



Chasing equilibrium passive sampling of hydrophobic organic compounds in water

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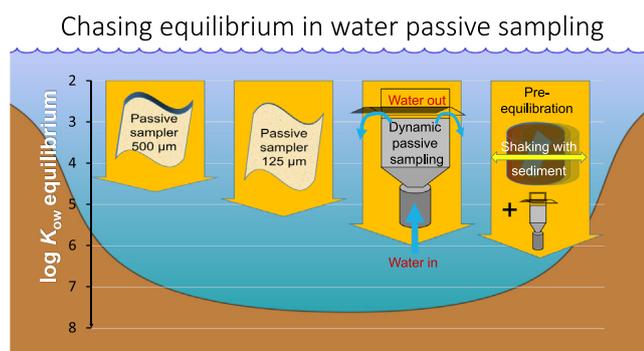
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HIGHLIGHTS

- Equilibrium passive sampling of hydrophobic compounds in water was investigated.
- Silicone passive samplers with different sheet thicknesses were tested.
- High water flow and long exposures extended the range of equilibrated compounds.
- Compounds with $\log K_{ow} \leq 5.5$ reached partition equilibrium with water.
- For compounds with $\log K_{ow} > 6$ equilibrium cannot be reached within a reasonable time.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigated a combination of approaches to extend the attainment of partition equilibria between silicone passive samplers (samplers) and surface or treated waste water towards more hydrophobic organic compounds (HOC). The aim was to identify the HOC hydrophobicity range for which silicone sampler equilibration in water is feasible within a reasonable sampler deployment period. Equilibrium partitioning of HOC between sampler and water is desirable for a simpler application as a “chemometer”, aiming to compare chemical activity gradients across environmental media (e.g. water, sediment, biota). The tested approaches included a) long sampler exposure periods and high water flow to maximize mass transfer from water to sampler; b) the use of samplers with reduced sheet thicknesses; and c) pre-equilibration of samplers with local bottom sediment, followed by their exposure in surface water at the same sampling site. These approaches were tested at three sites including a fish pond with a low level of pollution, a river impacted by an urban agglomeration and an effluent of municipal wastewater treatment plant. Tested compounds included polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH), DDT, its metabolites and their isomers, hexachlorobenzene (HCB) and polybrominated diphenyl ethers (PBDE). The study shows that samplers with a surface area of 400–800 cm² consisting of thin (100–500 μm) silicone sheets exposed at sampling rates of 10–40 L d⁻¹ for a time period of up to four months reach partition equilibrium with water for compounds with $\log K_{ow} \leq 5.5$. Nevertheless, for compounds beyond this limit it is challenging, within a reasonable time

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period, to reach equilibrium between sampler and water in an open system where water boundary layer resistance controls the mass transfer. For more hydrophobic HOC ($\log K_{ow} > 6$), the kinetic method using performance reference compounds is recommended instead.

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1. Introduction

Monitoring of hydrophobic organic compounds (HOC), such as polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), organochlorine pesticides, brominated flame retardants and others in the aquatic environment provides valuable information about their occurrence, transport, distribution between environmental compartments and exposure levels related to risk for aquatic organisms. The external exposure of chemicals to organisms in the aquatic environment is usually measured as the concentration of the compound in the compartment (e.g. water or sediment) to which the organism is dominantly exposed. Similarly, the internal exposure of aquatic organisms is often based on concentrations measured in their tissues. However, because the composition of water, sediment or biota is extremely different, concentrations of a HOC cannot be compared across these media and, consequently, concentration differences do not provide information on the direction of diffusive fluxes or levels of bioavailability (Lu et al., 2017; Schäfer et al., 2015).

Comparison of HOC levels across media is possible by application of partitioning passive samplers (further only 'samplers'; Mayer et al., 2003). A sampler spontaneously absorbs HOC from sampled medium until partitioning equilibrium is established. Since the sampler consist of a homogeneous polymer material with well-defined partitioning properties, HOC concentration accumulated in the sampler after equilibration with the environmental medium (e.g. water, sediment, biota) can be principally converted to the chemical activity of HOC in the sampled medium. According to the equilibrium partitioning theory (Di Toro et al., 1991), chemical activity difference represents the driving force for a spontaneous compound transport between environmental media. Thus, simply comparing equilibrium HOC concentration in polymer C_p^∞ after equilibration with two or more environmental media is equivalent to comparing chemical activities between those media. The sampler acts as a kind of "chemometer" (Gobas et al., 2009; Jahnke et al., 2014a, 2014b). To make measurement results independent of applied polymer type, and better understandable for public, C_p^∞ can be converted to equivalent concentrations in environmentally relevant media such as the free dissolved concentration (C_{free}) (Greenberg et al., 2014; Reichenberg and Mayer, 2006) or lipid-based concentration (Figueiredo et al., 2017; Jahnke et al., 2014a, 2014b).

The HOC concentration in the sampler at equilibrium with the sampled medium represents the chemical activity in that medium. When a polymer-based sampler is equilibrated with water, C_{free} can be estimated using the measured equilibrium concentration in the sampler C_p^∞ and the sampler-water partition coefficient, K_{pw} (Mayer et al., 2003):

$$C_{free} = \frac{C_p^\infty}{K_{pw}} = \frac{N_p^\infty}{K_{pw}m_p} \quad (1)$$

Here, N_p^∞ is the amount of compound absorbed by a sampler at equilibrium and m_p is the mass of the sampler. Required K_{pw} values can be measured under controlled laboratory conditions and are available in literature for many HOC and for polymers typically used in sampler construction, namely silicone and low-density polyethylene (Lohmann, 2012; Pintado-Herrera et al., 2016; Smedes et al., 2009; Smedes, 2018a).

Whereas partitioning equilibrium of HOC between sampler and sediment or soft tissues of aquatic biota can be achieved within a reasonable timeframe of days to weeks (Jahnke et al., 2011; Rojo-Nieto et al., 2019; Rusina et al., 2017; Smedes et al., 2013), equilibration of sampler in surface water takes a long time and is challenging to achieve, especially for very hydrophobic compounds (Allan et al., 2013).

During deployment in water a HOC amount absorbed by the sampler N_p^t exponentially rises with exposure time t , from the initial amount in the sampler N_p^0 , following the first-order kinetics, until it reaches the equilibrium value N_p^∞ (Vrana et al., 2001):

$$N_p^t = N_p^0 + (N_p^\infty - N_p^0) DEQ_p^t = C_p^0 m_p + (C_w K_{pw} - C_p^0) m_p DEQ_p^t \quad (2)$$

where DEQ_p^t , taking value between 0 and 1, is the degree of equilibrium that the compound attained during sampler exposure. In open aquatic systems such as streams or lakes DEQ_p^t is described by Booij et al. (2007):

$$DEQ_p^t = \left(1 - \exp\left(-\frac{R_s t}{K_{pw} m_p}\right) \right) \quad (3)$$

Here, R_s denotes the in situ sampling rate, i.e. the volume of water cleared of compound per unit of time. With R_s as the product of the overall mass transfer coefficient (k_o) and the sampler surface area (A_p) and further appreciating that m_p is equal to the product of polymer's density (ρ_p), sampler sheet thickness d_p and A_p , Eq. (3) modifies to:

$$DEQ_p^t = \left(1 - \exp\left(-\frac{k_o A_p t}{K_{pw} \rho_p d_p A_p}\right) \right) \quad (4)$$

DEQ_p approaches value of 1 when k_o and t values are as large as possible while K_{pw} and d_p are as low as possible. Of course, K_{pw} is mainly determined by compound properties, but in practical sampler application preference could be given to polymers with lower K_{pw} .

