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Uptake of hydrophobic organic compounds, including OCPs and PBDEs, and perfluoroalkyl acids (PFAAs) in fish and blue crabs of the lower Passaic River (NJ, USA)

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Abstract

The bioavailability and bioaccumulation of sedimentary hydrophobic organic compounds (HOCs) is of concern at contaminated sites. Passive samplers have emerged as a promising tool to measure the bioavailability of sedimentary HOCs and possibly to estimate their bioaccumulation. We thus analyzed HOCs including organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) in sediment, porewater and riverwater using low density polyethylene (LDPE) passive samplers, and in 11 different finfish species and blue crab from the lower Passaic River. Additionally, perfluorinated alkyl acids (PFAAs) were measured in grab water samples, sediment and fish. Best predictors of bioaccumulation in biota were either porewater concentrations (for PCBs and OCPs), or sediment organic carbon (PBDEs and PFAAs), including black carbon (OCPs, PCBs and some PCDD/F congeners) normalized concentrations. Measured lipid-based concentrations of the majority of HOCs exceeded the chemicals' activites in porewater by at least 2-fold, suggesting dietary uptake. Trophic magnification factors were > 1 for moderately hydrophobic analytes (log K_{OW} = 6.5 – 8.2) with low metabolic transformation rates (< 0.01 day^{-1}), including longer alkyl chain PFAAs. For analytes with lower (4.5 – 6.5) and higher (>8.2) K_{OW}s, metabolic transformation was more important in reducing trophic magnification.

INTRODUCTION

Rivers in highly urbanized/industrialized areas are impacted by various classes of chemicals, often resulting in adverse ecological effects, such as habitat destruction, and various physiological and reproductive disorders in the river fauna. Once in the ecosystem, pollutants can accumulate in biota from the surrounding water, sediments and/or porewater depending on the physicochemical properties of the pollutants, feeding habits, trophic position and metabolic rates. The significance of bioaccumulation in fish and the accompanied ecological and human health risks have been previously highlighted in studies performed by the U.S. EPA (US EPA 1992a; US EPA 1992b). Typically, organic chemicals are prioritized with respect to their persistence, bioaccumulation potential and toxicity (PBT chemicals) (Gobas et al. 2009). Recently, the use of chemical properties to predict the bioaccumulation potential of a chemical has been questioned (Borgå et al. 2012).

In our recent work (Khairy et al. 2014), we assessed the biomagnification of polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-*p*-dioxin/dibenzofurans (PCDD/Fs) in fish and crabs collected from the Passaic River estuary. In general, the dominant exposure pathways for legacy hydrophobic organic contaminants (HOCs) in biota were porewater and sediments rather than the riverwater. Here, we aimed to expand on these results by investigating a wider range of contaminants with more diverse structures and properties. Targeted compounds include organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs) and perfluorinated alkyl acids (PFAAs), including perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA). As PFAAs and some OCPs display much greater aqueous solubility than the legacy HOCs, it is unclear whether sediment-bound contamination remains a primary exposure pathway to biota in the river. These compounds also cover a wide range of resistance to metabolism (US EPA 2016a),

which should, in conjunction with varying degrees of lipophilicity, affect their uptake and magnification in the food web.

While recent work established the presence of PBDEs at relatively high concentrations in all the environmental compartments of the lower Passaic River, and deduced diffusive fluxes of PBDEs from sediment to overlying water (Khairy and Lohmann 2017), little is known regarding their uptake sources and their bioaccumulation potential.

Unlike legacy HOCs, PFAAs are ionic, amphiphilic compounds (Key et al. 1997), and thus have different physicochemical properties. They have been globally detected in all environmental compartments (Labadie and Chevreuil 2011; Loi et al. 2011; Fang et al. 2014). PFAAs are persistent and tend to bioaccumulate (PFAAs with longer fluorinated carbon chain) (Conder et al. 2008), undergo long range transport (LRT) and cause adverse ecological and health effects (Lau et al. 2007). Anionic PFAAs are proteinophilic and generally found at highest concentrations in blood and liver (Becker et al. 2010) in contrast to the lipophilic legacy pollutants.

