Comparing polyethylene and polyoxymethylene passive samplers for measuring sediment porewater concentrations of polychlorinated biphenyls: Mutual validation and possible correction by polymer-polymer partition experiment

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3 samplers for measuring sediment porewater

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6 partition experiment

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18 5005 words + 3 Figs. + 1 Table

19 Highlights

- 20 • PCBs in porewater were measured with polyoxymethylene (POM) and polyethylene (PE).
- 21 • Equilibrium was reached for PE within 28 d but not for POM even at 96 d.
- 22 • C_{free} from a 28 d exposure to sediment slurries were PE > POM by a factor of 2.
- 23 • POM/PE partition experiment may be useful to correct the observed differences.

24

25 Graphical Abstract

26

27

28 Abstract

29 Two sediment passive samplers, polyethylene (PE) and polyoxymethylene (POM), were compared
30 and mutually validated for measuring freely dissolved concentrations (C_{free}) of polychlorinated
31 biphenyls (PCBs) in sediment porewater. PE and POM strips in commonly used dimensions (30 and
32 76 μm in thickness, respectively) were exposed to sediment slurries for 28 d. The C_{free} values
33 calculated using literature polymer-water partition coefficients were consistently higher for PE than
34 for POM by a factor of 2 on average. Time series experiments over 96 d show that 28 d are
35 sufficient for attaining partition equilibrium of PCBs for PE, whereas even 96 d may not be enough
36 for POM. To gain additional insight, POM and PE strips were co-exposed to bovine serum albumin
37 suspension spiked with PCBs. The POM/PE concentration ratios increased over 56 d, and the ratios
38 at 28 d were in agreement with the POM-to-PE ratios of PCB concentrations from the 28-d
39 sediment slurry experiments. This agreement suggests that the use of apparent POM-water
40 partition coefficients (i.e., non-equilibrium concentration ratios) suitable for a 28-d exposure to
41 sediment slurries may correct the non-attainment of equilibrium and could provide more accurate
42 C_{free} values.

43

44 Keywords

45 Freely dissolved concentration, sediment porewater, passive sampling, sorption kinetics,
46 equilibrium partitioning

47

48 1. Introduction

49 Hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs), polycyclic
50 aromatic hydrocarbons (PAHs), and 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane and its
51 metabolites (DDTs) tend to accumulate in the sediment of aquatic environments. The freely
52 dissolved concentration (C_{free}) in porewater has been identified as a more suitable metric than the
53 whole-sediment concentration for assessing the bioaccumulation potential in and toxic effects on
54 benthic organisms, as C_{free} also reflects the bioavailability of the chemical (Di Toro et al., 1991). In
55 the past two decades, active research has been performed to develop and apply the concept of
56 passive sampling methods (PSMs) to infer C_{free} in sediment porewater (Mayer et al., 2000; Jonker
57 and Koelmans, 2001; Williamson et al., 2002; Vinturella et al., 2004; Cornelissen et al., 2006a;
58 Tomaszewski and Luthy, 2008; USEPA, 2012; Ghosh et al., 2014; Lydy et al., 2014; Mayer et al.,
59 2014; Arp et al., 2015; Booij et al., 2016). In PSMs for sediment, a polymeric phase (i.e., passive
60 sampler) is either buried in sediment *in situ* (e.g., Tomaszewski and Luthy (2008), Cornelissen et al.
61 (2008)) or exposed to sediment slurry in the laboratory (e.g., Mayer et al. (2000)) until the partition
62 equilibrium between the polymer and the sediment slurry is established. The polymer phase
63 concentration of the target chemical (C_p) is measured and then converted to C_{free} via Eq. (1).

$$64 \quad C_{\text{free}} = C_p / K_{\text{pw}} \quad (1)$$

65 K_{pw} is the polymer-water partition coefficient of the contaminant of concern. PSMs allow highly
66 sensitive measurements of C_{free} for HOCs, because K_{pw} , thus enrichment from water into the
67 polymer is generally high for HOCs. PSMs may be conducted in a non-equilibrium regime as well,
68 provided that appropriate corrections can be made, e.g., through performance reference
69 compounds (PRCs) that are pre-loaded to the polymer phase. The PSM-measured concentration is
70 the “truly” dissolved concentration in porewater, in contrast to the porewater concentration
71 measured by a conventional filtration or centrifugation method followed by solvent extraction,
72 which unavoidably co-extracts the dissolved organic matter (DOM)-bound fraction of the chemical
73 and over-estimates the freely dissolved concentration. A number of recent studies have shown that
74 C_{free} values measured by PSMs can explain and/or predict the extent of bioaccumulation in benthic
75 organisms (Kraaij et al., 2003; Cornelissen et al., 2006b; Sun and Ghosh, 2008; Tomaszewski et al.,
76 2008; Friedman et al., 2009; van der Heijden and Jonker, 2009; Ruus et al., 2010; Gschwend et al.,
77 2011; Muijs and Jonker, 2012; Fernandez and Gschwend, 2015; Maruya et al., 2015; Joyce et al.,