The time to reach 95% ($t_{0.95}$) of sampler-water equilibrium, i.e. when $N_p^t \approx (1 \pm 0.05) \times N_p^\infty$, can be estimated from a combination of Eqs. (2) and (4) as

$$t_{0.95} \approx - \ln \left(\frac{0.05 N_p^\infty}{N_p^\infty - N_p^0} \right) \frac{K_{pw} m_p}{R_s} = - \ln \left(\frac{0.05 N_p^\infty}{N_p^\infty - N_p^0} \right) \frac{K_{pw} \rho_p d_p A_p}{k_o A_p} \quad (5)$$

There are several options how to speed up attainment of sampler-water partition equilibrium.

Firstly, equilibrium is attained faster, when the mass transfer coefficient k_o is maximized. When using samplers consisting of thin silicone sheets (<1 mm), k_o of HOC is dominated by the mass transfer coefficient in water boundary layer (WBL), and the resistance to mass transfer in silicone can be neglected (Rusina et al., 2010) due to fast HOC diffusion in polymer material. Since the uptake from water to sampler limits the typically achievable $R_s = k_o A_p$ magnitude to tens of liters per day, for highly hydrophobic compounds with a very high sampler uptake capacity (i.e. $K_{pw} m_p$) equilibration of HOC in an open aquatic system may take up to months to years (Booij et al., 2007). The resistance to mass transfer in WBL can be minimized by exposing samplers in turbulent water (Allan et al., 2011; Booij et al., 2007), or by shaking them in dense sediment suspensions that disrupt the WBL at sampler surface and decrease the diffusion distance (Mayer et al., 2007; Smedes et al.,

2013). For estimation of k_o magnitude, in situ calibration of samplers is necessary, because k_o is an exposure specific parameter and depends on environmental variables, such as temperature, water flow and fouling. It is typically estimated from the release rate of performance reference compounds (PRCs) from samplers during exposure (Booij and Smedes, 2010; Huckins et al., 2002).

Secondly, sampler equilibration can be speeded up by minimizing the sampler thickness d_p , i.e. by using samplers in form of thin films (Mayer et al., 2003). This implies the need to increase the sampler surface area A_p in order to accumulate sufficient amount of compound for quantification. Note that a higher A_p increases R_s but at the same time it increases also the sampler capacity. Consequently, the time to attain a certain DEQ_p level is not affected by sampler surface area (Eq. (5)). Nevertheless, the product of $d_p A_p$ is important to assure that N_p^0 is sufficiently high to be well quantifiable. With this condition the limit of decreasing d_p lays in the samplers A_p that still can be practically handled in deployment.

Finally, equilibration time can be shortened when the initial amount of compound present in the sampler N_p^0 is in the range between zero and $2 \times N_p^\infty$. According to Eq. (5), when N_p^0 is 20% higher or lower than N_p^∞ , the equilibration time is shortened by half (Supplementary information, Fig. S2). In contrast, the equilibration time is extended when N_p^0 is higher than $2 \times N_p^\infty$. N_p^0 close to the equilibrium value N_p^∞ can be approached by sampler pre-exposure with another medium collected from the site of investigation, i.e. sediment, which faster attains equilibrium with sampler than water does (Belháčová-Minaříková et al., 2017; Mayer et al., 2014; Smedes et al., 2013; Witt et al., 2013)

In order to identify the HOC hydrophobicity range for which sampler equilibration in water is feasible within a reasonable sampler deployment period, we investigated a combination of the above mentioned approaches. Those included a) long sampler exposure periods of several months in a previously designed dynamic passive sampling device (DPS) (Vrana et al., 2018) that maximizes the k_o in the WBL; b) the use of thin samplers with different sheet thicknesses d_p ; and c) pre-equilibration of samplers with local bottom sediment, followed by their exposure in the water column in order to move N_p^0 closer to N_p^∞ . To our knowledge, a systematic testing of these parameters and conditions for equilibrium attainment of very hydrophobic compounds in aquatic passive sampling has not been done before.

2. Materials and methods

2.1. Chemicals

Acetone, diethylether, dichloromethane, ethyl acetate, hexane, hydrochloric acid, methanol and sulfuric acid were of analytical grade and obtained from Sigma-Aldrich (Germany) and Lab-Scan (Poland). Standards of 16 PAH, 7 indicator PCB congeners, DDT, its metabolites and their isomers and HCB were obtained from Supelco (Sigma-Aldrich, Prague, Czech Republic). Standards of polybrominated diphenyl ether (PBDE) congeners were purchased from AccuStandards (USA). The PRC mixture containing perdeuterated biphenyl (D_{10} -biphenyl) and 13 PCB congeners that do not occur in technical mixtures, (PCB 1, PCB

2, PCB 3, PCB 10, PCB 14, PCB 21, PCB 30, PCB 50, PCB 55, PCB 78, PCB 104, PCB 145, PCB 204) in ethyl acetate was kindly provided by Deltares, Utrecht, The Netherlands. D_8 -naphthalene, D_{10} -phenanthrene, D_{12} -perylene, PCB 4, PCB 29 and PCB 185 (Dr Ehrenstorfer, Germany) were used as recovery internal standards (RIS) and ^{13}C -labeled analogues of PBDE congeners (Wellington Laboratories, Canada) were used in isotope dilution method for determination of PBDE concentrations. PCB 121 and *p*-terphenyl were used as internal standards for quantification of PCB and PAH, respectively.

2.2. Materials

AlteSil™ translucent silicone sheets (further denoted sheets) 500 μm thick were purchased from Altec, UK. The sampler, further denoted as ALT, consisted of a single Altesil sheet cut into a 14×28 cm rectangle. The mass of the resulting ALT sheet was approximately 23 g. Specialty Silicone Products Inc. (SSP) translucent sheets 125 μm thick were purchased from Shielding Solutions Limited, UK. The sampler, further denoted as SSP, consisted of a single SSP sheet cut into a 14×28 cm rectangle and having the mass of approximately 5 g.

Before use, the samplers were extracted with ethyl acetate for 72 h to remove any additives and low-molecular weight polymers. Samplers were then spiked with 14 PRCs that are partially released during exposure. Samplers were spiked according to the procedure described in Smedes and Booij (2012). Briefly, sheets having a total mass of about 200 g were put into an amber glass bottle together with 250 mL of methanol and spiked with PRC mixture solution in ethylacetate containing $5\text{--}75 \mu g mL^{-1}$ individual PRCs, resulting in 20 ng per sampler for the most hydrophobic PRC, the PCB 204. The mixture was shaken in methanol for 1 h, followed by gradual addition of Milli-Q water over 10 days while shaking, ending up at 50% (v/v) methanol content. Sheets were stored and transported in wide mouth amber glass jars firmly closed by a screw cap with a metallic liner.

2.3. Equilibration of passive samplers with water

Samplers were deployed in water at three sampling sites (Table 1) located in South Moravian region in the Czech Republic. The sites were selected to represent different types of water with various level of HOC pollution, i.e. stagnant and streaming surface water, and effluent of a municipal wastewater treatment plant (WWTP). The site S1 (Table 1) was located in an artificial fish pond used for fish farming. The site is not impacted by any known industrial or municipal pollution source released directly into the water body. The site S2 (Table 1) was located in the river Svratka, downstream Brno city, and the site is impacted by treated wastewater discharge from a city with population equivalent of 400,000. A third sampling site (S3, Table 1) was located at the discharge of effluent from the main municipal WWTP in Brno, Czech Republic (capacity ca. 500,000 equivalent inhabitants). The sampling was conducted in an effluent basin that is used for measurement of flow and volume of discharged treated wastewater.

