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# Using Polyethylene Passive Samplers to Study the Partitioning and Fluxes of PBDEs in an Urban River

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27 (30 %); only 5 % of PDBEs were truly dissolved. Calculated sediment-water diffusive fluxes  
28 greatly overwhelmed the atmospheric depositional flux to the river.

29

### 30 **Introduction**

31 Polybrominated diphenyl ethers (PBDEs) are a class of hydrophobic brominated organic  
32 contaminants (HOCs) that were produced in three (penta-, octa- and deca-) technical  
33 formulations.<sup>1,2</sup> They were widely used in electronic equipment, textile paint and plastics to  
34 improve fire safety<sup>3</sup>. PBDEs have been detected in abiotic<sup>4-6</sup> and biotic environmental  
35 compartments <sup>7-10</sup> including remote areas<sup>11</sup>, and humans<sup>12</sup>. In North America, the production of  
36 the penta- and octa-BDE technical mixtures has been largely phased out<sup>13</sup>. However, PBDEs still  
37 exist in consumer products and continue to leach into the environment<sup>14</sup>. Once in the environment,  
38 they can persist and bioaccumulate leading to adverse health effects<sup>4</sup>. The penta-technical  
39 formulation has attracted the attention in recent years, due to its global consumption and higher  
40 ecotoxicities compared to the higher brominated formulations<sup>6</sup>. Tetra- through hepta-brominated  
41 congeners were listed as persistent organic pollutants (POPs) under the Stockholm Convention<sup>15</sup>.

42

43 In the aquatic environment, the transport, fate, effect and bioaccumulation of HOCs depends on  
44 their physicochemical properties, environmental conditions and sorption to solid phases. For  
45 instance, the uptake of HOCs by biota, their fate and transport are greatly influenced by the truly  
46 dissolved/colloidal/particulate phase distribution pattern. The truly dissolved fraction is highly  
47 bioavailable and can undergo diffusive exchange with the overlying air, underlying sediments, and  
48 the colloidal phase.

49 Passive sampling techniques were developed as an inexpensive/effective alternate for monitoring  
50 the truly dissolved HOCs in the atmosphere and water. Among the widely available passive

51 sampling matrices, low density polyethylene (LDPE) has been widely used for measuring HOCs  
52 in the atmosphere<sup>16-18</sup>, water<sup>16,18</sup>, porewater<sup>19-21</sup>, studying their diffusive fluxes<sup>16,18</sup> and  
53 investigating the bioaccumulation potential of POPs<sup>22,23</sup>.

54 In sediments, HOCs are typically strongly absorbed into organic matter.<sup>24</sup> Pyrogenic carbon  
55 particles such as black carbon (BC) may also play an important role in the sorption of HOCs (via  
56 adsorption) despite of its low contributions in sediments (1.0 – 20 % of the total organic  
57 carbon).<sup>25,26</sup> Black carbon has hence been referred to as a super sorbent for HOCs<sup>27,28</sup> including  
58 PBDEs<sup>4,27</sup>. As a result, BC is widely considered in studying the geochemistry of HOCs in  
59 sediments and soil<sup>21,27,29</sup>; including BC as a separate sorbent phase has greatly improved the  
60 prediction of the truly dissolved concentrations in sediments (porewater) when applying  
61 geochemical models<sup>5</sup>. HOCs are associated with BC and/or organic carbon during the transport  
62 and deposition away from their emission source if common for both.

63 Despite increasing concern over PBDEs in the environment, few studies have investigated the  
64 partitioning of PBDEs in the water column<sup>5,30</sup> and in sediments<sup>6,29</sup>. Additionally, no study has  
65 addressed the geochemistry of PBDEs in an aquatic environment comprehensively. In the current  
66 study, we used LDPE to investigate the temporal and spatial transport and fate of PBDEs in water,  
67 air, sediment and porewater samples in the lower tidal portion of the Passaic River, NJ which is  
68 greatly affected by the industrial activities<sup>31</sup> in the region. This region was selected because the  
69 presence of legacy and ongoing contaminants is well documented<sup>20,31-33</sup> in its environmental  
70 compartments, whereas none of the studies focused on PBDEs despite of the highly urbanized  
71 nature of the region.

72 Gaseous atmospheric and truly dissolved aqueous concentrations of PBDEs were determined by  
73 LDPE passive samplers concurrently at several locations. Adjacent samplers were used to calculate

74 the diffusive gaseous fluxes of PBDEs. Moreover, active water samples were collected to  
75 determine the particulate phase concentrations of PBDEs, compare the concentrations obtained  
76 from the passive and active samplers, and to determine the colloidal phase concentrations of  
77 PBDEs after measuring the dissolved organic carbon (DOC) in the water column. We were thus  
78 able to study the partitioning of PBDEs in the water column.

79 In the sediment, we used LDPE to measure porewater concentrations. By measuring the fractions  
80 of BC and OC, and PBDE concentrations in sediments, we were able to calculate the solid-water  
81 partitioning coefficients ( $K_{ds}$ ) and study the role played by the active sorbents in determining the  
82 fate of PBDEs in the river. Finally, we used particulate-phase PBDE concentrations, truly  
83 dissolved PBDE concentrations in the water column and the porewater to quantify the diffusive  
84 fluxes to or from the sediments. To our knowledge, this is the first comprehensive study that  
85 utilizes passive samplers to assess the partitioning of PBDEs between DOC, OC and BC in water  
86 and porewater and their transport between air, water and sediment in an urban river.

87

## 88 **Materials and Methods**

89 Detailed description of the sampling procedures, extraction, analysis, quality assurance, statistical  
90 analysis and the selected physicochemical properties are provided in the Supplementary  
91 information (SI). In addition, details on fluxes of PBDEs across air-water, water-sediment,  
92 suspended particulate matter (SPM)-sediment, and partitioning models of PBDEs between  
93 suspended particle-water, porewater - BC and OC in sediments, and uncertainty calculations are  
94 provided in the SI, Figures S1 and S2, Tables S1 – S6 and in Khairy et al.<sup>20,34</sup> and are briefly  
95 summarized below.

96 LDPE was pre-cleaned and spiked with performance reference compounds including deuterated  
97 polycyclic aromatic hydrocarbons (PAHs; naphthalene-d<sub>8</sub>, pyrene-d<sub>10</sub>, and benzo(a)pyrene-d<sub>12</sub>),  
98 brominated biphenyls (PBB 9, PBB 52, and PBB 103) and octachloronaphthalene according to the  
99 method outlined in Booij et al.<sup>35</sup> These samplers were deployed in the atmosphere (in two inverted  
100 bowls ~ 2 m above the ground as a shelter for protection against sunlight and precipitation) and  
101 the water (suspended ~1–2 m below the surface) along the lower portion of the Passaic River  
102 (Figure S1) during 6 deployments for 2 months each from September, 2011 to November, 2012.

103 Active water samples (100 L each passing on a glass fiber filter and three polyurethane foams at a  
104 flow rate of 2 l/min) were collected at three different locations (Figure S1) during November, 2011,  
105 March and July, 2012 using a water pump. Dissolved organic carbon (DOC) was measured in the  
106 water samples according to the EPA method 415.3<sup>36</sup>.

107 Sediment samples were collected from mudflats at low tide at 18 different locations (Figure S2)  
108 along the river and 4 locations from Newark Bay during September to November 2011. Detailed  
109 description of the sampling methodology and sampling locations can be found in Khairy et al.<sup>34</sup>.

110 Total organic carbon (TOC) and black carbon (BC) content in the sediments were determined as  
111 detailed in Gustafsson et al.<sup>26</sup>. Truly dissolved porewater concentrations of PBDEs were  
112 determined using a LDPE tumbling procedure as detailed in Lambert et al.<sup>21</sup>

113 Prior to extraction, all samples were spiked with 10 µL of a surrogate standard composed of  
114 labelled PBDE congeners (<sup>13</sup>C<sub>12</sub> BDE-28, 47, 99, 153 and 183; 4.0 ng/µl in nonane). After  
115 extraction and cleanup (see SI), purified extracts from all the samples were analyzed for 12 PBDE  
116 congeners (BDE-2, 8, 15, 28, 30, 47, 49, 99, 100, 153, 154, 183) using an Agilent GC 6890N  
117 equipped with a Quattro micro GC tandem MS (Waters) according to the method detailed in  
118 Khairy et al.<sup>37</sup>.

119 Procedural blanks, field blanks (LDPE), matrix spikes, and duplicate samples (20% of the total  
120 sediment samples) were included with each sample batch. BDE-47 was the only congener detected  
121 in the blanks and samples were corrected for blanks. Limits of detection (LOD) were determined  
122 in the different matrices based on a signal/noise ratio of 3.0 (Table S3). Recoveries of the surrogate  
123 standards generally ranged from 83 - 96%, 80 – 104 %, 72 – 85 %, 87 – 98 % and 78 – 83 % for  
124 the LDPE, sediments, filters and PUFs respectively. Matrix spikes recoveries were always >90%  
125 and < 110 % with a relative standard deviation < 20% (Table S4). Results of the replicate analysis  
126 of LDPE and the sediment samples indicated that the reproducibility of the analysis ranged from  
127 12.5 % – 21.3 %.

