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Uptake rates of alkylphenols, PAHs and carbazoles in semipermeable membrane devices (SPMDs) and polar organic chemical integrative samplers (POCIS)

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ABSTRACT

Passive sampling devices provide a useful contribution to the monitoring of contaminants in the aquatic environment. However, calibration data needed for the calculation of water concentrations from sampler accumulations are restricted to a limited number of compound classes. Thus uptake of a range of alkylated phenols (AP), polycyclic aromatic hydrocarbons (PAH) and carbazoles was determined for semipermeable membrane devices (SPMDs) and polar organic chemical integrative samplers (POCIS) using a flow through exposure system. Sampling rates ranged from 0.02 to 0.26 l d^{-1} for POCIS and 0.02 to 13.83 l d^{-1} for SPMDs. Observed SPMD uptake was also compared to that predicted by an empirical model including the use of performance reference compounds (PRCs). Predicted sampling rates did not differ by more than a factor of 1.3 from experimental values for PAH, providing further evidence that the PRC approach can be successfully used to determine in situ sampling rates for these compounds. Experimental sampling rates for AP in SPMDs were, however, much lower than predicted. This discrepancy was too large to be explained by small uncertainties in the calibration system or in the calculations. Based on these data we conclude that while hydrophobic AP are accumulated by SPMDs their partitioning cannot be predicted from their $\log K_{ow}$ using current methods. Due to this lower than expected uptake, sampling rates were only higher in SPMDs than POCIS in the range of $\log K_{ow} > 5.0$. Simultaneous deployment of both sampler types allows the study of compounds with a broad range of physicochemical properties.

1. Introduction

The relative persistence and potential toxicological effects of alkylphenols (AP) have led to increased concern about their presence in the environment. For example, it is reported that AP contribute to the estrogenicity of operational discharges from the offshore oil industry (Thomas et al., 2004) where they are readily found due to their natural occurrence in crude oils (Utvik, 1999; Boitsov et al., 2004). On land attention has been focused on octylphenol (OP) and nonylphenol (NP), which are present largely as a result of metabolism of alkylphenol ethoxylates (APEs). These commonly used surfactants have extensive domestic and industrial applications and generally enter the environment after partial removal within wastewater treatment plants (Nasu et al., 2001; Vogelsang et al., 2006; Tan et al., 2007; González et al., 2007; Loos et al., 2007). Their post treatment fate is largely influenced by degradation and sorption processes (Ying et al., 2002) and their eventual occurrence in coastal waters and sediments has been frequently reported (recently, Cheng et al., 2006; Koh et al., 2006; Zoller, 2006; Klecka et al., 2007).

AP have been found to accumulate and cause acute toxicity to algae, clams, shrimp, crustaceans and fish (McLeese et al., 1979, 1981; Saarikoski and Viluksela, 1982; Granmo et al., 1989; McCarty et al., 1993; Tollefsen et al., 1998). Many of these chemicals have also been reported to act as endocrine disruptors in aquatic species such as fish (Arukwe et al., 1997; Tollefsen, 2007; Tollefsen et al., 2008; Tollefsen and Nilsen, 2008) and crustaceans (Isidori et al., 2006), potentially causing interference with reproductive functions and normal development of organisms (Jobling et al., 1996; Ashfield et al., 1998; Gimeno et al., 1998; Seki et al., 2003). Whilst the overall ecological consequences of these compounds may be debated, concerns have led to the listing of NP and OP as 'priority substances' in annex X of the European Water Framework Directive (EU, 2000). Monitoring of these compounds is, therefore, obliged by EU member states. Such monitoring can be challenging due to rapid dilution of effluents and variable discharges and thus may require sensitive analytical techniques, intensive sampling programs and large volume samples.

