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Assessing benthic bioaccumulation of polychlorinated dioxins/ furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) in the lower Passaic River (NJ, USA) based on *in situ* passive sampling

Mohammed A. Khairy

Rainer Lohmann

University of Rhode Island, rlohmann@uri.edu

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1 **Field-testing Passive Multisamplers to Measure Freely Dissolved Concentrations and**
2 **Sedimentary Bioavailability of Dioxins/Furans and Polychlorinated Biphenyls**

3 **Mohammed A. Khairy^{†,‡*}, Rainer Lohmann[†]**

4 [†]Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island
5 02882 USA

6 [‡]Department of Environmental Sciences, Faculty of Science, Alexandria University, 21511
7 Moharam Bek, Alexandria, Egypt

8
9 *Corresponding author. E-mail address: rlohmann@uri.edu

10 Phone: 401-874-6612

11
12 **Abstract**

13
14 Passive sampling has emerged as a promising tool to better assess sediments contaminated with a
15 range of hydrophobic organic contaminants (HOC), such as polychlorinated biphenyls (PCBs) or
16 polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs). Previous work had evaluated the ability of
17 passive samplers to predict bioavailability of sedimentary HOCs in the laboratory, in particular for
18 marine organisms. The focus of the current study was to validate the use of *in situ* passive samplers
19 in porewater and surface water to derive freely dissolved concentrations of PCDD/Fs and PCBs
20 simultaneously. Passive multisamplers were also used to detect spatial trends of these HOCs, and
21 to predict their bioaccumulation by benthic organisms. Low density polyethylene samplers
22 (LDPE) were deployed at four locations along the lower Passaic River (NJ), where sediment and
23 benthic species samples were also collected. Good agreement was generally observed for PCB and
24 PCDD/F concentrations comparing *in situ* and the *ex situ* approaches (within 0.30 – 39%).
25 Including a higher chlorinated ¹³C₁₂ PCDD congener as a performance reference compound
26 improved results for PCDD/Fs. Significant linear relationships were observed between log LDPE
27 based –log lipid-based concentrations of PCDD/Fs and PCBs. The *in situ* multisampler showed

28 promise to estimate porewater concentrations of HOCs in shallow sediments and to predict the
29 bioaccumulation potential of HOCs in benthic biota.

30

31 **Introduction**

32 In aquatic ecosystems, sediments act as a sink that reflect past and ongoing discharges of
33 hydrophobic organic compounds (HOCs) and trace metals. Freely dissolved HOCs in sediment
34 porewater can be re-released to the overlying water column and bioaccumulate in the aquatic food
35 chain^{1,2} causing biological effects in the exposed species. Until recently, studying the fate and
36 transport of HOCs, and predicting their bioaccumulation potential and toxicity relied mainly on
37 the equilibrium partitioning theory using bulk sediment concentrations and organic carbon – water
38 partitioning coefficients (K_{OC})^{3,4}. Geochemical models using natural sorbents usually over-
39 predicted porewater concentrations due to the lack of site-specific partitioning coefficients (K_{OC})
40 ^{1,5,6}, and/or the inability of organic carbon alone to accurately explain the sorptive behavior of
41 HOCs in sediments^{3,7,8}. Using black carbon (BC) in addition to organic carbon greatly improved
42 the predictive ability, but BC is relatively difficult to quantify and accurately characterize².
43 Although direct measurement of porewater concentrations gave more accurate results¹, it was
44 rarely performed due to problems associated with the sample volume, corrections for the influence
45 of colloidal-bound fractions of HOCs and the difficulty of obtaining an accurate measurement for
46 HOCs with high octanol-water partitioning coefficients (K_{OWS})².

47 To overcome problems associated with direct measurement/prediction of porewater
48 concentrations, passive samplers have been developed to estimate the freely dissolved
49 concentrations of HOCs. Passive samplers such as low density polyethylene (LDPE)^{3,8-11},
50 polyoxymethylene (POM)^{1,12,13} and/or polydimethylsiloxane (PDMS)¹⁴ has been widely used to
51 estimate porewater and surface water concentrations of HOCs. LDPE have been widely used for

52 monitoring hydrophobic organic compounds (HOCs) in porewater^{3,4,8,9,11,15-17} and surface water.
53 ^{4,8,16} HOCs accumulate in LDPE via diffusion and absorption into the sampler matrix, with a high
54 enrichment in LDPE¹⁶ thus offering lower detection limits. Other advantages of LDPE include
55 simplicity (in its chemical makeup), low cost and ease of deployment¹⁸. For LDPE, complicated
56 cleanup techniques for extracts are rarely needed (except for PCDD/Fs), and it can be used both in
57 the linear uptake (kinetic) or equilibrium (thermodynamic) sampling mode by varying the
58 thickness of the PE, the use of performance reference compounds (PRCs) and the exposure time
59 (days, weeks and months).

60 Freely dissolved concentrations of HOCs in porewater have been previously measured either *in*
61 *situ* (field deployment by inserting samplers in sediments for a sufficient period of time)^{11,19-22} or
62 *ex situ* (equilibrating sediment-water slurry with passive sampler in the lab for a period of time
63 usually sufficient to attain equilibrium)^{3,4,8,9}. Although the *ex situ* approach is more widely used
64 due to the reduced equilibration time/enhanced mass transfer (continuous agitation of the
65 sediment-water-passive sampler system) and improved precision²³, the *in situ* approach is used
66 when it is required to capture field conditions (refer to Ghosh et al.² for more details on criteria for
67 selecting the *in situ* vs the *ex situ* approaches). As the *in situ* deployed passive samplers require
68 longer time to reach equilibrium with sediments, PRCs are needed and crucial for disequilibrium
69 corrections. Alternatively, deployed LDPE passive samplers with vibrating motors were
70 suggested^{11,19-22} to disrupt the depletion layer around the passive sampler and thus accelerate the
71 uptake of HOCs.

72 In our previous work, we used LDPE (25.5 μm thickness) *ex situ* to estimate porewater
73 concentrations of PCDD/Fs, PCBs, polycyclic aromatic hydrocarbons (PAHs), polybrominated
74 diphenyl ethers (PBDEs) and organochlorine pesticides in sediments of the lower Passaic

75 River^{3,7,8,24}. LDPE were spiked with PRCs for disequilibrium corrections. Estimated
76 concentrations of all the investigated HOCs were compared with measured concentrations of the
77 same HOCs in fish species and blue crabs. Results indicated that porewater concentrations were
78 the best predictors of tissue concentrations, and both porewater and diet were important uptake
79 sources of HOCs in higher level biota⁸.

80 In this work, we tested LDPE as a multisampler for the *in situ* estimation of porewater
81 concentrations along the lower Passaic River, known to be contaminated by dioxins/furans, PCBs
82 and other HOCs. This multisampling method could then be used as an effective tool to design and
83 implement projects at contaminated sites to aid in remediation decision making. The specific
84 objectives were: i) to construct of a new passive multi-sampler for the estimation of freely
85 dissolved concentrations of HOCs in porewater and the overlying water; ii) to ground-truth field-
86 deployed porewater concentrations by comparing them to porewater concentrations derived from
87 the *ex situ* approach; iii) to deploy the proposed sampler at several sites along the lower Passaic
88 River to demonstrate that the proposed multi sampler can yield representative spatial and temporal
89 interrogation of site contaminants and iv) to collect sediments and different benthic invertebrates
90 from the same sites of the proposed to assess the possibility of using the new proposed *in situ*
91 sampler as a proxy for bioaccumulation of HOCs by benthic invertebrates.

