting different trends. Linear correlation (Li et al., 2010), Gaussian trend, with a maximum sampling rate at log K_{ow} around 2 (Alvarez et al., 2007), and a curvilinear model (Mazzella et al., 2010) have been reported. In order to evaluate the relationship between R_s and log K_{ow} for this data set, R_s values have been calculated from the accumulated amount of APs in the POCIS, in the Oasis beads and in the PES alone. These concentrations were used as C_s in Equations (1) and (2), respectively. Fig. 4 shows the relationship between R_s and log K_{ow} and indicates that there is no clear correlation between the sampling rates calculated for uptake to the POCIS and log K_{ow} . A weak linear relationship is evident, but the fitting is poor ($R^2 = 0.43$) to extrapolate the R_s from the log K_{ow} . For the $R_{s,Oasis}$, the correlation appears to be Gaussian, with decreasing sampling rates at log K_{ow} 3–3.5; while for the $R_{s,PES}$ no clear trend is observed. The $R_{s,PES}$ values for 2-EtPhe, 2-iProPhe, 4-tBuPhe and 2-tBu-4-MePhe are almost constant over 28 days but for 4-HepPhe, 4-OctPhe and 4-NPhe a sharp increasing of the sampling rate is seen. This confirms that the hydrophobic APs (log $K_{ow} > 5$) are accumulated in the PES membranes, whilst the hydrophilic APs (log $K_{ow} < 4$) are barely accumulated in this phase. These considerations can be in part confirmed by Mazzella et al. (2010), who concluded that the water layer usually controls uptake of hydrophilic chemicals to POCIS (R_s increases with log K_{ow} increasing), while diffusion through the PES membranes is generally the rate limiting factor for the uptake of the hydrophobic compounds (R_s does not depend on flow rates). 2-PhPhe (log $K_{ow} = 3.09$) presents itself as an outlier in this data set, confirming the occurrence of a different uptake mechanisms for

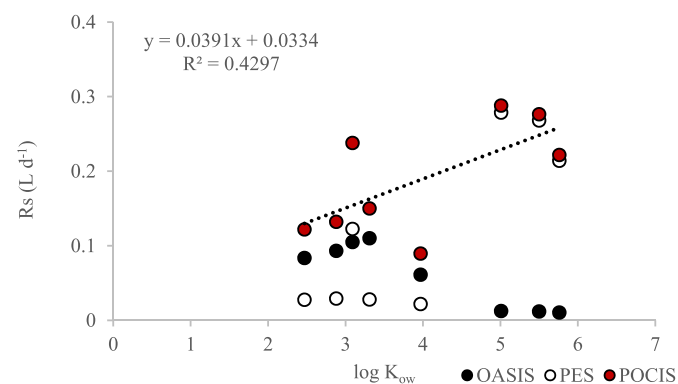


Fig. 4. Correlation between sampling rates R_s and log K_{ow} . The sampling rates were calculated from the amount of APs accumulated POCIS (fitted using linear model), in the Oasis beads and in the PES membranes.

this compound to the PES membranes that does not depend solely on compound hydrophobicity.

These observations imply that trends are strictly dependent on the phases that are extracted, the method used to calculate sampling rates, the physicochemical properties of the compounds being investigated (pharmaceuticals, pesticides, detergents, etc.), the type of POCIS configuration (“pharmaceutical” or “pesticide”) and the K_{ow} values used when making such correlations. This makes it difficult to reliably predict or extrapolate sampling rates from log K_{ow} . Difficulties in predicting sampling rates based on analyte molecular descriptors has been confirmed by Miller et al. (2016), who investigated the uptake of 73 compounds including pharmaceuticals, pesticides, and illegal drugs. These authors concluded that a priori information was not needed for the prediction of R_s and a simple model based on simplified molecular input line entry system (SMILES) of compounds performed as well as a model based on a multitude of molecular descriptors.