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Passive sampling devices (PSDs) may overcome these issues by permitting unattended large volume and time integrated sampling, which compensate for fluctuating discharges and give lower detection limits. The semipermeable membrane device (SPMD) developed by Huckins et al. (1990a) is such a PSD, with a large sampling capacity for hydrophobic organic chemicals. A wide range of contaminants have been reported to accumulate in SPMDs (for recent review see Esteve-Turrillas et al., 2007), including NP (Bennett and Metcalfe, 2000; Stuer-Lauridsen and Kjolholt, 2000). Also, the polar organic chemical integrative sampler (POCIS) (Alvarez et al., 2004) has been shown to concentrate some of the more hydrophilic AP (Petty et al., 2004; Alvarez et al., 2005; Harman et al., 2008). Both devices have been successfully used to monitor contaminants discharged from sewage treatment works (Petty et al., 2000; Stuer-Lauridsen and Kjolholt, 2000; Wang et al., 2001; Jones-Lepp et al., 2004; Alvarez et al., 2005; Augulyte and Bergqvist, 2007; Katsoyiannis and Samara, 2007) and simultaneous deployment allows for the detection of compounds with wide ranging physicochemical properties (Petty et al., 2004). However, in order for water concentrations to be calculated accurately from PSD accumulations, calibration data for those compounds is required. Whilst such data exists for a range of analytes (Huckins et al., 2006), none are available for AP. The overall objective of the present work is, therefore, to study the uptake kinetics of a range of AP and carbazoles by SPMDs and POCIS, allowing more quantitative analysis of these compounds from environmental exposures.

2. Theory and modelling

Consideration of the various uptake models, their theoretical basis, assumptions and weaknesses are described in depth by others (Huckins et al., 2006; Booij et al., 2007). Briefly, accumulation of hydrophobic chemicals in SPMDs can be explained by an initial linear uptake stage followed by curvilinear and equilibrium partitioning stages (Huckins et al., 1993). The linear stage is given by

$$C_s = K_{sw} k_e C_w t \quad (1)$$

where C_s and C_w are the concentrations in the sampler and water (freely dissolved), respectively (ng cm^{-3}), K_{sw} is the whole SPMD–water partition coefficient as one lipid equivalent volume (cm^3 cm^{-3}) (Huckins et al., 1999) and k_e is the release rate constant (d^{-1}). In order to provide comparison to traditional extraction methods, Eq. (1) can be re-expressed using a sampling rate term R_s (l d^{-1})

$$C_s = \frac{R_s C_w t}{V_s} \quad (2)$$

where V_s is the volume of the sampler (cm^3). With constant C_w and long exposures the concentration in the SPMD can be given simply by its equilibrium value.

$$C_s = C_w K_{sw} \quad (3)$$

In order to avoid arbitrary decisions about exactly when the different stages apply, uptake at any stage can be described by,

$$C_s = K_{sw} C_w \left(1 - \exp\left(-\frac{R_s t}{V_s K_{sw}}\right)\right) \quad (4)$$

(Huckins et al., 1993). The dependence of Eq. (4) on accurate sampling rates being available led to the development of using performance reference compounds (PRCs) to estimate them in situ (Booij et al., 2002; Huckins et al., 2002a). These compounds of medium fugacity are spiked into samplers before deployment. Theoretically their dissipation is governed by the same principles as the uptake of target compounds and so they are similarly affected by changes in, for example, water flow rates. The dissipation rate constant k_e is given by,

$$C_{sPRC} = C_{0PRC} \exp(-k_e t) \quad (5)$$

where C_{0PRC} and C_{sPRC} are the concentrations of PRCs before and after deployment.

The accumulation of chemicals by POCIS is not currently as well described as that for SPMDs. It is usually considered as (effectively) an infinite sink for contaminants, i.e. that saturation is not approached and thus uptake remains linear (Alvarez et al., 2004). Assuming linear uptake then Eq. (2) can simply be re stated,

$$C_s = \frac{R_s C_w t}{M_s} \quad (6)$$

where C_s represents the concentration in the sorbent (membrane not analysed) and M_s is its mass (Alvarez et al., 2004).

3. Materials and methods

3.1. Chemicals

Alkylphenols, 9-methyl and 3-ethylcarbazole were obtained from Chiron (Trondheim, Norway). All other chemicals (table 1) were from Sigma–Aldrich (Seelze, Germany) and were of at least 97% purity. Solvents were from Rathburn (Walkerburn, Scotland) except for cyclohexane (J.T. Baker, Deventer, Holland) and were of HPLC grade or better.