92 93 **Materials and Methods**

94 Detailed description of the sampling procedures, extraction and cleanup, instrumental analysis,
95 quality assurance, statistical analysis, selected physicochemical properties and uncertainty
96 calculations are provided in the Supporting Information (SI), are provided in the SI and Figures
97 S1-S4 and S2, and are briefly summarized below.

98 **Sediment collection:** Four surficial sediment samples (Figure S1) were collected during July,
99 2015 at 4 locations in the lower Passaic River (River km 29.6–0). This region was selected because
100 sediments are contaminated with various classes of HOCs^{3,7,8,24}. Sites were selected based on ease
101 of access. All sediment samples were collected from mudflats at low tide. A glass jar (previously
102 washed with soap and water and baked at 450 °C for 4 h) was filled by scooping mud by hand
103 using a shovel. The material from the dredge was kept in an ice box, and shipped frozen to the
104 laboratory. Samples were then kept in a freezer at –20 °C until extraction and analysis.

105 **Biota collection:** Deposit-feeding tube worms (*Pectinaria gouldii*; 1.0 g at each location) were
106 collected from 2 of locations [S1 (Riverbank Park) and S4 (Passaic Avenue)], and each of clams
107 (*Mya arenaria*; n = 60) and tiny mud crabs (n = 25; 1.0 – 1.5 cm in length) were collected from
108 only one location [S3 (Doremous Street) and S1 respectively]. No biota was found at S2.

109 **Multisampler deployments–sediment:** The proposed passive multisamplers were deployed at the
110 four locations as shown above (Figure S1). At each location, 4 deployments were performed (2
111 months each) from June, 2015 to February, 2016. During each deployment period, sediment and
112 biota samples were also collected and the analyzed samples represent a pooled sample of four
113 sampling occasions. The sediment multisampler consisted of a round, 1m frame that held the
114 LDPE strips (51 µm thickness; 10 × 86 cm strip of ~3.5–4 g each) in the upper 5 cm of sediment
115 *in situ* (Figure S2). Lead weights helped the multisampler penetrate into the sediment easily. As
116 the concentrations of PCDD/Fs in sediments are low (at the pg/g level)³, and their sorption to
117 carbonaceous particles is high^{3,7}, their mobility in the sediment is greatly reduced. The sampler is
118 thus designed to have a maximum expose surface area for a considerable length of time. Prior to
119 deployments, LDPEs were pre-cleaned and spiked with PRCs¹⁰.

120 As a control to the *in situ* porewater sampling system, *ex situ* estimation of porewater
121 concentrations was also performed (using LDPE sheets with 25 and 51 μm thickness) with the
122 same sediments as described previously⁴.

123 **Multisampler deployments- water:** To estimate the freely dissolved concentrations of HOCs in
124 the river's water, pre-cleaned and PRC spiked LDPE sheets (51 μm thickness; 10 \times 30 cm strip
125 each of \sim 2.0 g) were placed in a stainless steel-based housing (Figure S3) and deployed in
126 duplicates at each site attached to the porewater sampler.

127 **Extraction and analysis:** All LDPEs mentioned above were extracted with n-hexane for 24 hours
128 after spiking with surrogate standards. Extracts were then concentrated to \sim 1 mL, and further
129 concentrated to \sim 50 μL under a gentle stream of nitrogen. Sediment and biota samples were
130 Soxhlet extracted with n-hexane/methylene chloride (1:1, v:v). LDPE extracts were passed over
131 SPE cartridges filled with 1g active silica gel and 2 g 44 % H_2SO_4 impregnated silica gel. After
132 this step, samples were analyzed for PCBs. For PCDD/F analysis, extracts were brought to 1 mL
133 in hexane, and passed through an activated carbon column. PCDD/Fs were eluted with 100 mL of
134 toluene.²⁵ Toluene extracts were then concentrated, spiked with the internal standard and kept in
135 freezer until instrumental analysis.

136 All samples were separately analyzed for mono- through octa-chlorinated dioxins and furans, and
137 209 PCB congeners using gas chromatography coupled with to a triple quadrupole mass
138 spectrometry. For PCBs, a 30-m long \times 0.25-mm I.D. fused silica capillary column with DB-5MS
139 bonded phase, or equivalent was used for GC/MSMS analyses. The analytical method for PCB
140 detection is functionally equivalent to the U.S. EPA method 1668b²⁶ and the Japanese standard
141 method²⁵.

142

143 The 13 PCDD and 12 PCDF congeners were analyzed on the same GC/MSMS system equipped
144 with a 60-m long x 0.25-mm I.D. fused silica capillary column with DB-5MS HT bonded phase.
145 The PCDD/F analysis is functionally equivalent to USEPA method 1613. The targeted dioxin and
146 furan congeners include all 2,3,7,8-substituted ones (the WHO list).

147
148 **QA/QC:** All samples were spiked with surrogate standards composed of labeled PCDD/Fs and
149 PCBs. Average recoveries of $^{13}\text{C}_{12}$ PCB ranged from 68 ± 3.0 % ($^{13}\text{C}_{12}$ PCB 8) to 102 ± 3.0 % (PCB
150 180), whereas $^{13}\text{C}_{12}$ PCDD/Fs ranged from 63 ± 2.0 % (2,7-CDD) to 103 ± 6.0 % (1,2,3,4,6,7,8,9-
151 CDD). Field blanks (LDPE only) and procedural blanks (LDPE + biota) were included in the
152 analysis. PCB 18, 28, 52, 153 and 180 were detected in the field and procedural blanks (< 0.1 ng/g
153 dw for sediments and biota; < 0.50 pg/L for porewater) and samples were corrected for the blanks.
154 PCDD/Fs were not detected in any of the blanks. Limit of detections of PCBs and PCDDs/Fs were
155 calculated as the concentration of analytes in a sample giving a peak with a signal-to-noise (S/N)
156 of 3. Calculated concentrations of PCDD/Fs were reported as less than the limit of detection if
157 either the observed isotope ratio was not within 20% of the theoretical ratio or the peak area was
158 not greater than the specified threshold (3 times the noise).

159 Recoveries of PCBs in the matrix spikes ranged from 88 ± 3.0 % (PCB 1) to 103 ± 2.0 % (PCB 180)
160 and from 87 ± 3.0 % (PCB 1) to 97 ± 4.0 % (PCB 118) in LDPE (n = 6) and sediments + biota (n =
161 5 each) respectively. Recoveries of PCDD/Fs in the matrix spikes ranged from 89 ± 4.0 % (2-CDF)
162 to 103 ± 4.0 % (1,2,3,4,6,7,8,9-CDD) and from 83 ± 2.0 % (2-CDF) to 99 ± 3.0 % (2,3,7,8-CDD) in
163 LDPE and sediments + biota respectively. Relative standard deviations percentage (RSD %) for
164 all the analytes were < 20 %. Results of the replicate analysis of LDPE and sediment/biota samples
165 (20 % of each of the LDPE and sediment/biota samples) indicated that the reproducibility of the
166 analysis ranged from 3.0-24 % and 9.8-28 % for PCBs and PCDD/Fs respectively.