2016). Studies are also emerging that support the use of PSM-measured C_{free} for the assessment of toxicity to benthic organisms (Xu et al., 2007; McDonough et al., 2010; Harwood et al., 2013).

For validation of the PSMs, it would be desirable to compare the PSM-measured C_{free} with those measured based on a different measurement concept. However, other methods have various known problems (e.g., DOM interference as described above) or limited applicability (e.g., the air-bridge technique, restricted to relatively volatile compounds). Since PSMs appear to be the most reliable to measure C_{free} for now (Burgess et al., 2013), comparing the results obtained with two or more types of passive sampler, particularly those with substantially different characteristics, should be useful for validation purposes. Such comparative studies are available but still limited in the literature (Lydy et al., 2014).

As reviewed recently (Ghosh et al., 2014; Lydy et al., 2014), frequently used sediment passive samplers are polydimethylsiloxane (PDMS) fibers (Mayer et al., 2000; Maruya et al., 2009; Lang et al., 2015), polyethylene (PE) strips (Tomaszewski and Luthy, 2008; Fernandez et al., 2009), and polyoxymethylene (POM) strips (Jonker and Koelmans, 2001; Cornelissen et al., 2006a; Hawthorne et al., 2009; Hawthorne et al., 2011). Gschwend et al. (2011) compared the C_{free} values measured by several PSMs for 7 PCB congeners and showed, among others, that the differences in C_{free} were by up to a factor of 5 between PE and POM strips tumbled with sediment in pre-determined equilibration times. Oen et al. (2011) used PE and POM strips for profiling the vertical PCB distribution in field sediment, finding a factor of up to two difference between both methods (PRC-corrected). Perron et al. (2013a) measured C_{free} of PCBs and PAHs in the field and showed that, on average, a factor of 3 difference existed between POM and PE-measured C_{free} (PRC-corrected), though the authors also noted that the error can be much larger for other compounds in another article (Perron et al., 2013b). Fernandez et al. (2014) deployed PE strips, POM strips, and PDMS fibers in the field and reported an agreement within 1 order of magnitude in C_{free} between PE and POM even when the results were normalized with PRCs. The results from PDMS fibers, used without PRCs, were up to a factor of 230 off the PE results likely because of non-equilibrium caused by a limited mass transfer to PDMS fibers in their deployment, as discussed by the authors. Taking all these previous studies together, it may be concluded that differences between C_{free} measured by different PSMs are expected to be within a factor of 2 to 3 in many cases but can be an order of magnitude. This size of uncertainty may be considered acceptable for screening purposes, but it

108 may not, e.g., for a potential use in regulatory compliance measurements, which generally need
109 higher accuracy.

110 The accuracy of K_{pw} might explain a large fraction of the uncertainty in PSMs (Lydy et al.,
111 2014) because accurate determination of high K_{pw} values for HOCs is challenging. Recently, Gilbert
112 et al. (2016) proposed to measure and use polymer-polymer partition coefficients for calibration,
113 property evaluation, and data consistency tests of multiple passive samplers. This is a promising
114 approach for the consistency test of sediment passive samplers because polymer-polymer partition
115 coefficients can be much more accurately measured than polymer-water partition coefficients
116 (Gilbert et al., 2016), primarily due to the fact that the error-prone measurement of low aqueous
117 phase concentrations can be avoided. For two given polymers P1 and P2 equilibrated with the same
118 sediment sample, the following relationships exist.