3.2. Exposure system

Study compounds were chosen to cover a wide range of hydrophobicity and were a mix of AP, other uncalibrated compounds of relevance to North Sea offshore monitoring such as carbazoles, and polycyclic aromatic hydrocarbons (PAH). Considerable SPMD calibration data for PAH is available (Huckins et al., 1999, 2006; Luellen and Shea, 2002; Vrana and Schuurmann, 2002) so inclusion of these compounds allows for comparison. The flow through system consisted of a 200 l stainless steel, cylindrical tank that was shielded from ambient light and contained within a temperature controlled room (Supplementary material, Figure S1). All parts of the system were constructed of stainless steel, glass or PTFE and were solvent rinsed. Filtered seawater (200 μm, 1 l min^{-1}) and the acetone spike solution (0.2 ml min^{-1}) were mixed in a 5 l glass flask before being gravity fed to the system. Such a flow rate is required in order that the flushing rate Q of the exposure tank is much larger than the total (estimated) sampling rate, $Q \gg nR_s$ (Booij et al., 2003). The solution was fed into the bottom of the tank directly towards a stirring paddle (100 rpm). Samplers were placed ringwise around the stirrer. Laminar flow was estimated as 0.008 cm s^{-1} and with stirring surface flow was measured as approximately 4 cm s^{-1}. The exposure water temperature was 10 ± 1 °C. Final concentrations of test compounds in the exposure tank were 50–120 ng l^{-1}. This was determined by liquid–liquid extraction (using dichloromethane), of twice weekly water samples. The whole system was run for three days before adding samplers in an attempt to achieve steady state water concentrations and minimise the effects of adsorption to the exposure system.

3.3. SPMD extraction, clean up and quality control

Standard size SPMDs (91.4 × 2.5 cm LDPE tubing of 70–95 μm wall thickness, containing 1 ml triolein (Huckins et al., 2002b)) spiked with; acenaphthene-d10, fluorene-d10, phenanthrene-d10 and chrysene-d12 as PRCs, were obtained from ExposMeter (Tavelsjo, Sweden). Hexane dialysis of SPMDs was carried out as detailed

Table 1
Uptake rates R_s (l d^{-1}) for standard configurations of SPMDs and POCIS (defined in methods section), r^2 is from regression analysis of curve fits

Exposure compound	Log K_{ow}[a]	SPMD			POCIS		
		r^2	R_s	CV	r^2	R_s	CV
Alkylated phenols							
2,4-Dimethylphenol	2.30[b]	–	nd	–	0.68	0.111	28
2,5-Dimethylphenol	2.33[b]	–	nd	–	0.71	0.104	26
3,5-Dimethylphenol	2.35[b]	–	nd	–	0.72	0.105	25
4-Ethylphenol	2.58[b]	–	nd	–	0.80	0.159	23
2,4,6-Trimethylphenol	2.73[c]	0.98	0.06	6	0.83	0.189	29
2-*n*-Propylphenol	2.93[b]	0.97	0.06	6	0.75	0.075	30
2,3,5-Trimethylphenol	2.92[d]	0.99	0.02[g]	6	0.85	0.193	26
4-*n*-Propylphenol	3.20[c]	0.99	0.05	3	0.78	0.094	30
4-*tert*-Butylphenol	3.31[b]	0.99	0.05	6	0.88	0.170	23
4-Isopropyl-3-methylphenol	3.52[e]	–	[h]	–	0.88	0.150	25
4-*n*-Butylphenol	3.65[c]	0.98	0.05	6	0.80	0.036	29
2,6-Diiospropylphenol	3.79[b]	0.99	0.29	6	0.85	0.225	41
2-*tert*-Butyl-4-methylphenol	3.97[e]	0.98	0.15	7	0.88	0.218	31
4-*tert*-Butyl-2-methylphenol	3.97[e]	0.91	0.09	13	0.87	0.191	30
4-*n*-Pentylphenol	4.06[b]	0.98	0.06[i]	9	–	[k]	–
2,5-Diisopropylphenol	4.42[e]	0.99	0.18	6	0.83	0.065	42
2-*tert*-Butyl-4-ethylphenol	4.46[e]	0.99	0.22	7	0.86	0.161	44
6-*tert*-Butyl-2,4-dimethylphenol	4.52[e]	0.93	0.15	14	0.86	0.254	39
4-*n*-Heptylphenol	5.01[e]	–	1.43[i]	8	–	[k]	–
4-*tert*-Octylphenol	5.28[e]	0.97	0.40	11	0.63	0.058	40
4-*n*-Octylphenol	5.50[e]	–	4.25[i]	9	–	[k]	–
4-*n*-Nonylphenol	5.76[f]	–	7.43[i]	13	–	[k]	–
2-Methyl-4-*tert*-octylphenol	5.82[e]	0.99	1.82	6	–	[k]	–
PAH and other compounds							
Quinoline	2.03[b]	–	[h]	–	0.48	0.027	32
2,6-Dimethylquinoline	3.24[e]	–	[h]	–	0.50	0.017	57
Naphthalene	3.45	–	[h]	–	–	[k]	–
Carbazole	3.72[b]	0.99	0.30	7	–	[k]	–
9-Methylcarbazole	3.84[e]	0.98	5.43	5	–	[k]	–
2-Methylnaphthalene	3.86	0.90	8.45	5	–	[k]	–
trans-Decalin	4.20[e]	0.93	6.84	14	–	nd	–
cis-Decalin	4.20[e]	0.94	10.55	13	–	nd	–
3-Ethylcarbazole	4.33[e]	0.99	1.99	6	–	[k]	–
2,6-Dimethylnaphthalene	4.37	0.97	8.96	7	–	[k]	–
Fluorene	4.38	0.98	7.91	6	–	[k]	–
Dibenzothiophene	4.38	0.95	8.69	9	–	[k]	–
Anthracene	4.54	0.91	8.37	12	–	[k]	–
2-Methylanthracene	5.14	0.85	11.51	16	–	[k]	–
Pyrene	5.30	0.96	13.83[j]	14	–	[k]	–
Benzo[*a*]pyrene	6.35	0.82	11.37	18	–	[k]	–