167 **Estimation of Freely Dissolved Concentrations from LDPE:** PRCs were used to gauge
168 whether target analytes had achieved equilibrium and to adjust for disequilibrium in polyethylene
169 (C_{LDPE}) assuming that uptake and elimination rates are equivalent²⁷. Sampling rates were
170 calculated using the PRCs according to the method of Booij and Smedes²⁸. For porewater LDPE,
171 PRCs were used to correct for disequilibrium using the PRC calculator developed by Gschwend
172 et al.¹⁵ for sediment's deployed LDPE by applying a fixed-bed diffusive mass transfer model²⁹.

173
174 **Uncertainty Analysis:** Uncertainties associated with the estimated porewater and river water
175 concentrations (equation S6) from LDPE ranged from 64 – 68 % and 58 – 63 % respectively.
176 Uncertainties associated with predicted tissue concentrations (equations S8 – S10) from sediment's
177 OC were the lowest (22 – 67 %) followed by predicted concentrations from river water (62 –
178 86 %), porewater (65 – 91 %) and sediment's OC + BC (69 - 94 %).

179

180 **Results**

181 **Sediment Concentrations**

182 Concentrations of PCBs are given in Table S1, and for PCDD/Fs in Table S2, together with
183 fractions of black carbon (BC) and organic carbon (OC).

184 **PCBs:** We report concentrations of 89 PCB congeners that were detected in any of the investigated
185 environmental matrices (sediments, river water, porewater and biota). Σ_{89} PCBs ranged from 78
186 ng/g dw (S1) to 171 ng/g dw (S2) with an average concentration of 104 ng/g dw sediment. Detected
187 concentration at S2 was significantly higher than concentrations detected at the other three
188 locations (Repeated Measures ANOVA on Ranks, $p < 0.001$). All samples were dominated by tri-
189 through hepta- chlorinated congeners comprising > 80 % of the total detected concentrations of
190 PCBs in the sediments (Figure S4).

191
192 **PCDD/Fs:** Σ_{27} PCDD/Fs ranged from 1.7 ng/g dw (S4) to 4.6 ng/g dw (S2) with an average
193 concentration of 3.0 ng/g dw. As for PCBs, detected concentrations of PCDD/Fs at S2 were higher
194 than concentrations observed at the other locations, but it was not statistically significant. Detected
195 concentrations were within the same range as previously observed in sediments of the lower
196 Passaic River in 2011³. Sediments were dominated by 1,2,3,4,6,7,8,9-CDD comprising on average
197 53 % of the total detected concentrations followed by 1,2,3,4,6,7,8,9-CDF (11 %) (Figure S5).
198 In terms of the WHO toxic equivalents³⁰, concentrations ranged from 56 pg TEQ/g dw to 211 pg
199 TEQ/g dw with an average concentration of 147 pg TEQ/g dw. In all the samples 2,3,7,8-TCDD
200 dominated the total WHO-TEQ with contributions ranging from 71 – 81 % followed by hexa-
201 chlorinated furans (5.0 – 9.0 %).

202

203 **PCBs and PCDD/Fs in the *In Situ* Porewater Sampler**

204 **PCBs:** Average Σ_{89} PCB concentrations of the four deployment periods at each sampling location
205 ranged from $1.7 \pm 0.24 \mu\text{g/LDPE}$ (S1) to $6.3 \pm 1.4 \mu\text{g/LDPE}$ (S6). Average Σ_{89} PCB concentrations
206 at S4 were significantly higher (One Way Repeated Measures ANOVA, $p < 0.001$) than average
207 concentrations at all the other locations (Figure S6a). Similarly, average Σ_{89} PCB concentrations
208 at S2 and S3 were significantly higher than S1 (Figure S6a).

209
210 **PCDD/Fs:** Average PCDD/F concentrations ranged from $1.7 \pm 0.24 \text{ ng/LDPE}$ (S2) to 6.3 ± 1.4
211 ng/LDPE (S3). Unlike PCBs, no statistical significant difference was observed between
212 accumulated PCDD/Fs in the deployed LDPEs at the sampling sites. However, variabilities in the
213 detected PCDD/F congeners were observed (Figure S6b).

214 Results of the PCBs and PCDD/Fs show that the proposed *in situ* porewater sampler was able to
215 detect between site variabilities. The multisamplers and deployments were the same at all sites;
216 variations in the accumulated amounts/congeners hence reflect differences in freely dissolved
217 (porewater) concentrations.

218 219 **PRCs and Adjustment for Disequilibrium**

220 ***In situ* sampler:** All samples showed similar loss rates and % equilibrium values. Accordingly,
221 we selected one deployment site (Riverbank Park; S1) to illustrate the observed patterns (Figures
222 1 and 2). A typical sigmoidal curve was observed for the % equilibrium K_{PE-W} relationship for
223 each of PCBs (Figure 1b) and PCDD/Fs (Figure 2b), where congeners with $\log K_{PE-W}$ ranging from
224 3.9 to 4.9 for PCBs and 3.5 to 5.3 for PCDD/Fs were at or approaching equilibrium (66 – 82 %
225 and 71 – 99 % respectively). Congeners with K_{PE-W} ranging from 5.3 to 5.6 were in the curvilinear
226 uptake phase (53 – 60 %). All PCB and PCDD/F congeners with $K_{PE-W} > 5.6$ were still far from
227 reaching equilibrium in the linear uptake phase (% equilibrium < 40 %). Based on the PRC results,
228 average $C_{LDPE(eq)}$ of the four deployments at each site (Figure S5) ranged from 6.27 ± 0.03
229 $\mu\text{g/LDPE}$ (S2) to 14 ± 0.01 (S3) $\mu\text{g/LDPE}$ for PCBs and from 33 ± 3.0 (S2) to 56 ± 7.0 (S2) for
230 PCDD/Fs.

231 ***Ex situ* samplers:** This section discusses the results obtained from the tumbling experiment
232 performed in the laboratory. PRC loss rates and the related % equilibrium calculated for PCBs and
233 PCDD/Fs showed significant and consistent (observed for all sediments) variations between the
234 25 μm and 51 μm samplers. Percent equilibrium approached by the PCBs (Figure 1b) and
235 PCDD/Fs (Figure 2b) in the 25 μm thickness samplers were significantly higher (Mann-Whitney
236 Rank Sum Test, $p < 0.003$) than values observed for the 51 μm thickness samplers in all the
237 equilibrations. The major difference was observed for PCB and PCDD/F congeners with $\log K_{PE-}$

238 $w \geq 7.0$ and > 6.3 respectively, where congeners were approaching equilibrium in the 25 μm
239 samplers (average % equilibrium: 74 % and 62 % respectively), while still in the linear uptake
240 phase in the 51 μm samplers (average % equilibrium: 39 % and 35 % respectively) after 8 weeks
241 of shaking. Nevertheless, the shaking period applied in the current study was not sufficient to fully
242 attain sediment – LDPE equilibrium (based on the PRC loss rates) and thus longer period should
243 be considered.