At the fish pond discharge site S1A, samplers (both ALT and SSP) were mounted to a wire mesh frame and deployed where water is

Table 1
Passive sampler exposures.

Exposure	Site and exposure conditions	Deployment device	Sampler deployment period in water	Exposure time [d]	Mean water temperature [°C]	Mean pH value of water
S1A	Surface water, fish pond discharge	Wire mesh frame	2/6–14/10/2015	134	21.9	7.8
S1B	Surface water, fish pond	DPS	12/5–23/10/2015	164	21.5	7.8
S1C	Sampler equilibration with sediment collected at S1A in laboratory, followed by deployment in surface water, fish pond	DPS	1/9–23/10/2015	44 days equilibration in sediment slurry, followed by 52 days deployment in water	15.7	7.8
S2	Surface water, Svratka river	DPS	16/2/2016–12/4/2016	56	5.2	7.9
S3	Wastewater, effluent from a municipal WWTP	DPS	12/5–1/9/2015	112	21.6	7.6

discharged from the pond through an overflow. These samplers were exposed to running water from both sides and thus the exposed area was approximately 780 cm² per sheet. At all remaining locations, samplers were exposed in a DPS that has been described in our previous work (Vrana et al., 2018). Briefly, the device consists of a rectangular stainless-steel plate chamber open from two sides and fully immersed in water. The bottom end of the chamber is directly connected to a submersible electricity driven pump (cca 9 m³ h⁻¹) that forces water at high flow velocity (1–2 m s⁻¹) through the chamber. One ALT and one SSP sheet were mounted in the DPS. Samplers were exposed to water from only one side (Fig. 1). The exposed area was approximately 390 cm² per sheet. At all sites, samplers were deployed at approximately 50 cm depth below the water surface for a period of between 52 and 164 days. Samplers were mounted to the deployment devices just before exposure and removed immediately afterwards. All samplers were protected from direct sunlight to minimize photodegradation of the sampled compounds (Allan et al., 2016). Temperature and light intensity loggers (Hobo Pendant, Onset, Germany) were attached to all samplers during exposures. After exposure samplers were cleaned with local water using a scrubber, packed to closed amber glass vials, transported to the processing laboratory and stored in at –20 °C.

To monitor the equilibration progress, sampling rates R_s and associated DEQ_s were estimated from the dissipation of PRCs from samplers during exposure as described in Smedes and Booij (2012) using unweighted nonlinear least squares method by Booij and Smedes (2010), considering the retained PRC fraction, $f(\text{PRC})$, after exposure as a continuous function of their sampler-water partition coefficient:

$$\frac{N_{\text{PRC}}^t}{N_{\text{PRC}}^0} = f(\text{PRC}) = \exp\left(-\frac{R_s t}{K_{pw} m_p}\right) \approx \exp\left(-\frac{k_o A_p t}{K_{pw} \rho_p d_p A_p}\right) \quad (6)$$

where N_{PRC}^t and N_{PRC}^0 are the PRC amounts in the sampler after exposure time t and at the exposure start ($t = 0$), respectively. The model derived by Rusina et al. (2010) was applied to estimate target HOC sampling rates as a function of their molar mass M , i.e. $R_s = A_p B M^{-0.47}$, where B is an exposure specific factor related to the mass transfer coefficient in WBL (k_o).



2.4. Exposure of samplers pre-equilibrated in sediment

Assuming HOC in water and in surface sediment layer has approximately the same chemical activity, ALT samplers were first pre-equilibrated with surface sediment from site S1 in the laboratory under agitated conditions. In the following deployment in water that is expected to give the equilibration process a head start. To facilitate monitoring of the equilibration in water, two sub-samplers (from the sediment pre-equilibration) were prepared in which the HOC concentrations were respectively increased (H) and decreased (L) by a factor 1.2. This was done by means of extraction and consecutive extract dosing to fresh samplers following the scheme in Fig. 2. Briefly, in duplicate, three ALT sampler sheets (5 × 9.5 cm, 500 μm thick), 2.5 L of a sediment slurry (40% dry weight) from site S1, and 1 g of sodium azide were brought in a 5 L bottle and shaken at orbital shaker at room temperature in the dark for a total of 44 days. On day 30 methanol was added to obtain 20% (v/v) in order to accelerate the HOC equilibration. Then exposed sheets (total 6) were Soxhlet extracted in methanol as described in Section 2.5. The extract volume was reduced, quantitatively transferred to a 100 mL volumetric flask, which was filled to the mark. A 33% portion was set aside and analysed as described in Section 2.5. Then the 40% and 27% portions were each used for dosing a set of 2 clean ALT sheets analogically to the PRC spiking procedure (Smedes and Booij, 2012). These two dosed ALT samplers were then deployed at site S1 for 52 days (S1C, Table 1) in parallel with regular surface water samplers (S1B, Table 1) using the DPS device. After exposure, samplers were stored at –20 °C and analysed similar to the water-exposed sheets (2.5).

2.5. Sample processing

Before extraction, all exposed samplers were spiked with recovery internal standards (RIS) (50 ng of D₈-naphthalene, D₁₀-phenanthrene, D₁₂-perylene; 10 ng of PCB 4 and PCB 185; 1 ng of ¹³C-PBDE and Soxhlet extracted with methanol for 8 h. The obtained extract was concentrated by Kuderna-Danish evaporation to <2 mL. After addition of 20 mL hexane the extract was azeotropically transferred to hexane by Kuderna-Danish evaporation and volume-reduced to 1 mL. Mass of individual samplers was recorded after drying. A 30%



Fig. 1. Mounting silicone passive sampler in a deployment frame for exposure in water at site S1A (left) and in the dynamic passive sampling device for deployment at all remaining sites (right).

