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## Determination and comparison of freely dissolved PAHs using different types of passive samplers in freshwater

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**Title Page (with Author Details)**

**Determination and Comparison of Freely Dissolved PAHs Using Different Types of Passive Samplers in River and Lake, USA**

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1 **Determination and Comparison of Freely Dissolved PAHs Using Different Types of**  
2 **Passive Samplers in River and Lake, USA**

3  
4 **ABSTRACT**

5 Polycyclic aromatic hydrocarbons (PAHs) are well-known for their recalcitrant properties  
6 and biotoxicity in organism leading to serious environmental and health problems. Despite  
7 various analytical methods available, accurate determination of bioavailable fraction is  
8 warranted in order to evaluate the precise toxic potentials of these compounds. Currently, the  
9 passive sampler has been used worldwide to measure the bioavailable PAHs in the environment  
10 using the equilibrium partitioning principle. In this study, we co-deployed using different types  
11 of passive samplers which are linear low-density polyethylene (LLDPE) and low-density  
12 polyethylene (LDPE) to determine freely dissolved concentration ( $C_{free}$ ) of PAHs using the  
13 performance reference compounds (PRCs) in Kentucky Lake (KL), Ohio River (OH), and  
14 Mississippi River (MS). The release of PRCs with high molecular weight was faster in LLDPE  
15 than in LDPE over time. Particularly, the  $f_{eq}$  of BeP- $d_{12}$  was 4 times higher in LLDPE than in  
16 LDPE regardless of the short sampling period of 2 weeks due to the thin thickness of LLDPE.  
17 The average freely dissolved PAH concentrations in LLDPE and LDPE during the exposure  
18 period ranged from 2.89 and 1.27 ng/L in KL, 8.13 and 3.31 ng/L in OH, and 5.19 and 3.82  
19 ng/L in MS, respectively. The results revealed that LLDPE is a suitable alternative tool to  
20 LDPE for both short-term and long-term monitoring of PAHs.

21 **Highlights**

- 22 - Freely dissolved PAH concentrations measured using different types of passive  
23 sampler in river and lake.  
24 - The fractional equilibrium ( $f_{eq}$ ) of PRCs with high molecular weight was affected by  
25 the water flow velocity and thickness of passive sampler.

26 - LLDPE is applicable to measure the average freely dissolved concentration ( $C_{free}$ ) over  
27 a short exposure period.

28

## 29 **1. Introduction**

30

31 Among organic constituents, polycyclic aromatic hydrocarbons (PAHs) are known to pose  
32 environmental risks due to their high persistence and hydrophobic properties. The term "PAHs"  
33 refers to a class of hydrophobic and lipophilic substances with two or more aromatic rings,  
34 possessing remarkable environmental transport properties (Keyte et al., 2013; Purcaro et al.,  
35 2013; Ramesh et al., 2022; Yebra-Pimentel et al., 2015). PAHs have two to six benzene rings  
36 and are usually classified into three types: low molecular weight compounds with two benzene  
37 rings (LMW), medium molecular weight compounds with three to four benzene rings (MMW),  
38 and high molecular weight compounds with five to six benzene rings (HMW).

39 PAHs are typically generated by incomplete combustion, such as from coal, boating  
40 activities, forest fires, industrial food processing, and ocean dumping, and can then enter the  
41 ocean through estuaries, runoff or air transport and resuspend from sediment layers  
42 (Lapviboonsuk and Loganathan, 2007; Maruya et al., 1997; Veiga et al., 2014). Even low  
43 concentrations of PAH in water and sediment can have environmental impacts due to their  
44 ability to bioaccumulate in organisms (Albers et al., 2003; Carls and Thedinga, 2010; Yim et  
45 al., 2005; Qiu et al., 2009). In addition to seawater and sediments, PAHs can also accumulate  
46 through the feeding activities of organisms such as fish and plankton (Bandowe et al., 2014;  
47 Nacher-Mestre et al., 2010; Wang et al., 2021). Furthermore, PAHs can pose health risks to  
48 humans due to their mutagenic and carcinogenic properties, and the US Environmental  
49 Protection Agency (USEPA) has classified 16PAHs as "priority pollutants" (Durant et al., 1996;  
50 USEPA, 2003; USEPA, 2009; Ramesh et. al. 2022).

51 The total concentration of HOCs in aquatic environments includes particulate concentration  
52 and dissolved concentration, which includes freely dissolved concentration ( $C_{free}$ ), colloid- and  
53 dissolved organic carbon (DOC)-associated concentration. Some researchers have measured  
54 HOC concentrations in water (Anderson et al., 2008; Li et al., 2006), mostly describing samples  
55 by their total or dissolved concentrations without taking into account DOC and colloid phase.  
56 However, several studies have shown that HOCs linked with colloid, DOC, and particles are  
57 not bioavailable (Gustafson and Dickhut, 1997; MacRae and Hall, 1998), and have discussed  
58 the weak association between the total concentration and the amount absorbed by organisms  
59 (Gomez-Eyles et al., 2011).

60 Passive sampling technology is currently an alternative method that allows measurement of  
61 the freely dissolved HOC concentrations using equilibrium partitioning between the passive  
62 sampler and matrix such as porewater, air, and aquatic environment, while grab sampling  
63 provides the total concentration or dissolved concentration of HOC at the time of sampling  
64 (Booij et al., 2003a; Pevery et al., 2015). The advantages of the passive sampling approach  
65 include easier handling, cost-efficiency, and the ability to measure bioaccumulated and time-  
66 weighted average concentrations ( $C_{TWA}$ ). Among the various types of passive samplers, low-  
67 density polyethylene (LDPE), semipermeable membrane devices (SPMD), triolein-embedded  
68 cellulose acetate membranes (TECAME), and silicon rubber (SR) have been used for non-polar  
69 organic compounds such as PAHs and polychlorinated biphenyl (PCBs). For polar organic  
70 compounds, polar organic chemical integrative sampler (POCIS) and Chamcatcher have been  
71 used to monitor the bioavailable concentration (Emelogu et al., 2013; Fedorova et al., 2004;  
72 Greenwood et al., 2007; Huckins et al., 1993; Ke et al., 2006; King et al., 2020; Sobotka et al.,  
73 2022).