3.3.4. Considerations for using the POCIS and the proper calculation of the sampling rate

Several authors (Alvarez et al., 2004, 2007; Morin et al., 2012) have advocated that POCIS should be used to sample compounds that fall within the operational hydrophobicity range (log $K_{ow} \leq 4$) of the sampler. This study has gone one step further and demonstrated that log $K_{ow} \leq 4$ represents a critical value at which uptake of these APs to the PES membranes and the Oasis beads involves different processes. At this cut off point the APs begin to be accumulated in the PES membranes instead of reaching the Oasis beads. Thus far, POCIS has been calibrated for several hydrophilic APs, while it is known that the accumulation of hydrophobic APs is not very efficient (Harman et al., 2008a, 2009); this work demonstrated for the first time POCIS can be used to sample the more hydrophobic APs (log $K_{ow} > 4$) if the compounds concentration is measured in the PES membranes and not just in the Oasis beads. However as demonstrated here, certain hydrophilic compounds may present special behavior (for example 2-PhPhe), and thus it becomes even more paramount to extract both phases of the POCIS. Furthermore PSDs allow very low concentrations to be detected and by extracting both the Oasis beads and the PES membranes the APs accumulation becomes more efficient. In order to calculate robust R_s values and reliably determine environmental concentrations, the method used for evaluating the contaminants in the field must be consistent with that chosen to calibrate the POCIS. If the POCIS is calibrated by only extracting the Oasis beads, it is the Oasis beads that should then be extracted after laboratory or field deployment in order to evaluate contaminant concentrations. However based on this study this is not advocated.

This experiment was carried out in the laboratory, however additional factors must be considered when POCIS are deployed in the field. Sampling at great depths, the effect of membrane biofouling and salt in seawater may result in different sampling rates to those determined in laboratory. The effect of the salinity should be considered, although it has previously been reported that this effect can be corrected for using a constant, (Sacks and Lohmann, 2011), at least for the polyethylene equilibrium PSD. Biofouling (Morin et al., 2012) and thus reduced accumulation may be especially prominent for compounds that are accumulated to a greater extent in the PES membranes (4-HepPhe, 4-OctPhe and 4-NPhe), but may be negligible for APs accumulated mostly by the Oasis beads (2-EtPhe, 2-iProPhe, 4-tBuPhe, 2-tBu-4-MePhe and 2-PhPhe). Prior to use for PW monitoring, in situ calibration of the POCIS is therefore recommended to determine whether laboratory evaluated sampling rates are consistent with field observations.

4. Conclusions

A lag in accumulation of APs in the POCIS was observed with non-linear uptake (over 24 h) suggesting that the PES membranes initially hinder the APs diffusion from the water to the Oasis beads. These considerations provide useful information from the perspective of using the POCIS to assess the TWA concentrations of APs in PW as well as water and waste water, where deployment times i) long enough to avoid the lag phase (longer than 1 day) and, ii) short enough to satisfy using the POCIS in the integrative regime must be used.

Here the POCIS was calibrated and sampling rates were assessed by analyzing the AP concentrations in both the PES membranes and the Oasis beads. This study demonstrated that APs with $\log K_{ow} < 4$ were more effectively accumulated in the Oasis beads, while APs with $\log K_{ow} > 5$ were accumulated more efficiently in the PES membranes. A combination of decreased affinity of the Oasis beads for the APs with increased hydrophobicity, and increased sorption to the PES phase with increased hydrophobicity are likely explanations for these observations. It is therefore strongly advocated that in order to correctly determine uptake rates for compounds to be sampled by POCIS, both the PES membranes and the Oasis beads be extracted and the accumulated concentrations summed. This approach will then allow the accumulation of hydrophobic as well as hydrophilic APs using just one passive sampler. This may pave the way for the use of a single passive sampler to be deployed to monitor a greater range of common contaminants found in water.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2017.06.083>.

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