128

## 129 **Results and Discussion**

130 We first discuss PBDE concentrations in sediment, porewater and sediment-water sorption, then  
131 present results for PBDEs in the water column and discuss the influence of DOC on partitioning.  
132 This is followed by the gaseous atmospheric levels of PBDE. Lastly, we derive air-water exchange  
133 fluxes and a mass balance for PBDEs in this tidal river. The site of our study, the lower 24 km of  
134 the Passaic River, is a heavily industrialized and contaminated region, which is known for its  
135 contamination by PCDD/Fs<sup>21,34</sup>, but also contains other HOCs<sup>20</sup>, including PBDEs at elevated  
136 concentrations.

### 137 **PBDE Concentrations in Sediments**

138 Concentrations of  $\sum_{12}$  PBDEs ranged from 1.0 - 16 ng/g dw and 3.0 - 9.0 ng/g dw in Passaic River  
139 and Newark Bay (Table S7) respectively. Concentrations generally increased downriver from river  
140 km 24 (2.5 ng/g dw) to river km 11 (11 ng/g dw). In Newark Bay, PBDE concentrations increased  
141 compared to the last portion of the lower Passaic River (Figure S3) indicating either different

142 PBDE sources, difference in the emission levels from a given source, loadings from the Passaic  
143 River itself and/or the influence of sediment geochemistry (see below). Samples were dominated  
144 by BDE-47 and BDE-99 comprising on average 29 % and 28% respectively of the total  
145 concentrations (Figure S3). Higher brominated congeners (BDE-100, 154, 153 and 183) showed  
146 also considerable contributions, which could be attributed their enhanced sorption to sediments as  
147 a result of increasing partition to solids. The median sediment concentration of PBDEs (4.6 ng/g  
148 dw) in the Passaic River was much higher than those in the Niagara River (0.11 ng/g dw)<sup>38</sup> and  
149 Dialiao River Estuary, China (0.05 ng/g dw)<sup>39</sup>, and close to that of Beijiang River, China (6.1 ng/g  
150 dw)<sup>40</sup>. The mean concentration in the current study (5.5 ng/g dw) was also much higher than the  
151 mean concentration for sediments of Saginaw River, USA (0.50 ng/g dw)<sup>41</sup>. In contrast, average  
152 concentration in the current study was much lower than the average sediment concentration of  
153 Guiyu River China (3,212 ng/g dw)<sup>42</sup>. BDE-209 was excluded from all the comparison studies.

#### 154 **Porewater concentrations of PBDEs**

155 Porewater concentrations ranged from 12 pg/L (km 29.9) to 40 pg/L (km 1.8) in the river and from  
156 22 - 42 pg/L in Newark Bay (Table S8), which showed a significant increase ( $R^2 = 0.31$ ;  $p = 0.007$ )  
157 with the increase in sediment concentrations. BDE-47 was the dominant congener comprising 13  
158 – 50 % of the total concentrations followed by BDE-28 (6.0 – 30 %), BDE-49 (4.0 – 25 %), BDE-  
159 99 (1.0 – 23 %) and BDE-15 (2.0 – 20 %) (Figure S4). Overall relative uncertainty (equation S17)  
160 associated with the analytical errors and the estimation of the truly dissolved concentrations from  
161 LDPE deployments ranged from 64 – 66 %. There are very few other known porewater  
162 concentrations reported in the literature<sup>22,43</sup>. Our detected concentrations were much higher than  
163 the freely dissolved porewater concentrations of Narragansett Bay, RI ( $< 3.0$  pg/L)<sup>22</sup> but much



164 lower than the apparent porewater concentrations detected in marine sediments from China (170  
165 – 6,430 pg/L)<sup>43</sup>.

### 166 **Sediment Partitioning of PBDEs**

167 Overall sediment-water distribution coefficients,  $K_d$ s, were predicted using considering either just  
168 OC (equation 1), or both OC and BC (equation 2), and compared with observed  $K_d$  values:

$$169 \quad K_d = K_{OC} f_{OC} \quad (1)$$

170 where  $f_{OC}$  is the OC fraction in sediment (g/g sed), and

171  $K_{OC}$  is the OC-water partitioning coefficient (L/kg).

$$172 \quad K_d = K_{OC} f_{OC} + f_{BC} K_{BC} C_{PW}^{n-1} \quad (2)$$

173 where  $f_{BC}$  is the BC fraction in sediment (g/g sed),

174  $K_{BC}$  is the BC-water partitioning coefficient (L/kg),

175  $C_{PW}$  is porewater concentrations ( $\mu\text{g/L}$ ), and

176  $n$  is the Freundlich coefficient (0.7).

177 Predicted  $K_d$ s based on OC (RU: 8.0 – 42 %) were 2.0-106 folds lower (under-predicted) than  
178 observed  $K_d$ s in 81 % of the cases (Figure 1a). A similar trend was observed for PAHs and  
179 PCDD/Fs at the superfund site as part of the Passaic River<sup>21</sup>. The use of OC + BC (site specific  
180 values) dual model (Figure 1b) greatly improved the prediction, where predicted values over-  
181 estimated  $K_d$  values in 91 % of the data points by a factor of 1.0 – 2.0, and 2.0 – 5.5 in only 9.0 %  
182 of the data points. In both models, slopes of the regression lines were significantly different from  
183 zero ( $p < 0.05$ ) and ranged from 0.62-1.63. A slope of +1 is typically interpreted as being in

184 equilibrium, with the model capturing the key variable (i.e., interactions) of the observations<sup>44</sup>.  
185 Additionally, significant positive log-linear regression relationships ( $p < 0.05$ ) were observed  
186 between observed and predicted  $K_{ds}$  (Figure 1a, b). According to equation (2), BC accounted for  
187 12 – 99 % of total sorption of PBDEs to sediment. In conclusion, our results indicate the key role  
188 played by the BC in the sorption of PBDEs in sediment, in-line with previous results for PAHs,  
189 PCBs and PCDD/Fs<sup>20,21</sup>.

### 190 **PBDE Concentrations in the River Water**

191 PBDE concentrations obtained from the active samples are given in Table S9. Detected  
192 concentrations from the PUFs (truly dissolved + colloidal phase) ranged from 69 - 218 pg/L.  
193 Concentrations increased when moving downriver from river km 19 (average: 92 pg/L) to river  
194 km 9.6 (156 pg/L). Detected concentrations were greater than those previously reported for the  
195 Pearl River Estuary, China (2.15 – 127 pg/L)<sup>5</sup> and San Francisco Bay, USA (0.20 – 78.7 pg/L)<sup>45</sup>  
196 Concentrations of particulate matter in the river water ranged from 72 – 90 mg/L with minor  
197 variations between the sampling locations and within each sampling location at the different  
198 sampling periods. Particulate phase PBDE concentrations ranged from 62 - 886 pg/L (Figure S5).  
199 Concentrations of PBDEs in the particulate phase during the summer were 2.0 – 13-fold higher  
200 than concentrations reported during the autumn and spring (Figure S5); the reason for the higher  
201 summer concentrations is not known. All PUF and GFF samples were dominated by BDE-47 and  
202 BDE-99 comprising 30 - 43 % and 35 – 37 % respectively of the total PBDE concentrations in  
203 both phases.

204 As expected, truly dissolved concentrations of  $\sum_{12}$  PBDEs (obtained from the LDPE passive  
205 samplers) were lower than those from active sampling, and ranged from 5.5 - 51 pg/L with an  
206 average concentration of 23 pg/L (Table S10), and an overall uncertainty (equation S17) of 41 –

207 50 %. Detected truly dissolved concentrations were lower than concentrations recently detected in  
208 the lower Great Lakes (0.60 – 18 pg/L).<sup>18</sup> Comparable concentrations were generally observed at  
209 all the sampling locations (Figure S6) with slightly higher concentrations observed during the  
210 summer, autumn and spring seasons of 2012 with no significant correlation with water  
211 temperature. BDE-47 and BDE-99 dominated the samples comprising 41-49 % and 12-15 %  
212 respectively of the total PBDE concentrations (Figure S7). BDE-49 showed also considerable  
213 contributions (6.0 – 17 %).

#### 214 **Comparison between Active and Passive Water Concentrations**

215 Concentrations obtained from active PUF sampling ( $C_{ap}$ , in pg/L) represent both truly dissolved  
216 PBDEs and those in the colloidal phase. Accordingly, we derived the truly dissolved  
217 concentrations ( $C_w$ , in pg/L) by subtracting the colloidal-bound fraction of PBDEs (Equation 3):

$$218 \quad C_w = \frac{C_{ap}}{1 + [\text{DOC}] K_{\text{DOC}}} \quad (3)$$

219 where [DOC] is the aqueous DOC concentrations (kg/L), and

220  $K_{\text{DOC}}$  is the DOC-water partitioning coefficient (L/kg).

221 We predicted  $K_{\text{DOC}}$  values from  $K_{ow}$  according to the overall equation developed by Burkhard<sup>46</sup>  
222 ( $K_{\text{DOC}} = 0.08 K_{ow}$ ) for HOCs.

223 Good agreement was generally observed between passive and active concentrations corrected for  
224 DOC (Figure S8) with a factor difference ranging from 0.8 – 2.9 despite the difference in the  
225 sampling periods between both sampling techniques and the uncertainties associated with the  
226 analysis and calculations [64 – 66 % for the passive samples and 20 – 46 % for the PUFs (equation  
227 S18)].