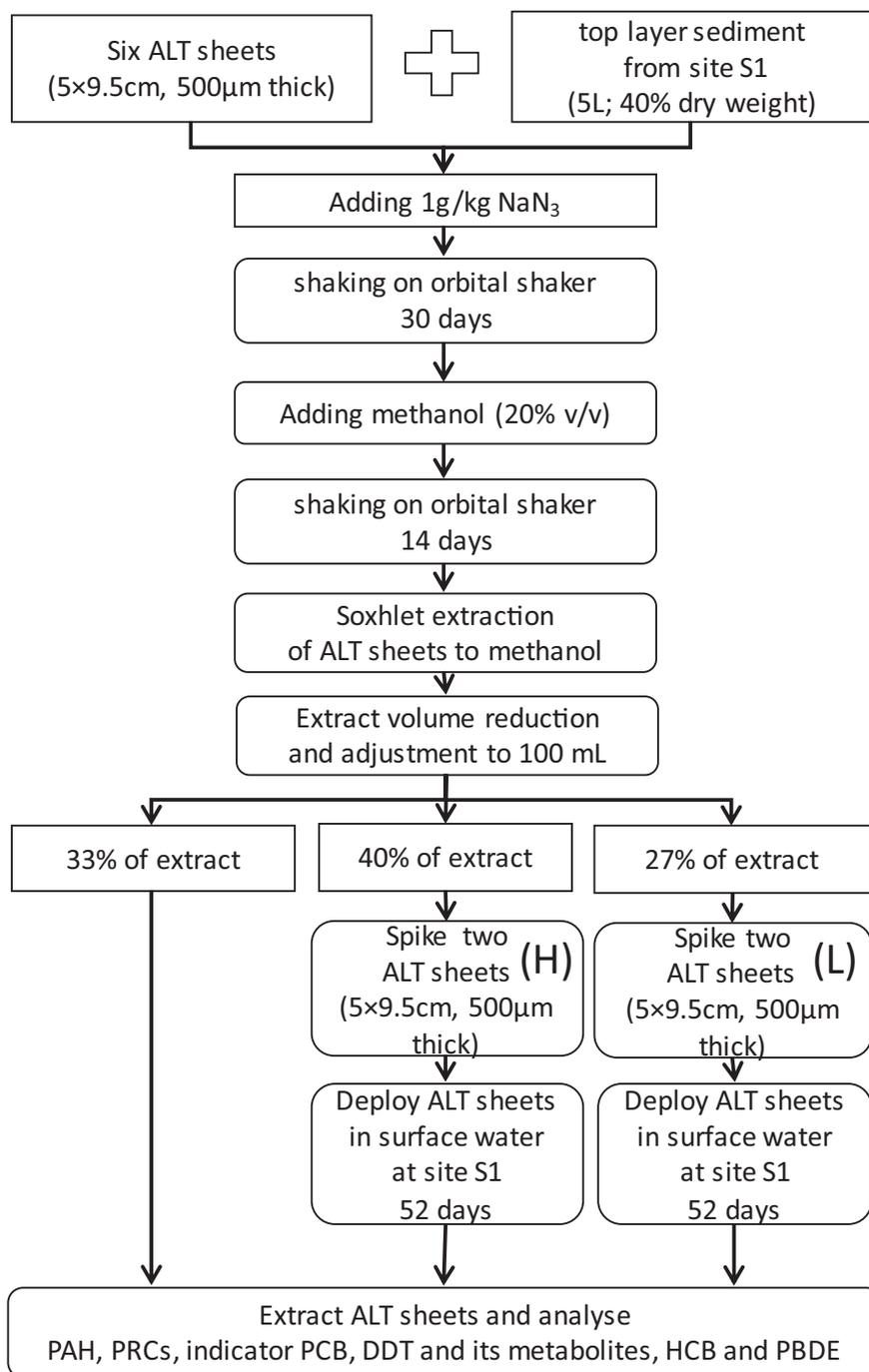


Fig. 2. Workflow of an experiment performed to investigate whether passive sampler pre-equilibration with surface layer of sediment, followed by passive sampler deployment in water column adjacent to the sediment, can speed up the sampler equilibration in water.

extract aliquot intended for analysis of PAHs was further cleaned-up on a silica gel column using diethylether/acetone elution. Subsequently, extracts were Kuderna-Danish reduced in volume, followed by evaporation with a gentle nitrogen flow. Finally, *p*-terphenyl was added as internal standard. The other 70% aliquot used for analysis of DDT, its metabolites and their isomers, HCB, PCB, PRC and PBDE was purified using activated silica gel modified with sulfuric acid, followed by PCB 121 addition as internal standard. All extracts were analysed using GC–MS/MS methods for PAH, PRC, indicator PCB, DDT, its metabolites and their isomers, HCB and PBDE. Applied quality assurance/quality control measures are described in Supplementary information.

2.6. Instrumental analysis

Analysis of PAH was performed using high performance gas chromatography GC–MS HP 7890 equipped with autosampler 7683B (Agilent, Germany). Analytes were separated on a 60 m DB-5MS column (0.25 mm I.D., film thickness: 0.25 µm; Agilent J&W, USA). The column was interfaced with MS/MS Triple Quadrupole 7000B (Agilent, Germany). Detection was performed in single ion monitoring mode, temperature of ionic source was 320 °C and quadrupole temperature 150 °C. One µL sample was injected in splitless mode at 280 °C. Helium (purity 5.5) was used as carrier gas at a flow of 1.5 mL min⁻¹. The GC instrument was operated with an initial oven temperature of 80 °C

(1 min hold), then ramped at $15\text{ }^{\circ}\text{C min}^{-1}$ to $180\text{ }^{\circ}\text{C}$ and at $5\text{ }^{\circ}\text{C min}^{-1}$ to $310\text{ }^{\circ}\text{C}$ which temperature was held for 20 min.

PCB, DDT, its metabolites and isomers, and HCB were analysed using GC–MS/MS 6890N GC (Agilent, USA) equipped with a $60\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ DB5-MS column (Agilent J&W, USA) coupled to Quattro Micro GC MS (Waters, Micromass, UK) operated in EI+ mode. At least 2 MRM transitions were recorded for each compound analysed. One μL of extract was injected in splitless mode at $280\text{ }^{\circ}\text{C}$. Helium was used as carrier gas at the flow of 1.5 mL min^{-1} . The GC temperature programme started $80\text{ }^{\circ}\text{C}$ (1 min hold), ramped at $15\text{ }^{\circ}\text{C min}^{-1}$ to $180\text{ }^{\circ}\text{C}$, and finally ramped at $5\text{ }^{\circ}\text{C min}^{-1}$ to $300\text{ }^{\circ}\text{C}$ (5 min hold).

PBDE were analysed using an Agilent 7890A GC equipped with $15\text{ m} \times 0.25\text{ mm} \times 0.10\text{ }\mu\text{m}$ Rtx-1614 capillary column (Restek, USA) coupled to an Autospec Premier HRMS (Waters, UK) operating in EI+ mode at the resolution of $>10,000$. Details are given in (Kukučka et al., 2015).

3. Results and discussion

3.1. Equilibration progress during long sampler exposure times

As stated above, higher DEQ_p^f can be achieved by maximizing the $R_s \times t$ or $k_o \times t$ product (Eqs. (3) and (4)). In this work we exposed thus samplers in a DPS, to achieve higher R_s for HOC uptake and PRC release.

Since the uptake of HOCs from water to sampler and their release from sampler to water are isokinetic processes (Booij et al., 2007),

equilibration progress can be assessed from the release of PRCs (Fig. 3). A complete release of PRC from the sampler indicates attainment of partitioning equilibrium for a compound present in water of a similar hydrophobicity. We considered the retained PRC fraction of $<5\%$ of the initial concentration in the sampler as a criterion of complete release. Equilibrium was thus confirmed for PRCs with $\log K_{ow} < 5$ from SSP samplers at all sites (Fig. 3).

We further estimated the maximum $K_{ow,0.95}$ value for which the sampler reaches 95% sampler–water equilibrium after the actual exposure time. Rearranging Eq. (5) for an exposure with negligible starting compound amount in the sampler ($N_p^0 = 0$) allows to estimate the maximum $K_{pw,0.95}$ value for which the sampler reaches 95% PS–water equilibrium after the actual sampler exposure time ($t_{0.95}$) as.

$$K_{pw,0.95} \approx -\ln 0.05 \frac{R_s t_{0.95}}{m_p} \quad (7)$$

The required sampling rates R_s were estimated from dissipation of PRCs from sampler using the model function described in Section 2.3 (Fig. 3). For illustration, we state here $^{300}R_s$ for a compound with molar mass of 300. $^{300}R_s$ values estimated for ALT polymer, for which published K_{pw} data are available, ranged from 10 to 45 L d^{-1} at sites S3 and S2, respectively (Table 2). The low R_s obtained during DPS application in wastewater effluent (S3) was likely due to a partial clogging of the DPS by fine threads of algae present in the water. On several occasions algae had to be removed from the DPS water intake during