$$119 \quad C_{free} = C_{P1}/K_{P1/w} = C_{P2}/K_{P2/w} \quad (2)$$

120 Here, C_{P1} and C_{P2} are the concentrations in P1 and P2, respectively, in equilibrium with the common
121 sediment, and $K_{P1/w}$ and $K_{P2/w}$ are P1-water and P2-water partition coefficients, respectively. From
122 the second relationship in Eq. (2), we can obtain

$$123 \quad C_{P2}/C_{P1} = K_{P2/w}/K_{P1/w} \quad (3)$$

124 From the thermodynamic cycle, we have $K_{P2/w}/K_{P1/w} = K_{P2/P1}$, where $K_{P2/P1}$ is the partition coefficient
125 between P2 and P1. Inserting this in Eq. (3), one can obtain $C_{P2}/C_{P1} = K_{P2/P1}$. Thus, the ratio of the
126 concentrations in two passive samplers should be equal to the respective polymer-polymer
127 partition coefficient. Thus, polymer-polymer partition coefficients may be useful to enhance mutual
128 comparison of two passive samplers.

129 Additional uncertainty in PSM measurements may come from non-equilibrium between the
130 sampler and porewater. A fixed (pre)equilibration time of, e.g., 28 d is often adopted for a practical
131 reason (Jonker et al., 2007), which however can result in non-attainment of equilibrium and thus
132 underestimation of C_{free} . POM, particularly, can have such problems because of its low diffusivity
133 for sorbing compounds (Rusina et al., 2007). Previous studies reported inconsistent equilibrium
134 times for POM. Hawthorne et al. (2009) concluded from their 84-d sediment slurry experiments
135 that 28 d are sufficient to obtain $\geq 87\%$ of the equilibrium concentrations for PCBs. However, Arp et

al. (2015) conducted a similar experiment and found 55–98% of equilibrium at 28 d, suggesting an underestimation of up to a factor of 2 if the experiment is terminated at 28 d.

In this study, PE and POM strips were used to measure PCB concentrations in sediment porewater. The results were compared with the aim to mutually validate both passive samplers. PE has apolar phase properties with high to moderate diffusivity, and some sediment particles adhered to the surface cannot be removed even with intensive wiping. In these regards, PE is similar to another frequently used passive sampler material, PDMS. In contrast, POM is a polar phase and its smooth surface makes it easy to be cleaned. A disadvantage of POM is its generally low diffusivity, as mentioned above. Thus, PE and POM have substantially different properties, and mutual validation of PE and POM passive samplers should put more reliability on both methods. In addition, time-series experiments with PE and POM in a sediment slurry system were performed to revisit the influence of exposure time on the measurements. Furthermore, a polymer-polymer partition experiment was conducted to gain additional insight into the sorption properties of PE and POM.

2. Materials and Methods

2.1. Materials

Acetone and *n*-hexane (PCB analysis 5000 grade), methanol (HPLC grade), bovine serum albumin (BSA, lyophilized powder), and silica gel (Wakogel® Q-22) were purchased from Wako Pure Chemical Industries, Japan. Granular copper was obtained from Kishida Chemical, Japan. NaN₃ powder (99.5%) was purchased from Sigma-Aldrich. PCB standard (EC-5085) containing 35 major congeners was obtained from Cambridge Isotope Laboratories, US. In the experiments that use sediments, 15 selected PCB congeners (IUPAC# 18, 52, 44, 66, 101, 87, 110, 149, 118, 153, 105, 187, 128, 180, 170) were quantified because of their relatively high abundance in our samples, frequent detection in other environmental samples in the literature (e.g., Mizukawa et al. (2009)) and the wide coverage of partition properties. In the POM/PE partition experiment (see below), all 35 congeners were considered to maximize the information obtainable from the experiment.

PE film (30 µm in thickness; Okura Industrial Co., Ltd., Japan) and POM film (76 µm in thickness, CS Hyde Company, US) were cut into strips with a size of 6 x 2 cm and 6 x 1.5 cm,

165 respectively. These strips were cleaned with *n*-hexane, acetone, and methanol in an ultrasonic bath
166 each for 1 h.

167 2.2. Sediment samples

168 Sediment samples were collected at seven sampling sites in the inner part of Osaka Bay (see Fig. S1)
169 on November 25, 2015. Six sites (O1–O5, Y) are in the immediate vicinity of the shore. More
170 specifically, Sites O2 to O5 are at the mouths of major rivers flowing into Osaka Bay, and Site Y is
171 located in the Osaka Nankou Bird Sanctuary, an artificial wetland constructed on reclaimed land.
172 Site O6 is 6–8 km off the shore. All sampling sites are close to the city of Osaka and highly
173 influenced by human activities.