## 228 **Water column partitioning of PBDEs**

229  $K_{\text{DOC}}$  values calculated in the current study (Table S11) were compared with literature  
230 values<sup>21,29,47</sup>.  $K_{\text{DOC}}$ s were plotted against  $K_{\text{OW}}$ s, and the slope of this significant relationship  
231 (Figure S9) was 0.18 ( $K_{\text{DOC}} = 0.18 \times K_{\text{OW}}$ ). This slope was higher than that calculated for PAHs  
232 and PCBs (0.08)<sup>46</sup>, indicating stronger affinity of PBDEs for DOC with increasing size relative to  
233 PAHs and PCBs; or in other words PBDEs sorb differently. Nevertheless, great variability was  
234 observed for  $K_{\text{DOC}}$  values reported in literature (Table S11)<sup>21,29,46-50</sup>. Our  $K_{\text{DOC}}$  values were only  
235 0.08 – 0.37 log units higher than those predicted in reference [<sup>46</sup>] indicating good agreement, and  
236 were similar to values calculated by ter Laak et al<sup>49</sup> for BDE-47, 99 and 153 (Figure S10). In  
237 contrast, our calculated values for BDE-28, 47, 99, 100, 153 and 183 were an order of magnitude  
238 higher than values reported by Wei-Haas et al.<sup>50</sup> for Arctic waters (Figure S10).

239 Observed organic carbon-water partitioning coefficients ( $K_{\text{OC}}$ s) were plotted against  $K_{\text{OW}}$ s.  $K_{\text{OC}}$ s  
240 were calculated thrice relative to PBDEs on particles - based on (i) apparent water concentrations  
241 ( $C_{\text{ap}}$ ) obtained from PUFs; (ii) truly dissolved water concentrations ( $C_{\text{d}}$ ) obtained from the LDPEs;  
242 and (iii) predicted ( $C_{\text{w}}$ ) obtained from PUFs after correcting for DOC (surrogate for colloidal  
243 phase). The correlation between  $K_{\text{OC}}$  and  $C_{\text{ap}}$  displayed significant log-linear relationships ( $p <$   
244 0.05) in the majority of the samples with slopes (0.10 – 0.49, Figure 2a) much shallower than those  
245 indicating non-equilibrium situation<sup>51</sup> or a significant sorption to colloids<sup>52</sup>. When  $C_{\text{d(w)}}$ s (both  
246 from LDPE and from PUFs after correction for DOC) were used, slopes were insignificantly ( $p <$   
247 0.05) different from 1 indicating an equilibrium partitioning situation<sup>5</sup>, and that the reason for the  
248 deviation using the apparent concentrations was the sorption to colloids.

249 In the Passaic River, the fraction of PBDEs sorbed to the colloids ranged from 3.7 % (BDE-2) to  
250 99 % (BDE-183) of the apparent concentrations, which were within the range observed for the

251 Hudson River<sup>53</sup> and slightly higher than values reported for the Pearl River Estuary, China (10 –  
252 98 %)<sup>5</sup>. This implies that only a small fraction (1.0 – 33 %) of tetra- through hepta-brominated  
253 diphenyl ethers is truly dissolved and could be available for either volatilization and/or diffusive  
254 uptake. Overall, though, POC was the most important PDBE reservoir in the water. The PBDEs  
255 (4-7 bromines) sorbed to particles represented on average 65 % of the total water concentrations  
256 followed by C<sub>DOC</sub> (30 %) and C<sub>d</sub> (5.0 %).

257 Our results confirm that active sampling severely overestimates truly dissolved concentrations,  
258 and a DOC correction needs to be performed. The K<sub>DOC</sub> values derived here could be used for that  
259 purpose. Yet, we argue that passive samplers are preferably used to study the water column  
260 partitioning of various hydrophobic organic compounds (HOCs) to yield dissolved concentrations  
261 directly.

262 Observed K<sub>p</sub> (using the freely dissolved concentrations obtained from the LDPE) in the water  
263 column were compared with predicted K<sub>p</sub> using the OC and OC + BC models. K<sub>OC</sub> values were  
264 obtained from ref [54]. Predicted K<sub>p</sub> values using OC (Figure 1c) generally under-predicted  
265 observed K<sub>p</sub> values (factor range: 1.5 – 101) in 80 % of the data points. In contrast, better  
266 predictions were observed when the OC + BC model (Figure 1d) was used, with a factor difference  
267 ranging from 1.0 to 5.0, indicating a slightly over-estimated K<sub>p</sub> values, which could be attributed  
268 to partitioning in the colloidal phase. Accordingly, we conclude that the partitioning of PBDEs  
269 between particulates and the dissolved phase was in equilibrium in the lower Passaic River and  
270 that BC significantly contributed to sorption of PBDEs (18 – 99 %) in the water column.

## 271 **In situ vs Literature Based K<sub>BC</sub> Values**

272 Greater variability was observed when site specific  $K_{BC}$  values were compared with literature  
273 values (see Figure 3, Table S11 and Figure S11 for more details). In the current study, we  
274 calculated in situ  $K_{BC}$  values using a Freundlich coefficient of 0.7.  $K_{BC}$ s were calculated twice for  
275 sorption in the water column (see below) and in sediments (Table S11). For comparison, we used  
276 the log-linear relationship between  $\log K_{BC}$  and aqueous solubility at saturation ( $C_w^{sat}$ ) developed  
277 by Lambert et al.<sup>21</sup> for furans in the same study area to derive values for PBDEs. We also derived  
278  $K_{BC}$  values for PBDEs based on the  $K_{BC} - K_{OW}$  relationship developed by Di Paolo et al.<sup>29</sup> for  
279 PBDEs. Finally, we estimated  $K_{soot}$  from Barring et al.<sup>47</sup> after correction for the influence of the  
280 non-linear adsorption onto soot (by normalizing to  $C_{PW}$  given in the same reference and using a  
281 Freundlich coefficient of 0.7). In their study, only two BDE congeners were included (BDE-47  
282 and BDE-99). However, a highly significant log-linear relationship was observed between  $K_{BC}$   
283 values for the two PBDE congeners and furans on one side, and  $-\log C_w^{sat}$  (Figure S11). For that  
284 reason, the equation developed by Lambert et al.<sup>21</sup> for furans (not the dioxins or PAHs) was used  
285 in our study to predict values for PBDEs.

286 When sediment  $K_{ds}$  were predicted with  $K_{BC}$  values specific for PBDEs<sup>29</sup>, predicted values were  
287 2.0 -85 folds lower (under-predicted) than observed values in 91 % of the data points.  $K_{BC}$  values  
288 from Lambert et al.<sup>21</sup> under-predicted  $K_d$  values by a factor ranging from 1.2 to 32 in 63 % of the  
289 data points, and over-estimated  $K_{ds}$  (by a factor 1.5 – 15) in 37 % of the data points. In contrast,  
290  $K_{BC}$  values from Barring et al.<sup>47</sup> over-predicted  $K_{ds}$  (factor differences ranging from 1.8 – 54) in  
291 almost all the data points (95 %).

292 Similar findings were observed for the partitioning of PBDEs in the water columns when literature  
293 based  $K_{BC}$  values were used. Several reasons could be responsible for these observed differences  
294 in the predictive ability of the literature based vs our site specific  $K_{BC}$  values, which may include

295 the difference in the composition of the black carbon, differences in the methods used to measure  
296 the truly dissolved concentrations (passive samplers in our study), and difference in the  
297 competitive sorption from other pollutants and from OC. Calculated  $K_{BC}$  values for the water  
298 column were also higher than values calculated for the sediments (Table S11) owing to the higher  
299 truly dissolved concentrations of PBDEs in the pore water (Table S8).

300 The following linear free energy relationships (Figure 3) were established between  $\log K_{BCS}$  and  
301 the final adjusted solubility values of PBDE ( $-\log C_w^{sat}$ ; mol/L) obtained from Yue and Li<sup>55</sup>:

$$302 \quad \text{Log } K_{BC} (\text{sediments}) = -\log C_w^{sat} * 0.95 + 0.36 \quad (4)$$

$$303 \quad (R^2 = 0.93; p < 0.001, SE = 0.21, n = 22)$$

$$304 \quad \text{Log } K_{BC} (\text{water column}) = -\log C_w^{sat} * 1.2 - 0.69 \quad (5)$$

$$305 \quad (R^2 = 0.98; p < 0.001, SE = 0.13; n = 9)$$

306 RUs associated with the predicted  $K_{ps}$  and  $K_{ds}$  (equation S20) based on the OC + literature based  
307 BC model were the highest (25 – 63 % and 68 – 89 % for water and sediments respectively)  
308 followed by OC + sample specific BC (equation S21; 32 – 52 % and 67 – 69 %), OC model  
309 (equation S19; 10 - 42 %) and observed  $K_{ps}$  and  $K_{ds}$  (equation S22; 30 %).

