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Chasing equilibrium in water passive sampling
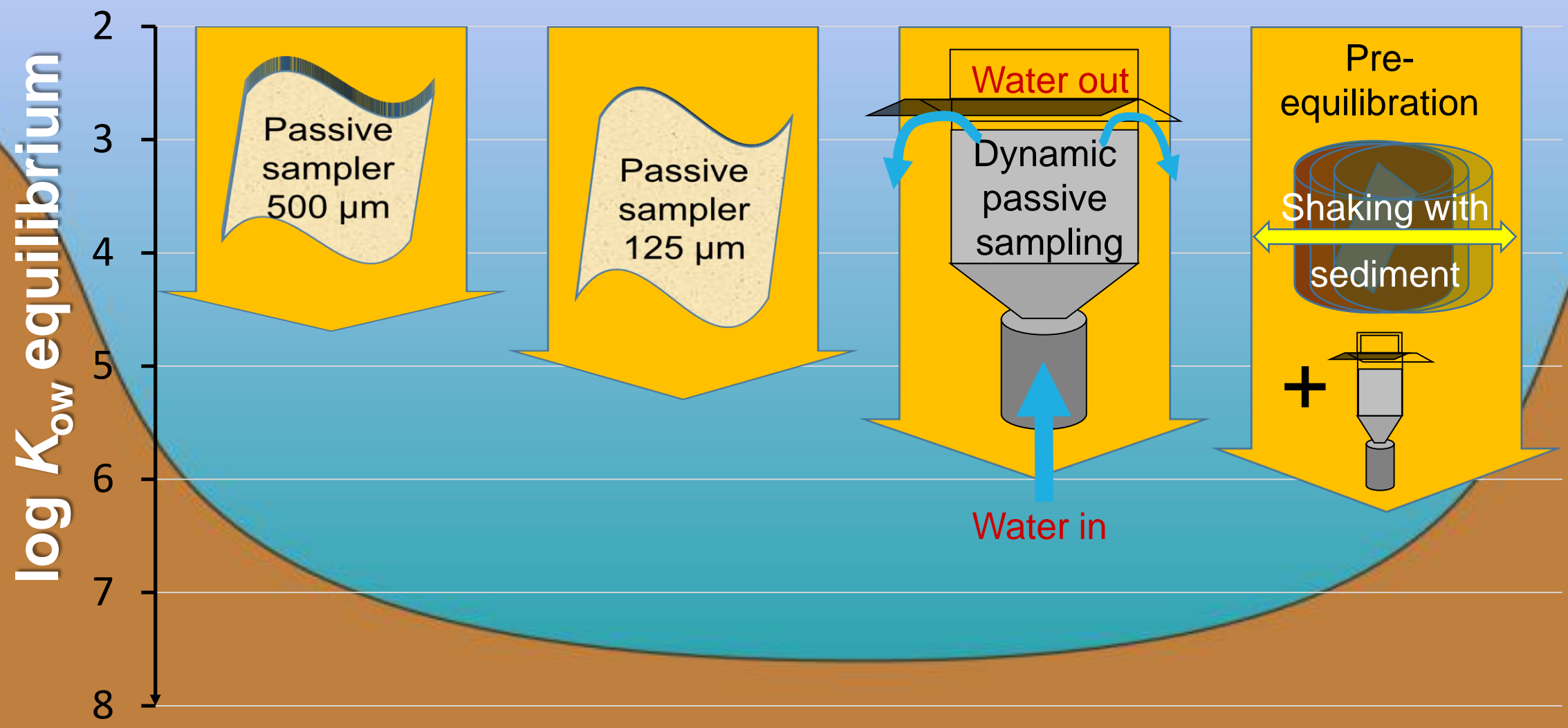
Highlights

- 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} ≤5.5 reached partition equilibrium with water

- For compounds with log K_{ow} >6 equilibrium cannot be reached within a reasonable time

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Chasing equilibrium passive sampling of
2
hydrophobic organic compounds in water

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23 **Keywords:** aquatic pollution; persistent organic pollutants; mass transfer; equilibrium partitioning;

24 passive sampling; silicone

25   Abstract

26   We investigated a combination of approaches to extend the attainment of partition equilibria

27   between silicone passive samplers (samplers) and surface or treated waste water towards more

28   hydrophobic organic compounds (HOC). The aim was to identify the HOC hydrophobicity range for

29   which silicone sampler equilibration in water is feasible within a reasonable sampler deployment

30   period. Equilibrium partitioning of HOC between sampler and water is desirable for a simpler

31   application as a "chemometer", aiming to compare chemical activity gradients across environmental

32   media (e.g. water, sediment, biota). The tested approaches included a) long sampler exposure

33   periods and high water flow to maximize mass transfer from water to PS; b) the use of samplers with

34   reduced sheet thicknesses; and c) pre-equilibration of samplers with local bottom sediment, followed

35   by their exposure in surface water at the same sampling site. These approaches were tested at three

36   sites including a fish pond with a low level of pollution, a river impacted by an urban agglomeration

37   and an effluent of municipal wastewater treatment plant. Tested compounds included

38   polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH), DDT, its metabolites and

39   their isomers, hexachlorobenzene (HCB) and polybrominated diphenyl ethers (PBDE). The study

40   shows that samplers with a surface area of 400-800 cm^2 consisting of thin (100-500 μm) silicone

41   sheets exposed at sampling rates of 10-40 L d^{-1} for a time period of up to four months reach partition

42   equilibrium with water for compounds with a log K_{ow} ≤5.5. Nevertheless, for compounds beyond this

43   limit it is challenging, within a reasonable time period, to reach equilibrium between sampler and

44   water in an open system where water boundary layer resistance controls the mass transfer. For more

45   hydrophobic HOC (log K_{ow}>6), the kinetic method using performance reference compounds is

46   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 the 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

75   free dissolved concentration (C_{free}) (Greenberg et al., 2014; Reichenberg and Mayer, 2006) or lipid-

76   based concentration (Figueiredo et al., 2017; Jahnke et al., 2014a, 2014b).

77   The HOC concentration in the sampler at equilibrium with the sampled medium represents the

78   chemical activity in that medium. When a polymer-based sampler is equilibrated with water, C_{free} can

79   be estimated using the measured equilibrium concentration in the sampler C_p^∞ and the sampler-

80   water partition coefficient, K_{pw} (Mayer et al., 2003):

81    $$C_{free} = \frac{C_p^\infty}{K_{pw}} = \frac{N_p^\infty}{K_{pw}m_p}$$ Equation 1

82   Here, N_p^∞ is the amount of compound absorbed by a sampler at equilibrium and m_p is the mass of

83   the sampler. Required K_{pw} values can be measured under controlled laboratory conditions and are

84   available in literature for many HOC and for polymers typically used in sampler construction, namely

85   silicone and low-density polyethylene (Lohmann, 2012; Pintado-Herrera et al., 2016; Smedes, 2018a;

86   Smedes et al., 2009).

87   Whereas partitioning equilibrium of HOC between sampler and sediment or soft tissues of aquatic

88   biota can be achieved within a reasonable timeframe of days to weeks (Jahnke et al., 2011; Rojo-

89   Nieto et al., 2019; Rusina et al., 2017; Smedes et al., 2013), equilibration of sampler in surface water

90   takes a long time and is challenging to achieve, especially for very hydrophobic compounds (Allan et

91   al., 2013).

