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

3
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12
13 **Abstract**

14 In the aquatic environment, the behavior of hydrophobic organic contaminants (HOCs), such as
15 polybrominated diphenyl ethers (PBDEs), depends on the congeners' physicochemical properties,
16 environmental conditions and the presence of competing natural sorbents, including particulate
17 and dissolved organic carbon (DOC) and black carbon (BC). Although BC is known as an
18 important sedimentary sorbent for HOCs, its affinity for PBDEs has been poorly constrained. To
19 better understand the biogeochemical controls on PBDEs, 12 PBDE congeners were measured in
20 air, water, sediment and porewater of the lower Passaic River. BDE-47 and BDE-99 dominated
21 in all media. In sediments and water, the dual OC + BC approach better predicted PBDE
22 partitioning compared to the simple OC isotherm. Field-derived K_{BC} for PBDEs were inversely
23 correlated with aqueous solubility [$\log K_{BC \text{ sediments (water)}} = -\log C_w^{\text{sat}} * 0.95 (1.2) + 0.36 (-0.69)$];
24 they reflected near background to highly contamination regions across the Passaic River. In the
25 water column, PBDEs appeared at equilibrium partitioning between particles and colloids: OC +
26 BC were responsible for the sorption of 65 % of the concentrations of PBDE, followed by colloids

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.^{1,2} They were widely used in electronic equipment, textile paint and plastics to
34 improve fire safety³. PBDEs have been detected in abiotic⁴⁻⁶ and biotic environmental
35 compartments ⁷⁻¹⁰ including remote areas¹¹, and humans¹². In North America, the production of
36 the penta- and octa-BDE technical mixtures has been largely phased out¹³. However, PBDEs still
37 exist in consumer products and continue to leach into the environment¹⁴. Once in the environment,
38 they can persist and bioaccumulate leading to adverse health effects⁴. 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 formulations⁶. Tetra- through hepta-brominated
41 congeners were listed as persistent organic pollutants (POPs) under the Stockholm Convention¹⁵.

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 atmosphere¹⁶⁻¹⁸, water^{16,18}, porewater¹⁹⁻²¹, studying their diffusive fluxes^{16,18} and
53 investigating the bioaccumulation potential of POPs^{22,23}.

54 In sediments, HOCs are typically strongly absorbed into organic matter.²⁴ 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).^{25,26} Black carbon has hence been referred to as a super sorbent for HOCs^{27,28} including
58 PBDEs^{4,27}. As a result, BC is widely considered in studying the geochemistry of HOCs in
59 sediments and soil^{21,27,29}; 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 models⁵. 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^{5,30} and in sediments^{6,29}. 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 activities³¹ in the region. This region was selected because the
69 presence of legacy and ongoing contaminants is well documented^{20,31-33} 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.^{20,34} 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-d₈, pyrene-d₁₀, and benzo(a)pyrene-d₁₂),
98 brominated biphenyls (PBB 9, PBB 52, and PBB 103) and octachloronaphthalene according to the
99 method outlined in Booij et al.³⁵ 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 415.3³⁶.

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.³⁴.

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

113 Prior to extraction, all samples were spiked with 10 µL of a surrogate standard composed of
114 labelled PBDE congeners (¹³C₁₂ 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.³⁷.

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^{21,34}, but also contains other HOCs²⁰, 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)³⁸ and
149 Dialiao River Estuary, China (0.05 ng/g dw)³⁹, and close to that of Beijiang River, China (6.1 ng/g
150 dw)⁴⁰. 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)⁴¹. 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)⁴². 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^{22,43}. Our detected concentrations were much higher than
163 the freely dissolved porewater concentrations of Narragansett Bay, RI (< 3.0 pg/L)²² but much

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

166 **Sediment Partitioning of PBDEs**

167 Overall sediment-water distribution coefficients, K_{dS} , 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_{dS} based on OC (RU: 8.0 – 42 %) were 2.0-106 folds lower (under-predicted) than
178 observed K_{dS} 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 River²¹. 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 observations⁴⁴.
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^{20,21}.

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)⁵ and San Francisco Bay, USA (0.20 – 78.7 pg/L)⁴⁵
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).¹⁸ 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_{DOC} is the DOC-water partitioning coefficient (L/kg).