310 Although calculated  $K_{BC}$  values in our study varied greatly from literature values (either field  
311 calculated or predicted from  $C_w^{sat}$ ), they represent the equilibrium distribution between BC and  
312 water in water and sediments in the field. Additionally,  $K_{BC}$  values were calculated for a wide  
313 range of samples ( $n = 29$ : 22 sediment and 9 water samples), with sites' contamination level  
314 ranging from near background to highly contaminated (standard deviation = 0.29 – 0.44 for  
315 sediments, 0.36 – 0.58 for water and 0.13 – 0.64 between sediments and water), which is an

316 advantage over laboratory driven values as these values represent the difference in the competitive  
317 sorption kinetics and the varying composition of BC between the different samples, and between  
318 sediments and water. Accordingly, we suggest that the  $K_{BC}$  values derived here are applicable for  
319 other urban-impacted water bodies. The log-linear relationships (equations 4 and 5) can hence be  
320 used to predict  $K_{BC}$  values from mono- through hepta-brominated BDE congeners.

321

### 322 **Atmospheric Concentrations of PBDEs**

323 Gaseous concentrations of  $\sum_{12}$ PBDEs ( $\text{pg}/\text{m}^3$ ) at all the sampling locations during each  
324 deployment period are given in Table S12. Concentrations ranged from 3.0 – 6.0  $\text{pg}/\text{m}^3$ , 3.0 – 8.0  
325  $\text{pg}/\text{m}^3$ , 6.0 – 19  $\text{pg}/\text{m}^3$ , 14 – 27  $\text{pg}/\text{m}^3$ , and 2.0 – 7.0  $\text{pg}/\text{m}^3$  in autumn, 2011, winter, spring, summer  
326 and autumn, 2012 respectively (Figure S12). Overall uncertainties associated with the estimation  
327 of gaseous concentrations (equation S17) from LDPE ranged from 48 – 50 % for the PBDE  
328 congeners. Atmospheric concentrations were slightly higher than concentrations recently reported  
329 for the lower Great Lakes (0.10 – 18  $\text{pg}/\text{m}^3$ )<sup>18</sup>, within the same range observed for Toronto, Canada  
330 (10 – 30  $\text{pg}/\text{m}^3$ )<sup>56</sup> and Western Europe (0.22 – 37  $\text{pg}/\text{m}^3$ )<sup>56</sup>, and much lower than concentrations  
331 reported for Istanbul, Turkey (110 – 620  $\text{pg}/\text{m}^3$ )<sup>57</sup>. Partial pressures of PBDE congeners were  
332 calculated from the ideal gas law as follows:

$$333 \quad pV = nRT \quad (6)$$

334 where  $p$  is the partial pressure (atm),

335  $V$  is the volume (L),

336  $n$  is the number of moles,

337  $R$  is the gas constant (0.082 L atm  $\text{K}^{-1}$   $\text{mol}^{-1}$ ) and



338 T is the temperature (K).

339 The natural log of P correlated significantly ( $R^2 = 0.34 - 0.67$ ,  $p < 0.05$ ,  $n = 34$ ) with inverse  
340 T, indicating an increase in volatilization with increasing temperature. This finding was similar to  
341 atmospheric PBDEs measured at the Great Lakes<sup>58</sup> as a part of the IADN program. Additionally,  
342 calculated enthalpy of phase values ( $\Delta H$ , in J/mol, see Table S13) from Clausius -Clapeyron  
343 equation (7) for BDE-47 and BDE-99 were within the range observed for both congeners at the  
344 Great Lakes<sup>58</sup>:

$$345 \ln P = (-\Delta H/R) * (1/T) + \text{constant} \quad (7)$$

346 In the water, relatively high truly dissolved concentrations were also observed during the  
347 summer and spring of 2012 (Figure S13) but the highest concentrations were observed in the  
348 autumn, which was different from the atmospheric trend suggesting a possible different source.  
349 All samples were dominated by BDE-47 (Figure S14) comprising 32 – 42 % of the total PBDE  
350 concentrations followed by BDE-2 (11 – 20 %) and BDE-99 (6.0 – 18 %).

351

## 352 **Fate of PBDEs**

### 353 **Air-Water Gaseous Diffusive Fluxes**

354 Atmospheric and truly dissolved water concentrations derived from the LDPE samplers were used  
355 to compute the gaseous diffusive fluxes. Fluxes thus represent the time weighed average  
356 concentrations that are absorbed by LDPE. Using the same approach, McDonough et al.<sup>18</sup>  
357 indicated that time-weighted fluxes obtained from the passive samplers for a given deployment  
358 time were in good agreement with the average calculated fluxes over a similar time period for

359 PBDE congeners that did not approach equilibrium (tetra-hepta-brominated congeners), and  
360 comparable to average calculated fluxes obtained from running active samplers over similar time  
361 scales of the LDPE.

362 Calculated gaseous fluxes of PBDEs are shown in Figure 4. Uncertainties associated with flux  
363 calculations (equation S23) ranged from 30 % to 430 % with 93 % of the data points ranging from  
364 30 to 95 % and 7.0 % (n = 30) above 100%. Accordingly, all the data points with uncertainties >  
365 100 % were assumed at equilibrium. Net volatilization fluxes ranged from 12 pg/m<sup>2</sup>/day (BDE-2  
366 at river km 28 during autumn 2011) to 1,860 pg/m<sup>2</sup>/day (BDE-47 at Newark Bay during autumn  
367 2012). Volatilization fluxes were generally observed for the lower brominated congeners (BDE-2,  
368 8, 15, 30, 28), whereas absorption fluxes were observed for the higher brominated ones (BDE-47,  
369 100, 99, 154, 153, 183) with a magnitude ranging from -22 pg/m<sup>2</sup>/day (BDE-30 at river km 28  
370 during winter 2012) to -5,670 pg/m<sup>2</sup>/day (BDE-183 at Newark Bay during winter 2012) (Figure  
371 4). Temporal variations in the calculated fluxes at each site were statistically insignificant  
372 (ANOVA test). Fluxes observed at river km 6.4 during the spring of 2012, and at Newark Bay  
373 during the summer of 2012 were significantly higher than fluxes observed at all the other sampling  
374 periods at all the samples (Repeated Measures of ANOVA, p < 0.001). The magnitude of the  
375 absorption fluxes was much higher than that for the volatilization fluxes in all the samples.  
376 Absorption fluxes were dominated by BDE-47 (-146 to -3360 pg/m<sup>2</sup>/day), BDE-183 (-146 to -  
377 3360 pg/m<sup>2</sup>/day) and BDE-99 (-148 to -3145pg/m<sup>2</sup>/day) (Figure 4). Absorption fluxes of PBDEs  
378 were previously observed at the Great Lakes<sup>18,59</sup> and the Atlantic Oceans<sup>60</sup> with BDE-47 and 99  
379 dominating those fluxes. Based on our results, the atmospheric deposition is considered an  
380 important source of PBDEs to the lower Passaic River and Newark Bay.

### 381 **Sediment-Water Fluxes**

382 Except for BDE-2, 47 and 99, all the other congeners showed positive diffusive fluxes (Figure  
383 S15a) with values ranging from 0.20 ng/m<sup>2</sup>/day (BDE-183 at river km 14) to 127 ng/m<sup>2</sup>/day (BDE-  
384 28 at Newark Bay) indicating that sediments are acting as a source of PBDEs to the overlying  
385 water column. In contrast, PBDEs at river km 28 (above Dundee Dam) showed negative fluxes (-  
386 157 ng/m<sup>2</sup>/day for BDE-47 to -0.10 ng/m<sup>2</sup>/day for BDE-30), probably due to the lower observed  
387 sediment concentrations (Figure S3). BDE-47 and 99 were depositing from the water column to  
388 the sediments at river kms 28, 19 and 6.4 (-18 to -157 ng/m<sup>2</sup>/day and -2.0 to -51 ng/m<sup>2</sup>/day for  
389 BDE-47 and 99 respectively), whereas both were released from sediments to the overlying water  
390 column at the other investigated sites (15 to 115 ng/m<sup>2</sup>/day and 14 to 58 ng/m<sup>2</sup>/day for BDE-47  
391 and 99 respectively). When both diffusive + sedimentation fluxes were combined (Figure S15b)<sup>61</sup>,  
392 a slight change was observed in the flux's magnitudes, whereas directional changes were only  
393 observed at river kms 14 (BDE-153, 154 and 183) and 9.6 (BDE-47, 49, 100, 99, 153, 154 and  
394 183) where net fluxes indicated that these congeners at those locations deposit from the water  
395 column to the sediments with a magnitude ranging from -0.30 to -14 ng/m<sup>2</sup>/day. This implies that  
396 sedimentation of PBDE is a significant process for the higher brominated PBDE congeners  
397 probably due to their strong absorption to OC and/or BC due to their higher hydrophobicity. We  
398 did not quantify the PBDEs potentially released from sediment resuspension in the current study.  
399 Sediment resuspension could be a significant source of PBDEs to the overlying water column and  
400 could balance the sedimentation process thus affecting the net flux calculated. Uncertainties  
401 (equations S24 and S25) for the calculated fluxes ranged from 82 to 84 % and 100 to 102 % for  
402 the diffusive and diffusive + sedimentation fluxes respectively.