92   During deployment in water a HOC amount absorbed by the sampler N_p^t exponentially rises with

93   exposure time t, from the initial amount in the sampler N_p^0, following the first-order kinetics, until it

94   reaches the equilibrium value N_p^∞ (Vrana et al., 2001):

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

96   where DEQ_p^t, taking value between 0 to 1, is the degree of equilibrium that the compound attained

97   during sampler exposure. In open aquatic systems such as streams or lakes DEQ_p^t is described by

98   Booij et al. (2007):

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

100   Here, R_S denotes the in situ sampling rate, i.e. the volume of water cleared of compound per unit of

101   time. With R_s as the product of the overall mass transfer coefficient (k_o) and the sampler surface area

102   (A_p) and further appreciating that m_p is equal to the product of polymer's density (ρ_p), sampler sheet

103   thickness d_p and A_p, equation 3 modifies to:

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

104   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

105   as possible. Of course, K_{pw} is mainly determined by compound properties, but in practical sampler

106   application preference could be given to polymers with lower K_{pw}.

107   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

108   estimated from a combination of equations 2 and 4 as

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

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

111   Firstly, equilibrium is attained faster, when the mass transfer coefficient k_o is maximized. When using

112   samplers consisting of thin silicone sheets (< 1mm), k_o of HOC is dominated by the mass transfer

113   coefficient in water boundary layer (WBL), and the resistance to mass transfer in silicone can be

114   neglected (Rusina et al., 2010) due to fast HOC diffusion in polymer material. Since the uptake from

115   water to sampler limits the typically achievable $R_S = k_o \times A_p$ magnitude to tens of liters per day, for

116 highly hydrophobic compounds with a very high sampler uptake capacity (i.e. $K_{pw} \times m_p$) equilibration

117 of HOC in an open aquatic system may take up to months to years (Booij et al., 2007). The resistance

118 to mass transfer in WBL can be minimized by exposing samplers in turbulent water (Allan et al., 2011;

119 Booij et al., 2007), or by shaking them in dense sediment suspensions that disrupt the WBL at

120 sampler surface and decrease the diffusion distance (Mayer et al., 2007; Smedes et al., 2013). For

121 estimation of k_o magnitude, in situ calibration of samplers is necessary, because k_o is an exposure

122 specific parameter and depends on environmental variables, such as temperature, water flow and

123 fouling. It is typically estimated from the release rate of performance reference compounds (PRCs)

124 from samplers during exposure (Booij and Smedes, 2010; Huckins et al., 2002).

125 Secondly, sampler equilibration can be speeded up by minimizing the sampler thickness d_p, i.e. by

126 using samplers in form of thin films (Mayer et al., 2003). This implies the need to increase the

127 sampler surface area A_p in order to accumulate sufficient amount of compound for quantification.

128 Note that a higher A_p increases R_s but at the same time the it increases also the sampler capacity.

129 Consequently, the time to attain a certain DEQ_p level is not affected by sampler surface area (eq 5).

130 Nevertheless, the product of $d_p \times A_p$ is important to assure that N_p^∞ is sufficiently high to be well

131 quantifiable. With this condition the limit of decreasing d_p lays in the samplers A_p that still can be

132 practically handled in deployment.

133 Finally, equilibration time can be shortened when the initial amount of compound present in the

134 sampler N_p^0 is in the range between zero and $2 \times N_p^\infty$. According to equation 5, when N_p^0 is 20% higher

135 or lower than N_p^∞, the equilibration time is shortened by half (Supplementary information, Figure

136 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

137 equilibrium value N_p^∞ can be approached by sampler pre-exposure with another medium collected

138 from the site of investigation, i.e. sediment, which faster attains equilibrium with sampler than water

139 does (Belháčová-Minaříková et al., 2017; Mayer et al., 2014; Smedes et al., 2013; Witt et al., 2013)

140 In order to identify the HOC hydrophobicity range for which sampler equilibration in water is feasible

141 within a reasonable sampler deployment period, we investigated a combination of the above

142 mentioned approaches. Those included a) long sampler exposure periods of several months in a

143 previously designed dynamic passive sampling device (DPS) (Vrana et al., 2018) that maximizes the k_o

144 in the WBL; b) the use of thin samplers with different sheet thicknesses d_p; and c) pre-equilibration of

145 samplers with local bottom sediment, followed by their exposure in the water column in order to

146 move N_p^0 closer to N_p^∞. To our knowledge, a systematic testing of these parameters and conditions

147 for equilibrium attainment of very hydrophobic compounds in aquatic passive sampling has not been

148 done before.

149 ## 2   Materials and Methods

150 ## 2.1   Chemicals

151 Acetone, diethylether, dichloromethane, ethyl acetate, hexane, hydrochloric acid, methanol and

152 sulphuric acid were of analytical grade and obtained from Sigma-Aldrich (Germany) and Lab-Scan

153 (Poland). Standards of 16 PAHs, 7 indicator PCB congeners, DDT, its metabolites and their isomers

154 and HCB were obtained from Supelco (Sigma-Aldrich, Prague, Czech Republic). Standards of

155 polybrominated diphenyl ether (PBDE) congeners were purchased from AccuStandards (USA). The

156 PRC mixture containing perdeuterated biphenyl (D_{10}-biphenyl) and 13 PCB congeners that do not

157 occur in technical mixtures, (PCB 1, PCB 2, PCB 3, PCB 10, PCB 14, PCB 21, PCB 30, PCB 50, PCB 55,

158 PCB 78, PCB 104, PCB 145, PCB 204) in ethyl acetate was kindly provided by Deltares, Utrecht, The

159 Netherlands. D_8-naphthalene, D_{10}-phenanthrene, D_{12}-perylene, PCB 4, PCB 29 and PCB 185 (Dr

160 Ehrenstorfer, Germany) were used as recovery internal standards (RIS) and ^{13}C-labeled analogues of

161 PBDE congeners (Wellington Laboratories, Canada) were used in isotope dilution method for

162 determination of PBDE concentrations. PCB 121 and p-terphenyl were used as internal standards for

163 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 $5-75$ $\mu g\,mL^{-1}$ 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

8

188   of 400 000. A third sampling site (S3, Table 1) was located at the discharge of effluent from the main

189   municipal WWTP in Brno, Czech Republic (capacity ca. 500 000 equivalent inhabitants). The sampling

190   was conducted in an effluent basin that is used for measurement of flow and volume of discharged

191   treated wastewater.

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 eqilibration 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

192

193   At the fish pond discharge site S1A, samplers (both ALT and SSP) were mounted to a wire mesh

194   frame and deployed where water is discharged from the pond through an overflow. These samplers

195   were exposed to running water from both sides and thus the exposed area was approximately 780

196   cm^2 per sheet. At all remaining locations, samplers were exposed in a DPS that has been described in

197   our previous work (Vrana et al., 2018). Briefly, the device consists of a rectangular stainless-steel

198   plate chamber open from two sides and fully immersed in water. The bottom end of the chamber is

199   directly connected to a submersible electricity driven pump (cca 9 m^3 h^{-1}) that forces water at high

200   flow velocity (1-2 m s^{-1}) through the chamber. One ALT and one SSP sheet were mounted in the DPS.