174 Sediment samples were collected using an Ekman grab sampler. The top layer (ca 2 cm) was
175 sampled with a stainless steel spoon and stored in a stainless steel container with a Teflon-lined lid.
176 At Site O3, in addition to the top 2 cm sample (O3-2cm), a larger amount of sediment was retrieved
177 from top ca 10 cm to be used for the kinetic experiments. This sample is referred to as O3-10cm.
178 The collected samples were transported on ice to the laboratory, transferred to glass bottles with
179 aluminum lining, and stored in a fridge. Samples were well homogenized, and large particles and
180 debris were removed by hand or avoided when the samples were used for the experiments.

181 Sample information is presented in Table S1. Water content was measured by drying the
182 sample at 105°C overnight. Organic carbon contents were measured using a JM3000N CN analyzer
183 (J-Science, Kyoto, Japan) after pre-treatment with HCl vapor to remove inorganic carbon.

184 2.3. Twenty-eight-day passive sampling experiments with sediment slurries

185 Porewater concentrations of PCBs were measured using POM and PE samplers in a laboratory
186 condition. Wet sediment sample (25 g) was weighed into a vial, which received 15 mL of 500 mg/L
187 NaN₃ solution and a preweighed POM or PE strip. Three replicate vials were prepared for each
188 sediment sample and each polymer type. The vials were closed with PTFE-lined caps and shaken on
189 an NR-10 horizontal shaker (Taitec, Japan) at 150 rpm. After 28 d, the polymer strips were taken
190 from the vials, cleaned thoroughly with moist Kimwipe, and ultrasonically extracted with two times
191 5 mL *n*-hexane/acetone (1:1 vol) for 2 h each. A few strips were extracted once again but no
192 detectable PCBs were found, confirming that the two times ultrasonic extraction is sufficient for
193 quantitative extraction of PCBs from the used polymer strips. Often, the cutting edge of polymer
194 strips was more difficult to clean. In this case, the edge was cut off before ultrasonic extraction and

195 polymer strips were weighed again after extraction and air-drying. A separate test confirmed no
196 change in polymer weight before and after ultrasonic extraction. The extract was treated with HCl-
197 activated copper to remove sulfur, dried under a nitrogen stream, reconstituted with a known
198 volume of *n*-hexane, and analyzed for PCBs.

199 2.4. Sampling kinetics

200 To assess passive sampling kinetics, 17 vials for each polymer type were prepared with sediment
201 O3-10cm, exactly as described above. For POM, three vials each were retrieved after 11, 20, 28, 42,
202 and 56 d. The remaining two vials, originally intended as backups, were collected at 96 d. Similarly,
203 for PE, three vials each were collected after 7, 14, 28, 42, and 56 d, and two vials after 96 d. The
204 slightly different sampling times for POM and PE were due to adaptation to the personal working
205 schedule. The collected polymer strips were treated exactly as described in the previous section.

206 The first order (Eq. (4)) and the second order (Eq. (5)) rate equations were fitted to the data,
207 as was done by Arp et al. (2015).

$$208 \quad C_p = C_{p,eq} \times (1 - e^{-k_1 t}) \quad (4)$$

$$209 \quad \frac{1}{C_{p,eq} - C_p} = \frac{1}{C_{p,eq}} + k_2 t \quad (5)$$

210 Where $C_{p,eq}$ is the equilibrium concentration in polymer, and k_1 and k_2 are the first order and the
211 second order rate constants, respectively. $C_{p,eq}$ and k_1 (or k_2) were adjusted to the data using
212 GraphPad Prism 6.

213 2.5. Whole-sediment PCB concentrations

214 A portion of each sediment sample was freeze-dried using an FD-550P freeze-dryer (Tokyo
215 Rikakikai, Tokyo, Japan). Dried samples were gently ground with a mortar and pestle. The
216 powdered sample (0.5 or 1 g) was ultrasonically extracted with 10 mL hexane/acetone (1:1 by
217 volume) three times, each for 10 min. The combined extract was then centrifuged at 350 *g* and
218 filtrated with a Whatman GF/F filter to remove sediment particles. After concentration to ca 5 mL,
219 the extract was treated with activated copper overnight and cleaned over silica gel deactivated with
220 5 wt% water. The resulting solution was dried, reconstituted with *n*-hexane and subjected to the
221 PCB analysis.