244 As expected, PRC loss rates and their related % equilibrium approached by each PCB and PCDD/F
245 congener were significantly lower *in situ* (Friedman Repeated Measures Analysis of Variance on
246 Ranks, $p < 0.001$) than values observed for the *ex situ* samplers (Figures 1b and 2b).

247 248 **Porewater concentrations**

249 Good agreement was generally observed for PCBs congeners measured with the tumbling
250 experiment using two different thicknesses and the *in situ* sampler (Figures 1d and S8 and Tables
251 S3- S6) with relative standard deviation % (RSD) ranging from 0.3 – 39 % in the four samples.

252 Our results contrast with those reported by Appell and Gschwend³¹, in which the authors observed
253 significantly lower *in situ* concentrations, presumably driven by bioirrigation.

254 Similarly, good agreement was generally for PCDD/Fs (Figures 2d and S9 and Tables S7 – S10)
255 with RSD % ranging from 1.0 – 22 %. Accordingly, we reason that the prototype *in situ* sampler
256 could successfully be used to estimate porewater concentrations of HOCs in shallow sediments if
257 properly pre-spiked with PRCs to correct for disequilibrium.

258 **Deuterated PAHs vs $^{13}\text{C}_{12}$ PCDDs as PRCs:** To investigate whether generic PRCs (d-PAHs)
259 were adequate for the accurate estimation of porewater concentrations of PCDD/Fs compared to
260 $^{13}\text{C}_{12}$ -PCDDs, we performed an additional field deployment (last deployment period) with LDPE
261 that were spiked with deuterated PAHs and one of each of $^{13}\text{C}_{12}$ di-, tetra- and hexa-chlorinated

262 dibenzo-p-dioxins (Figure 3a). These PRCs were also used in the accompanying *ex situ* tumbling
263 experiment, which represented the ‘true’ porewater concentrations (Figure 3b).
264 Slightly different results are obtained whether d-PAHs or ¹³C₁₂-PCDDs were used as PRCs in the
265 *in situ* (or the *ex situ* approaches). For the *in situ* samplers, relative percent difference (RPD %)
266 for PCDD/Fs in the four locations ranged from 1.0 % to 35 % for all PCDD/F congeners except
267 for 2,7/2,8-CDD, 2,3,7,8-CDF and 2,3,7,8-CDD at Passaic Avenue station (41 – 42 %) and
268 1,2,3,6,7,8-CDD at Doremous Street sampling site (52 %). For the *ex situ* samplers, lower
269 differences were observed (RPD %: 0.0 – 35 %) than in the *in situ* samplers. These calculated %
270 differences are within the estimated uncertainties for estimating porewater concentrations from
271 LDPE. Based on the obtained results, we conclude that d-PAHs could successfully be used as
272 PRCs for PCDD/Fs to correct for disequilibrium. We consider the use of ¹³C₁₂ PCDD/Fs as
273 optional, depending on budget constraints and needed certainty.

274 **Trends of Porewater concentrations**

276 Concentrations of 89 PCB congeners and 26 PCDD/F congeners from *in situ* sediment
277 deployments are given in Tables S3-S6 and S7-S10 respectively.

278 **PCBs:** Concentrations of Σ₈₉ PCBs ranged from 2.0 ng/L (S1) to 5.0 ng/L (S2) with an average
279 concentration of 3.0 ng/L. Concentrations of porewater at S2 were significantly higher (One-way
280 repeated measures of ANOVA, p < 0.01) than concentrations at all the other stations, which
281 showed comparable results (Tables S3-S6). The most abundant congeners were PCB 18, 16+32,
282 28+31, 43+52, and 42+44+59 comprising on average 67 % of the total PCB concentrations. As
283 shown in Figures 1, S8, samples were dominated by tri-, tetra- and di-chlorinated biphenyls
284 comprising 86 –89 % of the total PCB concentrations in the Passaic River.

285

286 **PCDD/Fs:** PCDD/F concentrations generally ranged from 24 pg/L (S1) to 41 pg/L (S3) with an
287 average concentration of 32 pg/L. In general, concentrations of furans were higher than dioxin
288 concentrations in the samples. All samples were dominated by the lower chlorinated furans (mon-
289 , di- and tri-) and 2,7/2,8-CDD (Figures 2, S9) comprising on average 97 % of the total PCDD/F
290 concentrations in the porewater. In terms of toxic equivalents, concentrations generally ranged
291 from 0.18 pg TEQ/L (S1) to 0.22 pg TEQ/L (S3), and all the samples were dominated by the
292 2,3,7,8-TCDD comprising 64 -73 % of the total TEQ concentrations in the porewater. The
293 dominance of 2,3,7,8-TCDD in the Passaic has been documented in previous studies³²⁻³⁵. Again,
294 these results confirm that ability of the LDPE-multisampler to detect spatial trends of HOCs.

295 296 **Riverwater concentrations**

297 Three LDPE deployments were performed at three sites including Sites 1, 3 and 4. No statistically
298 significant difference was observed between the detected freely dissolved concentrations of the
299 three deployments for PCBs and PCDD/Fs (except PCBs at Site 1). Accordingly, the discussion
300 here after will be based on the average concentration of the three deployments at each site.

301
302 **PCBs:** Estimated average freely dissolved concentrations of PCBs at the sampling sites are given
303 in Table (S11). \sum_{89} PCBs ranged from 1.3 ng/L to 1.8 ng/L, with no statistically significant
304 difference between the different sampling sites. Similar to porewater (Figure S8), samples were
305 dominated by the 3-Cl homologous group comprising 43 – 48 % (Figure S10) of the total PCB
306 concentrations followed 4-Cl (30 – 34 %) and 2-Cl homologous group (9.0 – 14 %).

307
308 **PCDD/Fs:** Estimated freely dissolved concentrations of PCDD/Fs at the three sampling sites
309 (samplers from one site were lost) are given in Table S12. Concentrations generally ranged from
310 19 pg/L (S1) to 39 pg/L (S4) with an average concentration of 25 pg/L. All the samples were

311 dominated by the lower chlorinated congeners (mono- through tri-chlorinated furans and di-
312 chlorinated dioxins) comprising > 93 % of the total concentrations (Figure S11). In terms of TEQ,
313 concentrations ranged from 0.16 pg TEQ/L to 0.33 pg TEQ/L. 2,3,7,8-TCDD was the dominant
314 congener comprising 27 – 82 % of the total TEQ concentrations.