221 We predicted K_{DOC} values from K_{ow} according to the overall equation developed by Burkhard⁴⁶
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_{DOC} values calculated in the current study (Table S11) were compared with literature
230 values^{21,29,47}. K_{DOC} s were plotted against K_{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)⁴⁶, 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_{DOC} values reported in literature (Table S11)^{21,29,46-50}. Our K_{DOC} values were only
235 0.08 – 0.37 log units higher than those predicted in reference [⁴⁶] indicating good agreement, and
236 were similar to values calculated by ter Laak et al⁴⁹ 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.⁵⁰ for Arctic waters (Figure S10).

239 Observed organic carbon-water partitioning coefficients (K_{OC} s) were plotted against K_{OW} s. K_{OC} s
240 were calculated thrice relative to PBDEs on particles - based on (i) apparent water concentrations
241 (C_{ap}) obtained from PUFs; (ii) truly dissolved water concentrations (C_{d}) obtained from the LDPEs;
242 and (iii) predicted (C_{w}) obtained from PUFs after correcting for DOC (surrogate for colloidal
243 phase). The correlation between K_{OC} and C_{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 situation⁵¹ or a significant sorption to colloids⁵². 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 situation⁵, 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 River⁵³ and slightly higher than values reported for the Pearl River Estuary, China (10 –
252 98 %)⁵. 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_{DOC} (30 %) and C_d (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_{DOC} 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_p (using the freely dissolved concentrations obtained from the LDPE) in the water
263 column were compared with predicted K_p using the OC and OC + BC models. K_{OC} values were
264 obtained from ref [⁵⁴]. Predicted K_p values using OC (Figure 1c) generally under-predicted
265 observed K_p 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_p 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_{BC} 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.²¹ 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.²⁹ for
279 PBDEs. Finally, we estimated K_{soot} from Barring et al.⁴⁷ 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.²¹ 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 PBDEs²⁹, 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.²¹ 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.⁴⁷ 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 Li⁵⁵:

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

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

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

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

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 (pg/m^3) at all the sampling locations during each
324 deployment period are given in Table S12. Concentrations ranged from 3.0 – 6.0 pg/m^3 , 3.0 – 8.0
325 pg/m^3 , 6.0 – 19 pg/m^3 , 14 – 27 pg/m^3 , and 2.0 – 7.0 pg/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 pg/m^3)¹⁸, within the same range observed for Toronto, Canada
330 (10 – 30 pg/m^3)⁵⁶ and Western Europe (0.22 – 37 pg/m^3)⁵⁶, and much lower than concentrations
331 reported for Istanbul, Turkey (110 – 620 pg/m^3)⁵⁷. 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 K^{-1} 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 Lakes⁵⁸ as a part of the IADN program. Additionally,
342 calculated enthalpy of phase values (ΔH , 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 Lakes⁵⁸:

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

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.¹⁸
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/m²/day (BDE-2
366 at river km 28 during autumn 2011) to 1,860 pg/m²/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/m²/day (BDE-30 at river km 28
370 during winter 2012) to -5,670 pg/m²/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/m²/day), BDE-183 (-146 to -
377 3360 pg/m²/day) and BDE-99 (-148 to -3145pg/m²/day) (Figure 4). Absorption fluxes of PBDEs
378 were previously observed at the Great Lakes^{18,59} and the Atlantic Oceans⁶⁰ 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/m²/day (BDE-183 at river km 14) to 127 ng/m²/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/m²/day for BDE-47 to -0.10 ng/m²/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/m²/day and -2.0 to -51 ng/m²/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/m²/day and 14 to 58 ng/m²/day for BDE-47
391 and 99 respectively). When both diffusive + sedimentation fluxes were combined (Figure S15b)⁶¹,
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/m²/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 km². 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 study²⁰. 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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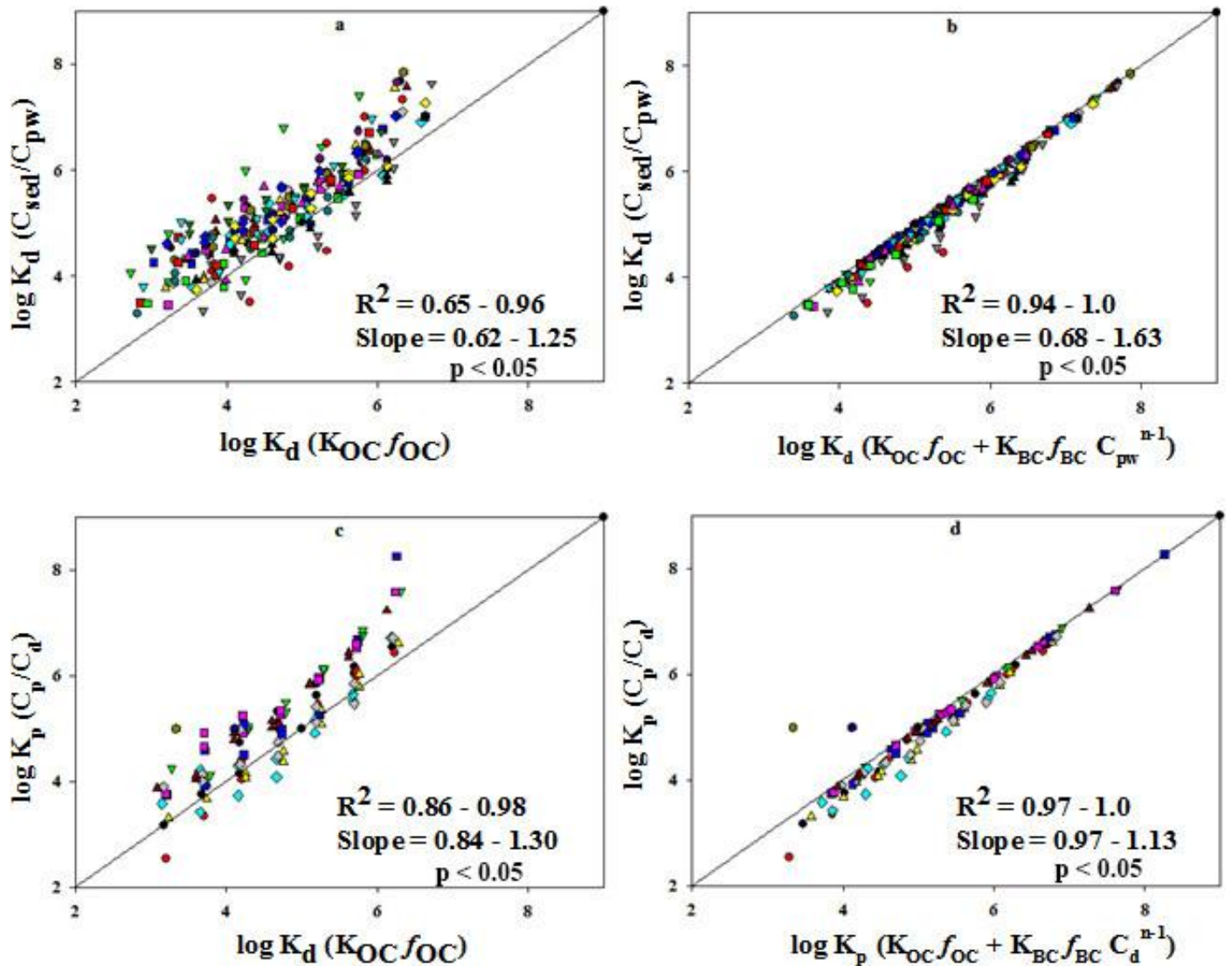
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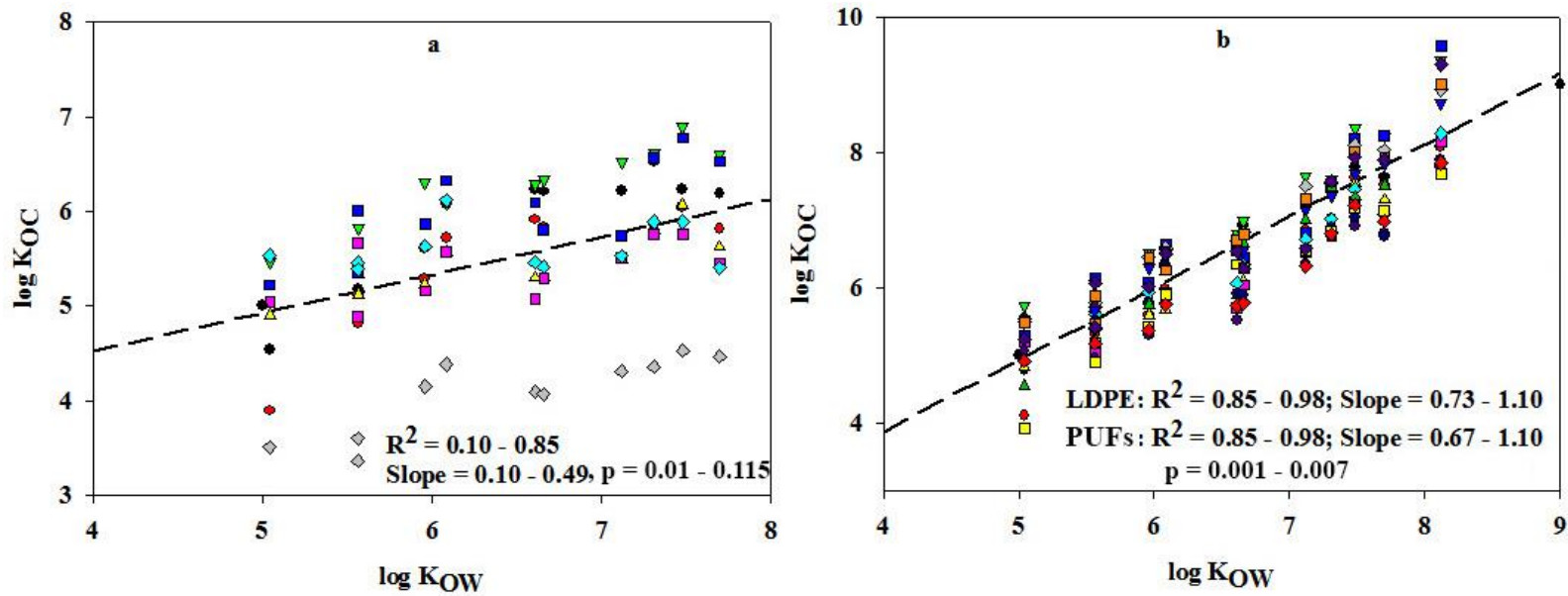