2.6. POM/PE partition experiment

In this experiment, PCBs were allowed to partition between POM and PE strips in aqueous solution of bovine serum albumin (BSA). BSA was added to water because it has been reported that BSA largely accelerates the mass transfer through the aqueous boundary layer between water and the polymer phase (Kramer et al., 2007; Endo and Goss, 2011; Zhang et al., 2011). In the literature, it was shown that benzo[ghi]perylene, a highly hydrophobic PAH, reached three-phase partition equilibrium in a BSA-water-PDMS fiber system within 24 h (Endo and Goss, 2011), whereas it would need weeks or longer for equilibration in a pure water-fiber system (Endo et al., 2011). A previous study (Gilbert et al., 2016) used 40% methanol/water mixture to enhance the polymer-polymer partitioning, yet the authors of the study noted that a possible cosolvent effect of methanol dissolved in polymer can be significant. This effect could be larger for POM than PE and PDMS, as POM is a polar, H-bond acceptor phase, which is expected to absorb a substantial amount of methanol. BSA is unlikely to enter the polymer matrix and thus may be more suitable than methanol. Indeed, no significant effect of BSA addition on polymer sorption properties has been confirmed by previous studies (Heringa et al., 2006; Jahnke and Mayer, 2010; Endo and Goss, 2011; Oemisch et al., 2014).

POM and PE strips (3 × 1 cm) were cut out and cleaned, as described above. Nine vials were prepared, and each vial received 10 µL of PCB solution in *n*-nonane (250 ng/mL for each congener). The solvent was completely dried with a gentle stream of nitrogen gas. One piece each of POM and PE was inserted in the vial and mixed with 4 mL of 1 g/L BSA solution containing 500 mg/L NaN₃. The vials were shaken horizontally (100 rpm) and three vials each were collected after 8, 28, and 56 d. The POM and PE strips were retrieved, cleaned, and extracted as described above. For the POM/PE partition experiment, all 35 congeners contained in the used PCB standard were quantified.

2.7. PCB analysis

Measurements were performed with a gas chromatograph equipped with an electron capture detector (7890B GC-ECD, Agilent Technologies). Helium was used as carrier gas and a DB-5ms column (30 m × 0.25 mm i. d., 0.25 µm coating thickness; Agilent Technologies) for separation. Details for GC conditions were provided in the electronic supplementary file.

252 3. Results and Discussion

253 3.1. Whole-sediment concentrations

254 The measured whole-sediment concentrations of PCBs are shown in Table S2. The sum of the
255 concentrations for the 15 PCBs were similar in the sampled locations (10–26 µg/kg-dry), except for
256 relatively high concentrations detected in O3-2cm and O3-10cm samples (80 and 303 µg/kg-dry,
257 respectively). Organic carbon normalized distribution coefficients (K_{oc}) were calculated as $K_{oc} =$
258 $C_{sediment}/(f_{oc} C_{free})$, where $C_{sediment}$ is the whole-sediment concentration, C_{free} is the freely dissolved
259 concentration measured with PE (as explained in detail below), and f_{oc} is the fraction of organic
260 carbon. The K_{oc} values obtained for each congener were within 1 log unit (Table S3, Fig. S2). The
261 lowest values were well in line with Karickhoff's relationship with the octanol-water partition
262 coefficient (K_{ow}) (Karickhoff et al., 1981). These results suggest that PCB sorption by the sediment
263 samples used is governed mainly by recent, amorphous organic matter with possible additional
264 sorption by condensed carbonaceous sorbents in some samples (Cornelissen et al., 2005).

265 3.2. Twenty-eight day passive sampling experiments with sediment slurries

266 The concentrations of PCBs in POM and PE strips after a 28 d exposure to sediment slurries are
267 given in Tables S4 and S5. The depletion of the concentration in sediment due to the passive
268 sampling was estimated for each congener and sediment sample, and it was 10 ± 5 % (POM) and 9
269 ± 42 % (PE) of the original concentration with 29 % in the worst case (outlier). While a common
270 criterion for negligible depletion (5 %) was exceeded, these depletions were still considered low
271 and thus no correction was made for the following discussions.