CVs are the average from individual sampling times.
[a] Values taken from Huckins et al. (2006) where available to increase comparability to existing SPMD data, otherwise taken from the literature or by fragment constant methods as indicated.
[b] Hansch et al. (1995).
[c] Sangster (1993).
[d] Sabljic et al. (1995)
[e] EPA (2000).
[f] Itokawa et al. (1989).
[g] No data at 7 days.
[h] No curve fit.
[i] Calculated using 7 day data only.
[j] Data from 14 days excluded due to analytical interference and $n = 2$ at 28 day sampling.
[k] Low and variable accumulations with poor linearity. nd = not detected.

by Huckins et al. (1990b). Extracts were combined and reduced with nitrogen before clean up using gel permeation chromatography as described previously (Harman et al., 2008). Three replicates of each type of sampler for each sampling time were analysed, together with fabrication, field and transport blanks. These blanks are used to correct for possible contamination during manufacture, transport, storage, during deployment and retrieval, in the subsequent laboratory procedures and to determine initial PRC concentrations (Huckins et al., 2006).

3.4. POCIS handling and extraction

Standard POCIS with a surface area per mass of sorbent ratio of ca. 180 cm^2 g^{-1} (Alvarez et al., 2004) were obtained from Exposmeter (Tavelsjo, Sweden). The pharmaceuticals configuration was used, containing Oasis HLB sorbent between two discs of polyethersulphone membrane. Preliminary trials showed this type of POCIS to be more suitable for AP uptake than the other commercially available configuration, 'POCIS-pesticides'. POCIS were extracted with methanol as described by Alvarez et al. (2004). Extracts were reduced in volume with a gentle stream of nitrogen and solvent changed to cyclohexane.

3.5. Instrumental analysis

Analysis proceeded by gas chromatography with mass spectrometric detection (GC–MS). Samples were run twice, once for alkylphenols and once for PAH, carbazoles, etc. An Agilent Technologies

(Santa Clara, USA) 6890 GC linked to a 5973 mass selective detector in selected ion monitoring (SIM) mode was used. The GC was equipped with a 30 m column with a stationary phase of 5% phenyl polysiloxane (0.25 mm internal diameter and 0.1 μm film thickness) with a column flow rate of 1.2 m l min^{-1}. The inlet was operated in the splitless mode. The initial column temperature was 40 °C, which was raised stepwise to 310 °C over 46 min.

3.6. Data evaluation

Accumulation of analytes during the exposure was modelled by linear and non-linear regression using Eq. (1) and (4), (assumption of constant C_w), depending on whether half saturation was approached or not during the exposure period (Vrana and Schuurmann, 2002). Prism 4.1® (GraphPad Software, San Diego, USA) was used to fit curves directly to the data and sampling rates were then calculated from the linear part or the whole of those fitted curves. In order to calculate the dissipation rate constants of PRCs the same software was used to fit the decay equation (Eq. (5) to the experimentally determined time course PRC concentrations using a forced zero expected equilibrium point. Estimating sampling rates by using the PRC data and an empirical model (Huckins et al., 2006) is detailed in Supplementary material.