201   Samplers were exposed to water from only one side (Figure 1). The exposed area was approximately

202   390 cm^2 per sheet. At all sites, samplers were deployed at approximately 50 cm depth below the

203   water surface for a period of between 52 and 164 days. Samplers were mounted to the deployment

204   devices just before exposure and removed immediately afterwards. All samplers were protected

205   from direct sunlight to minimize photodegradation of the sampled compounds (Allan et al., 2016).

206 Temperature and light intensity loggers (Hobo Pendant, Onset, Germany) were attached to all

207 samplers during exposures. After exposure samplers were cleaned with local water using a scrubber,

208 packed to closed amber glass vials, transported to the processing laboratory and stored in at -20°C.

209 To monitor the equilibration progress, sampling rates R_S and associated DEQ_s were estimated from

210 the dissipation of PRCs from samplers during exposure as described in Smedes and Booij (2012) using

211 unweighted nonlinear least squares method by Booij and Smedes (2010), considering the retained

212 PRC fraction, f(PRC), after exposure as a continuous function of their sampler-water partition

213 coefficient:

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

214

215 where N_{PRC}^{t} and N_{PRC}^{0} are the PRC amounts in the sampler after exposure time t and at the exposure

216 start(t = 0), respectively. The model derived by Rusina et al., (2010) was applied to estimate target

217 HOC sampling rates as a function of their molar mass M, i.e. $R_S = A_p \times B \times M^{-0.47}$, where B is an exposure

218 specific factor related to the mass transfer coefficient in WBL (k_o).

2.4 Exposure of samplers pre-equilibrated in sediment

220 Assuming HOC in water and in surface sediment layer has approximately the same chemical activity,

221 ALT samplers were first pre-equilibrated with surface sediment from site S1 in the laboratory under

222 agitated conditions. In the following deployment in water that is expected to give the equilibration

223 process a head start. To facilitate monitoring of the equilibration in water, two sub-samplers (from

224 the sediment pre-equilibration) were prepared in which the HOC concentrations were respectively

225 increased (H) and decreased (L) by a factor 1.2. This was done by means of extraction and

226 consecutive dosing of fresh samplers following the scheme in Figure 2. Briefly, in duplicate, three ALT

227 sampler sheets (5×9.5cm, 500µm thick), 2.5 L of a sediment slurry (40% dry weight) from site S1, and

228 one gram of sodium azide were brought in a 5 L bottle and shaken at orbital shaker at room

229 temperature in the dark for a total of 44 days . On day 30 methanol was added to obtain 20% (v/v) in

230 order to accelerate the HOC equilibration. Then exposed sheets (total 6) were Soxhlet extracted in

231 methanol as described in section 2.5. The extract volume was reduced, quantitatively transferred to

232 a 100 mL volumetric flask, which was filled to the mark. A 33% portion was set aside and analysed as

233 described in section 2.5. Then the 40% and 27% portions were each used for dosing a set of 2 clean

234 ALT sheets analogically to the PRC spiking procedure (Smedes and Booij, 2012). These two dosed ALT

235 samplers were then deployed at site S1 for 52 days (S1C, Table 1) in parallel with regular surface

236 water samplers (S1B, Table 1) using the DPS device. After exposure, samplers were stored at -20°C

237 and analyzed similar to the water-exposed sheets (2.5).

2.5   Sample processing

239 Before extraction, all exposed samplers were spiked with recovery internal standards (RIS) (50 ng of

240 D_8-naphthalene, D_{10}-phenanthrene, D_{12}-perylene; 10 ng of PCB 4 and PCB 185; 1 ng of ^{13}C-PBDE and

241 Soxhlet extracted with methanol for 8 hours. The obtained extract was concentrated by Kuderna-

242 Danish evaporation to less than 2 mL. After addition of 20 mL hexane the extract was azeotropically

243 transferred to hexane by Kuderna-Danish evaporation and volume-reduced to 1 mL. Mass of

244 individual samplers was recorded after drying. A 30% extract aliquot intended for analysis of PAHs

245 was further cleaned-up on a silica gel column using diethylether/acetone elution. Subsequently,

246 extracts were Kuderna-Danish reduced in volume, followed by evaporation with a gentle nitrogen

247 flow. Finally, p-terphenyl was added as internal standard. The other 70% aliquot used for analysis of

248 DDT, its metabolites and their isomers, HCB, PCB, PRC and PBDE was purified using activated silica gel

249 modified with sulfuric acid, followed by PCB 121 addition as internal standard. All extracts were

250 analyzed using GC-MS/MS methods for PAH, PRC, indicator PCB, DDT, its metabolites and their

251 isomers, HCB and PBDE. Applied quality assurance/quality control measures are described in

252 Supplementary information.

2.6   Instrumental analysis

Analysis of PAHs 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°C min^{-1} to 180°C and at 5°C min^{-1} to 310°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 m x 0.25 mm x 0.25µm 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°C. Helium was used as carrier gas at the flow of 1.5 ml min^{-1}. The GC temperature programme started 80°C (1 min hold), ramped at 15°C min^{-1} to 180°C, and finally ramped at 5°C min^{-1} to 300°C (5 min hold).

PBDE were analysed using an Agilent 7890A GC equipped with 15 m x 0.25 mm × 0.10 µm 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

275 As stated above, higher DEQ_p^t can be achieved by maximizing the $R_s \times t$ or $k_o \times t$ product (Eqs. 3 and 4).

276 In this work we exposed thus samplers in a DPS, to achieve higher R_s for HOC uptake and PRC release.

277 Since the uptake of HOCs from water to sampler and their release from sampler to water are

278 isokinetic processes (Booij et al., 2007), equilibration progress can be assessed from the release of

279 PRCs (Figure 3). A complete release of PRC from the sampler indicates attainment of partitioning

280 equilibrium for a compound present in water of a similar hydrophobicity. We considered the retained

281 PRC fraction of less than 5% of the initial concentration in the sampler as a criterion of complete

282 release. Equilibrium was thus confirmed for PRCs with log K_{ow} < 5 from SSP samplers at all sites

283 (Figure 3).

284 We further estimated the maximum $K_{ow,0.95}$ value for which the sampler reaches 95% sampler-water

285 equilibrium after the actual exposure time. Rearranging equation 5 for an exposure with negligible

286 starting compound amount in the sampler ($N_p^0 = 0$) allows to estimate the maximum $K_{pw,0.95}$ value

287 for which the sampler reaches 95% PS-water equilibrium after the actual samplerexposure time (t$_{0.95}$)

288 as

289 $$K_{pw,0.95} \approx -\ln 0.05 \frac{R_S t_{0.95}}{m_p}$$ Equation 7

290 The required sampling rates R_S were estimated from dissipation of PRCs from sampler using the

291 model function described in 2.3 (Figure 3). For illustration, we state here $^{300}R_S$ for a compound with

292 molar mass of 300. $^{300}R_s$ values estimated for ALT polymer, for which published K_{pw} data are

293 available, ranged from 10 to 45 L d^{-1} at sites S3 and S2, respectively (Table 2). The low R_s obtained

294 during DPS application in wastewater effluent (S3) was likely due to a partial clogging of the DPS by

295 fine threads of algae present in the water. On several occasions algae had to be removed from the

296 DPS water intake during exposure. In contrast, the DPS performed very well at the riverine site S2,

297 reaching R_s of 45 L d^{-1}, comparable with our previous study in the Danube river (Vrana et al., 2018).