#### 403 **Inventory of PBDE fluxes across the Passaic River**

404 In the current study, the magnitude of the sedimentation fluxes of PBDEs (sorbed on particles)  
405 greatly exceeded diffusive fluxes from sediments to water or water to sediments and the gaseous  
406 diffusive fluxes either volatilization or deposition (Figure S16). The study area (lower 17 miles of  
407 the river) is 3.80 km<sup>2</sup>. We computed the net annual fluxes for PBDEs in the river assuming that  
408 our collected samples are representative of the entire area of the lower Passaic River. We also  
409 assumed that particulate phase concentrations of PBDEs obtained from our sampling periods could  
410 be applied on the annual scale since only minor difference between (3 samples) and within sample  
411 (three sampling periods at each location) particle content in the water column (70 – 92 mg/L) was  
412 observed. Passive sampler deployments covered the entire year at each location in the air and  
413 water; derived PBDE concentrations already represent time weighted averages.

414 Accordingly, the net particle sedimentation fluxes of PBDEs from the water column ranged from  
415 -0.60 to -139 g/yr, whereas diffusion fluxes of dissolved PBDEs from sediments to the water  
416 ranged from 0.10 to 84 g/yr, and was observed for all the congeners except BDE-47 and 183  
417 (Figure S16). Compared to the net volatilization gaseous fluxes (0.007 – 0.26 g/yr), sediments  
418 acted as the main source of PBDEs to the water column in the river. Similarly, deposition of  
419 dissolved PBDEs to sediments (for BDE-47 and 183; 0.40 to 28 g/yr) greatly exceeds those  
420 depositing from the atmosphere (0.50 to 1.5 g/yr). Thus, we conclude that sediments play a key  
421 role in the fate and transport of PBDEs in the lower Passaic River, which supports the importance  
422 of sediments as a source of PBDEs to their bioaccumulation in nekton as was observed in our  
423 previous study<sup>20</sup>. Additionally, the magnitude of fluxes to and from the water column suggest that  
424 other important removal processes such as degradation, discharge from the river, uptake by  
425 organisms, partitioning to the colloidal phase and particulate phase and storm runoff should be  
426 considered.

## 427 **Implications**

428 In the current study, we investigated the sorptive behavior of PBDEs in the water column and  
429 sediments, and fate in the tidal portion of the lower Passaic River using LDPE passive samplers.  
430 Derived partitioning constants indicated stronger sorption of PBDEs to DOC compared to other  
431 HOCs, in contrast to results obtained in the Arctic. Due to the low solubility of HOCs in water,  
432 measuring the truly dissolved concentrations using the conventional sampling techniques is  
433 challenging, and correcting for the influence of the DOC could be misleading. Considering the  
434 above-mentioned drawbacks and the high cost of active sampling, the use of passive samplers as  
435 a cost-effective way of measuring dissolved concentrations is greatly encouraged. In the current  
436 study, we also used LDPE for measuring the truly dissolved PBDE fraction in the porewater and  
437 the atmosphere. Thus, we demonstrated the wide applicability of passive samplers to study the  
438 partitioning, transport and fate of PBDEs at one study area, and accordingly should be considered  
439 in similar future studies.

440 The current study highlighted the important role played by the natural sorbents and particles in  
441 affecting the behavior of PBDEs in the river as was previously observed for other HOCs. PBDEs  
442 sorbed to particles represented on average 65 % of the total water concentrations followed by  
443 sorption to DOC/colloids (30 %) and being truly dissolved (5.0 %). Our results indicates that BC  
444 is the dominant factor in the solid-water partitioning in the river despite of its lower abundance  
445 compared to OC, and is responsible on average on 73 % and 44 % of the total PBDE concentrations  
446 in sediments and water respectively. Accordingly, BC (in sediments and water) and DOC/colloids  
447 (in water) play a significant role in controlling the bioavailability and mobility of PBDEs; this in  
448 terns will influence the diffusive flux (reducing the freely dissolved fraction) and sedimentation  
449 (increase the concentrations of PBDEs sorbed to particulates) flux calculations. Accordingly,

450 quantifying BC and DOC should be included in bioaccumulation/biomagnification and fate studies  
451 of PBDEs and the other HOCs.

## 452 **Supporting Information**

453 Details on the sampling, chemical analysis, statistical analysis. Uncertainties, sorption models and  
454 flux calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## 458 **References**

- 459 (1) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed Polybrominated Diphenyl Ether  
460 (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE  
461 Technical Flame-retardant Mixtures. *Environ. Sci. Technol.* **2006**, *40* (20), 6247–6254.
- 462 (2) He, M.-J.; Luo, X.-J.; Chen, M.-Y.; Sun, Y.-X.; Chen, S.-J.; Mai, B.-X. Bioaccumulation  
463 of polybrominated diphenyl ethers and decabromodiphenyl ethane in fish from a river  
464 system in a highly industrialized area, South China. *Sci. Total Environ.* **2012**, *419*, 109–  
465 115.
- 466 (3) Voorspoels, S.; Covaci, A.; Jaspers; Neels, H.; Schepens, P. Biomagnification of PBDEs  
467 in Three Small Terrestrial Food Chains. *Environ. Sci. Technol.* **2007**, *41* (2), 411–416.
- 468 (4) Ali, U.; Mahmood, A.; Syed, J. H.; Li, J.; Zhang, G.; Katsoyiannis, A.; Jones, K. C.;  
469 Malik, R. N. Assessing the combined influence of TOC and black carbon in soil–air  
470 partitioning of PBDEs and DPs from the Indus River Basin, Pakistan. *Environ. Pollut.*  
471 **2015**, *201*, 131–140.
- 472 (5) Chen, M.-Y.; Yu, M.; Luo, X.-J.; Chen, S.-J.; Mai, B.-X. The factors controlling the  
473 partitioning of polybrominated diphenyl ethers and polychlorinated biphenyls in the  
474 water-column of the Pearl River Estuary in South China. *Mar. Pollut. Bull.* **2011**, *62* (1),  
475 29–35.
- 476 (6) Jia, F.; Gan, J. Comparing black carbon types in sequestering polybrominated diphenyl  
477 ethers (PBDEs) in sediments. *Environ. Pollut.* **2014**, *184*, 131–137.
- 478 (7) Guo, L.; Qiu, Y.; Zhang, G.; Zheng, G. J.; Lam, P. K. S.; Li, X. Levels and  
479 bioaccumulation of organochlorine pesticides (OCPs) and polybrominated diphenyl ethers  
480 (PBDEs) in fishes from the Pearl River estuary and Daya Bay, South China. *Environ.*

- 481 *Pollut.* **2008**, 152 (3), 604–611.
- 482 (8) Houde, M.; Muir, D. Influence of lake characteristics on the biomagnification of persistent  
483 organic pollutants in lake trout food webs. *Environ. Toxicol. Chem.* **2008**, 27 (10), 2169–  
484 2178.
- 485 (9) Streets, S. S.; Henderson, S. A.; Stoner, A. D.; Carlson, D. L.; Simcik, M. F.;  
486 Swackhamer, D. L. Partitioning and Bioaccumulation of PBDEs and PCBs in Lake  
487 Michigan †. *Environ. Sci. Technol.* **2006**, 40 (23), 7263–7269.
- 488 (10) Wu, J.-P.; Luo, X.-J.; Zhang, Y.; Luo, Y.; Chen, S.-J.; Mai, B.-X.; Yang, Z.-Y.  
489 Bioaccumulation of polybrominated diphenyl ethers (PBDEs) and polychlorinated  
490 biphenyls (PCBs) in wild aquatic species from an electronic waste (e-waste) recycling site  
491 in South China. *Environ. Int.* **2008**, 34 (8), 1109–1113.
- 492 (11) Jansson, B.; Asplund, L.; Olsson, M. Brominated flame retardants — Ubiquitous  
493 environmental pollutants? *Chemosphere* **1987**, 16 (10), 2343–2349.
- 494 (12) Toms, L.-M. L.; Hearn, L.; Kennedy, K.; Harden, F.; Bartkow, M.; Temme, C.; Mueller,  
495 J. F. Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of  
496 human milk, dust and indoor air. *Environ. Int.* **2009**, 35 (6), 864–869.
- 497 (13) Hites, R. A. Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-  
498 Analysis of Concentrations. *Environ. Sci. Technol.* **2004**, 38 (4), 945–956.
- 499 (14) Abbasi, G.; Buser, A. M.; Soehl, A.; Murray, M. W.; Diamond, M. L. Stocks and Flows of  
500 PBDEs in Products from Use to Waste in the U.S. and Canada from 1970 to 2020.  
501 *Environ. Sci. Technol.* **2015**, 49 (3), 1521–1528.
- 502 (15) UNEP, U. Report of the Conference of the Parties of the Stockholm Convention on  
503 Persistent Organic Pollutants on the work of its fourth meeting. In *United Nations*  
504 *Environment Programme: Stockholm Convention on Persistent Organic Pollutants.*  
505 *Geneva*; 2009; p 112.
- 506 (16) Khairy, M.; Muir, D.; Teixeira, C.; Lohmann, R. Spatial Distribution, Air-Water Fugacity  
507 Ratios and Source Apportionment of Polychlorinated Biphenyls in the Lower Great Lakes  
508 Basin. *Environ. Sci. Technol.* **2015**, 49 (23), 13787–13797.
- 509 (17) Meire, R. O.; Khairy, M.; Targino, A. C.; Galvão, P. M. A.; Torres, J. P. M.; Malm, O.;  
510 Lohmann, R. Use of passive samplers to detect organochlorine pesticides in air and water  
511 at wetland mountain region sites (S-SE Brazil). *Chemosphere* **2016**, 144, 2175–2182.
- 512 (18) McDonough, C. A.; Puggioni, G.; Helm, P. A.; Muir, D.; Lohmann, R. Spatial  
513 Distribution and Air–Water Exchange of Organic Flame Retardants in the Lower Great  
514 Lakes. *Environ. Sci. Technol.* **2016**, 50 (17), 9133–9141.
- 515 (19) Fernandez, L. A.; MacFarlane, J. K.; Tcaciuc, A. P.; Gschwend, P. M. Measurement of  
516 Freely Dissolved PAH Concentrations in Sediment Beds Using Passive Sampling with  
517 Low-Density Polyethylene Strips. *Environ. Sci. Technol.* **2009**, 43 (5), 1430–1436.
- 518 (20) Khairy, M. A.; Weinstein, M. P.; Lohmann, R. Trophodynamic behavior of hydrophobic  
519 organic contaminants in the aquatic food web of a tidal river. *Environ. Sci. Technol.* **2014**,