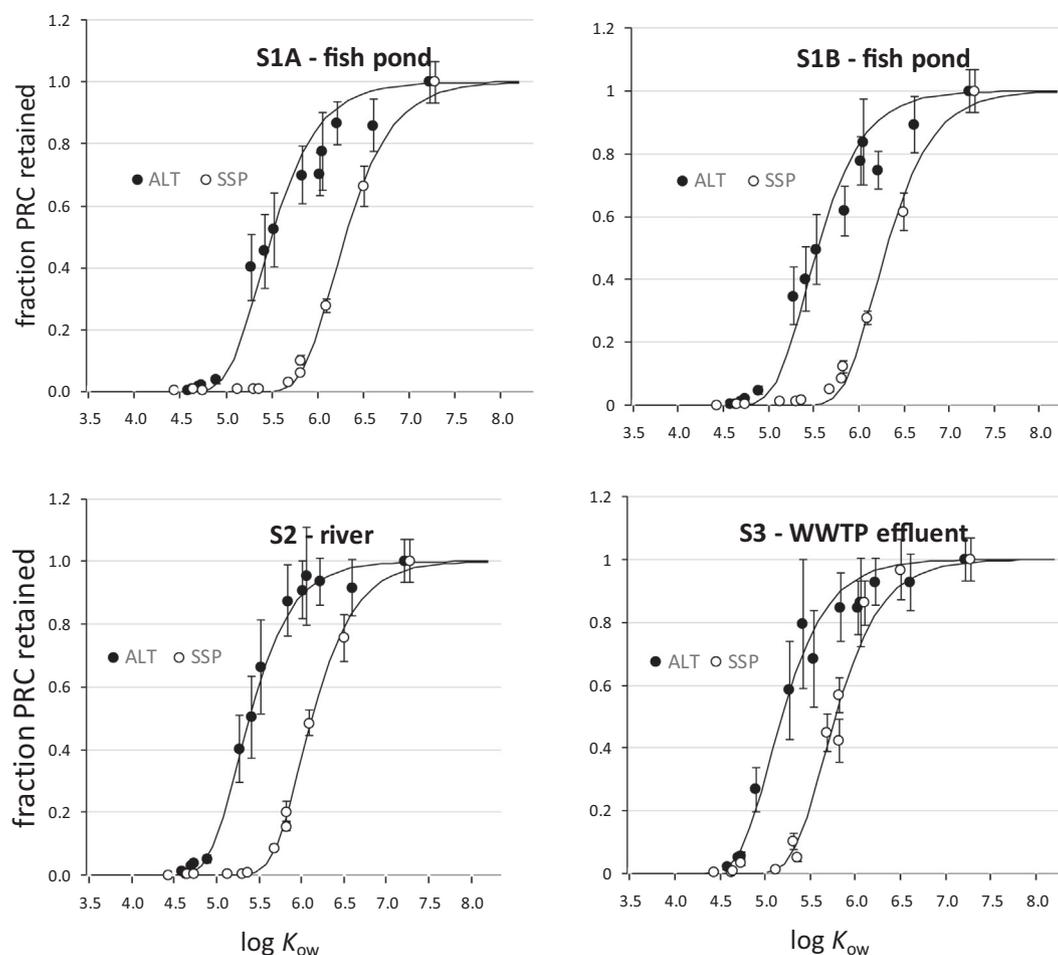


Fig. 3. Retained PRC fractions in two co-deployed silicone passive samplers ALT and SSP with film thicknesses of 500 and $125\text{ }\mu\text{m}$ (marked by black and white dots), respectively, as a function of $\log K_{ow}$. Error bars represent 2 standard deviations and are estimated from typical sampling repeatability. The model fits of experimental data (Eq. (6)) are displayed as drawn lines.

Table 2
Sampler properties and field performance characteristics obtained from the release of PRCs.

Sampling site	Passive sampler	m_p [g]	d_p [μm]	A [cm ²]	t [d]	³⁰⁰ R _s [L d ⁻¹] ^a	³⁰⁰ V [L] ^b	log $K_{pw,0.95}$ [L kg ⁻¹] ^c	log $K_{ow,0.95}$ ^d
S1A – fish pond	ALT	24.9	500	780	134	26.9	3600	4.7	4.8
	SSP	5.3	125	780	134			5.4	5.5
S1B – fish pond	ALT	22.4	500	390	164	17.2	2815	4.6	4.9
	SSP	5.3	125	390	164			5.2	5.4
S2 – river	ALT	27.0	500	390	56	44.7	2504	4.5	4.7
	SSP	5.5	125	390	56			5.2	5.3
S3 WWTP effluent	ALT	22.3	500	390	112	10.2	1147	4.2	4.5
	SSP	5.1	125	390	112			4.9	5.1

^a Sampling rate of a compound with a molar mass of 300 g mol⁻¹.

^b Sampled water volume for a compound with molar mass 300 g mol⁻¹, calculated as ³⁰⁰R_st.

^c Estimated maximum log K_{pw} of a compound reaching 95% equilibrium between ALT sampler and water.

^d Estimated maximum log K_{ow} of a compound reaching 95% equilibrium between ALT sampler and water, derived from a correlation log $K_{pw} = 1.14 \times \log K_{ow} - 0.92$ for PRCs. log K_{pw} values of PRCs were taken from (Smedes, 2018b).

exposure. In contrast, the DPS performed very well at the riverine site S2, reaching R_s of 45 L d⁻¹, comparable with our previous study in the Danube river (Vrana et al., 2018). The ³⁰⁰R_s at the site S1A, where samplers were deployed in running water, was higher (27 L d⁻¹) than that obtained using the DPS at site S1B (17 L d⁻¹). This was likely due to several power cuts in DPS that occurred during the long exposure period and also because the sampler at S1A had two times higher sampler surface area exposed to water (Table 2).

The product of sampling rate and exposure time ($R_s t$) presents the maximum sampled volume of water during exposures at different sites, which for the ALT sampler ranged from 1100 L to 3600 L at sites S3 and S1A, respectively.

The calculation shows that in ALT samplers under exposure conditions and within the deployment periods stated in Tables 1 and 2, all analysed compounds with log K_{pw} lower than 4.2–4.7 attained partition equilibrium in water. Since log K_{pw} is correlated with log K_{ow} , this corresponds with a log K_{ow} range of 4.5 to 4.9 (Table 2). The calculation confirms the observation made by inspection of PRC data (Fig. 3).

3.2. Equilibration of thinner silicone in water

Sampler equilibration can be further extended to more hydrophobic compounds by minimizing the sampler thickness d_p .

3.2.1. Assessment from PRC release

The calculation using Eq. (7) shows that in SSP sampler the threshold log $K_{pw,0.95}$ values reached 4.9 to 5.4, which corresponds with log $K_{ow,0.95}$ values in the range between 5.1 and 5.5. The calculation assumes in the first approximation equal R_s and K_{pw} values in both ALT and SSP samplers. Equality of R_s in samplers of the same geometry (14 × 28 cm sheets) exposed in the same arrangement has been demonstrated previously (Vrana et al., 2018). There may be small differences in K_{pw} values between ALT and SSP polymer, however, these were neglected for the purpose of our comparison. Comparison of log $K_{ow,0.95}$ in co-deployed ALT and SSP samplers shows that fourfold reduction of sampler thickness increased the threshold $K_{ow,0.95}$ value by 0.6 to 0.7 log units. In practice, this means that equilibrium establishment for ALT was most likely reached for PAHs with less than five condensed aromatic rings and for mono- and di-chlorinated PCBs. The SSP sampler could reach equilibrium for PAHs with less than six aromatic rings and for mono- to tetra-chlorinated PCBs.