298 The $^{300}R_S$ 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

300 occurred during the long exposure period and also because the sampler at S1A had two times higher

301 sampler surface area exposed to water (Table 2).

302 The product of sampling rate and exposure time ($R_s \times t$) presents the maximum sampled volume of

303 water during exposures at different sites, which for the ALT sampler ranged from 1100 L to 3600 L at

304 sites S3 and S1A, respectively.

305 The calculation shows that in ALT samplers under exposure conditions and within the deployment

306 periods stated in Tables 1 and 2, all analysed compounds with log K_{pw} lower than 4.2-4.7 attained

307 partition equilibrium in water. Since log K_{pw} is correlated with log K_{ow}, this corresponds with a log K_{ow}

308 range of 4.5 to 4.9 (Table 2). The calculation confirms the observation made by inspection of PRC

309 data (Figure 3).

310 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 [cm²]	t [d]	^{300}Rs [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

311 [a]Sampling rate of a compound with a molar mass of 300 g mol^{-1}

312 [b]Sampled water volume for a compound with molar mass 300 g mol^{-1}, calculated as $^{300}R_S \times t$

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

314 [d]Estimated maximum log K_{ow} of a compound reaching 95% equilibrium between ALT sampler and water, derived

315 from a correlation log K_{pw} = 1.14×log K_{ow} - 0.92 for PRCs. log K_{pw} values of PRCs were taken from (Smedes,

316 2018b)

3.2   Equilibration of thinner silicone in water

317

318   Sampler equilibration can be further extended to more hydrophobic compounds by minimizing the

319   sampler thickness d_p.

320   ### 3.2.1   Assessment from PRC release

321   The calculation using Equation 7 shows that in SSP sampler the threshold log $K_{pw,0.95}$ values reached

322   4.9 to 5.4, which corresponds with log $K_{ow,0.95}$ values in the range between 5.1 to 5.5. The calculation

323   assumes in the first approximation equal R_s and K_{pw} values in both ALT and SSP samplers. Equality of

324   R_S in samplers of the same geometry (14×28 cm sheets) exposed in the same arrangement has been

325   demonstrated previously (Vrana et al., 2018). There may be small differences in K_{pw} values between

326   ALT and SSP polymer, however, these were neglected for the purpose of our comparison.

327   Comparison of log $K_{ow,0.95}$ in co-deployed ALT and SSP samplers shows that fourfold reduction of

328   sampler thickness increased the threshold $K_{ow,0.95}$ value by 0.6 to 0.7 log units. In practice, this means

329   that equilibrium establishment for ALT was most likely reached for PAHs with less than five

330   condensed aromatic rings and for mono- and di-chlorinated PCBs. The SSP sampler could reach

331   equilibrium for PAHs with less than six aromatic rings and for mono- to tetra-chlorinated PCBs.

332   ### 3.2.2   Assessment from compound uptake

333   Another approach to assess which compounds attained partition equilibrium is based on comparison

334   of HOC uptake from water to samplers with different thicknesses. The ratio of HOC amounts

335   accumulated in ALT and SSP samplers, in which the initial concentration N_p^0 is close to zero, can be

336   derived from equation 2:

337
$$\frac{N_{ALT}^t}{N_{SSP}^t} = \frac{K_{ALT,w} m_{ALT} DEQ_{ALT}^t}{K_{SSP,w} m_{SSP} DEQ_{SSP}^t}$$
Equation 8

338   Booij et al. (2007) have further shown that at short exposure times when DEQ^t is close to 0 and the

339   initial concentration N_p^0 is close to zero, Equation 2 can be simplified to:

340
$$N_p^t = C_w R_S t$$
Equation 9

341 In that situation, since both samplers were exposed to the same water for equal time period, the

342 ratio of HOC amounts accumulated in samplers ALT and SSP is:

343
$$\frac{N_{ALT}^t}{N_{SSP}^t} = \frac{R_{s,ALT}}{R_{s,SSP}}$$
Equation 10

344 As mentioned earlier, WBL-controlled R_s of co-deployed silicone samplers are expected to be equal

345 (Vrana et al., 2018). Therefore, the ratio N_{ALT}^t/N_{SSP}^t close to one identifies the range of compounds

346 that are far from reaching partitioning equilibrium with water in both samplers. When the sampler

347 capacity ($K_{pw} \times m_p$) starts playing a role in uptake, the ratio becomes higher than one, indicating

348 equilibrium attainment in one or both samplers. The N_{ALT}^t/N_{SSP}^t ratio as a function of compound`s

349 hydrophobicity is shown in Figure 4.

350 The ratio decreases with increasing log K_{ow} of the compound, and for compounds with a log $K_{ow} > 6.5$,

351 the ratio is close to one, i.e., the compounds did not reach equilibrium with the passive sampler.

352 These results are in agreement with the non-equilibrium range identified from PRC release for

353 compounds exceeding the threshold log $K_{ow,0.95}$ log stated in Table 2.

354 The equation 8 can be further transformed to compare the degree of partition equilibrium attained

355 in the two co-deployed samplers.

356
$$\frac{DEQ_{ALT}^t}{DEQ_{SSP}^t} = \frac{N_{ALT}^t K_{SSP,w} m_{SSP}}{N_{SSP}^t K_{ALT,w} m_{ALT}}$$
Equation 11

357 The DEQ_{ALT}^t/DEQ_{SSP}^t ratio, plotted as a function of compound`s log K_{ow}, is shown in Figure 5. The

358 ratio varies approximately in the range from zero and one, and in all cases it decreases with the

359 increasing log K_{ow} of the compound. The data from sampler exposures at site S1 show clearly that for

360 log $K_{ow} < 5$ the ratio levels off and attains values close to one. The ratio approaching one is expected

361 when both co-deployed samplers are close to partition equilibrium with the water. In theory, ratios

362 higher than one are not expected since the uptake capacity ($K_{pw} \times m_p$) of ALT is always higher

363 compared to SSP. The observed ratios higher than one in some cases may be attributed to the

364 uncertainty related to the *DEQ*p ratio calculation. Data in Figure 5 shows that in all exposures,

365 partition equilibrium between water and ALT and SSP was attained for compounds with log K_{ow} < 5

366 and for some compounds in the log K_{ow} range between 5 and 6.

367 Both projections of the HOC uptake (Figures 4 and 5) confirm that with selected samplers and

368 exposure conditions partition equilibrium of compounds with log K_{ow} < 5 is attained within an

369 exposure period of 5 months.

370

3.3 Exposure of samplers pre-equilibrated in sediment slurry

372 Further, we investigated whether sampler pre-equilibration with surface layer of sediment collected

373 at the fish pond site, followed by sampler deployment in water column adjacent to the sediment, can

374 speed up the sampler equilibration in water (exposure S1C in Table 1).