315 **Porewater vs River water Concentrations and Profiles**

316 Derived porewater concentrations of PCBs (2.0 – 3.0 ng/L) and PCDD/Fs (25 – 41 pg/L) from *in*
317 *situ* samplers were slightly higher than estimated river water concentrations (1.3 – 1.8 ng/L and 12
318 – 39 pg/L for PCBs and PCDD/Fs respectively) at the same locations. Both porewater and river
319 water PCB profiles were dominated by the tri-, tetra- and di-chlorinated PCB congeners. Similarly,
320 profiles of PCDD/Fs in both porewater and riverwater were dominated by the lower chlorinated
321 congeners (mono- through tri-chlorinated congeners) (Figures S8-S11 and Tables S3-S12).
322 Calculated activities (equation S2) of PCBs and PCDD/Fs in porewater were higher than that of
323 the river water (Figure S12) indicating that porewater possibly act as a diffusive source of HOCs
324 to the overlying water and aquatic life.

325 **Biota Concentrations**

326 **PCBs:** Concentrations (ng/g lipid) of PCBs in the benthic species are given in Table (S13). Σ_{89}
327 PCB concentrations ranged from 2,700 ng/g lipid (shrimp) to 10,100 ng/g lipid (tube worms at S4)
328 with an average concentration of 6,450 ng/g lipid. Detected concentration of PCBs in the shrimp
329 was significantly lower than concentrations reported for the other species (Repeated Measures
330 Analysis of Variance on Ranks, $p < 0.001$). Additionally, concentration of PCBs in the tube worms
331 sampled at Passaic Ave (S4) was significantly higher than detected concentrations in the mud crabs
332 and the tube worms collected from River Bank Park (Site 1) (Repeated Measures Analysis of

336 Variance on Ranks, $p < 0.001$). Similar PCB profiles were observed in all the investigated benthic
337 species, where PCBs were dominated by tri- through hepta-chlorinated homologous groups (like
338 sediments) comprising 83 – 94 % of the total lipid normalized PCB concentrations (Figure S13).
339 **PCDD/Fs:** Concentrations of \sum_{26} PCDD/Fs in the benthic species ranged from 12 ng/g lipids
340 (shrimp) to 34 ng/g (clams) lipid with an average concentration of 23 ng/g lipid (Table S14). No
341 statistical significant difference was observed for the detected PCDD/F concentrations in the
342 different investigated benthic species. Unlike for PCBs, different patterns were observed in the
343 benthic species (see Figure S14). Concentrations of the most toxic 2,3,7,8-CDD congener ranged
344 from 0.70 ng/g lipid (tube worms at S1) to 2.0 ng/g lipid (mud crab at S1) comprising 2.0 – 9.0 %
345 of the total lipid normalized PCDD/F concentrations.

346 In terms of TEQ, concentrations ranged from 0.80 ng TEQ/g lipid to 2.2 ng TEQ/g lipid. As
347 expected, 2,3,7,8-TCDD dominated the TEQ concentrations contributing on average 87 % of the
348 total WHO-TEQ concentrations followed by penta- and hexa- CDF congeners (4.0 % and 3.0 %
349 respectively).

350

351 **Profiles of PCBs and PCDD/Fs in Porewater vs Riverwater vs Sediments vs Biota**

352 To investigate the similarities/dissimilarities in the observed profiles of PCBs and PCDD/Fs in
353 sediments, porewater, biota and river water, factor analysis was performed. The factor analysis
354 (Tables S15-S17) generated 3 factors that explained 96 % of the total variability in the data. Factor
355 1 explained 42 % of the total variability and was heavily loaded on all the porewater and riverwater
356 profiles at all the sampling sites (> 0.95). This is a reflection of the similar freely dissolved profiles
357 of OCBs and PCDD/Fs (dominance of the lower chlorinated congeners). Factor 2 explained 29 %
358 of the total variability and was heavily loaded (> 0.90) on all the sediment samples and moderately
359 loaded (0.54 – 0.63) on some of the benthic species. This explains some of the similarities in the

360 profiles of HOCs in the sediments and the benthic species (abundance of the higher chlorinated
361 PCB and PCDD/F congeners). Factor 3 explained 25 % of the total variability in the data and was
362 loaded on the biota samples. Although biota samples had high contributions from 1,2,3,4,6,7,8,9-
363 CDD, tetra- and penta-chlorinated PCBs like in sediments, they also showed significant
364 contributions from the lower chlorinated PCDD/F congeners and less contribution of the hexa- and
365 hepta-chlorinated PCBs compared to sediments and accordingly, they were heavily loaded on a
366 separate factor than sediments.

367
368 ***In situ* passive sampler- biota relationship:** We report the regression lines developed in the
369 current study for PCBs + PCDD/Fs (combined) in addition to literature relationships previously
370 obtained for LDPE and other passive samplers in field studies^{19,36-43}. For ease of comparison and
371 visualization, we plotted logarithmic- converted concentrations for better visualization. A factor
372 of ± 10 was incorporated into the relationship (Figure 4) as previously suggested by Joyce et al.⁴⁰.

373
374 As shown in Figure 4 and Table S18, all the regression relationships obtained in the current study
375 between LDPE concentrations and lipid-based concentrations in mud crabs, tube worms (at two
376 sites), clams and shrimp were within the order of magnitude range (factor 10) and were above
377 the 1:1 relationship (lipid-based concentrations were higher than LDPE concentrations).
378 Additionally, coefficient of variation (R^2) in the current study ranged from 0.81 to 0.91 (SE: 0.27
379 – 0.37), and slopes were statistically insignificant from 1.0 [0.80 – 1.06 (SE: 0.04 – 0.06), $p <$
380 0.001]. Overall, the regressions indicate that the affinity of PCBs and PCDD/Fs to LDPE passive
381 samplers are rather similar (slope of 1) to that of lipids in the investigated organisms.

382 In our previous work⁷, LDPE concentrations of HOCs (PCBs, PCDD/Fs, PBDEs and
383 organochlorine pesticides) obtained from the *ex situ* approach also displayed significant log-log

384 linear relationship with their corresponding lipid-based concentrations in various fish species (R^2
385 = 0.79, SE = 0.62, slope = 1.2, $p < 0.001$) of the lower Passaic River. Lipid based concentrations
386 were higher than LDPE concentrations as was also observed in the current and other studies (see
387 Figure 4). Coefficient of determinations (R^2) for the regression analysis in the current study (0.81
388 – 0.91) were among the highest observed in previous studies.^{19,36–43}

389 Porewater passive samplers also yielded better correlations than those (Table S18) obtained by
390 using sediment OC, OC + BC or riverwater to predict lipid-based concentrations (Figure S15). This
391 implies that the accumulated amounts of HOCs in LDPE sheets deployed in sediments are better
392 predictors of lipid-based concentrations of HOCs and that the proposed porewater *in situ* LDPE
393 based sampler could be effectively used to predict the bioaccumulation of HOCs in biota.

394
395 **Influence of lipophilicity on the affinities of HOCs to LDPE and lipids:** $\log(C_{lip}/C_{passive})$ was
396 calculated and plotted against $\log K_{lip-w}$ as a surrogate for lipophilicity (Figure 5). $\log(C_{lip}/C_{passive})$
397 values ranged from -0.37 ± 0.37 to 1.6 ± 0.50 with an average value of 0.51 ± 0.33 . The average
398 value of the current study was similar to that calculated for DDTs and PCBs using various passive
399 samplers in Joyce et al.⁴⁰, albeit with a lower standard deviation in our work (0.52 ± 0.49).