4. Results and discussion

4.1. Blanks and procedural recoveries

The described methods were not able to provide reproducible results at low concentrations for phenol or for 2-methyl, 3-methyl and 4-methylphenol, due to their volatility and background contamination. These data have therefore, been excluded. Procedural recoveries of target compounds averaged 90% for SPMDs (average CV 9%, $n = 5$) and 68% for POCIS (average CV 7%, $n = 5$). Recovery for the more polar alkylphenols ($\log K_{ow} < 4.0$) from POCIS was noticeably lower, typically <50%. Several compounds were present in PSD blanks. Naphthalenes were consistently found in both SPMD and POCIS (10–90 ng) as were small amounts of 4-*tert*-octylphenol (20 ng). 6-*tert*-Butyl-2,4-dimethylphenol and 2-*tert*-butyl-4-ethylphenol were also present in trace levels in SPMDs and POCIS, respectively. Apparent instability of 2,6-di-*tert*-butylphenol in analytical standards and high blank values in POCIS, possibly from the membrane, resulted in these data being disregarded. No target compounds were detected in solvent blanks.

4.2. Exposure system concentrations

The flow of spiked water remained constant throughout the study at 1 ± 0.01 l min^{-1} ($n = 56$). Measured exposure water concentrations were generally within 20% of nominal concentrations, with little variation between samples (average CV 12%, $n = 8$). Notable exceptions were the 4-*n*-alkylphenols which reduced in concentration after 14 days, probably due to biodegradation as reported elsewhere (Ekelund et al., 1993). This degradation appeared to be more significant with increasing chain length and was clearly replicated in SPMD uptake curves. Concentrations of several other compounds were more variable including, naphthalene, pyrene and carbazoles. Calibration sampling rates (R_s) are highly dependent on the accuracy of the freely dissolved, 'available for sampling' exposure concentrations (C_w), here determined by partitioning with dichloromethane. This method may have overestimated C_w (and thus resulted in underestimation of R_s) as any fraction of analytes bound to organic carbon (OC) will have been extracted by dichloromethane but was not available for sampling. Correcting C_w for OC as described by Meadows et al. (1998) revealed that concentrations of only six compounds, those with $\log K_{ow} > 5.0$, could have been overestimated by more than 10% (Supplementary material). Benzo[*a*]pyrene was the only target compound whose concentration could have been seriously affected (70%) and this seems highly unlikely based on the observed uptake. We conclude, therefore, that partitioning to OC has not affected the presented sampling rates greatly.

4.3. Uptake and sampling rates – POCIS

All AP were quantifiable in POCIS with the exception of 4-*n*-pentyl, 4-*n*-heptyl, 4-*n*-octyl, 4-*n*-nonyl and 2-methyl-4-*tert*-octylphenol. The absence of these compounds was probably due to a combination of their hydrophobic nature ($\log K_{ow}$ 4.06–5.82) and degradation of the *n*-alkylphenols, as mentioned earlier. Uptake of the other exposure compounds, PAH, carbazoles, etc. was generally at low ng $POCIS^{-1}$ levels with high variability and poor linear fit. The more polar quinoline and 2,6-dimethylquinoline ($\log K_{ow}$ 2.03 and 3.24, respectively), were exceptions. POCIS is generally not recommended for sampling hydrophobic compounds (Alvarez et al., 2007). Variation between POCIS was relatively high (average CV 30%, Table 1) possibly due to individual samplers experiencing different hydrodynamic conditions because of positioning relative to water flow (Vrana and Schuurmann, 2002). POCIS were placed in the exposure tank using a randomised block design and there was no discernable pattern to the variation apart from that it was higher for 21 day samples. Uptake of AP remained linear during the 28 day exposure, (average r^2 0.80, non-linearity runs test $P > 0.5$) although uptake of dimethylphenols and 4-ethylphenol appeared to be slowing down at 28 days (Supplementary material, Figure S2). Uptake of quinoline may also have reached a plateau, but interpretation is difficult due to considerable variation. Non-linear POCIS uptake and desorption was recently reported for the first time (Mazzella et al., 2007) and further sampling points would be required in order to adequately test for non-linearity. What takes place at eventual 'equilibrium' or saturation in POCIS and to what extent, if any, there is partitioning or desorption due to competitive processes are questions that warrant further investigation. Linear fits were not forced through zero in order that calculated R_s values allowed for non-zero intercepts. Intercepts appeared to be related to hydrophobicity (r^2 0.59) with more polar compounds ($\log K_{ow} < 3.1$) exhibiting 'burst' uptake in the initial stages and more hydrophobic ones ($\log K_{ow} > 3.1$) a 'lag' stage as shown in Fig. 1. It has been reported that a burst effect represents initial wetting of the membrane and sorbent and thus can be reduced by deploying POCIS pre-wetted (Alvarez, 1999). Lag uptake for more hydrophobic compounds may be due to sorption to the