74 Highly hydrophobic compounds ( $\log K_{OW} > 5$ ) take a long time to reach equilibrium in  
75 aquatic environments due to their high molecular weight (Lohmann, 2012). As a result,

76 biofouling can grow on the surface of the passive sampler over time. Performance reference  
77 compounds (PRCs), which have similar physicochemical properties to target compounds and  
78 are not present in the environment, have been used in several investigations to minimize  
79 biofouling and correct non-equilibrium compounds (Booij et al., 2010; Schintu et al., 2018).  
80 PRCs have been used to determine the degree of equilibrium achieved and subsequently correct  
81 for non-equilibrium if target compounds cannot reach equilibrium between passive sampler  
82 and matrix (Adams et al., 2007; Joyce et al., 2015). The time to reach equilibrium depends on  
83 the molecular weight of the target compound, water flow velocity, and the thickness of the  
84 passive sampler (Lohmann, 2012). Particularly, a passive sampler with a thin thickness is faster  
85 to reach equilibrium than a thick sampler and then PRCs would be rapidly reach equilibrium.  
86 As linear low-density polyethylene (LLDPE) with a thin thickness of 10  $\mu m$  was found to be  
87 a useful passive sampler in our previous study (Kim et al., 2020), we used LLDPE as a new  
88 passive sampler to measure freely dissolved PAH concentrations in river and lake to compared  
89 with LDPE, which has been widely used until now and compared the fractional equilibrium  
90 ( $f_{eq}$ ) of high molecular weight PRC compounds between two passive samplers to confirm which  
91 one reaches equilibrium faster between LLDPE and LDPE. Finally, we evaluated which  
92 method, passive sampling or conventional sampling, was better.

## 93 2. Theory

94

95 Passive sampler-water partition coefficient ( $K_{PW}$ ) (mL/g) is crucial to calculating freely  
96 dissolved concentration.

$$97 \quad K_{PW} = \frac{C_{PS}^{\infty}}{C_W^{\infty}} \quad (1)$$

98 Here,  $C_{PS}^{\infty}$  and  $C_W^{\infty}$  are concentration in passive sampler (ng/kg) and in water (ng/L) at  
99 equilibrium state, respectively. The log  $K_{PW}$  values of LLDPE were obtained from a previous

100 study (Kim et al., 2020) and additional experiment (not published), while the log  $K_{PW}$  values  
101 of LDPE were obtained from Lohmann (2012) and detailed in Table S1.

102 The  $K_{PW}$  value is known to be affected by changes in temperature (Booij et al., 2003b),  
103 therefore a modified version of the van't Hoff equation (eq. 2) (Lohmann, 2012) can be used  
104 to calculate different  $K_{PW}$  values at various temperatures.

$$105 \quad K_{PW}(T) = K_{PW}(298) \times e^{\left\{\frac{\Delta H_{PW}}{R} \times \left(\frac{1}{298} - \frac{1}{T}\right)\right\}} \quad (2)$$

106 where,  $K_{PW}(T)$  and  $K_{PW}(298)$  are constants at temperature T (K) and 298 K, respectively.  
107  $\Delta H_{PW}$  and  $R$  are the enthalpy of passive sampler-water partitioning (kJ/mol) and the universal  
108 gas constant (8.3143 J/mol/K), respectively.

109 Prior to deployment in the field, PRCs can be added into a passive sampler to assess the extent  
110 of equilibrium during the exposure time (Adams et al., 2007). When exposed to the  
111 environment, the PRCs in a passive sampler would be released into the water and the target  
112 compound would be absorbed into the passive sampler. The  $f_{eq}$  can be determined by equation  
113 3:

$$114 \quad f_{eq} = 1 - \frac{C_{PRC}^t}{C_{PRC}^0} \quad (3)$$

115 where,  $C_{PRC}^t$  and  $C_{PRC}^0$  are concentration of PRCs remaining after deploying in the  
116 environment (ng/g) and initial concentration of PRCs in passive sampler (ng/g), respectively.

$$117 \quad C_{free} = \frac{C_{PS}^t}{K_{PW}(T)} \times \frac{1}{f_{eq}} \quad (4)$$

118 where,  $C_{free}$  and  $C_{PS}^t$  are freely dissolved concentration in water (ng/L) and concentration  
119 of target compounds in passive sampler at exposure time (ng/kg), respectively.