400 Calculated $C_{lip}/C_{passive}$ decreased with the increase in K_{lip-w} indicating that the affinity of HOCs to
401 lipids and LDPE becomes more similar with the increase in hydrophobicity. Future work should
402 measure the exact difference between animal lipids and LDPE to be able to correct for this
403 divergence, as far as it is caused by physico-chemical partitioning differences.

404 The lower chlorinated PCBs (1- and 2-Cl) had a higher affinity towards lipids, which could
405 possibly be attributed to their higher solubilities, and thus more uptake from porewater and
406 riverwater. In the study performed by Joyce et al.⁴⁰, a completely different pattern was observed,
407 where higher ratio values were observed for analytes with higher $\log K_{OW}$ values. This observed

408 variation could also be attributed to the differences in the passive samplers used, differences in the
409 investigated species and accordingly their metabolic rates and differences in the level of
410 contamination of the sediments with HOCs among the different studies.

411
412 **Implications**

413 Joyce et al.⁴⁰ reviewed the use of passive samplers as surrogates to predict the bioaccumulation of
414 HOCs in aquatic organisms and indicated the existence of several basic and conceptual data gaps
415 currently limiting their use. Previous work had evaluated the bioaccumulation predictive ability of
416 LDPE only for marine organisms, and most studies were laboratory-based. The current study
417 addressed some of the knowledge gaps.

418 Our study indicated that *in situ* porewater passive samplers are good predictors of lipid-based
419 concentrations in freshwater aquatic organisms and that the predictive ability of the passive
420 samplers was better than sediments using the common equilibrium partitioning theory.
421 Additionally, the current results indicated the good agreement between estimated porewater
422 concentrations using both the *in situ* and *ex situ* approaches. We therefore suggest that the *ex situ*
423 laboratory approach, while easier, is not necessarily superior or needed^{2,36}. By and large, we report
424 similar results for PCDD/Fs and PCBs both *in situ* and *ex situ* for 2 key groups of HOCs. These
425 results also indicate the absence of significant bioirrigation at those sites³¹. It remains important to
426 select representative PRCs that covers the entire range of analytes investigated. In our previous
427 work^{3,7,8,24}, we indicated that (*ex situ*) porewater was a better predictor of the bioaccumulation of
428 various HOCs in fish of different trophic levels. An *in situ* comparison might yield more
429 representative results but should also include the analysis of trophic status of benthic biota to better
430 explain the observed results.

431 A comparison of the detected sediment and porewater concentrations also showed that total
432 sediment concentration of PCBs, and particularly PCDD/Fs is not necessarily a good predictor of
433 porewater concentrations. In addition, while we observed gradients in sediment and porewater
434 concentrations, there were no significant spatial differences in riverwater itself for PCBs and
435 PCDD/Fs in this study. This makes riverwater potentially a useful medium for establishing
436 temporal trends, but much less powerful for assessing spatial trends.

437 Future work should then concentrate on studying the ability the proposed *in situ* sampler to predict
438 the bioaccumulation potential in an entire food web and that whether one regression equation could
439 be used as a representative of the entire foodweb or not. Given the recent diverging results from a
440 porewater interlaboratory comparison⁴⁴, performing field-based comparisons of different passive
441 sampling approaches will be needed to further increase the confidence in their results.

442

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445

446 **Supplementary Information:**

447 Detailed information about sampling, extraction and cleanup of samples, instrumental analysis,
448 quality assurance/quality control, physicochemical properties of PCBs and PCDD/Fs, uncertainty
449 analysis and statistical analysis. This information is available free of charge via the Internet at
450 <http://pubs.acs.org>.

451

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453

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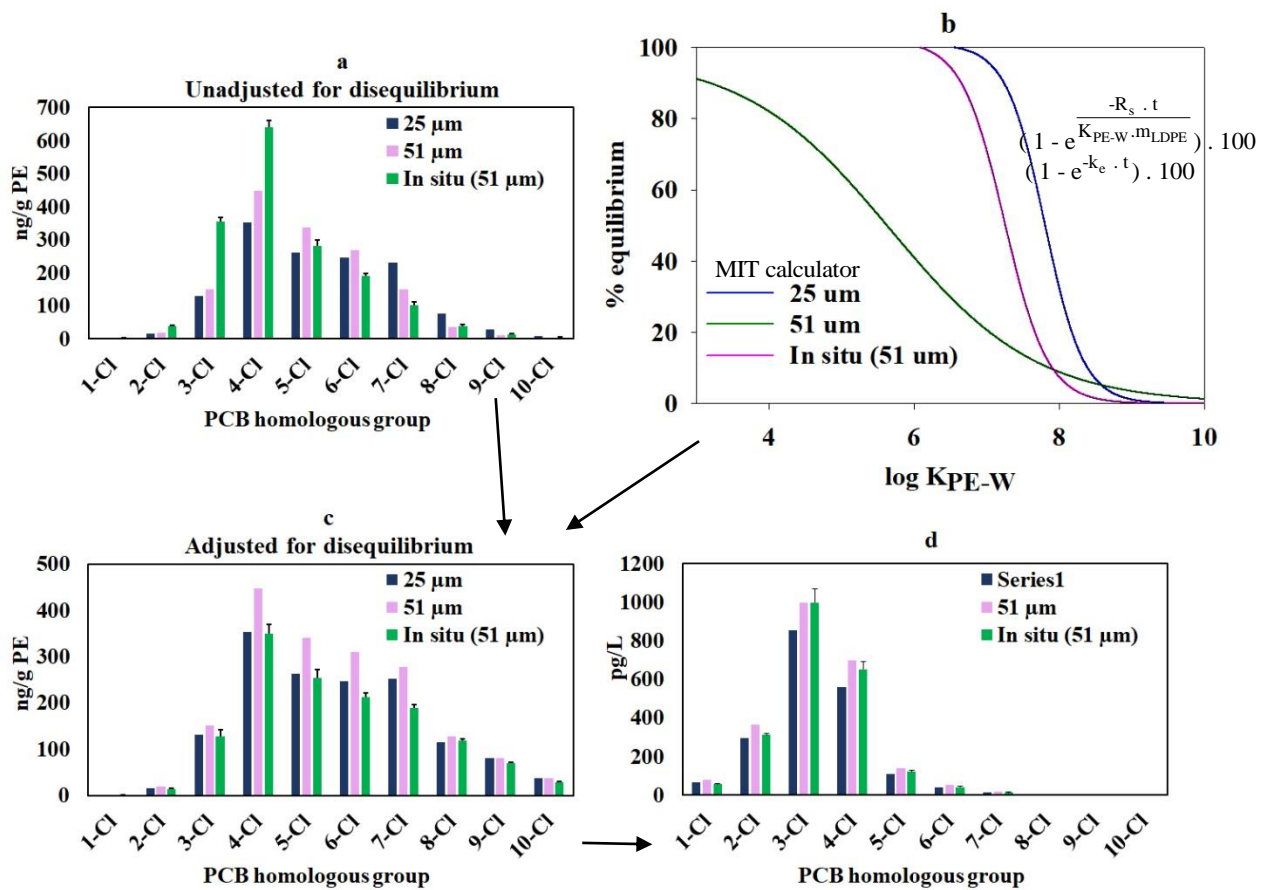
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637 Figure 1: Concentrations of PCBs (ng/g PE) in the LDPE of the proposed *in situ* porewater sampler

638 before (a) and after (c) correction for disequilibrium using PRCs (b) and the estimated

639 porewater concentrations (d) at S1 (Riverbank Park).