3.2.2. Assessment from compound uptake

Another approach to assess which compounds attained partition equilibrium is based on comparison of HOC uptake from water to samplers with different thicknesses. The ratio of HOC amounts accumulated

in ALT and SSP samplers, in which the initial concentration N_p^0 is close to zero, can be derived from Eq. (2):

$$\frac{N_{ALT}^t}{N_{SSP}^t} = \frac{K_{ALT,w} m_{ALT} DEQ_{ALT}^t}{K_{SSP,w} m_{SSP} DEQ_{SSP}^t} \quad (8)$$

Booij et al. (2007) have further shown that at short exposure times when DEQ^t is close to 0 and the initial concentration N_p^0 is close to zero, Eq. (2) can be simplified to:

$$N_p^t = C_w R_s t \quad (9)$$

In that situation, since both samplers were exposed to the same water for equal time period, the ratio of HOC amounts accumulated in samplers ALT and SSP is:

$$\frac{N_{ALT}^t}{N_{SSP}^t} = \frac{R_{s,ALT}}{R_{s,SSP}} \quad (10)$$

As mentioned earlier, WBL-controlled R_s of co-deployed silicone samplers are expected to be equal (Vrana et al., 2018). Therefore, the ratio N_{ALT}^t/N_{SSP}^t close to one identifies the range of compounds that are far from reaching partitioning equilibrium with water in both samplers. When the sampler capacity ($K_{pw} m_p$) starts playing a role in uptake, the ratio becomes higher than one, indicating equilibrium attainment in one or both samplers. The N_{ALT}^t/N_{SSP}^t ratio as a function of compound's hydrophobicity is shown in Fig. 4.

The ratio decreases with increasing log K_{ow} of the compound, and for compounds with a log $K_{ow} > 6.5$, the ratio is close to one, i.e., the compounds did not reach equilibrium with the passive sampler. These results are in agreement with the non-equilibrium range identified from PRC release for compounds exceeding the threshold log $K_{ow,0.95}$ log stated in Table 2.

The Eq. (8) can be further transformed to compare the degree of partition equilibrium attained in the two co-deployed samplers.

$$\frac{DEQ_{ALT}^t}{DEQ_{SSP}^t} = \frac{N_{ALT}^t K_{SSP,w} m_{SSP}}{N_{SSP}^t K_{ALT,w} m_{ALT}} \quad (11)$$

The DEQ_{ALT}^t/DEQ_{SSP}^t ratio, plotted as a function of compound's log K_{ow} , is shown in Fig. 5. The ratio varies approximately in the range from zero and one, and in all cases it decreases with the increasing log K_{ow} of the compound. The data from sampler exposures at site S1 show clearly that for log $K_{ow} < 5$ the ratio levels off and attains values close to one. The ratio approaching one is expected when both co-deployed samplers are close to partition equilibrium with the water. In theory, ratios higher than one are not expected since the uptake capacity ($K_{pw} m_p$) of ALT is

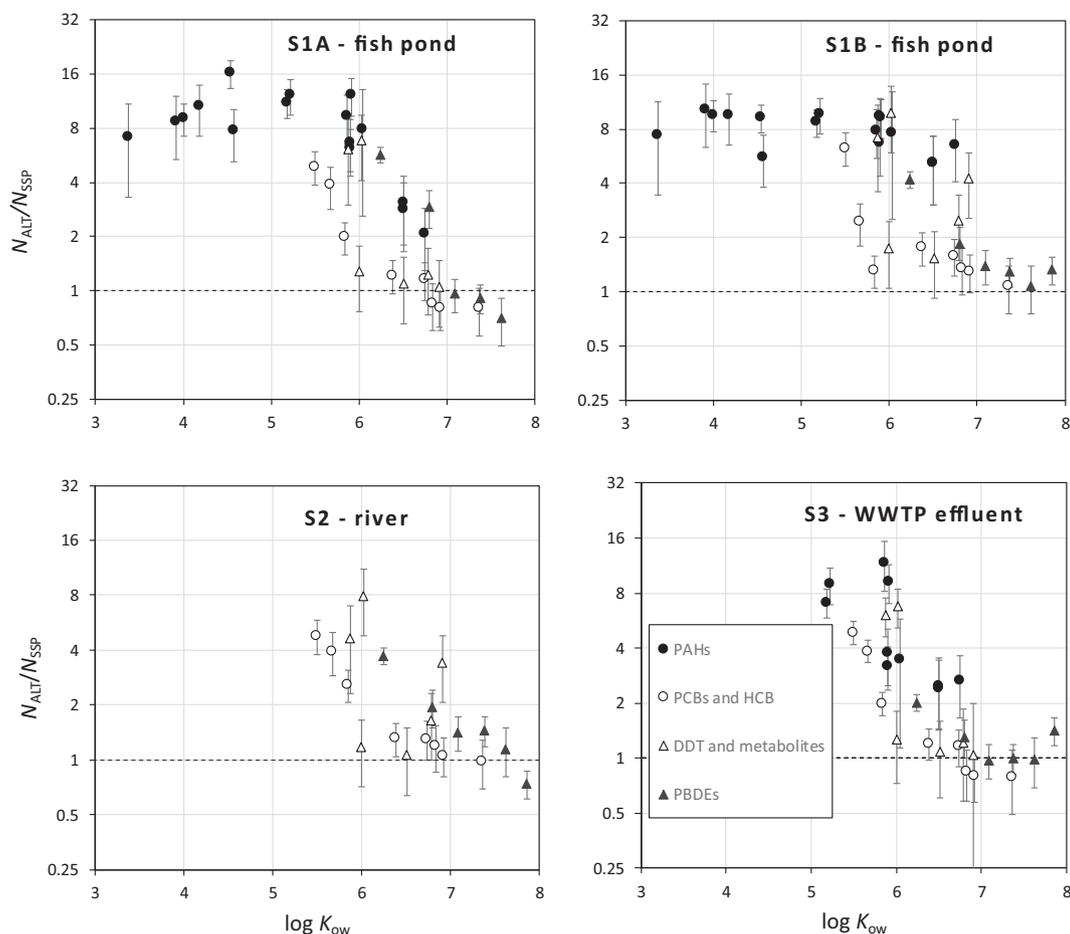


Fig. 4. Ratio of compound amounts (N_{ALT}/N_{SSP}) absorbed by two co-deployed silicone passive samplers ALT and SSP with film thicknesses of 500 and 125 μm , respectively, plotted versus $\log K_{ow}$. Error bars represent 2 standard deviations and are estimated from typical sampling repeatability. The dashed line represents unity and indicates fully integrative sampling in both samplers. Sampling sites (S1–S3) and exposure conditions are described in Table 1.

always higher compared to SSP. The observed ratios higher than one in some cases may be attributed to the uncertainty related to the DEQ_p ratio calculation. Data in Fig. 5 shows that in all exposures, partition equilibrium between water and ALT and SSP was attained for compounds with $\log K_{ow} < 5$ and for some compounds in the $\log K_{ow}$ range between 5 and 6.

Both projections of the HOC uptake (Figs. 4 and 5) confirm that with selected samplers and exposure conditions partition equilibrium of compounds with $\log K_{ow} < 5$ is attained within an exposure period of 5 months.

3.3. Exposure of samplers pre-equilibrated in sediment slurry

Further, we investigated whether sampler pre-equilibration with surface layer of sediment collected at the fish pond site, followed by sampler deployment in water column adjacent to the sediment, can speed up the sampler equilibration in water (exposure S1C in Table 1).

The chemical activity of HOC in the top sediment layer (upper 5 cm) and the water column is expected to be very similar. Hence, a sampler equilibrated with the upper layer of the sediment and further with overlaying water would contain similar levels of HOC as a sampler equilibrated with water only. Sampler equilibrium in sediment is established much faster than in water and can be obtained even for very hydrophobic compounds (Smedes et al., 2013), especially when applying a co-solvent method that enhances the HOC mass transfer (Belháčová-Minaříková et al., 2017).