120

121

### 122 3. Materials and Methods

#### 123 3.1. Materials and reagents

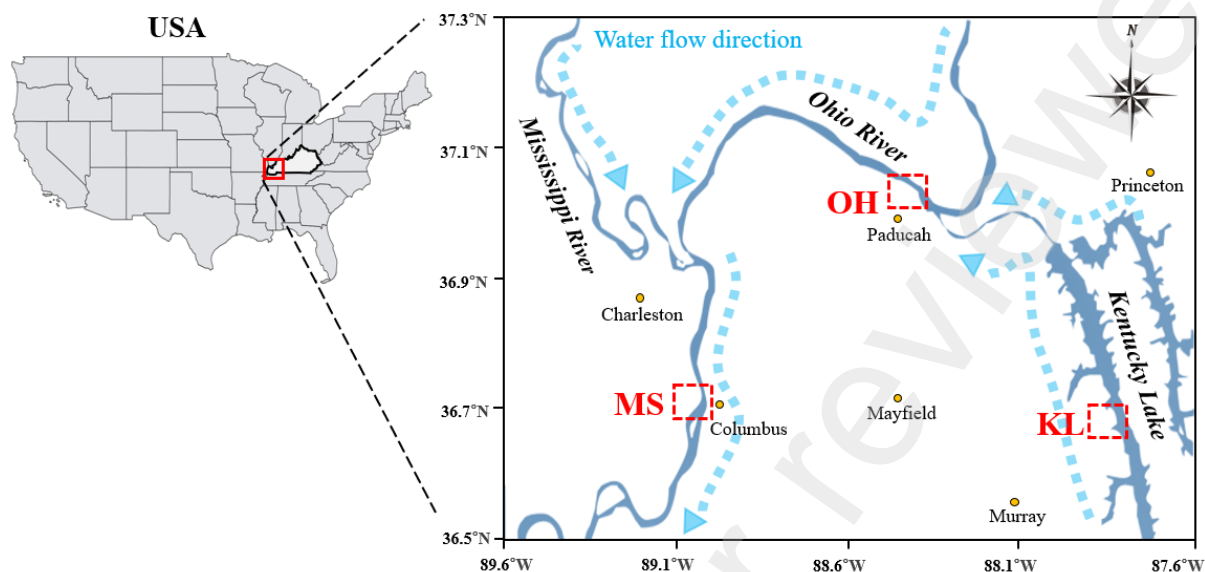
124 High purity dichloromethane and n-hexane were purchased from Fisher scientific, USA.  
125 Target compounds analyzed were 16 priority PAH compounds viz. naphthalene (NAP),  
126 acenaphthylene (ACY), acenaphthene (ACP), fluorene (FLR), phenanthrene (PHE),  
127 anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene  
128 (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP),  
129 indeno(1,2,3-cd)pyrene (IcP), dibenzo(a,h)perylene (DhA), and benzo(g,h,i)perylene (BgP)  
130 (Table S1).

131 For quality assurance and quality control purposes, we used five surrogate standards and  
132 one internal standard: naphthalene- $d_8$  (NAP- $d_8$ ), acenaphthene- $d_8$  (ACP- $d_8$ ), phenanthrene- $d_{10}$   
133 (PHE- $d_{10}$ ), chrysene- $d_{12}$  (CHR- $d_{12}$ ), perylene- $d_{12}$  (PER- $d_{12}$ ) and terphenyl- $d_{14}$  were obtained  
134 from AccuStandard (USA). PRCs included fluorene- $d_{10}$  (FLR- $d_{10}$ , MW:176.28), fluoranthene-  
135  $d_{10}$  (FLT- $d_{10}$ , MW:212.31) and benzo(e)pyrene- $d_{12}$  (BeP- $d_{12}$ , MW:264.4) obtained from  
136 AccuStandard (USA), and benzo(a)anthracene- $d_{12}$  (BaA- $d_{12}$ , MW:240.4) obtained from  
137 CHIRON (Norway).

138 LLDPE (10  $\mu\text{m}$  thickness) and LDPE (25.4  $\mu\text{m}$  thickness) were purchased from  
139 Cleanwrap, Korea and Film Gard, USA, respectively. Both passive samplers were cut into  
140 strips (~2 g) and pre-extracted in triplicate following hexane, dichloromethane, methanol, and  
141 deionized water using a sonication extractor (Hwashin Technology, Korea) to remove  
142 interfering substances. The pre-cleaned passive samplers were dried in a clean hood overnight  
143 to remove remaining water. Passive samplers were exposed to methanol:water (8:2, v/v)  
144 solution containing PRCs (con.: 10  $\mu\text{g}/\text{mL}$ ) for 19 days on the horizontal shaker at 120 rpm  
145 before deployment (Booij et al., 2002). PRCs-loaded passive samplers were immersed in  
146 deionized water for 1 day to remove methanol and then dried and kept at  $-20^\circ\text{C}$  until exposure.



147 3.2. Co-deployed passive samplers



148  
149 **Fig 1. LLDPE and LDPE were co-deployed at three stations in Kentucky, USA:**

150 **Kentucky Lake (KL), Ohio River (OH), and Mississippi River (MS). The blue dotted**  
151 **arrow indicates the direction of water flow.**

152  
153 The exposure was performed at three locations in the USA: Kentucky Lake (KL), Ohio  
154 River (OH), and Mississippi River (MS) (Fig 1, Table S2). Kentucky Lake is an artificial lake  
155 located in the southeastern region of the USA and is a mooring site for large vessels. The  
156 Mississippi River is the largest inland waterway in the USA and the seventh-largest river in the  
157 world, while the Ohio River is a major river in the eastern USA, flowing approximately 981  
158 miles (1,579 km) from Pittsburgh, Pennsylvania to Cairo, Illinois, where it meets the  
159 Mississippi River. These three regions can be influenced by the byproducts of fossil fuel  
160 combustion and biomass burning (e.g., wood-burning stoves, automobile exhaust, coal  
161 combustion). PAHs are still detected in these three locations and are being monitored to  
162 identify contamination sources (Lapviboonsuk and Loganathan, 2007).