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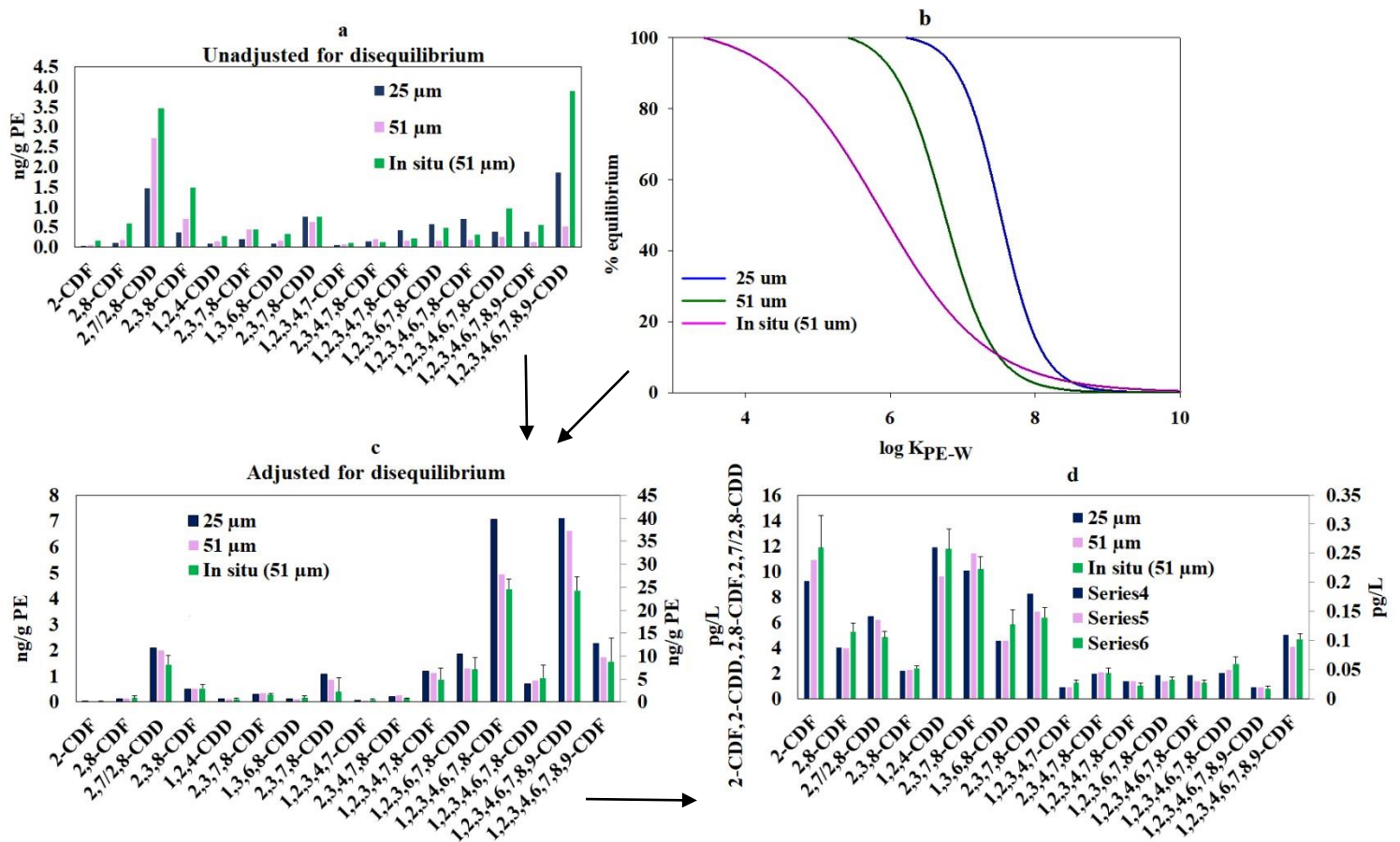
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664 Figure 2: Concentrations of PCDD/Fs (ng/g PE) in the LDPE of the proposed *in situ* porewater

665 sampler before (a) and after (c) correction for disequilibrium using PRCs (b) and the

666 estimated porewater concentrations (d) at S1 (Riverbank Park).

