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

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Abstract

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

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

Introduction

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

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

Passive sampling techniques were developed as an inexpensive/effective alternate for monitoring the truly dissolved HOCs in the atmosphere and water. Among the widely available passive sampling matrices, low density polyethylene (LDPE) has been widely used for measuring HOCs in the atmosphere[16–18], water[16,18], porewater[19–21], studying their diffusive fluxes[16,18] and investigating the bioaccumulation potential of POPs[22,23].

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

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

Gaseous atmospheric and truly dissolved aqueous concentrations of PBDEs were determined by LDPE passive samplers concurrently at several locations. Adjacent samplers were used to calculate the diffusive gaseous fluxes of PBDEs. Moreover, active water samples were collected to determine the particulate phase concentrations of PBDEs, compare the concentrations obtained from the passive and active samplers, and to determine the colloidal phase concentrations of PBDEs after measuring the dissolved organic carbon (DOC) in the water column. We were thus able to study the partitioning of PBDEs in the water column.

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

Materials and Methods

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

LDPE was pre-cleaned and spiked with performance reference compounds including deuterated polycyclic aromatic hydrocarbons (PAHs; naphthalene-d_8, pyrene-d_{10}, and benzo(a)pyrene-d_{12}), brominated biphenyls (PBB 9, PBB 52, and PBB 103) and octachloronaphthalene according to the method outlined in Booij et al.[35] These samplers were deployed in the atmosphere (in two inverted bowls ~ 2 m above the ground as a shelter for protection against sunlight and precipitation) and the water (suspended ∼1−2 m below the surface) along the lower portion of the Passaic River (Figure S1) during 6 deployments for 2 months each from September, 2011 to November, 2012.

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

Sediment samples were collected from mudflats at low tide at 18 different locations (Figure S2) along the river and 4 locations from Newark Bay during September to November 2011. Detailed description of the sampling methodology and sampling locations can be found in Khairy et al.[34]. Total organic carbon (TOC) and black carbon (BC) content in the sediments were determined as detailed in Gustafsson et al.[26]. Truly dissolved porewater concentrations of PBDEs were determined using a LDPE tumbling procedure as detailed in Lambert et al.[21]

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

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

Results and Discussion

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

PBDE Concentrations in Sediments

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

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

Porewater concentrations of PBDEs

Porewater concentrations ranged from 12 pg/L (km 29.9) to 40 pg/L (km 1.8) in the river and from 22 - 42 pg/L in Newark Bay (Table S8), which showed a significant increase ($R^2 = 0.31$; $p = 0.007$) with the increase in sediment concentrations. BDE-47 was the dominant congener comprising 13 – 50 % of the total concentrations followed by BDE-28 (6.0 – 30 %), BDE-49 (4.0 – 25 %), BDE-99 (1.0 – 23 %) and BDE-15 (2.0 – 20 %) (Figure S4). Overall relative uncertainty (equation S17) associated with the analytical errors and the estimation of the truly dissolved concentrations from LDPE deployments ranged from 64 – 66 %. There are very few other known porewater concentrations reported in the literature[22,43]. Our detected concentrations were much higher than the freely dissolved porewater concentrations of Narragansett Bay, RI (< 3.0 pg/L)[22] but much lower than the apparent porewater concentrations detected in marine sediments from China (170 – 6,430 pg/L)[43].

Sediment Partitioning of PBDEs

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

$$K_d = K_{OC}\, f_{OC} \tag{1}$$

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

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

$$K_d = K_{OC}\, f_{OC} + f_{BC}\, K_{BC}\, C_{PW}^{n-1} \tag{2}$$

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

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

C_{PW} is porewater concentrations (μg/L), and

n is the Freundlich coefficient (0.7).

Predicted K_ds based on OC (RU: 8.0 – 42 %) were 2.0-106 folds lower (under-predicted) than observed K_ds in 81 % of the cases (Figure 1a). A similar trend was observed for PAHs and PCDD/Fs at the superfund site as part of the Passaic River[21]. The use of OC + BC (site specific values) dual model (Figure 1b) greatly improved the prediction, where predicted values over-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 % of the data points. In both models, slopes of the regression lines were significantly different from zero ($p < 0.05$) and ranged from 0.62-1.63. A slope of +1 is typically interpreted as being in equilibrium, with the model capturing the key variable (i.e., interactions) of the observations[44]. Additionally, significant positive log-linear regression relationships ($p < 0.05$) were observed between observed and predicted K_ds (Figure 1a, b). According to equation (2), BC accounted for 12 – 99 % of total sorption of PBDEs to sediment. In conclusion, our results indicate the key role played by the BC in the sorption of PBDEs in sediment, in-line with previous results for PAHs, PCBs and PCDD/Fs[20,21].