163 Passive samplers loaded with PRCs (~2 g) were hung on a handmade stainless-steel frame  
164 to prevent them from being lost and were exposed below 1 m in KL and OH for 1, 2, 4, and 6  
165 weeks (April 14-21, April 14-28, April 14-May 12, and April 14-May 26, 2022, respectively)  
166 (Fig S1). In addition, passive samplers were exposed in MS for 1, 2, 3, and 4 weeks (May 23-  
167 30, May 30-June 6, June 6-13, and June 13-20, 2022, respectively). Field blank samples of  
168 LLDPE and LDPE were unfolded to absorb contamination compounds in the air when  
169 deploying and retrieving. The retrieved passive samplers were cleaned with deionized water  
170 and Kimwipes to remove biofouling on the surface of the passive samplers. Water samples  
171 were collected using a grab sampler to measure dissolved PAH concentrations and compare  
172 them with freely dissolved PAH concentrations under the same conditions. All samples were  
173 kept in a freezer until analysis.

### 174 3.3. Chemical analysis

175 Passive samplers were cut into small pieces and placed into 250 mL flasks with 30  $\mu$ L of  
176 surrogate standard mixture (con.: 10  $\mu$ g/mL), and triplicate extracted with dichloromethane  
177 using a sonication. Water samples were filtered through GF/F filters to remove particulate  
178 matter and then extracted using a liquid-liquid extraction method to measure dissolved  
179 concentrations. The extracts were combined and concentrated using a rotary evaporator  
180 (Rotavapor R3000, BUCHI, Switzerland). The concentrated samples were purified in a column  
181 packed with 5 g of deactivated silica gel (5%), 2.5 g of alumina (1%), and anhydrous sodium  
182 sulfate ( $\text{Na}_2\text{SO}_4$ ). The eluates were concentrated and exchanged to hexane using rotary  
183 evaporation and then concentrated by  $\text{N}_2$  gas until 0.2 mL. To remove oligomers, the  
184 concentrated samples were transferred to 0.7  $\mu$ L of insert vials in microcentrifuge tubes and  
185 frozen, then centrifuged for 5 minutes at 5000 rpm. The supernatant was separated and

186 transferred to insert vials containing 1.5 mL GC vials. All samples were spiked with 30  $\mu$ L of  
187 GC/IS (con.: 10  $\mu$ g/mL) and analyzed.

### 188 3.4. Instrumental analysis and QA/QC

189 All samples were quantitated using a gas chromatography-mass spectrometer (GC-MS)  
190 (7890B/5977B, Agilent). Helium was used as the mobile phase gas, and a capillary column  
191 (DB-5MS, 30 m x 0.25 mm x 0.25  $\mu$ m) was utilized. The injection sample volume was 2  $\mu$ L.  
192 The temperature of the sample inlet was maintained at 300°C, taking into account the boiling  
193 point of the analyte, and detected using selective ion monitoring (SIM).

194 The average recovery rates of surrogate standards, excluding NAP- $d_8$ , for LLDPE and LDPE  
195 ranged from 40% to 69% and 40% to 60% in KL, 40% to 68% and 42% to 68% in OH, and  
196 40% to 56% and 40% to 57% in MS, respectively. In the case of the MS at 4 weeks, the  
197 recoveries of NAP-  $d_8$  and ACY-  $d_{10}$  in LDPE were below 40%, so they were excluded. The  
198 concentrations of PAHs in the procedural blank water ranged from 0.10 (IcP) to 13 (PHE) ng/L.  
199 Additionally, a higher expected qualitative ion of ACY was detected in LLDPE and LDPE, so  
200 this compound was excluded from the calculation in this study. For the field blank, the average  
201 recovery rates of surrogate standards for sampling periods, excluding NAP- $d_8$ , ranged from 40%  
202 to 72%. The concentrations of 16PAHs in field blank from LLDPE and LDPE ranged from  
203 0.007 (CHR) to 14 (PHE) ng/g and 0.007 (CHR) to 7.4 (PHE) ng/g in KL and 0.059 (IcP) to  
204 17 (PHE) ng/g and 0.059 (BaP) to 8.7 (PHE) ng/g in OH, and 0.86 (FLT) to 6.8 (FLR) ng/g  
205 and 0.053 (CHR) to 3.8 (PHE) ng/g, respectively. The average recovery rates of surrogate  
206 standards excluding NAP- $d_8$ , for water samples ranged from 43% to 72% in KL, 40% to 83%  
207 in OH, and 45% to 60% in MS.

208

## 209 4. Results and Discussions

210

#### 211 4.1. Comparison of $f_{eq}$ in LLDPE and LDPE

212

213

214 Four PRCs including FLR- $d_{10}$ , FLT-  $d_{10}$ , BaA- $d_{12}$ , and BeP-  $d_{12}$  were used to correct the

215 concentration of target compounds for non-equilibrium between passive sampler and water.

216 The  $f_{eq}$  calculated by using equation 3 for the PRCs in LLDPE and LDPE ranged from 0.18 to

217 1 and 0.14 to 1 in KL and 0.13 to 1 and 0.22 to 1 in OH, and from 0.5 to 1 and 0.28 to 1 in MS,

218 respectively, except for  $f_{eq} < 0.1$  (Fig 2). The  $f_{eq}$  for each sampling period are detailed in Table

219 S3.

220 While FLR- $d_{10}$  and FLT-  $d_{10}$  reached equilibrium at all sampling periods, the  $f_{eq}$  of BaA- $d_{12}$

221 and BeP-  $d_{12}$  with HMW increased over time. BeP- $d_{12}$  was released slowly from LLDPE in KL

222 and from LDPE in OH and MS and its  $f_{eq}$  was too low ( $< 0.1$ ) to correct the concentration of

223 target compounds until 2 weeks in KL and 1-2 weeks in OH and MS. The  $f_{eq}$  of PRCs in passive

224 sampler varied depending on the molecular weight and showed a pattern similar to that in the

225 previous study (Lohmann, 2012).