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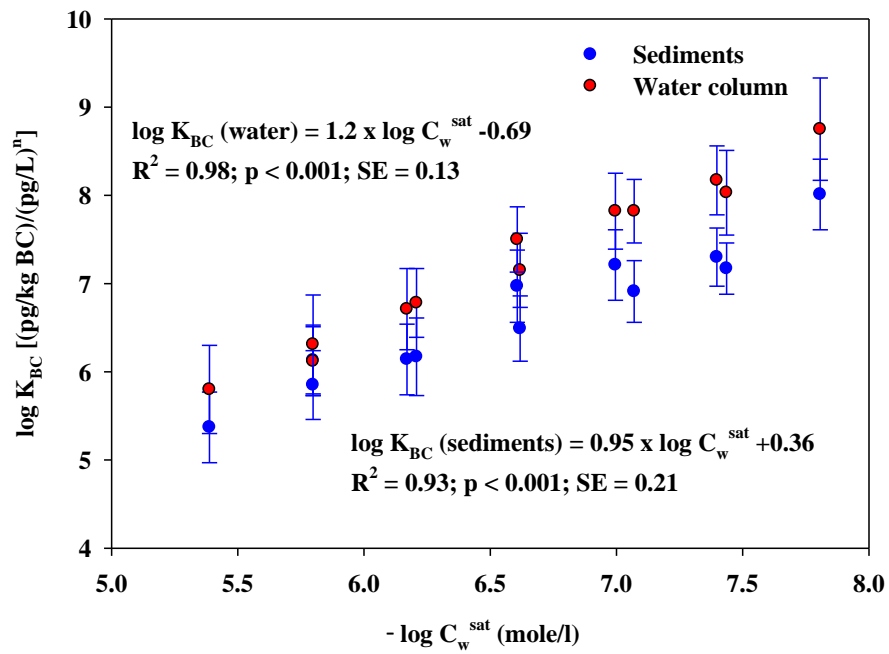
646 **Figure 1: Log linear relationships between observed and predicted solid-water partitioning**
 647 **coefficients in sediments based on OC (a) and OC + BC (b) sorption models, and**
 648 **in water (c, d). Site specific K_{BC} values were used. Predicted K_{AS} were calculated**
 649 **using a Freundlich coefficient (n) of 0.7²⁹. 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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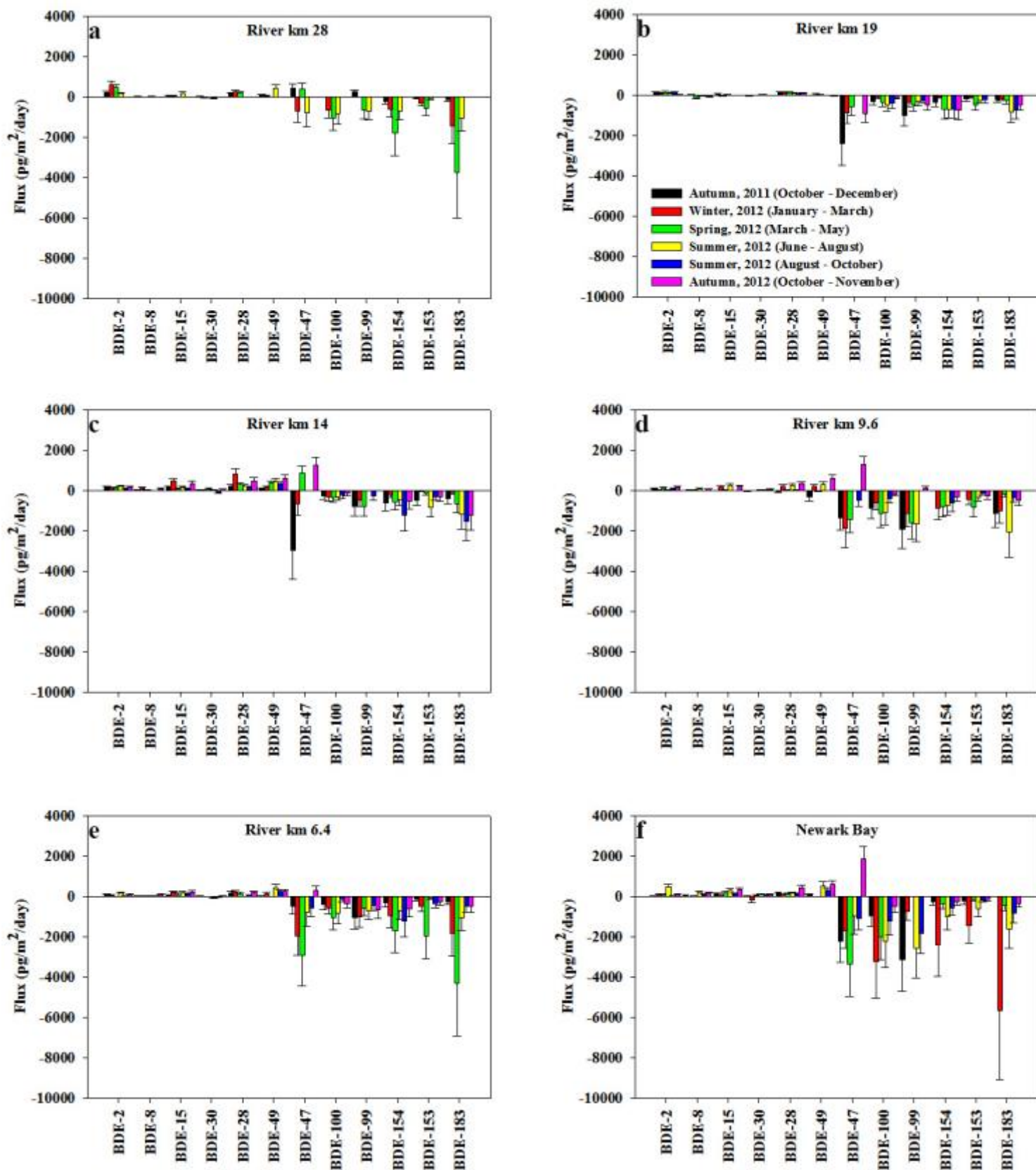
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700 **Figure 4: Calculated air-water gaseous fluxes ($\text{pg}/\text{m}^2/\text{day}$) of PBDEs at the lower Passaic**
 701 **River.**

702 TOC

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