PBDE Concentrations in the River Water

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

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

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

Comparison between Active and Passive Water Concentrations

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

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

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

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

We predicted K_{DOC} values from K_{OW} according to the overall equation developed by Burkhard[46] ($K_{DOC} = 0.08\ K_{OW}$) for HOCs.

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

Water column partitioning of PBDEs

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

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

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

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

Our results confirm that active sampling severely overestimates truly dissolved concentrations, and a DOC correction needs to be performed. The K_{DOC} values derived here could be used for that purpose. Yet, we argue that passive samplers are preferably used to study the water column partitioning of various hydrophobic organic compounds (HOCs) to yield dissolved concentrations directly.

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

In situ vs Literature Based K_{BC} Values

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

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

Similar findings were observed for the partitioning of PBDEs in the water columns when literature based K_{BC} values were used. Several reasons could be responsible for these observed differences in the predictive ability of the literature based vs our site specific K_{BC} values, which may include the difference in the composition of the black carbon, differences in the methods used to measure the truly dissolved concentrations (passive samplers in our study), and difference in the competitive sorption from other pollutants and from OC. Calculated K_{BC} values for the water column were also higher than values calculated for the sediments (Table S11) owing to the higher truly dissolved concentrations of PBDEs in the pore water (Table S8).

The following linear free energy relationships (Figure 3) were established between log K_{BC}s and the final adjusted solubility values of PBDE (-log C_w^{sat}; mol/L) obtained from Yue and Li[55]:

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

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

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

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

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

Although calculated K_{BC} values in our study varied greatly from literature values (either field calculated or predicted from C_w^{sat}), they represent the equilibrium distribution between BC and water in water and sediments in the field. Additionally, K_{BC} values were calculated for a wide range of samples (n = 29: 22 sediment and 9 water samples), with sites' contamination level ranging from near background to highly contaminated (standard deviation = 0.29 – 0.44 for sediments, 0.36 – 0.58 for water and 0.13 – 0.64 between sediments and water), which is an advantage over laboratory driven values as these values represent the difference in the competitive sorption kinetics and the varying composition of BC between the different samples, and between sediments and water. Accordingly, we suggest that the K_{BC} values derived here are applicable for other urban-impacted water bodies. The log-linear relationships (equations 4 and 5) can hence be used to predict K_{BC} values from mono- through hepta-brominated BDE congeners.

Atmospheric Concentrations of PBDEs

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

$$pV = nRT \qquad (6)$$

where p is the partial pressure (atm),

V is the volume (L),

n is the number of moles,

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

T is the temperature (K).

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

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

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

Fate of PBDEs

Air-Water Gaseous Diffusive Fluxes

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

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

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

Sediment-Water Fluxes

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

Inventory of PBDE fluxes across the Passaic River

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

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

Implications

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

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

Supporting Information

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

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References

(1) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures. *Environ. Sci. Technol.* **2006**, *40* (20), 6247–6254.

(2) He, M.-J.; Luo, X.-J.; Chen, M.-Y.; Sun, Y.-X.; Chen, S.-J.; Mai, B.-X. Bioaccumulation of polybrominated diphenyl ethers and decabromodiphenyl ethane in fish from a river system in a highly industrialized area, South China. *Sci. Total Environ.* **2012**, *419*, 109–115.

(3) Voorspoels, S.; Covaci, A.; Jaspers; Neels, H.; Schepens, P. Biomagnification of PBDEs in Three Small Terrestrial Food Chains. *Environ. Sci. Technol.* **2007**, *41* (2), 411–416.

(4) Ali, U.; Mahmood, A.; Syed, J. H.; Li, J.; Zhang, G.; Katsoyiannis, A.; Jones, K. C.; Malik, R. N. Assessing the combined influence of TOC and black carbon in soil–air partitioning of PBDEs and DPs from the Indus River Basin, Pakistan. *Environ. Pollut.* **2015**, *201*, 131–140.

(5) Chen, M.-Y.; Yu, M.; Luo, X.-J.; Chen, S.-J.; Mai, B.-X. The factors controlling the partitioning of polybrominated diphenyl ethers and polychlorinated biphenyls in the water-column of the Pearl River Estuary in South China. *Mar. Pollut. Bull.* **2011**, *62* (1), 29–35.

(6) Jia, F.; Gan, J. Comparing black carbon types in sequestering polybrominated diphenyl ethers (PBDEs) in sediments. *Environ. Pollut.* **2014**, *184*, 131–137.

(7) Guo, L.; Qiu, Y.; Zhang, G.; Zheng, G. J.; Lam, P. K. S.; Li, X. Levels and bioaccumulation of organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) in fishes from the Pearl River estuary and Daya Bay, South China. *Environ.*

Pollut. **2008**, *152* (3), 604–611.

(8) Houde, M.; Muir, D. Influence of lake characteristics on the biomagnification of persistent organic pollutants in lake trout food webs. *Environ. Toxicol. Chem.* **2008**, *27* (10), 2169–2178.