375 The chemical activity of HOC in the top sediment layer (upper 5 cm) and the water column is

376 expected to be very similar. Hence, a sampler equilibrated with the upper layer of the sediment and

377 further with overlaying water would contain similar levels of HOC as a sampler equilibrated with

378 water only. Sampler equilibrium in sediment is established much faster than in water and can be

379 obtained even for very hydrophobic compounds (Smedes et al., 2013), especially when applying a co-

380 solvent method that enhances the HOC mass transfer (Belháčová-Minaříková et al., 2017).

381 In the first step, we derived an assumed equilibrium HOC concentration in a sampler deployed in

382 water column, C_p^∞ (exposure S1B). This value was then applied as equilibrium assessment criterion

383 for sampler pre-incubated in sediment (C_{p_sed}) (exposure S1C). C_p^∞ was calculated from equation 2,

384 assuming negligible starting compound concentration in the sampler ($C_p^0 = 0$):

385 $$C_p^\infty = C_p^t / DEQ_p^t$$ Equation 12

386   The necessary DEQ_p^t was estimated from the PRC elimination data. This step was necessary since (as

387   has been shown in paragraph 2.3) a full partition equilibrium in water has not been reached for very

388   hydrophobic compounds.

389   Figure 6 shows a ratio of HOC concentrations in PS, incubated with top layer of sediment from the

390   fish pond site S1 and then exposed to water at the same site (C_{p_sed}), to calculated concentrations of

391   samplers at equilibrium with water C_p^∞. For most of the investigated HOCs, the equilibration of

392   silicone with sediment resulted in C_{p_sed} concentrations that were within a factor of 10 from C_p^∞. For

393   some compounds, even a lower C_{p_sed}/C_p^∞ value was attained. For indeno(123cd)pyrene,

394   benzo(g,h,i)perylene, PCB 28, PCB 52, PCB 101, PCB 118, *p,p´*-DDE and *o,p´*-DDD the difference

395   between C_{p_sed} and C_p^∞ was less than a factor of 2. However, a larger C_{p_sed}/C_p^∞ factor difference

396   was observed for fluorene (0.03), benzo(k)fluoranthene (43), benzo(a)pyrene (12), BDE 99 (0.07), BDE

397   153 (0.07), *o,p'*-DDE (41), *o,p'*-DDT (0.01) and *p,p'*-DDT (0.03). This indicates a different chemical

398   activity of HOC in sediment and in water column, which may be caused by various factors, e.g. a

399   faster compound degradation in one of the phases, temporal variability in water, collection of

400   sediment recently emerged from deeper layers that did not have sufficient time to equilibrate with

401   water, etc.

402   The subsequent water deployment of ALT sheets spiked with the extract of the sediment-equilibrated

403   sampler, resulted for most compounds with a log K_{ow}<6 in a further shift of the C_{p_sed}/C_p^∞ ratio

404   towards one, i.e. to the assumed PS/water equilibrium. The difference between C_{p_sed} and C_p^∞ was

405   reduced to less than a factor of four for PAHs with up to 4 aromatic rings and for HCB. Some decrease

406   (less than a factor of 2) in C_{p_sed}/C_p^∞ was also observed for PAHs with 5 aromatic rings. In agreement

407   with theory (Equation 4) a fast re-equilibration was confirmed for compounds with low

408   hydrophobicity. The estimated sampling rate of sheets during water deployment was approximately 6

409   L day^{-1}. This value was calculated from sampling rate of co-deployed sheets spiked with PRCs,

410   assuming equality of k_0 in both samplers. In agreement with the observation, Equation 5 predicts re-

411 equilibration of PAHs with up to 4 aromatic rings in the molecule during 52 days of deployment in

412 water. The more hydrophobic compounds (log K_{ow}>6) re-equilibrate much slower, and when the

413 concentration in the sampler equilibrated with sediment differs from C_p^∞, even extended deployment

414 in water does not help to attain the desired equilibrium C_p^∞ value for compounds with log K_{ow} higher

415 than 6.

3.4   Perspective

417 In situ equilibrium passive sampling of HOC in surface water offers several potential advantages over

418 other passive sampling techniques (Table 3). When data on HOC chemical activity is needed for

419 exposure assessment of pelagic organisms, equilibrium passive sampling in water column obviously

420 reflects their exposure level better than passive sampling in sediment. Ex-situ passive sampling in

421 water allows intensive agitation to attain equilibrium for very hydrophobic HOC, but it heavily suffers

422 from compound depletion and is a poor insensitive alternative to in situ sampling. In analogy to in

423 situ sampling in water, in situ sampling in sediment also suffers from HOC depletion near the sampler

424 surface. Because the HOC uptake capacity in sediment is much larger than in water, ex-situ sampling

425 in sediment is feasible without depletion.

426 In situ integrative passive sampling of HOC in surface water shares all the advantages with in situ

427 equilibrium passive sampling in the same matrix, except that modeling approach is needed for

428 estimation of C_{free} or C_p^∞. This work investigated how equilibrium passive sampling with thinner

429 samplers can extend the K_{ow} equilibrium range. Theoretically, this can be carried further by applying

430 even thinner samplers but such approach has practical handling limits. For long term monitoring

431 programmes an easier way is to extend exposure time to a year or longer. In all other situations

432 estimation of C_p^∞ will need to rely on modelling and availability of adequate K_{pw} of target HOC and

433 PRC.

4   Conclusions

435   The study shows that a combination of various exposure conditions shortens the time needed for a

436   silicone passive sampler to reach equilibrium with water. Thin (125 μm) samplers exposed in a strong

437   water current for several months may reach equilibrium for compounds with a log K_{ow} $\leq$6.

438   Nevertheless, for compounds with a higher K_{ow} such as for PAH with five condensed rings, PCB with

439   more than five chlorine atoms in the molecule or BDE with more than four bromine atoms per

440   molecule, it is challenging to attempt equilibrium attainment in an open system with WBL resistance

441   controls the uptake. Although it is possible to further decrease sampler thickness in order to extend

442   the equilibration range towards more hydrophobic compounds, it would require a change of sampler

443   construction. Sampler sheets thinner than 100 μm are not available, and if they were, they would

444   most likely be fragile and not suitable for exposure in running water. Use of silicone layer of less than

445   20 μm range with increased sampler surface area is applicable e.g. in form of silicone-coated glass

446   surfaces (Reichenberg et al., 2008).

447   The „equilibration" of samplers previously pre-incubated with upper layer of the sediment followed

448   by deployment in the overlaying water column enabled to attain HOC concentrations in samplers

449   close to the equilibrium with water for a broad range of compounds, approximately up to ~log K_{ow} of

450   5.5. If the HOC concentration in the sampler that has been pre-equilibrated with sediment was close

451   enough to the equilibrium value with water (e.g. within 20%), the following equilibration with water

452   could be achieved after significantly shorter time period than in a situation when the uptake in water

453   proceeded from a zero initial sampler concentration. However, the possibility to extend the $K_{pw,0.95}$

454   range to higher values by using this approach is limited. It can be shown (from Equation 5) that the

455    $K_{pw,0.95}$ of a sampler pre-equilibrated to DEQ_p of 80% and then exposed in water, is only by a factor of

456   two higher than that of a sampler exposed only in water (without pre-equilibration). This

457   corresponds to $K_{pw,0.95}$ range extension barely by 0.3 log units. Nevertheless, even this approach does

458   not seem to be applicable in general, since chemical activity of some specific compounds (e.g. some

459   DDT metabolites or PBDE in our case) seem to deviate in sediment and water column. This difference

460   is critical especially for very hydrophobic compounds, for which accumulation or desorption from

20

461 sampler proceeds very slowly in reflection of the change of chemical activity in the exposure

462 medium. Still, the outlined approach can be useful since during re-equilibration in water, the sampler

463 may gain or lose HOC, and the direction of C_p change will directly indicate the difference in chemical

464 activity between water and sediment.