In the first step, we derived an assumed equilibrium HOC concentration in a sampler deployed in water column, C_p^∞ (exposure S1B). This

value was then applied as equilibrium assessment criterion for sampler pre-incubated in sediment (C_{p_sed}) (exposure S1C). C_p^∞ was calculated from Eq. (2), assuming negligible starting compound concentration in the sampler ($C_p^0 = 0$):

$$C_p^\infty = C_p^t / DEQ_p^t \quad (12)$$

The necessary DEQ_p^t was estimated from the PRC elimination data. This step was necessary since (as has been shown in Section 2.3) a full partition equilibrium in water has not been reached for very hydrophobic compounds.

Fig. 6 shows a ratio of HOC concentrations in PS, incubated with top layer of sediment from the fish pond site S1 and then exposed to water at the same site (C_{p_sed}), to calculated concentrations of samplers at equilibrium with water C_p^∞ . For most of the investigated HOCs, the equilibration of silicone with sediment resulted in C_{p_sed} concentrations that were within a factor of 10 from C_p^∞ . For some compounds, even a lower C_{p_sed}/C_p^∞ value was attained. For indeno(123 cd)pyrene, benzo(g,h,i)perylene, PCB 28, PCB 52, PCB 101, PCB 118, *p,p'*-DDE and *o,p'*-DDD the difference between C_{p_sed} and C_p^∞ was less than a factor of 2. However, a larger C_{p_sed}/C_p^∞ factor difference was observed for fluorene (0.03), benzo(k)fluoranthene (43), benzo(a)pyrene (12), BDE 99 (0.07), BDE 153 (0.07), *o,p'*-DDE (41), *o,p'*-DDT (0.01) and *p,p'*-DDT (0.03). This indicates a different chemical activity of HOC in sediment and in water column, which may be caused by various factors, e.g. a faster compound degradation in one of the phases, temporal variability in water, collection of sediment recently emerged from deeper layers that did not have sufficient time to equilibrate with water, etc.

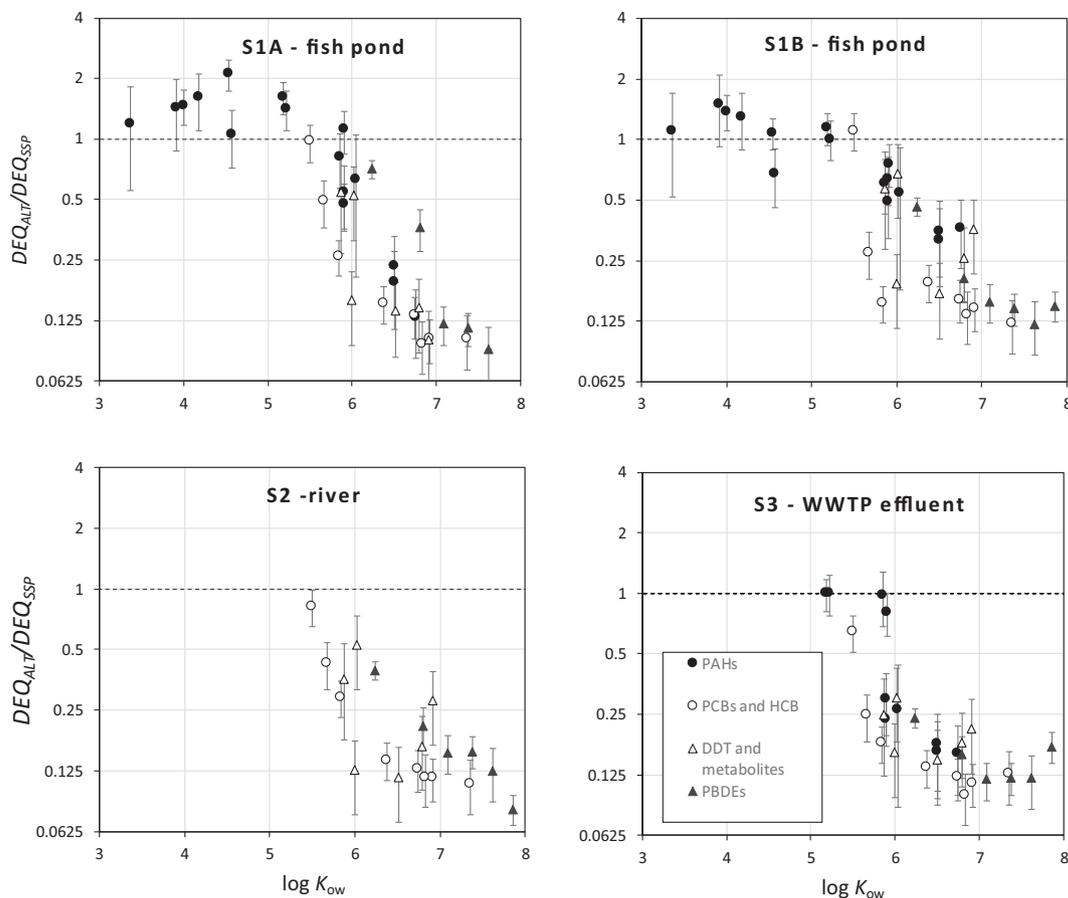


Fig. 5. Ratio of equilibrium degree (DEQ_{ALT}/DEQ_{SSP}) attained by the two co-deployed samplers, i.e. ALT and SSP with film thicknesses of 500 and 125 μm , respectively, plotted versus $\log K_{ow}$. The ratio was calculated using Eq. (11). Error bars represent 2 standard deviations and are estimated from typical sampling repeatability. Sampling sites and exposure conditions are described in Table 1. The dashed line indicates the maximum theoretical DEQ_p ratio of 1, when partition equilibrium has been attained in both samplers.

The subsequent water deployment of ALT sheets spiked with the extract of the sediment-equilibrated sampler, resulted for most compounds with a $\log K_{ow} < 6$ in a further shift of the C_{p_sed}/C_p^∞ ratio towards one, i.e. to the assumed PS/water equilibrium. The difference between C_{p_sed} and C_p^∞ was reduced to less than a factor of four for PAHs with

up to 4 aromatic rings and for HCB. Some decrease (less than a factor of 2) in C_{p_sed}/C_p^∞ was also observed for PAHs with 5 aromatic rings. In agreement with theory (Eq. (4)) a fast re-equilibration was confirmed for compounds with low hydrophobicity. The estimated sampling rate of sheets during water deployment was approximately 6 L day^{-1} . This