(9) Streets, S. S.; Henderson, S. A.; Stoner, A. D.; Carlson, D. L.; Simcik, M. F.; Swackhamer, D. L. Partitioning and Bioaccumulation of PBDEs and PCBs in Lake Michigan †. *Environ. Sci. Technol.* **2006**, *40* (23), 7263–7269.

(10) Wu, J.-P.; Luo, X.-J.; Zhang, Y.; Luo, Y.; Chen, S.-J.; Mai, B.-X.; Yang, Z.-Y. Bioaccumulation of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in wild aquatic species from an electronic waste (e-waste) recycling site in South China. *Environ. Int.* **2008**, *34* (8), 1109–1113.

(11) Jansson, B.; Asplund, L.; Olsson, M. Brominated flame retardants — Ubiquitous environmental pollutants? *Chemosphere* **1987**, *16* (10), 2343–2349.

(12) Toms, L.-M. L.; Hearn, L.; Kennedy, K.; Harden, F.; Bartkow, M.; Temme, C.; Mueller, J. F. Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of human milk, dust and indoor air. *Environ. Int.* **2009**, *35* (6), 864–869.

(13) Hites, R. A. Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-Analysis of Concentrations. *Environ. Sci. Technol.* **2004**, *38* (4), 945–956.

(14) Abbasi, G.; Buser, A. M.; Soehl, A.; Murray, M. W.; Diamond, M. L. Stocks and Flows of PBDEs in Products from Use to Waste in the U.S. and Canada from 1970 to 2020. *Environ. Sci. Technol.* **2015**, *49* (3), 1521–1528.

(15) UNEP, U. Report of the Conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants on the work of its fourth meeting. In *United Nations Environment Programme: Stockholm Convention on Persistent Organic Pollutants. Geneva*; 2009; p 112.

(16) Khairy, M.; Muir, D.; Teixeira, C.; Lohmann, R. Spatial Distribution, Air-Water Fugacity Ratios and Source Apportionment of Polychlorinated Biphenyls in the Lower Great Lakes Basin. *Environ. Sci. Technol.* **2015**, *49* (23), 13787–13797.

(17) Meire, R. O.; Khairy, M.; Targino, A. C.; Galvão, P. M. A.; Torres, J. P. M.; Malm, O.; Lohmann, R. Use of passive samplers to detect organochlorine pesticides in air and water at wetland mountain region sites (S-SE Brazil). *Chemosphere* **2016**, *144*, 2175–2182.

(18) McDonough, C. A.; Puggioni, G.; Helm, P. A.; Muir, D.; Lohmann, R. Spatial Distribution and Air–Water Exchange of Organic Flame Retardants in the Lower Great Lakes. *Environ. Sci. Technol.* **2016**, *50* (17), 9133–9141.

(19) Fernandez, L. A.; MacFarlane, J. K.; Tcaciuc, A. P.; Gschwend, P. M. Measurement of Freely Dissolved PAH Concentrations in Sediment Beds Using Passive Sampling with Low-Density Polyethylene Strips. *Environ. Sci. Technol.* **2009**, *43* (5), 1430–1436.

(20) Khairy, M. A.; Weinstein, M. P.; Lohmann, R. Trophodynamic behavior of hydrophobic organic contaminants in the aquatic food web of a tidal river. *Environ. Sci. Technol.* **2014**,

48 (21), 12533–12542.

(21) Lambert, M.; Friedman, C.; Luey, P.; Lohmann, R. Role of Black Carbon in the Sorption of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans at the Diamond Alkali Superfund Site, Newark Bay, New Jersey. *Environ. Sci. Technol.* **2011**, *45* (10), 4331–4338.

(22) Sacks, V. P.; Lohmann, R. Freely dissolved PBDEs in water and porewater of an urban estuary. *Environ. Pollut.* **2012**, *162*, 287–293.

(23) Khairy, M. A.; Lohmann, R. Field calibration of low density polyethylene passive samplers for gaseous POPs. *Environ. Sci. Process. Impacts* **2014**, *16* (3), 414–421.

(24) Burgess, R. M.; Lohmann, R. Role of black carbon in the partitioning and bioavailability of organic pollutants. *Environ. Toxicol. Chem.* **2004**, *23* (11), 2531–2533.

(25) Gustafsson, Ö.; Gschwend, P. M. The Flux of Black Carbon to Surface Sediments on the New England Continental Shelf. *Geochim. Cosmochim. Acta* **1998**, *62* (3), 465–472.

(26) Gustafsson, Ö.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. Quantification of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and Bioavailability. *Environ. Sci. Technol.* **1997**, *31* (1), 203–209.

(27) Nam, J. J.; Gustafsson, O.; Kurt-Karakus, P.; Breivik, K.; Steinnes, E.; Jones, K. C. Relationships between organic matter, black carbon and persistent organic pollutants in European background soils: Implications for sources and environmental fate. *Environ. Pollut.* **2008**, *156* (3), 809–817.