272 Assuming that partition equilibrium was established within 28 d, C_{free} in sediment porewater
273 were calculated from the measured PCB concentrations in POM and PE via Eq. (1). For the POM-
274 water partition coefficients ($K_{POM/w}$), those measured by Hawthorne et al. (2009) were used. This
275 choice is appropriate, because the POM sheet used in this study was the same brand from the same
276 provider as in the study by Hawthorne et al. (2009). The PE-water partition coefficients ($K_{PE/w}$) were
277 from Smedes et al. (2009). $K_{PE/w}$ values in the literature were in good agreement, often with ± 0.1
278 log unit variation irrespective of the sources of PE (Lohmann, 2012). The values of $K_{POM/w}$ and $K_{PE/w}$
279 used are shown in Table 1. Fig. 1A compares the C_{free} obtained with POM ($C_{free-POM}$) and PE (C_{free-}
280 PE). While there is a positive correlation between $C_{free-POM}$ and $C_{free-PE}$, one can note that C_{free-}
281 POM is consistently lower than $C_{free-PE}$. The $C_{free-POM}/C_{free-PE}$ ratio is from 0.27 to 1.25 with a

282 geometric mean (GM) of 0.54 and a geometric standard deviation (GSD) of 1.4 (see Table S6). Thus,
283 on average $C_{\text{free-PE}}$ is roughly twice as much as $C_{\text{free-POM}}$. The differences are more congener-
284 specific than site-specific. The GM of $C_{\text{free-POM}}/C_{\text{free-PE}}$ ratios in seven sediment samples is 0.35
285 (PCB 153) to 1.09 (PCB 170) for each congener, while the GM of $C_{\text{free-POM}}/C_{\text{free-PE}}$ ratios across 15
286 congeners is 0.49 (Y) to 0.61 (O4) for each sediment sample. Possible reasons for this discrepancy
287 between POM and PE are discussed in the following sections.

288

Table 1. Logarithmic partition coefficients between passive sampling polymers and water for the studied PCBs.^a

PCB#	$K_{\text{POM/w}}^b$	$K'_{\text{POM/w-28d}}^c$	$K_{\text{PE/w}}^d$
18	5.12	4.90	4.90
52	5.65	5.33	5.55
44	5.65	5.30	5.48
66	6.08	5.67	5.95
101	5.90	5.72	6.18
87	6.05	5.77	6.18
110	6.20	5.79	6.16
149	6.11	5.97	6.59
118	6.32	6.07	6.53
153	6.64	6.14	6.81
105	6.38	5.98	6.44
187	6.44	6.09	7.01
128	6.35	6.11	6.74
180	6.67	6.38	7.24
170	6.54	6.39	7.25

^aL_{water}/kg_{polymer}. ^bHawthorne et al. (2009). ^cApparent partition coefficient from this study. See the text. ^dSmedes et al. (2009).

Fig. 1. Freely dissolved concentrations of PCB congeners in sediment porewater (C_{free}) measured with POM and PE passive samplers. (A) $K_{\text{POM/w}}$ from literature and (B) $K'_{\text{POM/w-28d}}$ from this study was used to obtain C_{free} by POM. The equilibration time was 28 d.

3.3. Sampling kinetics

Fig. 2 shows the concentration-time plots of PCBs 18, 52, 101 and 180 in POM and PE over 96 d. These four congeners cover the entire range of hydrophobicity tested. Plots for the other congeners are shown in the supplementary file (Figs. S3 to S5).

Fig. 2. Concentration-time profiles of four selected PCB congeners in POM (left) and PE (right) strips in sediment slurry. Solid curves indicate the fitted second order rate equation. Straight lines for PCBs 18, 52, and 101 in PE indicate the mean of all data and are shown because fitting of both the first and the second order rate equations to these data did not converge. Dotted lines are the respective 95% confidential intervals.

The PCB concentrations in POM increased over time without a clear indication of equilibrium within 96 d. The curve shapes for POM were closely similar for all congeners (Fig. S3). The model fit was slightly better with the second-order than the first-order rate equation, with R^2 0.24–0.79 and 0.16–0.75, respectively. The relatively low R^2 is mainly due to an unexpected drop of concentration at 56 d. If we remove the data at 56 d, R^2 improves to 0.50–0.92 and 0.42–0.93 for the second- and the first-order models, respectively. The concentration at 28 d was 63–83% of the second order model-extrapolated equilibrium concentrations, and 47–76% of the concentration at 96 d. These values agree well with the values reported by Arp et al. (2015), who found that C_{POM} at