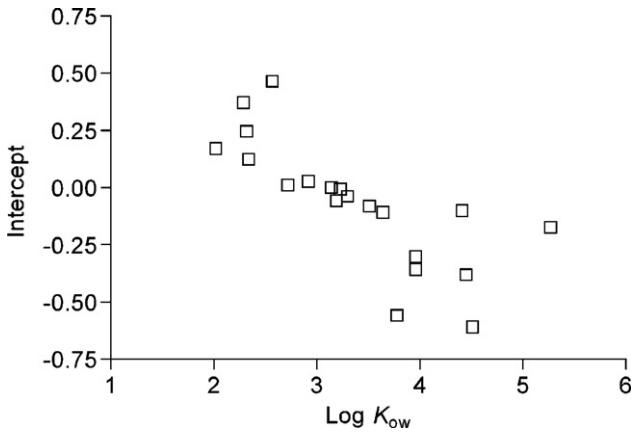

Fig. 1. Intercepts from fitted POCIS uptake curves as a function of $\log K_{ow}$.

membrane surfaces dominating in the early stages, which may suggest biphasic uptake. Mass transfer through the polymer matrix itself may also be a significant factor and analysis of both membranes and sorbents during calibration studies would allow a more detailed description. In any case this may not be a critical issue as the effect is small during a typical 4 week exposure and also as POCIS is unlikely to be routinely used to measure hydrophobic compounds (Alvarez et al., 2007).

Calculated sampling rates ranged from 0.017 to 0.254 l d^{-1} (2,6-dimethylquinoline and 6-*tert*-butyl-2,4-dimethylphenol, respectively, Table 1). To our knowledge 4-*tert*-butylphenol is the only one of our exposure compounds that POCIS has been calibrated for previously with a sampling rate of 0.120 l d^{-1} (Harman et al., 2008), compared to 0.170 l d^{-1}. This discrepancy is most probably due to differences in flow rates between these studies, and highlights the need for the standardisation of POCIS calibrations. Overall the presented POCIS sampling rates are similar to those reported by others using renewal type exposures for herbicides and pharmaceuticals (Alvarez et al., 2004; Macleod et al., 2007; Mazzella et al., 2007; Togola and Budzinski, 2007).

Recent work has provided some evidence of a Gaussian shaped relationship between POCIS R_s and log K_{ow} for herbicides (Mazzella et al., 2007) and tentatively within some classes of pharmaceuticals (Macleod et al., 2007), that is similar to that seen for SPMDs (Huckins et al., 2006). However, it is unlikely that K_{ow} is a powerful enough descriptor to be able to predict sampling rates for polar compounds with diverse functional groups. Even within the alkylphenols used in this study some compounds with similar structure had almost identical sampling rates but differed from those of other compounds with roughly the same log K_{ow}. For example 2-*n*-propyl and 4-*n*-propylphenol (log K_{ow} 2.93 and 3.20) had sampling rates of 0.075 and 0.094 l d^{-1} compared to 0.189 and 0.193 l d^{-1} for 2,4,6-trimethyl and 2,3,5-trimethylphenol (log K_{ow} 2.73 and 2.92, respectively).