465 For estimation of C_w or other related measures of chemical activity in water for very hydrophobic

466 HOC the kinetic method using PRCs remains the method of choice, as outlined in the available

467 guidance document (Smedes and Booij, 2012). Since the concentrations of HOCs in water are often

468 very low, the integrative character of passive sampling renders long sampler exposures using thin

469 samplers exposed in turbulent water a favorable exposure method. Estimation of R_S values necessary

470 for C_w estimation depends on the accuracy of PRC measurement that are partially eliminated from

471 samplers during exposure as well as to the accuracy of their K_{pw} values. Moreover, R_S accuracy can be

472 improved by applying more PRCs in the hydrophobicity range where a partial PRC release

473 (approximately between 20 and 80%) is expected during exposure. During long sampler exposures

474 that range is shifted towards more hydrophobic compounds, which implicates two important issues

475 to be considered in future studies: a) selection of a suitable range of more PRCs equally distributed

476 over the range of log K_{ow} between 6 and 8; and b) determination of accurate K_{pw} values for those

477 compounds.

478 ## Acknowledgment

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

Passive sampling method / Advantageous property	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	j,k,l

487 [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,
488 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)

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Figure 1
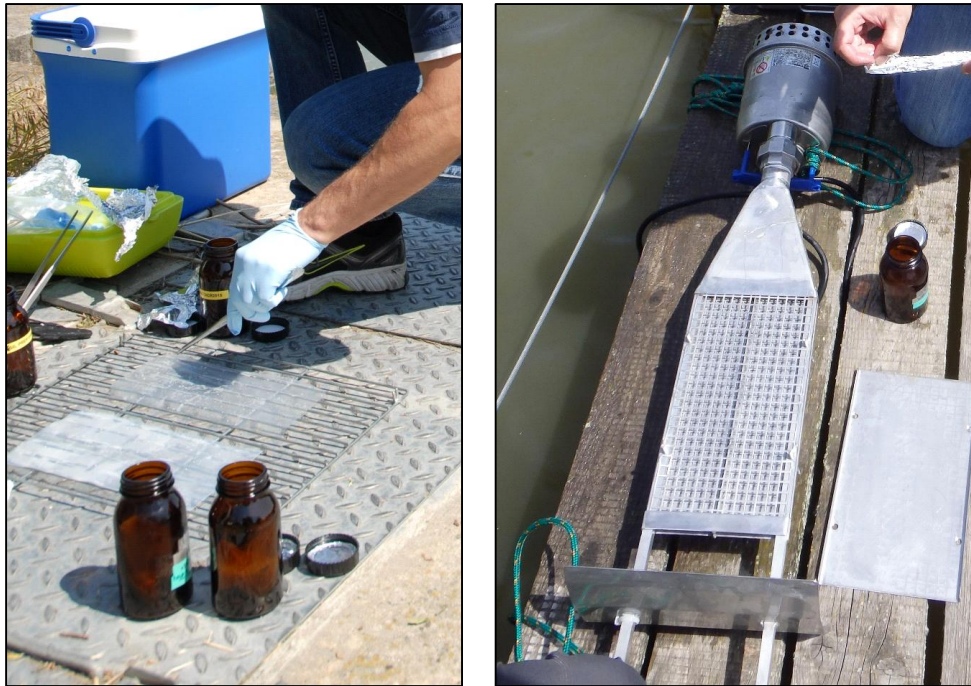**Click here to download Figure: Figure 1.docx**