- 520 48 (21), 12533–12542.
- 521 (21) Lambert, M.; Friedman, C.; Luey, P.; Lohmann, R. Role of Black Carbon in the Sorption  
522 of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans at the Diamond Alkali  
523 Superfund Site, Newark Bay, New Jersey. *Environ. Sci. Technol.* **2011**, *45* (10), 4331–  
524 4338.
- 525 (22) Sacks, V. P.; Lohmann, R. Freely dissolved PBDEs in water and porewater of an urban  
526 estuary. *Environ. Pollut.* **2012**, *162*, 287–293.
- 527 (23) Khairy, M. A.; Lohmann, R. Field calibration of low density polyethylene passive  
528 samplers for gaseous POPs. *Environ. Sci. Process. Impacts* **2014**, *16* (3), 414–421.
- 529 (24) Burgess, R. M.; Lohmann, R. Role of black carbon in the partitioning and bioavailability  
530 of organic pollutants. *Environ. Toxicol. Chem.* **2004**, *23* (11), 2531–2533.
- 531 (25) Gustafsson, Ö.; Gschwend, P. M. The Flux of Black Carbon to Surface Sediments on the  
532 New England Continental Shelf. *Geochim. Cosmochim. Acta* **1998**, *62* (3), 465–472.
- 533 (26) Gustafsson, Ö.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. Quantification  
534 of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and  
535 Bioavailability. *Environ. Sci. Technol.* **1997**, *31* (1), 203–209.
- 536 (27) Nam, J. J.; Gustafsson, O.; Kurt-Karakus, P.; Breivik, K.; Steinnes, E.; Jones, K. C.  
537 Relationships between organic matter, black carbon and persistent organic pollutants in  
538 European background soils: Implications for sources and environmental fate. *Environ.*  
539 *Pollut.* **2008**, *156* (3), 809–817.
- 540 (28) Cornelissen, G.; Haftka, J.; Parsons, J.; Gustafsson, Ö. Sorption to Black Carbon of  
541 Organic Compounds with Varying Polarity and Planarity. *Environ. Sci. Technol.* **2005**, *39*  
542 (10), 3688–3694.
- 543 (29) Di Paolo, C.; Gandhi, N.; Bhavsar, S. P.; Van den Heuvel-Greve, M.; Koelmans, A. A.  
544 Black Carbon Inclusive Multichemical Modeling of PBDE and PCB Biomagnification and  
545 -Transformation in Estuarine Food Webs. *Environ. Sci. Technol.* **2010**, *44* (19), 7548–  
546 7554.
- 547 (30) Guan, Y.-F.; Sojini, O. S. S.; Li, S.-M.; Zeng, E. Y. Fate of polybrominated diphenyl  
548 ethers in the environment of the Pearl River Estuary, South China. *Environ. Pollut.* **2009**,  
549 *157* (7), 2166–2172.
- 550 (31) Iannuzzi, J.; Butcher, M.; Iannuzzi, T. Evaluation of potential relationships between  
551 chemical contaminants in sediments and aquatic organisms from the lower Passaic River,  
552 New Jersey, USA. *Environ. Toxicol. Chem.* **2011**, *30* (7), 1721–1728.
- 553 (32) Adams, D.; O'Connor, J.; Weisberg, S. Final Report: Sediment Quality of the NY/NJ  
554 Harbor System—An Investigation under the Regional Environmental Monitoring and  
555 Assessment Program (R-EMAP). 1998.
- 556 (33) Bopp, R. F.; Chillrud, S. N.; Shuster, E. L.; Simpson, H. J.; Estabrooks, F. D. Trends in  
557 chlorinated hydrocarbon levels in Hudson River basin sediments. *Environ. Heal. Perspect.*  
558 **1998**, *106*, 1075–1081.



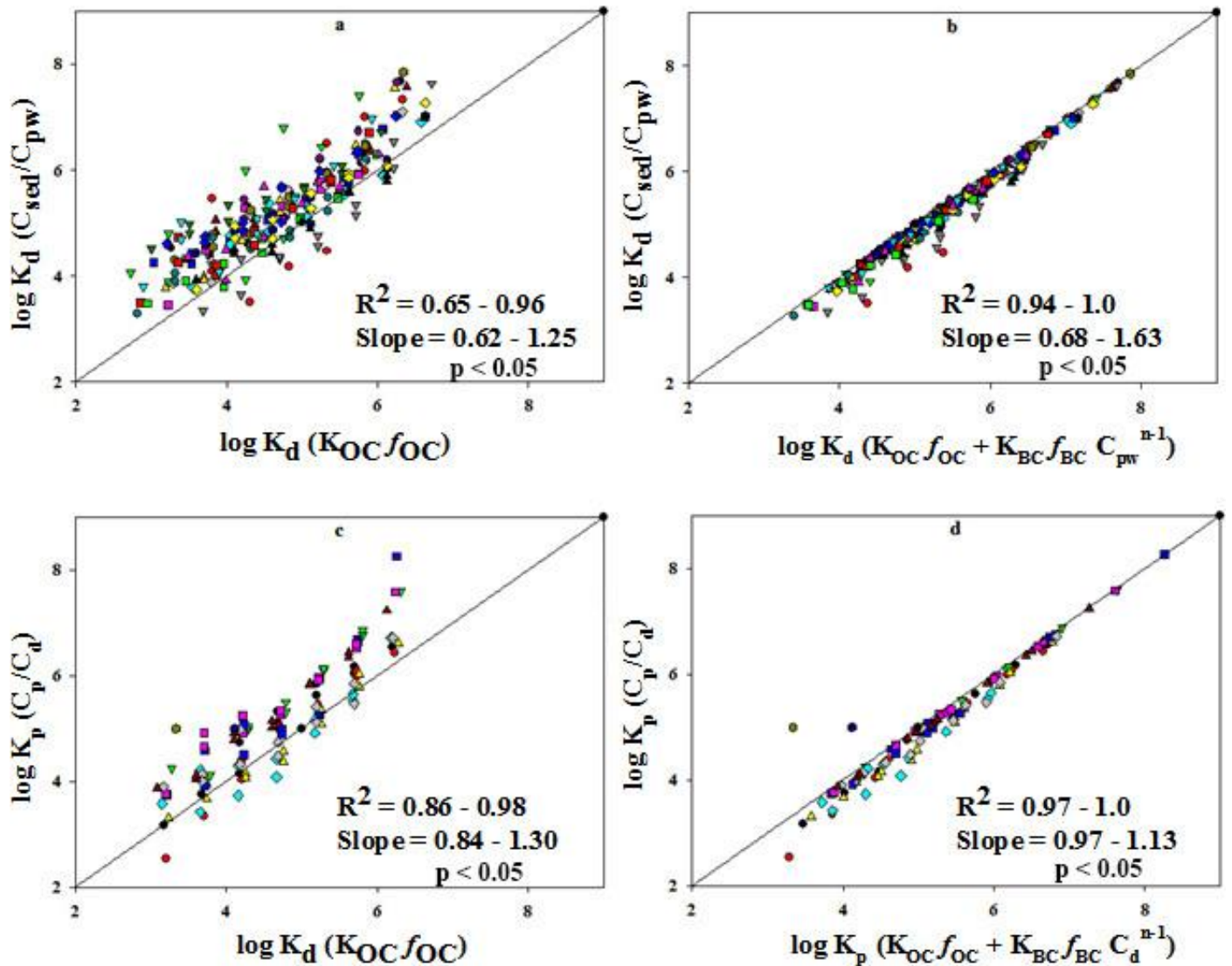
- 559 (34) Khairy, M.; Barrett, K.; Lohmann, R. Changing sources of polychlorinated dibenzo-p-  
560 dioxins and furans in sediments and ecological risk for nekton in the lower Passaic River  
561 and Newark Bay, New Jersey, USA. *Environ. Toxicol. Chem.* **2016**, *35* (3), 550–562.
- 562 (35) Booij, K.; Smedes, F.; van Weerlee, E. M. Spiking of performance reference compounds  
563 in low density polyethylene and silicone passive water samplers. *Chemosphere* **2002**, *46*  
564 (8), 1157–1161.
- 565 (36) Potter, B. B.; Wimsatt, J. C. Method 415.3. Measurement of total organic carbon,  
566 dissolved organic carbon and specific UV absorbance at 254 nm in source water and  
567 drinking water. *Washington, DC, US Environ. Prot. Agency* **2005**.
- 568 (37) Khairy, M. A.; Luek, J. L.; Dickhut, R.; Lohmann, R. Levels, sources and chemical fate of  
569 persistent organic pollutants in the atmosphere and snow along the western Antarctic  
570 Peninsula. *Environ. Pollut.* **2016**, *216*, 304–313.
- 571 (38) Samara, F.; Tsai, C. W.; Aga, D. S. Determination of potential sources of PCBs and  
572 PBDEs in sediments of the Niagara River. *Environ. Pollut.* **2006**, *139* (3), 489–497.
- 573 (39) Zhao, X.; Zhang, H.; Ni, Y.; Lu, X.; Zhang, X.; Su, F.; Fan, J.; Guan, D.; Chen, J.  
574 Polybrominated diphenyl ethers in sediments of the Daliao River Estuary, China: Levels,  
575 distribution and their influencing factors. *Chemosphere* **2011**, *82* (9), 1262–1267.
- 576 (40) Chen, L.; Huang, Y.; Peng, X.; Xu, Z.; Zhang, S.; Ren, M.; Ye, Z.; Wang, X. PBDEs in  
577 sediments of the Beijiang River, China: Levels, distribution, and influence of total organic  
578 carbon. *Chemosphere* **2009**, *76* (2), 226–231.
- 579 (41) Yun, S. H.; Addink, R.; McCabe, J. M.; Ostaszewski, A.; Mackenzie-Taylor, D.; Taylor,  
580 A. B.; Kannan, K. Polybrominated Diphenyl Ethers and Polybrominated Biphenyls in  
581 Sediment and Floodplain Soils of the Saginaw River Watershed, Michigan, USA. *Arch.*  
582 *Environ. Contam. Toxicol.* **2008**, *55* (1), 1–10.
- 583 (42) Luo, Q.; Cai, Z. W.; Wong, M. H. Polybrominated diphenyl ethers in fish and sediment  
584 from river polluted by electronic waste. *Sci. Total Environ.* **2007**, *383* (1), 115–127.
- 585 (43) Li, Q.; Yan, C.; Luo, Z.; Zhang, X. Occurrence and levels of polybrominated diphenyl  
586 ethers (PBDEs) in recent sediments and marine organisms from Xiamen offshore areas,  
587 China. *Mar. Pollut. Bull.* **2010**, *60* (3), 464–469.
- 588 (44) Lohmann, R.; Burgess, R. M.; Cantwell, M. G.; Ryba, S. a; MacFarlane, J. K.; Gschwend,  
589 P. M. Dependency of polychlorinated biphenyl and polycyclic aromatic hydrocarbon  
590 bioaccumulation in *Mya arenaria* on both water column and sediment bed chemical  
591 activities. *Environ. Toxicol. Chem.* **2004**, *23* (11), 2551–2562.
- 592 (45) Daniel R. Oros, \*, †; Dale Hoover, ‡; Francois Rodigari, §; David Crane, ¶ and; Sericano, L.,  
593 J. Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface  
594 Sediments, and Bivalves from the San Francisco Estuary. **2004**.
- 595 (46) Burkhard, L. P. Estimating Dissolved Organic Carbon Partition Coefficients for Nonionic  
596 Organic Chemicals. *Environ. Sci. Technol.* **2000**, *34* (22), 4663–4668.
- 597 (47) Barring, H.; Bucheli, T. D.; Broman, D.; Gustafsson, Ö. Soot–water distribution