4.4. Uptake and sampling rates – SPMDs

With the exception of the most polar AP (ethyl and di-methylphenols) all exposure compounds were detected in SPMDs. Uptake for quinolines and 4-isopropyl-3-methylphenol was, however, very low and for naphthalene somewhat higher but with large variation. Curves were not able to be fitted to these three compounds. There was generally little variation between SPMDs, CVs 3–18% (average of CV from individual sampling times) and less than that found for POCIS (Table 1). Uptake curves were fitted directly to the data and it was apparent that the more polar AP had reached or were approaching equilibrium and that most other compounds appeared to be in a curve linear uptake stage after 28 days (Supplementary material, Figure S2). For several of the more hydrophobic PAHs, e.g. benzo[*a*]pyrene and 2-methylanthrancene, higher than expected accumulations at 14 days appeared to influence those curve fits. Regression analysis revealed that curves fitted the data well (r^2 0.88–0.99), although this is perhaps an inappropriate assessment for compounds which had reached equilibrium. Sampling rates calculated from fitted curves, ranged from 0.02 to 7.43 l d^{-1} for AP, 7.91 to 13.83 l d^{-1} for PAH, 0.30 to 5.43 l d^{-1} for carbazoles and 6.84 and 10.55 l d^{-1} for *cis* and *trans*-decalin, respectively (Table 1). Because uptake was lower than expected for AP in SPMDs, POCIS was more effective (comparison of commercially available configurations) at sampling certain compounds of moderate hydrophobicity, e.g. 6-*tert*-butyl-2,4-dimethylphenol (log K_{ow} 4.52).

In order to provide verification of experimental SPMD sampling rates, they were compared to those predicted using an empirical uptake model (Huckins et al., 2006). This model is based on data from 19 different calibration studies of PCBs, PAH and PCDDs/PCDFs and the relationship of sampling rates and water–SPMD partition coefficients (K_{sw}) with K_{ow}. In addition, analysis of the dissipation of PRCs provides correction for differing external factors and allows a sampling rate to be estimated that is both compound and exposure specific (Supplementary material). For PAH there was good agreement between predicted and experimental sampling rates (R_{sPRED} and R_{sEXP}) with none of these compounds falling out of the range of the error factor ($R_s \times/\div$ 1.36) as shown in Fig. 2. For example sampling rates were 11.31 compared to 11.51 l d^{-1} for 2-methylanthracene and 9.46 compared to 8.96 l d^{-1} for 2,6-dimethylnaphthalene (R_{sPRED} and R_{sEXP}, respectively). Estimates of C_w using predicted sampling rates were also, therefore, reasonably similar (average difference 30%) to those measured directly. For AP, carbazole and 3-ethylcarbazole there was generally poor agreement between experimental and predicted sampling rates. Differences in sampling rates for 4-*n*-alkylphenols are confounded by their degradation during the exposure, however, this had the greatest effect on nonylphenol and yet the difference between R_s is the smallest. Furthermore, the differences in R_s for the other 4-*n*-alkylphenols are not consistently lower than for the other AP with similar log K_{ow} (table 1). Several other factors may be contributing to the observed differences. For the more polar AP equilibrium might have been reached before the first sampling time of 7 days leading to underestimation of the slope of the linear part of the uptake curve. Also, as resistance by the membrane is more important at lower log K_{ow} (<4.0), the use of an empirical model that is based largely on the uptake studies of compounds under boundary layer control is somewhat inappropriate. However, the differences between R_{sPRED} and R_{sEXP} cover a considerable range of hydrophobicity including 9 AP with log K_{ow} > 4.0 and yet model predicted sampling rates were only approached by nonylphenol (R_{sEXP} 7.43 l d^{-1}, R_{sPRED} 10.48 $\times/\div$ 1.36). Furthermore, applying a model for membrane controlled uptake (Booij et al., 2003) did not fit the data better for those medium polar compounds that were accumulated. This suggests that, at experimental exposure