Figure 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).
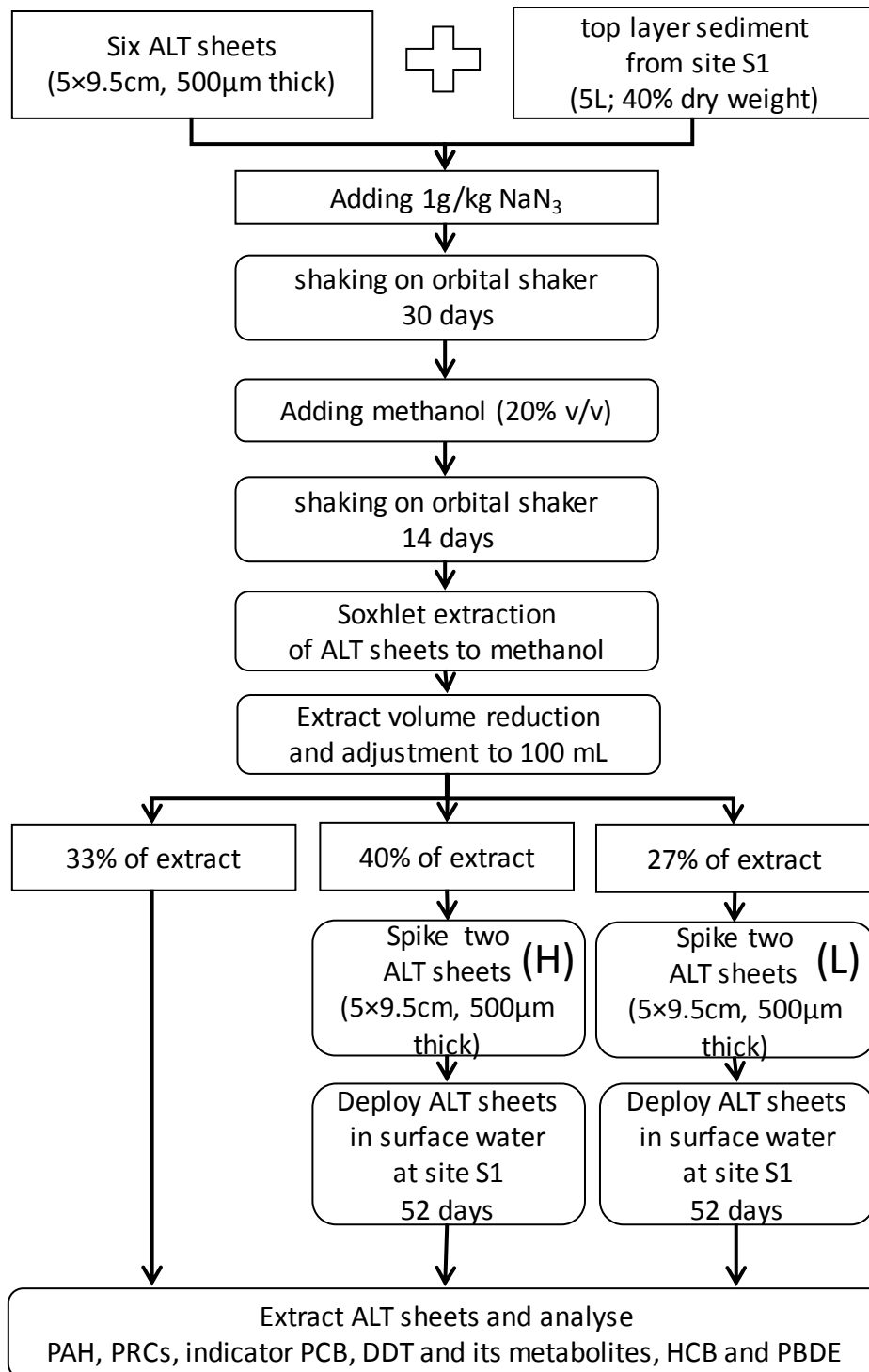
Figure 2
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Figure 2. Workflow of an experiment performed to investigate whether passive sampler pre-equilibration with surface layer of sediment, followed by passive sampler deployment in water column adjacent to the sediment, can speed up the sampler equilibration in water.
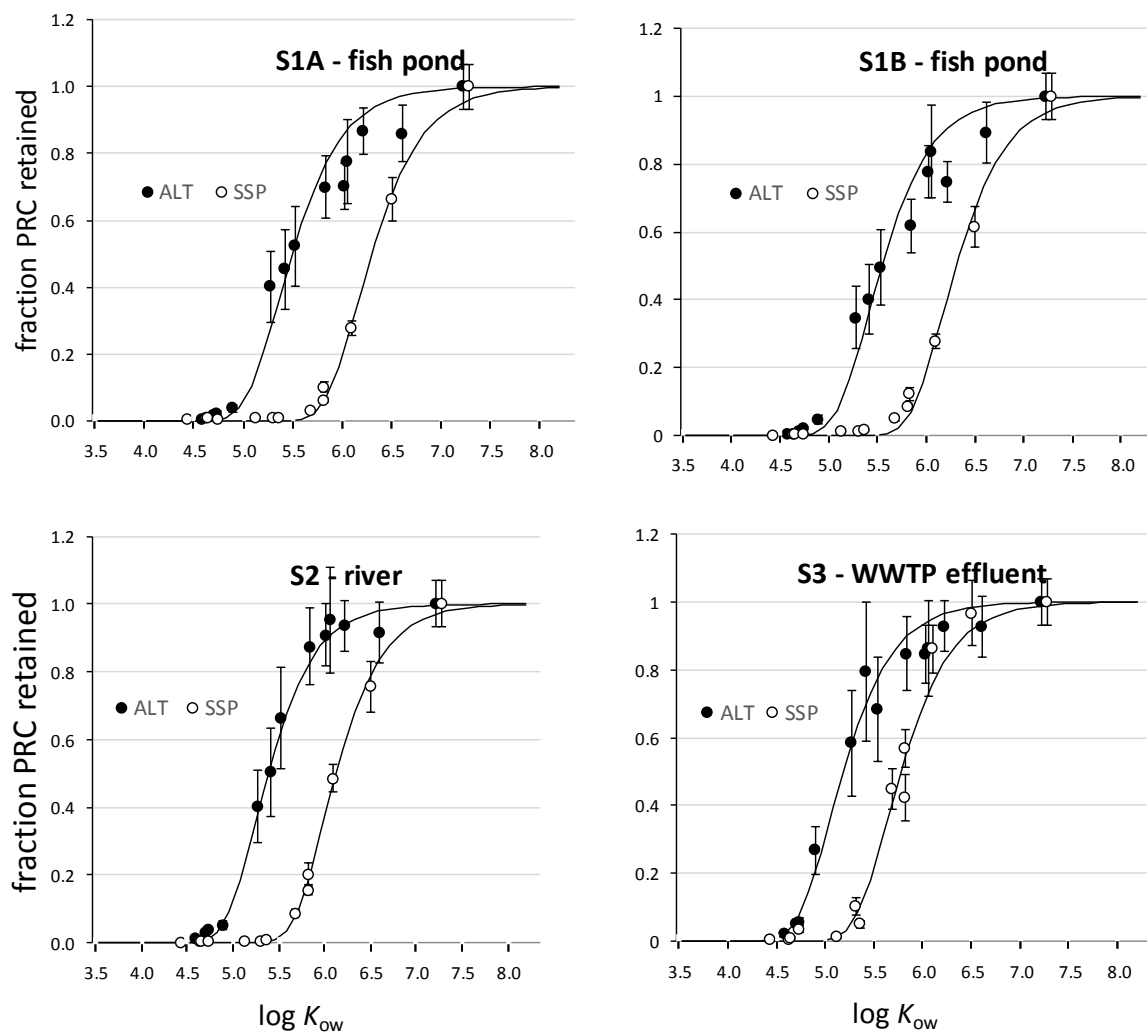
Figure 3. Retained PRC fractions in two co-deployed silicone passive samplers ALT and SSP with film thicknesses of 500 and 125 μm (marked by black and white dots), respectively, as a function of log K_{ow}. Error bars represent 2 standard deviations and are estimated from typical sampling repeatability. The model fits of experimental data (Equation 6) are displayed as drawn lines
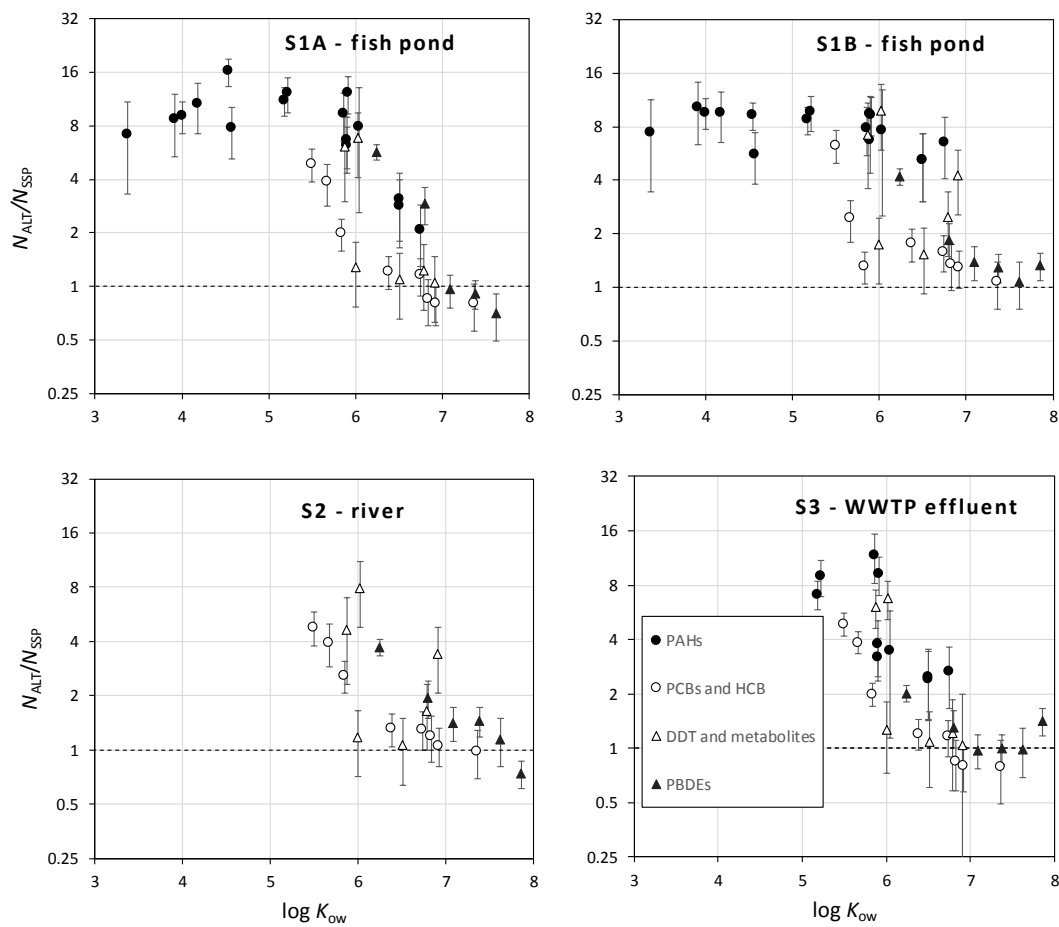
Figure 4 Ratio of compound amounts (N_{ALT}^{t}/N_{SSP}^{t}) absorbed by two co-deployed silicone passive samplers ALT and SSP with film thicknesses of 500 and 125 μm, respectively, plotted versus log K_{ow}. Error bars represent 2 standard deviations and are estimated from typical sampling repeatability. 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.