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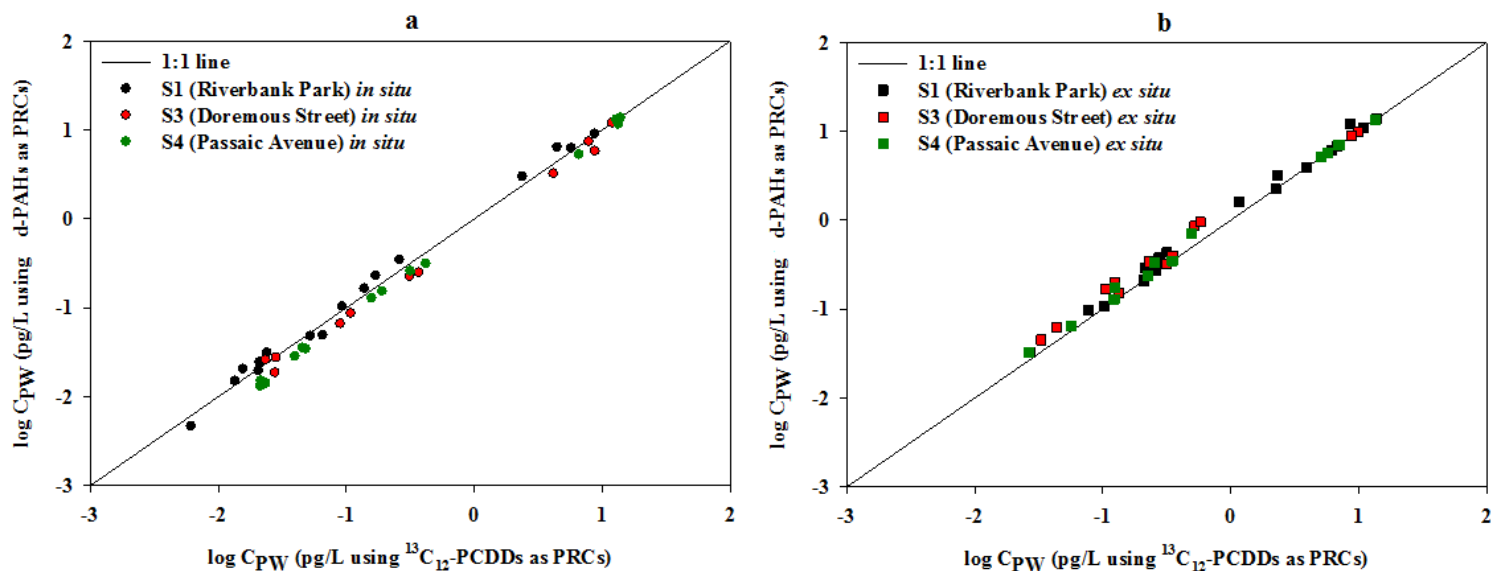
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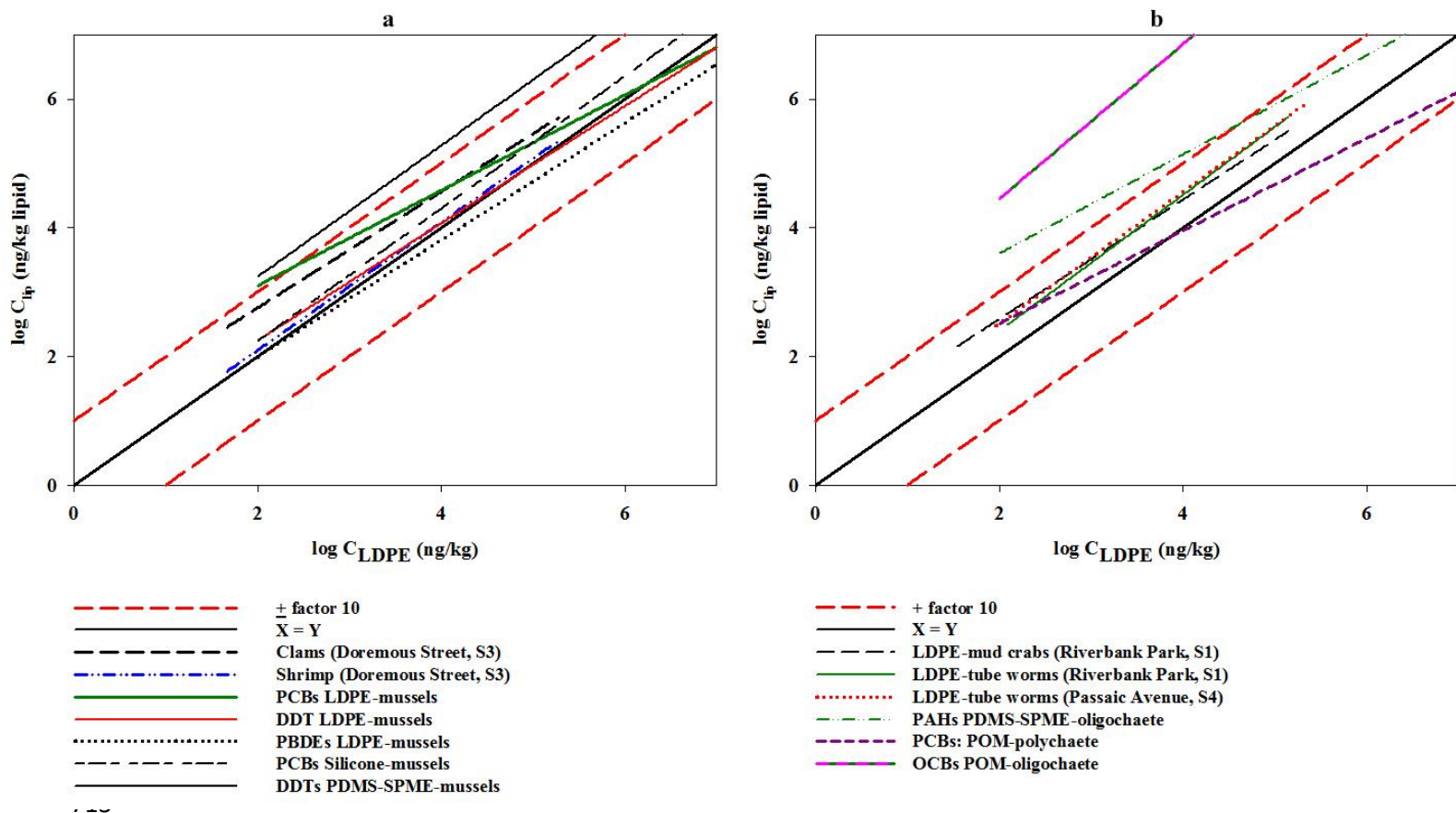
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688 Figure 3: Comparison between using either d-PAHs or ¹³C -PCDDs as PRCs for correcting
689 porewater passive samplers for non-equilibrium using *in situ* (a) and *ex situ* (b)
690 approaches at the sampling sites.

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714 Figure 4. Log-log linear relationships between lipid-based tissue concentrations (C_{lip}) in clams and
 715 mussels (a) and in crabs, oligochaete and polychaetes (b) vs passive sampler's
 716 concentrations in the current and previous studies. The continuous black line represents
 717 a 1:1 correlation. The two dashed red lines represent plus or minus a factor of 10. PCBs
 718 LDPE-mussels relationship from Burgess et al.³⁸; DDT-LDPE and PBDE-LDPE
 719 relationships from Joyce et al.⁴⁰; PCBs silicone-mussels relationship from Smedes⁴⁵;
 720 DDTs PDMS-SPME relationship from Pirogovsky⁴²; PCBs POM-polychaete
 721 relationship from Janssen et al.⁴⁶; PCBs POM-oligochaete relationship from
 722 Beckingham and Ghosh¹⁹. Regression parameters are given in Table S18.

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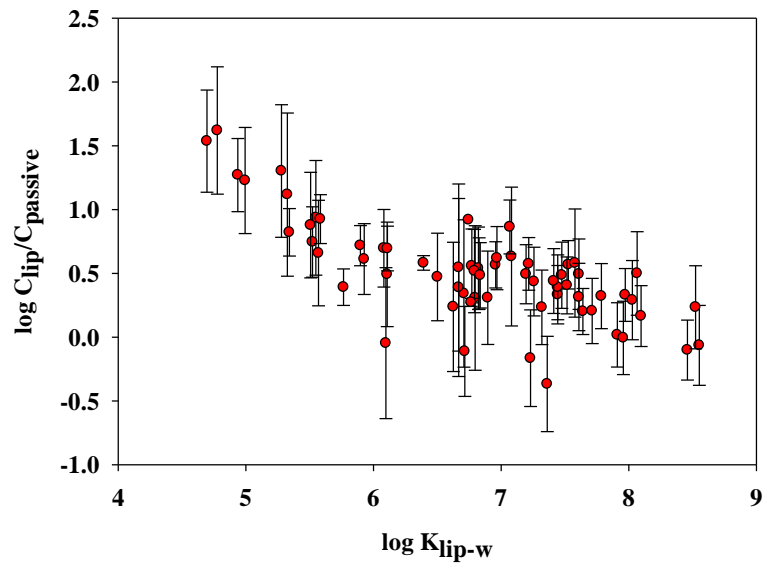


Figure 5: Ratio of lipid normalized concentrations to LDPE-based concentrations plotted against lipid-water partitioning coefficient (K_{lip-w}). Circles represent average values of all the investigated species and the error bars represent the standard deviation.

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