226 In general, the passive samplers loaded with PRCs should be exposed to the environment

227 for at least 28 days to release PRCs with HMW to obtain  $f_{eq}$  above 0.1 (Allan et al., 2010).

228 However, in this study, clear differences were observed in the  $f_{eq}$  of BeP- $d_{12}$  between LLDPE

229 and LDPE for each exposure time and location. The  $f_{eq}$  of BeP- $d_{12}$  in passive samplers at

230 sampling sites increased over time. The  $f_{eq}$  of BeP- $d_{12}$  in KL showed a similar pattern between

231 LLDPE and LDPE, possibly due to KL being a large lake with relatively low water velocity.

232 In contrast, the  $f_{eq}$  was highest in MS (average water velocity 1.93 km/h) followed by OH (1.77

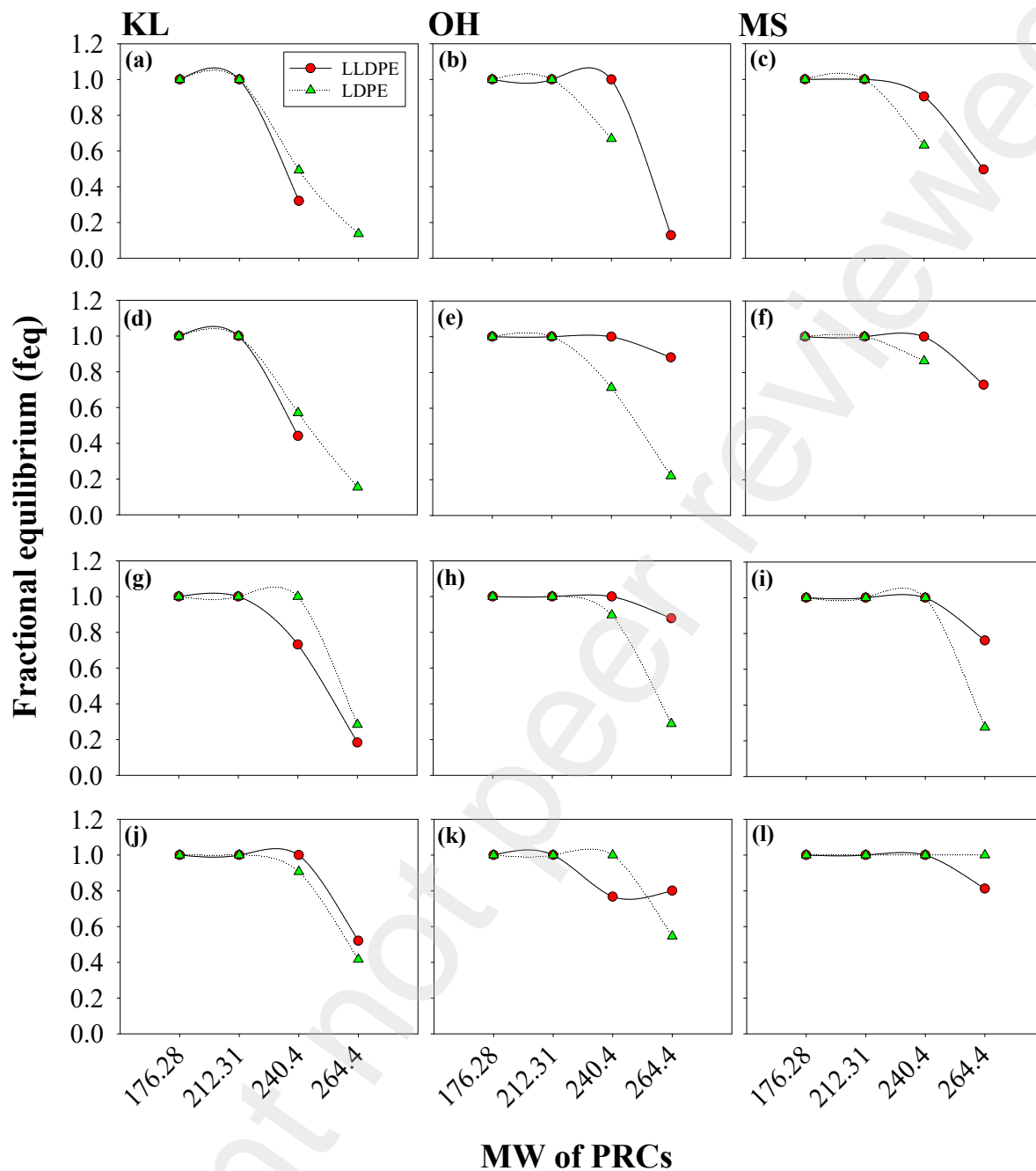
233 km/h) and KL, suggesting that the  $f_{eq}$  of PRCs with HMW can be influenced by water velocity,

234 as shown in Fig S2 (Estoppey et al., 2014; National Park Service; ORSANCO).

235 Moreover, the  $f_{eq}$  of BeP- $d_{12}$  in LLDPE was 4.0, 3.0, 1.5 and 2.8 times higher than that in

236 LDPE for 2, 4, 6 weeks of exposure in OH and, 3 weeks in MS, excepting 1 week in OH and

237 1 and 2 weeks in MS due to  $f_{eq} < 0.1$ . This result indicated that the thinner LLDPE sampler had  
238 better release for PRCs and faster absorption for the target compound and was consistent with  
239 the result of Smith et al. (2022), which showed that the  $f_{eq}$  of PRCs can increase with thickness  
240 thinning and the sampler can rapidly absorb target compounds even with a short sampling  
241 period. Thus, LLDPE is a more suitable tool for short- and long-term monitoring of organic  
242 pollutants than LDPE.