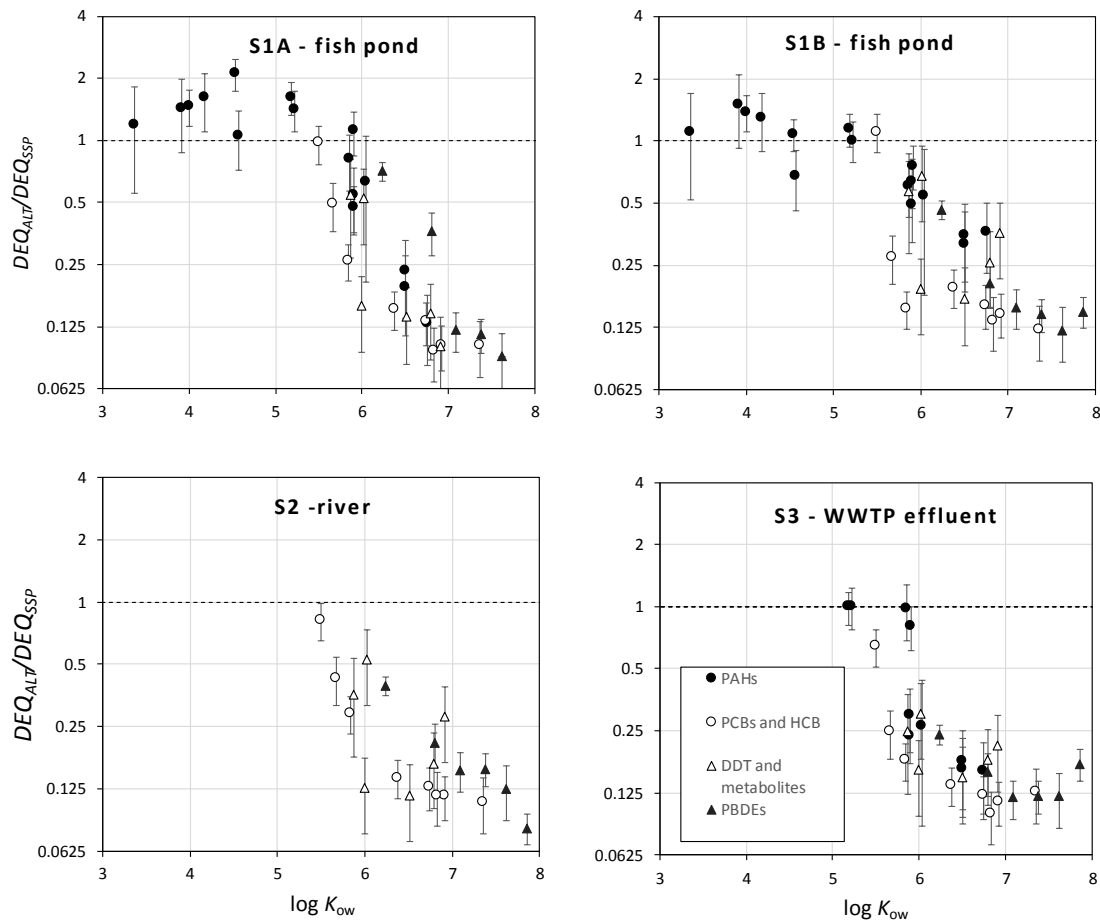
Figure5 Ratio of equilibrium degree (DEQ_{ALT}/DEQ_{SSP}) attained by the two co-deployed samplers, i.e. ALT and SSP with film thicknesses of 500 and 125 µm, respectively, plotted versus log K_{ow}. The ratio was calculated using Equation 11. Error bars represent 2 standard deviations and are estimated 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.
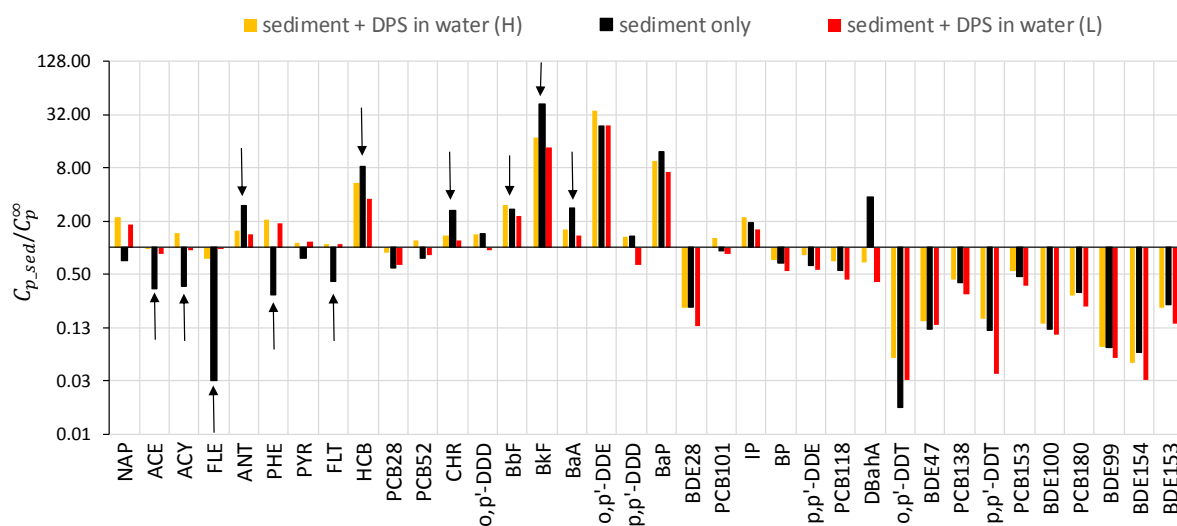
Figure 6. Ratios of the HOC concentrations in the sediment pre-equilibrated ALT samplers deployed for 52 days, with those in samplers deployed in a regular way and converted to equilibrium (C_p^∞) using Equation 12. The black bar represents this ratio for the unexposed sediment pre-equilibrated sampler, 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. 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 chapter 2.4

Supplementary information revised

Supplementary information revised with track changes visible