(28) Cornelissen, G.; Haftka, J.; Parsons, J.; Gustafsson, Ö. Sorption to Black Carbon of Organic Compounds with Varying Polarity and Planarity. *Environ. Sci. Technol.* **2005**, *39* (10), 3688–3694.

(29) Di Paolo, C.; Gandhi, N.; Bhavsar, S. P.; Van den Heuvel-Greve, M.; Koelmans, A. A. Black Carbon Inclusive Multichemical Modeling of PBDE and PCB Biomagnification and -Transformation in Estuarine Food Webs. *Environ. Sci. Technol.* **2010**, *44* (19), 7548–7554.

(30) Guan, Y.-F.; Sojinu, O. S. S.; Li, S.-M.; Zeng, E. Y. Fate of polybrominated diphenyl ethers in the environment of the Pearl River Estuary, South China. *Environ. Pollut.* **2009**, *157* (7), 2166–2172.

(31) Iannuzzi, J.; Butcher, M.; Iannuzzi, T. Evaluation of potential relationships between chemical contaminants in sediments and aquatic organisms from the lower Passaic River, New Jersey, USA. *Environ. Toxicol. Chem.* **2011**, *30* (7), 1721–1728.

(32) Adams, D.; O’Connor, J.; Weisberg, S. Final Report: Sediment Quality of the NY/NJ Harbor System–An Investigation under the Regional Environmental Monitoring and Assessment Program (R-EMAP). 1998.

(33) Bopp, R. F.; Chillrud, S. N.; Shuster, E. L.; Simpson, H. J.; Estabrooks, F. D. Trends in chlorinated hydrocarbon levels in Hudson River basin sediments. *Environ. Heal. Perspect.* **1998**, *106*, 1075–1081.

(34) Khairy, M.; Barrett, K.; Lohmann, R. Changing sources of polychlorinated dibenzo-p-dioxins and furans in sediments and ecological risk for nekton in the lower Passaic River and Newark Bay, New Jersey, USA. *Environ. Toxicol. Chem.* **2016**, *35* (3), 550–562.

(35) Booij, K.; Smedes, F.; van Weerlee, E. M. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* **2002**, *46* (8), 1157–1161.

(36) Potter, B. B.; Wimsatt, J. C. Method 415.3. Measurement of total organic carbon, dissolved organic carbon and specific UV absorbance at 254 nm in source water and drinking water. *Washington, DC, US Environ. Prot. Agency* **2005**.

(37) Khairy, M. A.; Luek, J. L.; Dickhut, R.; Lohmann, R. Levels, sources and chemical fate of persistent organic pollutants in the atmosphere and snow along the western Antarctic Peninsula. *Environ. Pollut.* **2016**, *216*, 304–313.

(38) Samara, F.; Tsai, C. W.; Aga, D. S. Determination of potential sources of PCBs and PBDEs in sediments of the Niagara River. *Environ. Pollut.* **2006**, *139* (3), 489–497.

(39) Zhao, X.; Zhang, H.; Ni, Y.; Lu, X.; Zhang, X.; Su, F.; Fan, J.; Guan, D.; Chen, J. Polybrominated diphenyl ethers in sediments of the Daliao River Estuary, China: Levels, distribution and their influencing factors. *Chemosphere* **2011**, *82* (9), 1262–1267.

(40) Chen, L.; Huang, Y.; Peng, X.; Xu, Z.; Zhang, S.; Ren, M.; Ye, Z.; Wang, X. PBDEs in sediments of the Beijiang River, China: Levels, distribution, and influence of total organic carbon. *Chemosphere* **2009**, *76* (2), 226–231.

(41) Yun, S. H.; Addink, R.; McCabe, J. M.; Ostaszewski, A.; Mackenzie-Taylor, D.; Taylor, A. B.; Kannan, K. Polybrominated Diphenyl Ethers and Polybrominated Biphenyls in Sediment and Floodplain Soils of the Saginaw River Watershed, Michigan, USA. *Arch. Environ. Contam. Toxicol.* **2008**, *55* (1), 1–10.

(42) Luo, Q.; Cai, Z. W.; Wong, M. H. Polybrominated diphenyl ethers in fish and sediment from river polluted by electronic waste. *Sci. Total Environ.* **2007**, *383* (1), 115–127.

(43) Li, Q.; Yan, C.; Luo, Z.; Zhang, X. Occurrence and levels of polybrominated diphenyl ethers (PBDEs) in recent sediments and marine organisms from Xiamen offshore areas, China. *Mar. Pollut. Bull.* **2010**, *60* (3), 464–469.

(44) Lohmann, R.; Burgess, R. M.; Cantwell, M. G.; Ryba, S. a; MacFarlane, J. K.; Gschwend, P. M. Dependency of polychlorinated biphenyl and polycyclic aromatic hydrocarbon bioaccumulation in Mya arenaria on both water column and sediment bed chemical activities. *Environ. Toxicol. Chem.* **2004**, *23* (11), 2551–2562.