243

244 **Figure 2. Fractional equilibrium of LLDPE and LDPE according to exposure time at each**  
 245 **sampling site: (a) to (c) for 1 week, (d) to (f) for 2 weeks in KL, OH, and MS, (g) and (h)**  
 246 **for 4 weeks in Kentucky Lake (KL) and Ohio River (OH), (i) for 3 weeks in Mississippi**  
 247 **River (MS), (j) and (k) in 6 weeks in KL and OH, and (l) for 4 weeks in MS. (MW:**  
 248 **Molecular Weight)**

249

250

251

#### 252 4.2. Comparison of $C_{free}$ in a different types of passive samplers

253  
254 The information regarding water temperature and  $\log K_{pw}$  values of LLDPE and LDPE,  
255 which were corrected using equation 2, are presented in Table S3 and Table S4, respectively.

256 The average freely dissolved PAH concentrations calculated using equations 2 and 4, in  
257 LLDPE and LDPE during the exposure period were 2.89 and 1.27 ng/L in KL, 8.13 and 3.31  
258 ng/L in OH, and 5.19 and 3.82 ng/L in MS, respectively. Burgess et al. (2015) reported that the  
259 freely dissolved PCB concentrations measured by three different types of passive samplers  
260 were generally within a factor of 2 to 3 of each other, which was similar to our results. The  
261 concentration patterns of each sampling site were similar and the average freely dissolved PAH  
262 concentrations was in the same order between different passive samplers as shown in Fig. 3.  
263 The average freely dissolved PAH concentrations decreased in KL and OH at 6 weeks and in  
264 MS at 4 weeks.

265 KL and OH join the MS and flow into the lower Gulf of Mexico. In a previous study, Allan  
266 et al. (2012) measured freely dissolved PAH concentrations using passive samplers in the Gulf  
267 of Mexico area, including Grand Isle (LA), Gulfport (MS), Gulf Shores (AL), and Gulf Breeze  
268 (FL). The freely dissolved concentration of 33PAHs in LA was  $3.8 \pm 0.64$  ng/L in May 2010  
269 but increased to  $170 \pm 14$  ng/L in June 2010 after the oiling occurred, and then decreased in  
270 July 2010. Since 2011, the freely dissolved PAH concentrations in all sampling sites were  
271 below 20 ng/L. The freely dissolved PAH concentrations measured in this study in OH, KL,  
272 and the upper MS river were similar to those ( $<10$  ng/L) in the sampling area around the Gulf  
273 of Mexico (data extracted from Fig 2, Allan et al., 2012).

274 The composition of the 14PAH compounds in each sampling site was similar between  
275 different passive samplers (Fig. 4), indicating that LLDPE and LDPE have similar absorption  
276 properties for various PAHs. The target compounds with 3 rings in the MS at 4 weeks did not  
277 appear (Fig. 4f) because, as described above, the recoveries of LMW compounds were below

278 40%, so they were excluded. In general, the freely dissolved and total PAHs around the Gulf  
279 of Mexico and Louisiana were composed primarily of compounds with 3 or 4 rings (Allan et  
280 al., 2012; Zhang et al., 2007). Similarly, the freely dissolved PAHs with 3 or 4 rings in this  
281 study ranged from 52% to 94% and were major compounds.

282 In another study, Amdany et al. (2014) reported that the freely dissolved PAH concentrations  
283 ranged from 22.1 to 126.7 ng/L in Johannesburg City, South Africa, including rivers, lakes,  
284 and dams, over a period of 14 days using SPMDs (Table 1). Furthermore, freely dissolved PAH  
285 concentrations, except for NAP, was found to range from 2.8 to 29 ng/L in the Danube River,  
286 Europe, using SPMDs for 14 days (Vrana et al., 2014). In the case of a different matrix, such  
287 as the marine environment, Monteyne et al. (2013) reported that the freely dissolved PAH  
288 concentrations ranged from 3.9 to 170 ng/L in three Belgian coastal harbors using PDMS for  
289 2 months. In the open sea, the freely dissolved PAH concentrations ranged from 3.8 to 16 ng/L  
290 using LDPE (Bao et al., 2012) and 2.56 to 4.46 ng/L using SR (Sobotka et al., 2021). Compared  
291 with the previous studies, this study showed that the concentrations in all sampling sites,  
292 including KL, OH, and MS, were lower than those in rivers, lakes, and seawater and were  
293 similar to those in the open sea, indicating that this study area was relatively clean for PAHs.