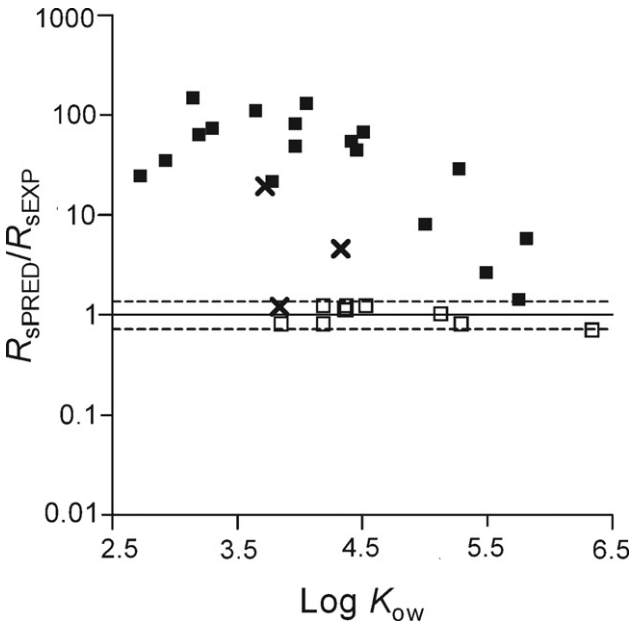

Fig. 2. Ratio of empirical model (Huckins et al., 2006) predicted (R_{sPRED}) and experimental (R_{sEXP}) sampling rates versus log K_{ow} for AP, PAH and carbazoles (closed squares, open squares, and crosses, respectively) in SPMDs. The horizontal straight line represents no difference between predicted and experimental sampling rates. Dotted lines represent uncertainty of predicted sampling rates as an 'error factor', here $R_s \times/\div$ 1.36. This is estimated from the standard deviation of the intercepts of individual PRC fits (a_{0PRC}) to the model (Huckins et al., 2006).

conditions, uptake was under water boundary layer control even at $\log K_{ow} \approx 3.0$. Further experiments, measuring uptake under different flow conditions are required in order to verify this point. During development of the empirical model a better fit was obtained for regression analysis of $\log K_{sw}$ and $\log K_{ow}$ when a different intercept was used for some polar pesticides (−3.20) than that proposed for PCBs, PAHs, etc. (−2.61). Applying this 'polar' intercept reduced differences between R_{sPRED} and R_{sEXP} approximately 4-fold but they remained large (R_{sPRED}/R_{sEXP} up to 40) for all but the most hydrophobic compounds and the new curve still did not describe the data.

Discrepancies between literature $\log K_{ow}$ values will affect R_{sPRED} as the SPMD–water partition coefficient (K_{sw}) and the compound specific term (α) are estimated from those (described in Supplementary material). However, using the compound for which we found the greatest difference in reported $\log K_{ow}$ values, 'nonylphenol' and substituting the $\log K_{ow}$ we used of 5.76 (4-*n*-nonylphenol, Itokawa et al., 1989) by that reported by Ahel and Giger (1993) of 4.48 (technical nonylphenol), only changes R_{sPRED} from 10.48 to 9.81 l d^{-1}. The $\log K_{ow}$ values used for AP would have to be on average 2.2 log units less for the sampling rates to correspond, which is improbable. Similarly, small uncertainties in exposure concentrations (described in Section 4.2) will affect sampling rates but also not significantly enough to explain the observed differences. It is likely that a more fundamental explanation is responsible, i.e. that K_{sw} (or more specifically the water-membrane partitioning coefficient) cannot be estimated from K_{ow} for AP using the equation proposed for PAH, PCB, etc. by Huckins et al. (2006). This is perhaps unsurprising considering the OH functional group, the amphiphilic nature and the excellent surfactant properties of AP. The lower than expected sampling rates for carbazole, (R_{sPRED} 5.80 l d^{-1}, R_{sEXP} 0.30 l d^{-1}) and 3-ethylcarbazole (R_{sPRED} 9.14 l d^{-1}, R_{sEXP} 1.99 l d^{-1}), are also probably explained by the presence of a functional group (NH). If this is the case then the similarity of predicted and experimental sampling rates for 9-methylcarbazole (R_{sPRED} 6.49 l d^{-1}, R_{sEXP} 5.43 l d^{-1}) is due to the methyl group being attached at the N position thus reducing its 'influence'. Lastly, it is pertinent to note that proponents of the empirical model used have not stated that it can be applied to other chemical classes outside of those used in the data sets from which it was created (Huckins et al., 2006). From the perspective of environmental monitoring, the calculation of time-weighted concentrations of AP based on models and PRC dissipation of hydrophobic compounds should be questioned. Further studies under different exposure conditions are required to examine this issue sufficiently.

5. Conclusion

SPMDs are excellent samplers of hydrophobic non-ionic compounds. Isotropic exchange means that the PRC approach can estimate sampling rates in situ with reasonable accuracy for such compounds. Applying the same models for other compounds which have been shown to accumulate in SPMDs but may have reduced partitioning due to structure, such as alkylphenols, may not be appropriate. The pharmaceuticals version of POCIS is well suited to sampling alkylphenols up to about $\log K_{ow}$ 4.5, thus the simultaneous deployment of both PSDs allows the study of environmental contaminants with wide ranging physicochemical characteristics. Sampling rates of several l d^{-1} for SPMDs and 100–200 ml d^{-1} for POCIS offers significant improvements in detection limits for those compounds compared to standard monitoring methods.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.04.091.

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