(45) Daniel R. Oros, *,†; Dale Hoover, ‡; Francois Rodigari, §; David Crane, ∥ and; Sericano⊥, J. Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from the San Francisco Estuary. **2004**.

(46) Burkhard, L. P. Estimating Dissolved Organic Carbon Partition Coefficients for Nonionic Organic Chemicals. *Environ. Sci. Technol.* **2000**, *34* (22), 4663–4668.

(47) Bärring, H.; Bucheli, T. D.; Broman, D.; Gustafsson, Ö. Soot–water distribution

coefficients for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polybrominated diphenylethers determined with the soot cosolvency-column method. *Chemosphere* **2002**, *49* (6), 515–523.

(48) Kuivikko, M.; Sorsa, K.; Kukkonen, J. V. K.; Akkanen, J.; Kotiaho, T.; Vähätalo, A. V. Partitioning of tetra- and pentabromo diphenyl ether and benzo[a]pyrene among water and dissolved and particulate organic carbon along a salinity gradient in coastal waters. *Environ. Toxicol. Chem.* **2010**, *29* (11), 2443–2449.

(49) ter Laak, T. L.; van Eijkeren, J. C. H.; Busser, F. J. M.; van Leeuwen, H. P.; Hermens, J. L. M. Facilitated Transport of Polychlorinated Biphenyls and Polybrominated Diphenyl Ethers by Dissolved Organic Matter. *Environ. Sci. Technol.* **2009**, *43* (5), 1379–1385.

(50) Wei-Haas, M. L.; Hageman, K. J.; Chin, Y.-P. Partitioning of Polybrominated Diphenyl Ethers to Dissolved Organic Matter Isolated from Arctic Surface Waters. *Environ. Sci. Technol.* **2014**, *48* (9), 4852–4859.

(51) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **1979**, *13* (3), 241–248.

(52) Totten, L. A.; Brunciak, P. A.; Gigliotti, C. L.; Dachs, J.; Glenn; Nelson, E. D.; Eisenreich, S. J. Dynamic Air−Water Exchange of Polychlorinated Biphenyls in the New York−New Jersey Harbor Estuary. *Environ. Sci. Technol.* **2001**, *35* (19), 3834–3840.

(53) Zarnadze, A.; Rodenburg, L. A. Water-column concentrations and partitioning of polybrominated diphenyl ethers in the New York/New Jersey Harbor, USA. *Environ. Toxicol. Chem.* **2008**, *27* (8), 1636–1642.

(54) Xia, G. *Sorption behavior of nonpolar organic chemicals on natural sorbents*; 1998.

(55) Yue, C.; Li, L. Y. Filling the gap: Estimating physicochemical properties of the full array of polybrominated diphenyl ethers (PBDEs). *Environ. Pollut.* **2013**, *180*, 312–323.

(56) Harner, T.; Shoeib, M.; Diamond, M.; Ikonomou, M.; Stern, G. Passive sampler derived air concentrations of PBDEs along an urban–rural transect: Spatial and temporal trends. *Chemosphere* **2006**, *64* (2), 262–267.

(57) Kurt-Karakus, P. B.; Alegria, H.; Jantunen, L.; Birgul, A.; Topcu, A.; Jones, K. C.; Turgut, C. Polybrominated diphenyl ethers (PBDEs) and alternative flame retardants (NFRs) in indoor and outdoor air and indoor dust from Istanbul-Turkey: Levels and an assessment of human exposure. *Atmos. Pollut. Res.* **2017**.

(58) Venier, M.; Hites, R. A. Flame Retardants in the Atmosphere near the Great Lakes. *Environ. Sci. Technol.* **2008**, *42* (13), 4745–4751.

(59) Ruge, Z.; Muir, D.; Helm, P.; Lohmann, R. Concentrations, Trends, and Air–Water Exchange of PAHs and PBDEs Derived from Passive Samplers in Lake Superior in 2011. *Environ. Sci. Technol.* **2015**, *49* (23), 13777–13786.

(60) Xie, Z.; Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Brominated Flame Retardants in Seawater and Atmosphere of the Atlantic and the Southern Ocean. *Environ. Sci. Technol.* **2011**, *45* (5), 1820–1826.