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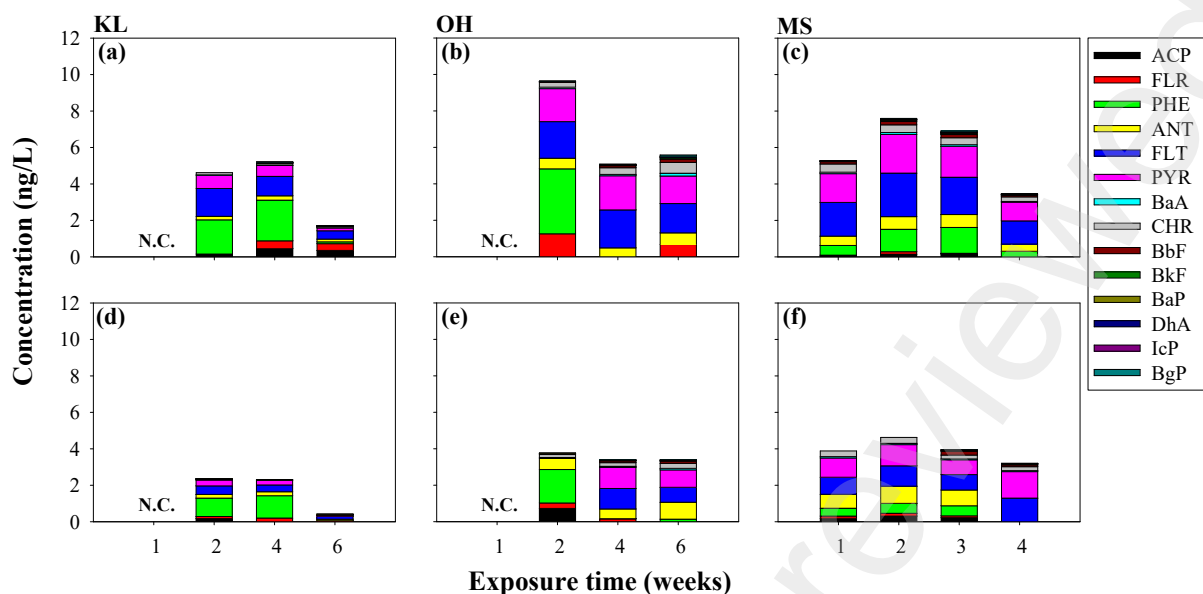
302



303 **Table 1. Comparison of freely dissolved PAH concentrations in different of passive**  
 304 **samplers and locations**

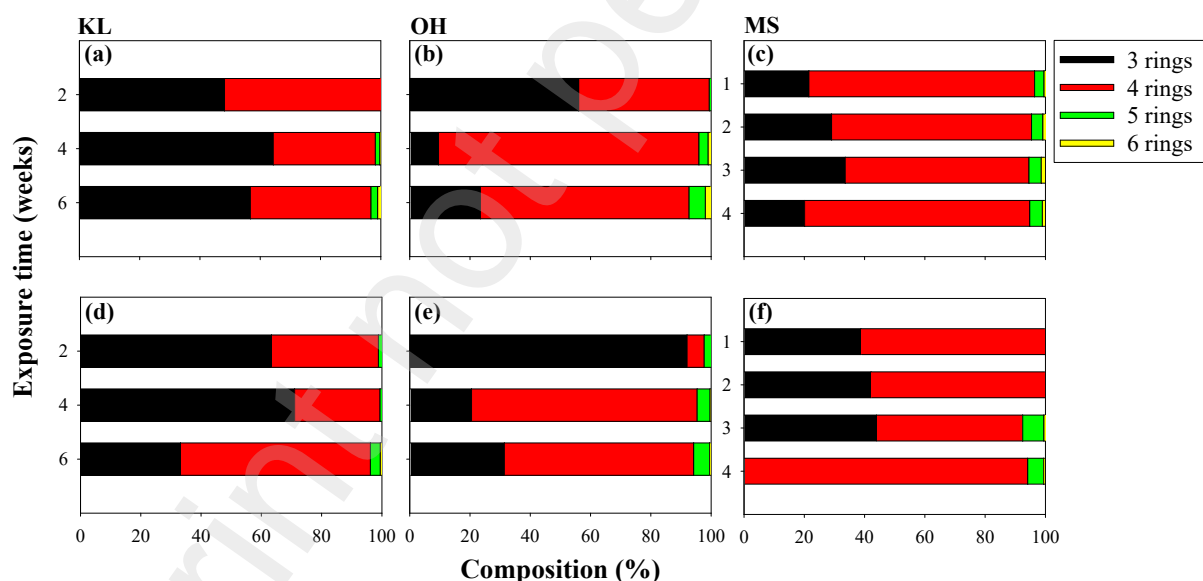
Environmental	Location	No. of PAHs	Concentration (ng/L)	Passive samplers	Ref.
Seawater	Johannesburg City	16	22.1-126.7	SPMDs	Amdany et al., 2014
	Belgian coastal harbors	15	3.9-170	PDMS	Monteyne et al., 2013
	Alexandroupolis Port	21	55.1±7.6- 61.5±4.2	PDMS	Apostolopoulou et al., 2014
	Narragansett Bay	15	0.16-5.7	LDPE	Lohmann et al., 2011
Open sea	Hailing Bay	14	3.8-16	LDPE	Bao et al., 2012
	Black Sea	15	2.56-4.46	SR	Sobotka et al., 2021
	Yellow Sea	16	0.67-1.9	LDPE	Jang et al., 2022
Freshwater	Danube River,	15	2.8-29	SPMDs	Vrana et al., 2014
	Lower Yangtze River	15	0.2-33	LDPE	Yao et al., 2017
	Yellow River	3	26.32	LDPE	Xia et al., 2013
	Willamette River	15	70-2150 (dry season) 80-560 (wet season)	SPMDs	Sower and Anderson, 2008
	Ontario lake	6	113.1	SPME	Ouyang et al., 2007
	Kentucky Lake	14	1.72-5.21	LLDPE	Present study
			0.42-2.37	LDPE	”
	Mississippi River	14	3.47-7.59	LLDPE	”
			3.21-4.62	LDPE	”
	Ohio River	14	5.09-9.63	LLDPE	”
			3.39-3.77	LDPE	”

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 308 **Figure 3. Total freely dissolved concentration (ng/L) in LLDPE (a to c) and LDPE (d to**  
 309 **f) in each sampling site. The concentration at 1 week in KL and OH in both passive**  
 310 **samplers was not calculated (N.C.).**

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 315 **Figure 4. The composition of freely dissolved PAHs (%) in LLDPE (a to c) and LDPE (d**  
 316 **to f).**

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### 321 4.3. Comparison of $C_{free}$ and $C_{dissolved}$