28 d were 55–98% of equilibrium. The agreement is less good with the results by Hawthorne et al. (2009) showing faster attainment of equilibrium. Arp et al. (2015) also reported decreasing relative uptake kinetics with increasing hydrophobicity of PCBs, yet such a trend was not recognizable in the present study. Arp et al. (2015) claim that the POM-to-sediment weight ratio has a significant influence on the kinetics, and generally, the higher the ratio, the faster the uptake, thus the earlier the attainment of equilibrium. The weight ratio adapted in this work is $0.1 \text{ g}_{\text{POM}}/25 \text{ g}_{\text{wet sediment}}$, which is ca $0.01 \text{ g}_{\text{POM}}/\text{g}_{\text{dry sediment}}$. This is only slightly smaller than $0.03 \text{ g}_{\text{POM}}/\text{g}_{\text{dry sediment}}$ by Hawthorne et al. (2009) and Arp et al. (2015). The organic carbon content is about 3% in all three studies. Apparently, the weight ratio alone cannot account for the differential kinetic behavior. Note that, in the present kinetic study, the depletions of the PCB concentrations by POM were relatively large, i.e., 7–33% at 96 d. This is because K_{oc} for sample O3-10cm were relatively low (Table S3). A strong mass depletion in sediment could lead to a longer equilibration time, because a substantial fraction of the chemical has to desorb from the sediment particles and that intraparticle diffusion could play a significant role in the overall mass transfer from sediment to the sampler. Conversely, a mass depletion could also accelerate the equilibration, because a depletion in sediment means that the equilibrium concentration in POM that has to be achieved also becomes lower than that for the non-depletion case. However, neither of these effects appear to be important here, as concentration-time profiles for POM were similar for all congeners and independent of the extent of the depletions (Fig. S3). Since congeners with different $K_{\text{POM/w}}$ showed similar uptake profiles, it is expected that the mass transfer to the 76 μm thick POM strip is rate-limited by the internal diffusion in POM matrix rather than the aqueous boundary layer (Arp et al., 2015).

The concentrations in PE increased rapidly from the beginning of the experiment to the first sampling day (7 d) and stayed more or less constant to 96 d with some fluctuations. This observation suggests that 7 d are sufficient for partition equilibrium. Exceptions are PCBs 180 and 187, which needed a longer time (ca 28 d) to reach equilibrium. Fitting of the first- and second-order rate equations was not successful for most of the congeners, as data are missing within the first 7 d where the concentration increased. Booij et al. (2003) reported that most of PCBs reached equilibrium within 60 d in a system with sediment slurry and a 70 μm -thick PE strip. Assuming a linear relationship, this translates into the attainment of equilibrium within 25 d with 30 μm -thick PE, which agrees well with the results of this work.

To summarize, all target PCB congeners reach equilibrium within 28 d with PE in the experimental setting and samples used in this work, whereas 28 d appear to be insufficient for POM. It follows that 30 μm thick PE is more convenient passive sampler than 76 μm thick POM. In terms of the quicker equilibration. The concentrations of PCBs in POM at 28 d appear to be 50-80 % of the equilibrium, largely in line with Arp et al. (2015). This means that the termination of equilibration with POM at 28 d can cause at most an underestimation by a factor of 2 or 0.3 log units. These results can well explain the systematically and consistently lower values of C_{free} obtained with POM as compared to PE (Fig. 1A). The slower equilibration with POM may be related to the low diffusivity in POM matrix and its 2.5 times greater thickness than that of the used.

3.4. POM/PE partitioning ratios and their use for mutual validation of sediment passive samplers

Before evaluating the results of the POM/PE partition experiment, the recovery of PCBs was calculated. The recovery here is defined as the sum of the amounts detected in the POM and PE strips divided by the amount initially added to the vial. The recoveries of 35 congeners were 70 ± 8 , 81 ± 6 and 59 ± 5 % after an equilibration time of 8, 28, and 56 d, respectively (see Table S7 for all data). The unrecovered fraction should have remained in the BSA suspension or been lost from the test vial. To examine to what extent the former can account for the observed recoveries, we calculated the BSA-water partition coefficients ($K_{\text{BSA/w}}$) based on the mass balance calculations, assuming no loss of PCBs up to 28 d and near equilibrium between PE, water, and BSA (but not POM). The calculated $\log K_{\text{BSA/w}}$ from the data at 8 and 28 d was 5.4 to 7.2 and correlated with $\log K_{\text{ow}}$ (R^2 : 0.67 and 0.62 for 8 and 28 d, respectively). The obtained values are in line with literature experimental values, i.e., 5.02–5.23 for PCBs 78, 103, and 136 (Endo and Goss, 2011) and 6.78 for PCB 153 (Mäenpää et al., 2015). Particularly, the $\log K_{\text{BSA/w}}$ value we obtained for PCB 153 (i.e., 6.9, 6.7) is in excellent agreement with the literature value. Thus, we surmise that the 10–40% fraction that was not recovered from 8 d and 28 d samples is mainly due to the binding to BSA in the suspension. Nevertheless, the reduced recovery at 56 d may suggest some loss of PCBs from the vial, for example, due to a diffusive loss through the Teflon liner of the cap. As the recovery at 56 d is relatively low, the results from 56 d should be considered tentative.