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

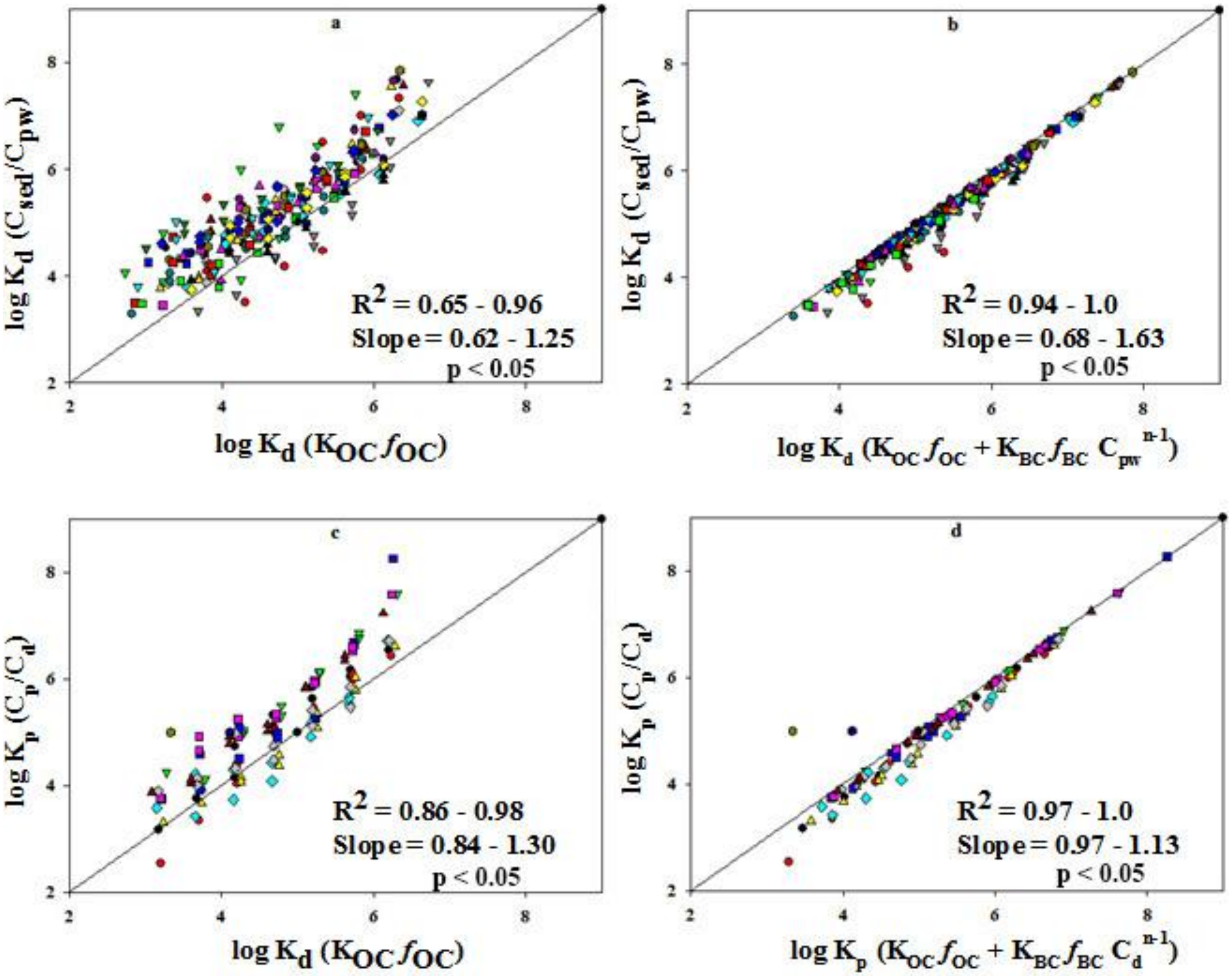


Figure 1: Log linear relationships between observed and predicted solid-water partitioning coefficients in sediments based on OC (a) and OC + BC (b) sorption models, and in water (c, d). Site specific K_{BC} values were used. Predicted K_ds were calculated using a Freundlich coefficient (n) of 0.7[29].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