- 598 coefficients for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and  
599 polybrominated diphenylethers determined with the soot cosolvency-column method.  
600 *Chemosphere* **2002**, 49 (6), 515–523.
- 601 (48) Kuivikko, M.; Sorsa, K.; Kukkonen, J. V. K.; Akkanen, J.; Kotiaho, T.; Vähätalo, A. V.  
602 Partitioning of tetra- and pentabromo diphenyl ether and benzo[a]pyrene among water and  
603 dissolved and particulate organic carbon along a salinity gradient in coastal waters.  
604 *Environ. Toxicol. Chem.* **2010**, 29 (11), 2443–2449.
- 605 (49) ter Laak, T. L.; van Eijkeren, J. C. H.; Busser, F. J. M.; van Leeuwen, H. P.; Hermens, J.  
606 L. M. Facilitated Transport of Polychlorinated Biphenyls and Polybrominated Diphenyl  
607 Ethers by Dissolved Organic Matter. *Environ. Sci. Technol.* **2009**, 43 (5), 1379–1385.
- 608 (50) Wei-Haas, M. L.; Hageman, K. J.; Chin, Y.-P. Partitioning of Polybrominated Diphenyl  
609 Ethers to Dissolved Organic Matter Isolated from Arctic Surface Waters. *Environ. Sci.*  
610 *Technol.* **2014**, 48 (9), 4852–4859.
- 611 (51) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. Sorption of hydrophobic pollutants on  
612 natural sediments. *Water Res.* **1979**, 13 (3), 241–248.
- 613 (52) Totten, L. A.; Brunciak, P. A.; Gigliotti, C. L.; Dachs, J.; Glenn, Nelson, E. D.;  
614 Eisenreich, S. J. Dynamic Air–Water Exchange of Polychlorinated Biphenyls in the New  
615 York–New Jersey Harbor Estuary. *Environ. Sci. Technol.* **2001**, 35 (19), 3834–3840.
- 616 (53) Zarnadze, A.; Rodenburg, L. A. Water-column concentrations and partitioning of  
617 polybrominated diphenyl ethers in the New York/New Jersey Harbor, USA. *Environ.*  
618 *Toxicol. Chem.* **2008**, 27 (8), 1636–1642.
- 619 (54) Xia, G. *Sorption behavior of nonpolar organic chemicals on natural sorbents*; 1998.
- 620 (55) Yue, C.; Li, L. Y. Filling the gap: Estimating physicochemical properties of the full array  
621 of polybrominated diphenyl ethers (PBDEs). *Environ. Pollut.* **2013**, 180, 312–323.
- 622 (56) Harner, T.; Shoeib, M.; Diamond, M.; Ikonomou, M.; Stern, G. Passive sampler derived  
623 air concentrations of PBDEs along an urban–rural transect: Spatial and temporal trends.  
624 *Chemosphere* **2006**, 64 (2), 262–267.
- 625 (57) Kurt-Karakus, P. B.; Alegria, H.; Jantunen, L.; Birgul, A.; Topcu, A.; Jones, K. C.;  
626 Turgut, C. Polybrominated diphenyl ethers (PBDEs) and alternative flame retardants  
627 (NFRs) in indoor and outdoor air and indoor dust from Istanbul-Turkey: Levels and an  
628 assessment of human exposure. *Atmos. Pollut. Res.* **2017**.
- 629 (58) Venier, M.; Hites, R. A. Flame Retardants in the Atmosphere near the Great Lakes.  
630 *Environ. Sci. Technol.* **2008**, 42 (13), 4745–4751.
- 631 (59) Ruge, Z.; Muir, D.; Helm, P.; Lohmann, R. Concentrations, Trends, and Air–Water  
632 Exchange of PAHs and PBDEs Derived from Passive Samplers in Lake Superior in 2011.  
633 *Environ. Sci. Technol.* **2015**, 49 (23), 13777–13786.
- 634 (60) Xie, Z.; Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Brominated Flame Retardants in  
635 Seawater and Atmosphere of the Atlantic and the Southern Ocean. *Environ. Sci. Technol.*  
636 **2011**, 45 (5), 1820–1826.

637 (61) Sabin, L. D.; Maruya, K. A.; Lao, W.; Diehl, D.; Tsukada, D.; Stolzenbach, K. D.; Schiff,  
638 K. C. Exchange of polycyclic aromatic hydrocarbons among the atmosphere, water, and  
639 sediment in coastal embayments of southern California, USA. *Environ. Toxicol. Chem.*  
640 **2010**, 29 (2), 265–274.