The values of POM/PE concentration ratios ($C_{\text{POM}}/C_{\text{PE}}$) increased from 8 d to 56 d and approached the values of $K_{\text{POM/w}}/K_{\text{PE/w}}$ calculated based on the literature partition coefficients (Fig. 3, Table S8). The results can be interpreted that the equilibrium between POM and PE was not

376 established within 28 d but could be closely approached within 56 d. As the internal diffusion in PE
 377 is relatively quick and the aqueous boundary layer diffusion is accelerated by BSA, the observed
 378 non-equilibrium should be attributable to slow diffusion in POM. Fig. 3 also includes the ratio of
 379 PCB concentrations in POM and PE strips from the 28 d passive sampling experiments with
 380 sediment slurries (see section 3.2). Interestingly, this ratio closely agrees with $C_{\text{POM}}/C_{\text{PE}}$ from the
 381 POM/PE partition experiment at 28 d. Both ratios are ca a factor of 2 lower than $K_{\text{POM/w}}/K_{\text{PE/w}}$.
 382 Apparently, both sediment slurry and BSA suspension systems did not reach complete partition
 383 equilibrium, as also discussed above, but the extent of equilibration appears to be similar in these
 384 two systems.

385
 386 **Fig. 3. POM/PE partition coefficients ($K_{\text{POM/PE}}$) derived from literature $K_{\text{POM/w}}$ and $K_{\text{PE/w}}$, and**
 387 **POM/PE concentration ratios ($C_{\text{POM}}/C_{\text{PE}}$) from 28-d sediment passive sampling experiments (mean**
 388 **of 7 sediment samples) and POM/PE partition experiments (mean of 3 replicates). Error bars**
 389 **represent the standard deviations.**

390
 391 For the illustration purpose, $K'_{\text{POM/w-28 d}}$, an apparent partition coefficient between POM
 392 and water was calculated using $C_{\text{POM}}/C_{\text{PE}}$ from the 28-d co-exposure to BSA suspension and $K_{\text{PE/w}}$
 393 from the literature, as $K'_{\text{POM/w-28 d}} = (C_{\text{POM}}/C_{\text{PE}})/K_{\text{PE/w}}$ (Table 1). The concentrations in POM from the

394 28-d passive sampling experiments were divided by $K'_{\text{POM/w-28 d}}$ to give C_{free} . The results show that
395 C_{free} calculated this way agree well with C_{free} from PE (Fig. 1B). Although this agreement can be
396 expected from the results shown in Fig. 3, it can more clearly illustrate the possibility that the use of
397 apparent POM-water partition coefficients (i.e., non-equilibrium concentration ratios) could be
398 used to obtain C_{free} from passive sampling experiments in a pre-equilibrium condition. Obviously,
399 $K'_{\text{POM/w-28 d}}$ is not an equilibrium value and thus can be system-dependent. This non-equilibrium
400 approach without PRCs can only work if the uptake kinetics by POM is sufficiently similar in
401 sediment slurries and in BSA solution. Nevertheless, if the sampler uptake kinetics is largely
402 controlled by the internal diffusion in POM, the uptake kinetics should not be much dependent on
403 the external factors, and thus such non-equilibrium sampling with a non-equilibrium concentration
404 ratio may be justified.

405 This study mutually validated the accuracy of the 28 d ex-situ sediment slurry methods with
406 POM (76 μm) and PE (30 μm) strips, which gave C_{free} within around a factor of 2. The PE strip
407 appears to be more convenient material because of faster equilibration. While we were unable to
408 determine equilibrium POM-PE partition coefficients, possible correction to the POM results using
409 apparent partition coefficients derived from the polymer-polymer partition experiment was
410 suggested, which may render POM more useful alternative material particularly if particle adhesion
411 to other samplers is an issue. Further research is warranted as to how POM's uptake kinetics
412 depend on the experimental conditions, because consistent uptake kinetics is a prerequisite for
413 such correction.

414

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419

420 [Appendix A. Supplementary data](#)

421 Supplementary data related to this article can be found at ...

422

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