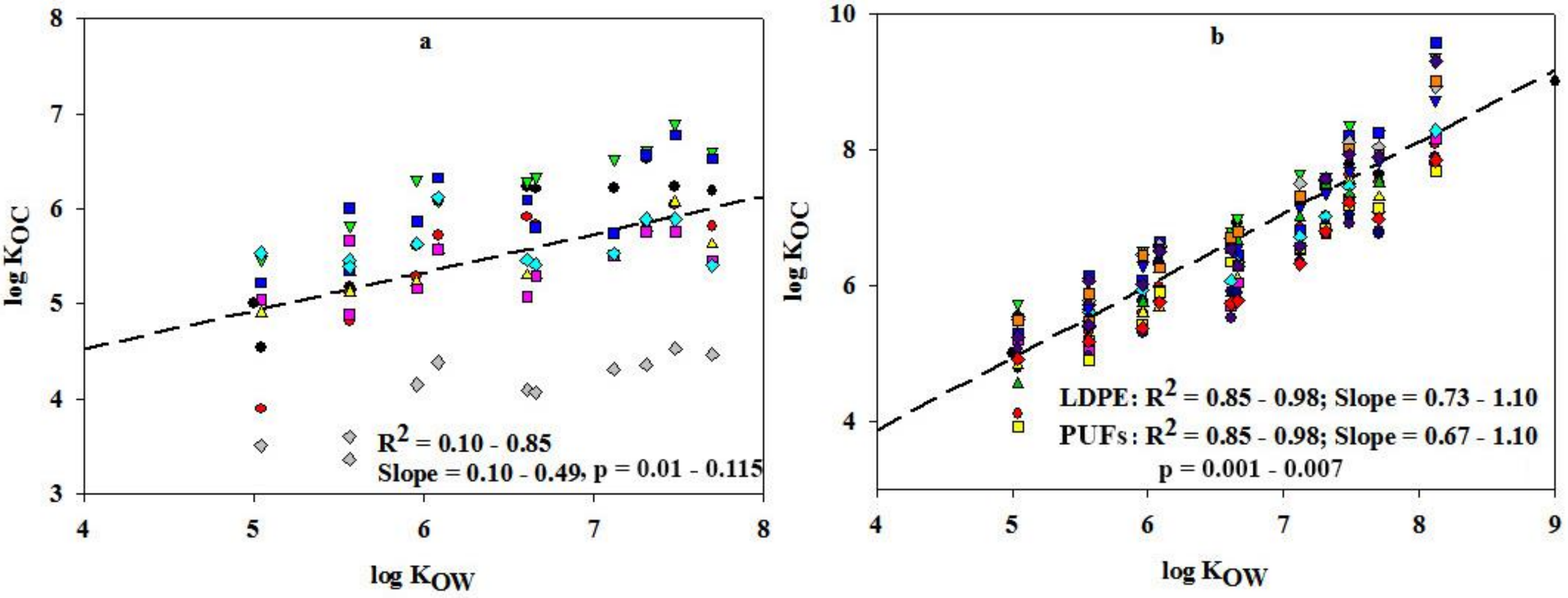


Figure 2: Log linear relationships between K_{OC}s and K_{OW}s for apparent (a) and truly dissolved concentrations (b) of PBDEs in the water column of the lower Passaic River. Symbols represent calculated K_{OC} values for 12 PBDE congener at each sampling site (n = 3 x 3 sampling periods). Data points in panel b represent the truly dissolved values obtained from LDPE and from PUFs after DOC correction.

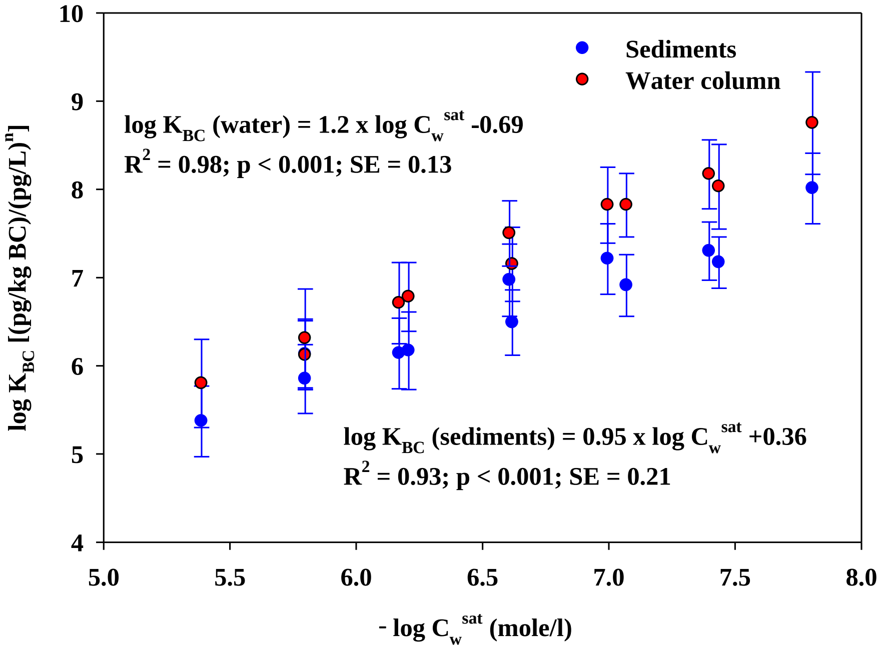


Figure 3: Log -linear relationship between observed K_{BC} (L/kg) and C_w^{sat} (mol/L) in sediments (n = 22) and water (n = 9) of the lower Passaic River. Error bars represent the standard deviation.