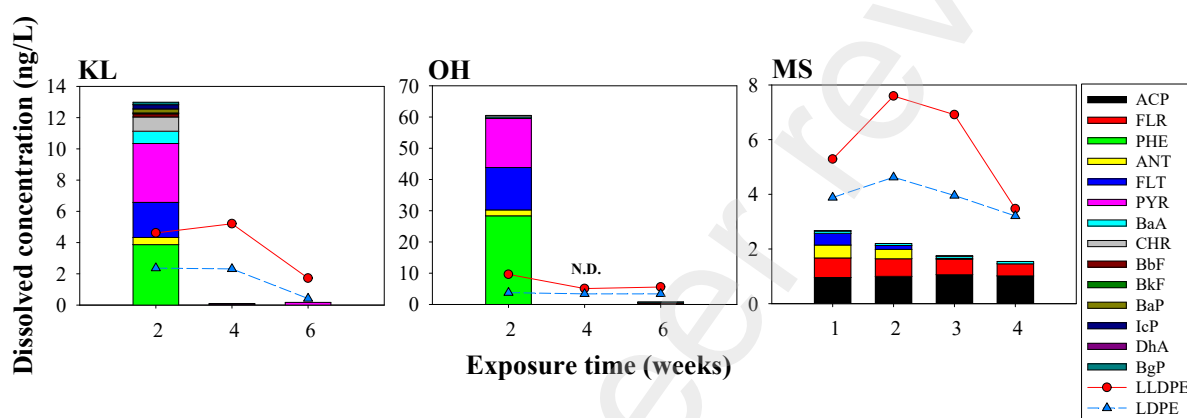
322

323 The dissolved PAH concentrations obtained from conventional method ranged from 0.1 (4  
324 weeks) to 13 (2 weeks) ng/L in KL, N.D. (4 weeks) to 60.5 (2 weeks) ng/L in OH, and 1.54 (4  
325 weeks) to 2.67 (1 week) ng/L in MS, respectively. The dissolved concentration trend was  
326 similar to the freely dissolved concentration, as both showed a decrease over time (Fig. 5).

327 In general, the concentration of compounds in the dissolved phase was higher than that in  
328 the freely dissolved phase, since the dissolved phase includes colloid-, dissolved organic  
329 carbon-, and the freely dissolved-phase. Additionally, Particulate or dissolved organic carbon  
330 (DOC) associated concentration showed a good correlation with the log  $K_{OW}$  values of the  
331 PAHs due to high affinity so that as the PAH concentrations in POC/DOC phase increased, the  
332 freely dissolved concentration decreased (Xia et al., 2013). While  $C_{free}/C_{dissolved}$  ratio (%) from  
333 LLDPE and LDPE in KL and OH at 2 weeks showed 35.6% and 18.2%, and 15.9% and 6.23%,  
334 respectively, and was very similar to the previous studies (Apostolopoulou et al., 2014), the  
335 dissolved concentrations at 4 and 6 weeks in KL and OH were extremely low, resulting in  
336  $C_{free}/C_{dissolved}$  ratio (%) above 100% contrary to expectations. Although the low dissolved  
337 concentrations at 4 and 6 weeks in KL and OH could be attributed to the sampling of water  
338 diluted by high precipitation several days before the grab sampling for the determination of  
339 dissolved PAHs, the freely dissolved concentration was representative of the time-weighted  
340 average concentration during the entire exposure period. As a result, the  $C_{free}/C_{dissolved}$  ratio (%)  
341 showed the values above 100%. In the case of MS, despite using a large volume of water and  
342 conventional liquid-liquid extraction, the dissolved PAH concentrations were lower than the  
343 freely dissolved PAH concentrations. In fact, the number of PAHs detected in the dissolved  
344 phase of MS ranged from zero to 11 compounds with the average of 5, while the number of  
345 freely dissolved PAHs detected ranged from 7 to 13 compounds with average of 11, which is  
346 similar pattern to the results obtained in KL and OH. Kim et al. (2020) and Burgess et al. (2015)

347 reported the same result that freely dissolved concentration (passive sampler) was higher than  
 348 dissolved concentration (spot sampling). Therefore, unlike grab sampling for the determination  
 349 of dissolved concentration, passive sampling provides the time-weighted average concentration  
 350 during the sampling period, enabling accurate predictions and detection of more target  
 351 compounds.

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353 **Figure 5.** The total dissolved concentration for each sampling period in all sampling sites  
 354 and the total freely dissolved concentration in LLDPE and LDPE were plotted on the  
 355 figure.  
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## 360 5. Conclusions

361  
 362 The freely dissolved PAH concentrations were compared between LLDPE, a new passive  
 363 sampler, and LDPE, a normal passive sampler. The  $f_{eq}$  of BeP- $d_{12}$  was 4 times higher in LLDPE  
 364 than in LDPE regardless of the short sampling period of 2 weeks. This result showed that  
 365 LLDPE was as suitable a passive sampler to short-term monitoring and could correct non-  
 366 equilibrium compounds in water. The freely dissolved PAH concentrations were in same order  
 367 between both passive samplers. Additionally, the trend of freely dissolved PAH concentration  
 368 and their composition in Kentucky Lake (KL), Ohio River (OH), and Mississippi River (MS)  
 369 were similar for both passive samplers during each sampling period. Therefore, LLDPE was a  
 370 more suitable alternative tool than LDPE for short and long-term monitoring of trace

371 contaminated compounds. Furthermore, the conventional method can show a spot  
372 concentration due to rapid fluctuations in environmental factors such as precipitation. On the  
373 other hand, passive samplers can form a regulatory baseline by presenting time-weighted  
374 average concentrations.

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