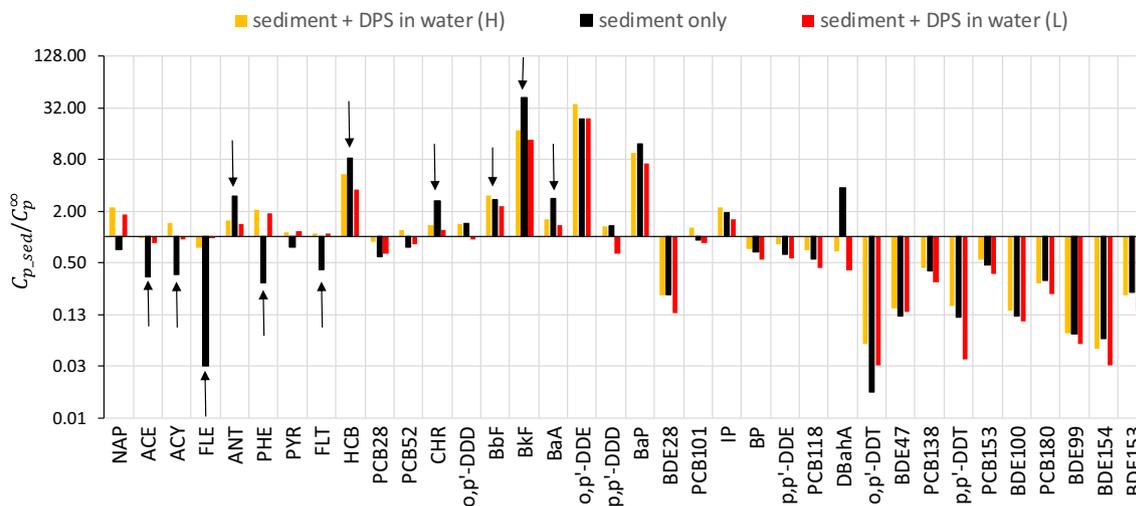


Fig. 6. Ratios of the HOC concentrations in the sediment pre-equilibrated ALT samplers deployed for 52 days, with those in samplers deployed in a regular way and converted to equilibrium (C_p^∞) using Eq. (12). The black bar represents this ratio for the unexposed sediment pre-equilibrated sampler, and the yellow and red bar for the samplers re-dosed to a factor 1.2 higher (H) and lower (L) concentration, respectively. Arrows show the direction in which the C_{p_sed}/C_p^∞ ratio shifted after deployment in water. The compounds are ordered according to their $\log K_{ow}$ values. Abbreviations of compound names are listed in Supplementary information, Table S1. For details see Section 2.4. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Comparison of various passive sampling approaches applicable for monitoring HOC in the aquatic environment.

Advantageous property	Passive sampling method				
	Water			Sediment	
	Equilibrium		Integrative	Equilibrium	
	In situ	Ex situ	In situ	In situ	Ex situ
Assessing exposure of benthic organisms	–	–	–	+	+
Assessing exposure of pelagic organisms	+	+	+	–	–
Limit of quantification is sufficiently low for environmental monitoring	+	–	+	+	+
Negligible analyte depletion during sampling	+	–	+	–	+
Time-integrative character of sampling	–	–	+	–	–
No need to use models for calculating the equilibrium value	+	+	–	–	+
Equilibrium attainment for compounds with $\log K_{ow} > 6$	–	–	Not required	–	+
References	This work, a, b		c,d	e,f	g,h,i

^a(Fernandez et al., 2012), ^b(Perron et al., 2013), ^c(van Pinxteren et al., 2010), ^d(David and Sandra, 2007), ^e(Booij et al., 2007), ^f(Roll and Halden, 2016), ^g(Fernandez et al., 2009), ^h(Witt et al., 2013), ⁱ(Cornelissen et al., 2008), ^j(Jonker et al., 2018), ^k(Endo et al., 2017), ^l(Greenberg et al., 2014)

value was calculated from sampling rate of co-deployed sheets spiked with PRCs, assuming equality of k_0 in both samplers. In agreement with the observation, Eq. (5) predicts re-equilibration of PAHs with up to 4 aromatic rings in the molecule during 52 days of deployment in water. The more hydrophobic compounds ($\log K_{ow} > 6$) re-equilibrate much slower, and when the concentration in the sampler equilibrated with sediment differs from C_p^∞ , even extended deployment in water does not help to attain the desired equilibrium C_p^∞ value for compounds with $\log K_{ow}$ higher than 6.

3.4. Perspective

In situ equilibrium passive sampling of HOC in surface water offers several potential advantages over other passive sampling techniques (Table 3). When data on HOC chemical activity is needed for exposure assessment of pelagic organisms, equilibrium passive sampling in water column obviously reflects their exposure level better than passive sampling in sediment. Ex-situ passive sampling in water allows intensive agitation to attain equilibrium for very hydrophobic HOC, but it heavily suffers from compound depletion and is a poor insensitive alternative to in situ sampling. In analogy to in situ sampling in water, in situ sampling in sediment also suffers from HOC depletion near the sampler surface. Because the HOC uptake capacity in sediment is much larger than in water, ex-situ sampling in sediment is feasible without depletion.

In situ integrative passive sampling of HOC in surface water shares all the advantages with in situ equilibrium passive sampling in the same matrix, except that modeling approach is needed for estimation of C_{free} or C_p^∞ . This work investigated how equilibrium passive sampling with thinner samplers can extend the K_{ow} equilibrium range. Theoretically, this can be carried further by applying even thinner samplers but such approach has practical handling limits. For long term monitoring programmes an easier way is to extend exposure time to a year or longer. In all other situations estimation of C_p^∞ will need to rely on modeling and availability of adequate K_{pw} of target HOC and PRC.

4. Conclusions

The study shows that a combination of various exposure conditions shortens the time needed for a silicone passive sampler to reach equilibrium with water. Thin (125 μm) samplers exposed in a strong water current for several months may reach equilibrium for compounds with a $\log K_{ow} \leq 6$. Nevertheless, for compounds with a higher K_{ow} such as for PAH with five condensed rings, PCB with more than five chlorine atoms in the molecule or BDE with more than four bromine atoms per molecule, it is challenging to attempt equilibrium attainment in an open system with WBL resistance controlling the uptake. Although it is possible to further decrease sampler thickness in order to extend the equilibration range towards more hydrophobic compounds, it

would require a change of sampler construction. Sampler sheets thinner than 100 μm are not available, and if they were, they would most likely be fragile and not suitable for exposure in running water. Use of silicone layer of <20 μm range with increased sampler surface area is applicable e.g. in form of silicone-coated glass surfaces (Reichenberg et al., 2008).

The “equilibration” of samplers previously pre-incubated with upper layer of the sediment followed by deployment in the overlaying water column enabled to attain HOC concentrations in samplers close to the equilibrium with water for a broad range of compounds, approximately up to $-\log K_{ow}$ of 5.5. If the HOC concentration in the sampler that has been pre-equilibrated with sediment was close enough to the equilibrium value with water (e.g. within 20%), the following equilibration with water could be achieved after significantly shorter time period than in a situation when the uptake in water proceeded from a zero initial sampler concentration. However, the possibility to extend the $K_{pw,0.95}$ range to higher values by using this approach is limited. It can be shown (from Eq. (5)) that the $K_{pw,0.95}$ of a sampler pre-equilibrated to DEQ_p of 80% and then exposed in water, is only by a factor of two higher than that of a sampler exposed only in water (without pre-equilibration). This corresponds to $K_{pw,0.95}$ range extension barely by 0.3 log units. Nevertheless, even this approach does not seem to be applicable in general, since chemical activity of some specific compounds (e.g. some DDT metabolites or PBDE in our case) seem to deviate in sediment and water column. This difference is critical especially for very hydrophobic compounds, for which accumulation or desorption from sampler proceeds very slowly in reflection of the change of chemical activity in the exposure medium. Still, the outlined approach can be useful since during re-equilibration in water, the sampler may gain or lose HOC, and the direction of C_p change will directly indicate the difference in chemical activity between water and sediment.

For estimation of C_w or other related measures of chemical activity in water for very hydrophobic HOC the kinetic method using PRCs remains the method of choice, as outlined in the available guidance document (Smedes and Booij, 2012). Since the concentrations of HOC in water are often very low, the integrative character of passive sampling renders long sampler exposures using thin samplers exposed in turbulent water a favorable exposure method. Estimation of R_S values necessary for C_w estimation depends on the accuracy of PRC measurement that are partially eliminated from samplers during exposure as well as to the accuracy of their K_{pw} values. Moreover, R_S accuracy can be improved by applying more PRCs in the hydrophobicity range where a partial PRC release (approximately between 20 and 80%) is expected during exposure. During long sampler exposures that range is shifted towards more hydrophobic compounds, which implicates two important issues to be considered in future studies: a) selection of a suitable range of more PRCs equally distributed over the range of $\log K_{ow}$ between 6 and 8; and b) determination of accurate K_{pw} values for those compounds.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.01.242>.

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