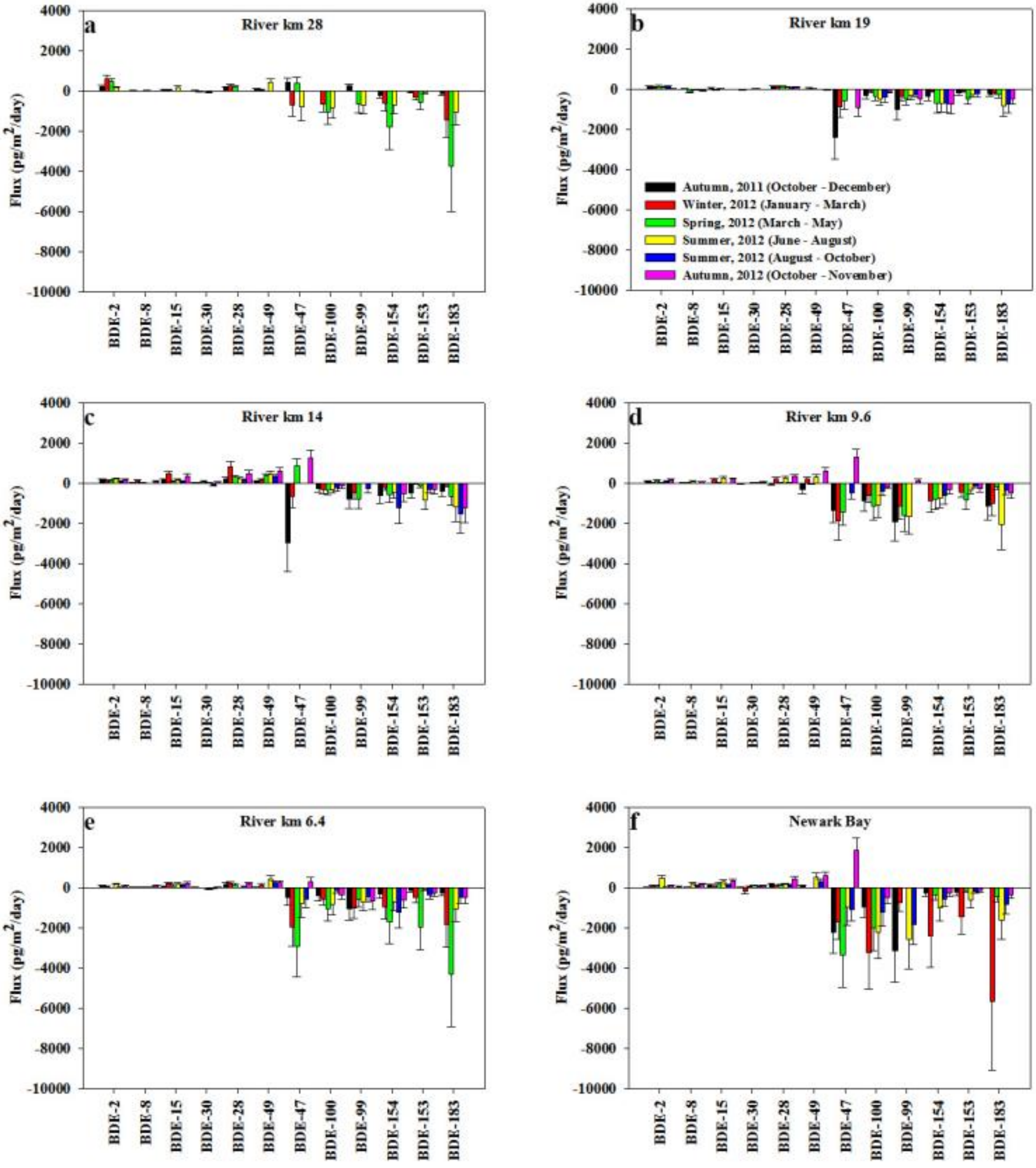
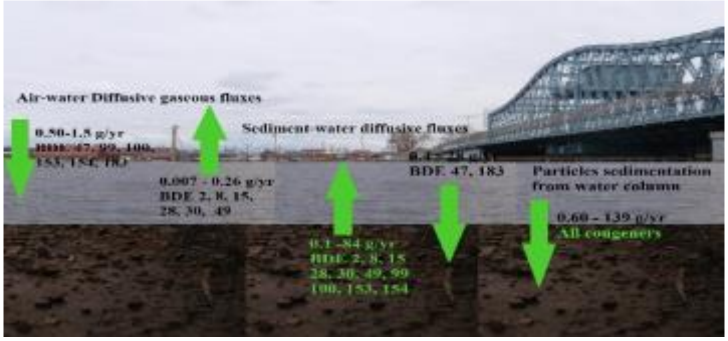


Figure 4: Calculated air-water gaseous fluxes (pg/m^2/day) of PBDEs at the lower Passaic River.

TOC


Air-water Diffusive gaseous fluxes
0.50-1.5 g/yr
BDE 47, 99, 100,
153, 154, 183
0.007 - 0.26 g/yr
BDE 2, 8, 15,
28, 30, 49
Sediment-water diffusive fluxes
0.1 -84 g/yr
BDE 2, 8, 15
28, 30, 49, 99
100, 153, 154
BDE 47, 183
Particles sedimentation
from water column
0.60 - 139 g/yr
All congeners