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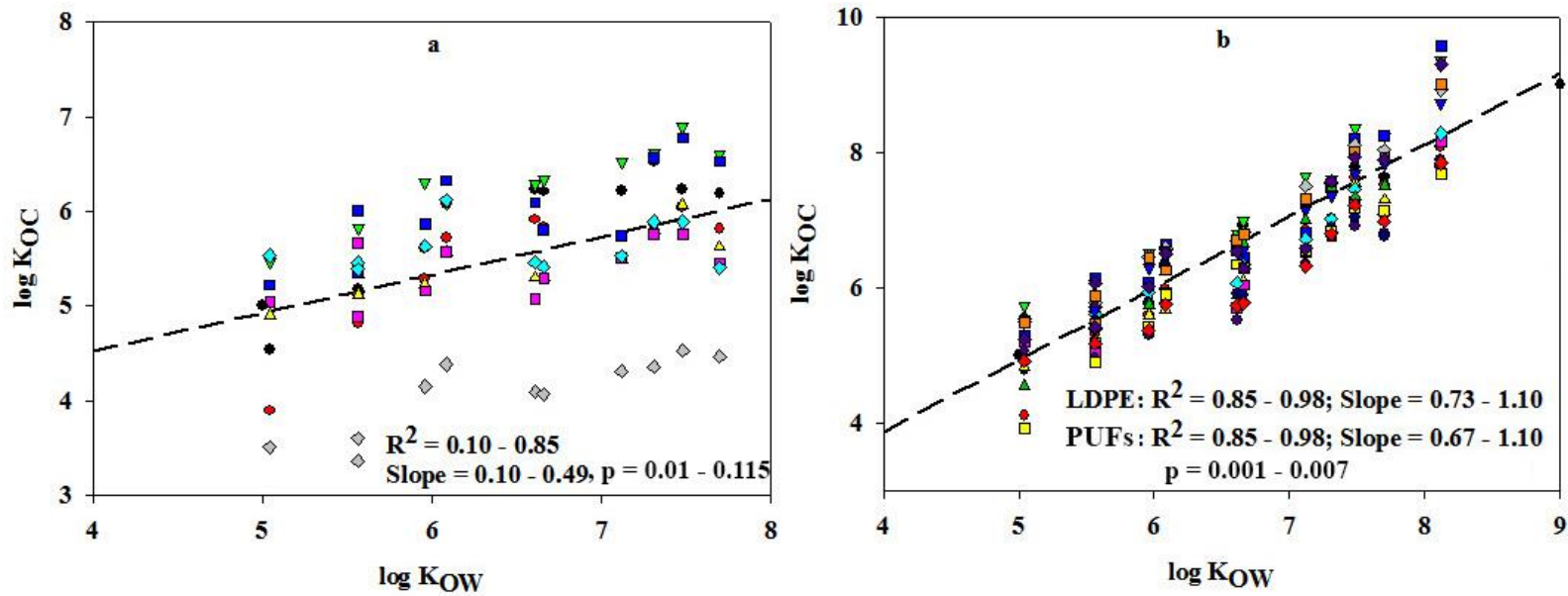


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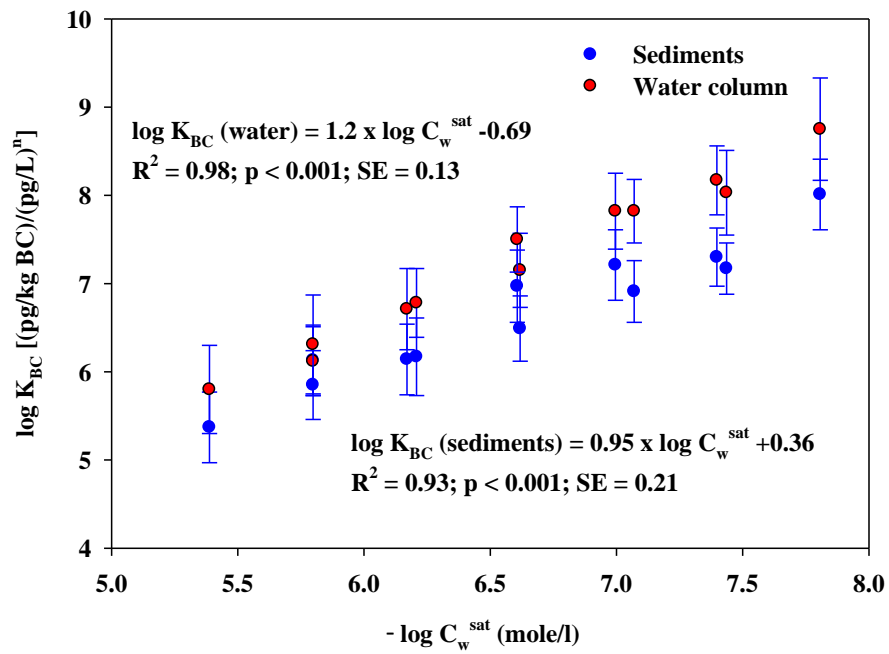
646 **Figure 1: Log linear relationships between observed and predicted solid-water partitioning**  
 647 **coefficients in sediments based on OC (a) and OC + BC (b) sorption models, and**  
 648 **in water (c, d). Site specific  $K_{BC}$  values were used. Predicted  $K_{AS}$  were calculated**  
 649 **using a Freundlich coefficient ( $n$ ) of 0.7<sup>29</sup>. Symbols represent calculated  $K_{d(p)}$  for**  
 650 **12 PBDE congeners at each sampling site ( $n = 22$  for sediments and 9 for water).**

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653 **Figure 2: Log linear relationships between Kocs and Kows for apparent (a) and truly**  
 654 **dissolved concentrations (b) of PBDEs in the water column of the lower Passaic**  
 655 **River. Symbols represent calculated Koc values for 12 PBDE congener at each**  
 656 **sampling site (n = 3 x 3 sampling periods). Data points in panel b represent the**  
 657 **truly dissolved values obtained from LDPE and from PUFs after DOC correction.**



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659 **Figure 3: Log -linear relationship between observed  $K_{BC}$  (L/kg) and  $C_w^{sat}$  (mol/L) in**  
 660 **sediments (n = 22) and water (n = 9) of the lower Passaic River. Error bars**  
 661 **represent the standard deviation.**

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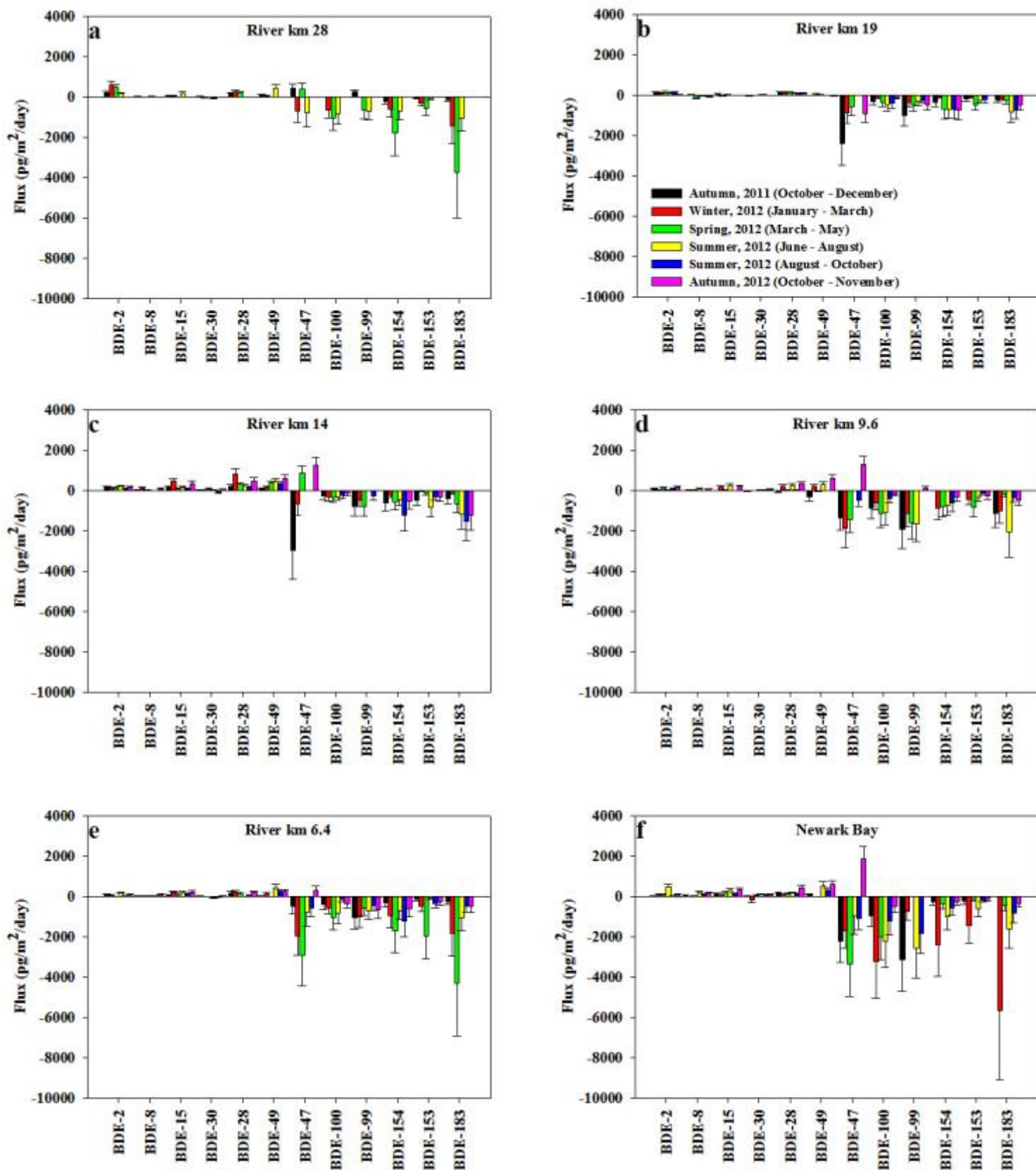
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700 **Figure 4: Calculated air-water gaseous fluxes (pg/m<sup>2</sup>/day) of PBDEs at the lower Passaic**  
 701 **River.**

702 TOC

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