Studying the bioaccumulation potential of HOCs requires the ability to measure the freely dissolved fraction in sediments (porewater) and/or the water column, where bioavailability is expected to increase with an increase in the dissolved concentrations (You et al. 2006). Passive samplers, such as low density polyethylene (LDPE) sheets, have emerged as an inexpensive and effective technique for measuring the freely dissolved concentrations of HOCs. Traditionally, geochemical approaches have been used to predict porewater concentrations (sediment concentrations and organic carbon content), due to the difficulties associated with the measurement of the dissolved fraction in sediment's porewater directly. However, since the development of

88 passive sampling devices, estimation of porewater concentrations have become feasible (
89 Fernandez et al. 2009; Ghosh et al. 2014; Khairy and Lohmann 2017).

90
91 The original equilibrium partitioning theory (Di Toro et al. 1991) linked porewater concentrations
92 of HOCs to their accumulation in the lipid of organisms. As LDPE samplers similarly accumulate
93 HOCs from porewater, recent studies indicated that LDPE concentrations of HOCs (at
94 equilibrium) can be used to predict their bioaccumulation (Friedman et al. 2009). In fact, recent
95 work by Jahnke et al. (2014) suggested that passive sampling can be used to estimate the
96 bioaccumulation potential of HOCs, and indicated that the majority of studies resulted in tissue
97 concentrations below the equilibrium concentration with porewater (Jahnke et al. 2014). Being
98 able to rely on passive samplers to predict (maximum) bioaccumulation in aqueous foodwebs
99 would certainly be very useful for the assessment of contaminated sites.

100
101 In the current study, we investigated the bioaccumulation of OCPs and PBDEs in 11 fish species
102 and *Callinectes sapidus* (blue crab), collected from the fresh-brackish portion of the Passaic River
103 estuary. PFAAs data for only 8 fish species were included in the current study. To that end, we
104 calculated the bioaccumulation factors (BAFs) for OCPs, PBDEs and PFAAs, compared the
105 accumulated amounts of HOCs in LDPE and in the biota and investigated the best predictors for
106 HOCs and PFAAs in biota using sediment geochemistry and LDPE (active water samples for
107 PFAAs). Since sampling of biotic and abiotic compartments were done at the same time intervals
108 and all the samples were analyzed in the same lab, we present here a uniquely consistent set of
109 BAFs. Our objectives were to (i) assess the sources of contaminants accumulated by the biota
110 (sediments, porewater, diet, or overlying water), (ii) assess the suitability of using LDPE to predict

111 the bioaccumulation of HOCs in biota and (iii) derive bioaccumulation factors and assess the
112 trophic magnification (or dilution) of target analytes.

113

114 **MATERIALS AND METHODS**

115 *Samples collection, extraction, analysis for OCPs and PBDEs*

116 Detailed description of the sampling of biota and sediments, preparation and deployment of the
117 LDPE in the river water (for OCPs and PBDEs), the stable isotope analysis in the biota tissues, the
118 determination of porewater concentrations using LDPE tumbling experiment and the uncertainty
119 analysis can be found in in Figures S1-S3, Table S1,text in the Supplementary information (SI)
120 and in Khairy et al. (2014, 2015) and Khairy and Lohmann (2017). More information about the
121 extraction of all matrices, instrumental analysis, quality assurance and the determination of
122 porewater concentrations is available in the SI (Tables S2-S6) and is briefly summarized below.

123 Finfish specimens (n = 350 representing 10 species) including benthic feeders (*Callinectes*
124 *sapidus*, *Anguilla rostrata*, *Fundulus heteroclitus*, *Hybognathus regius*, *Morone americana*),
125 bentho-pelagic taxa (*Fundulus diaphanus*, *Lepomis spp*., *Esox americanus*, and juvenile *Morone*
126 *saxatilis*), and pelagic species (*Menidia menidia* and *Dorosoma cepedianum*) and 7 *Callinectes*
127 *sapidus* (blue crab) specimens were collected during August-November, 2011 at three locations in
128 the Passaic River estuary (Figure S1). For marine transients, fish collections were restricted to the
129 extent practical to young-of-year that had a recent history of exposure to contaminants in the
130 system. See Table (S1) for more details on the biota samples.

131 Sediment samples were collected from 18 different locations (Figure S2) along the lower Passaic
132 River during September to November, 2011, from the mudflats at low tide. Detailed description

of the sampling methodology and sampling locations can be found in Khairy et al. (2015). Total organic carbon (TOC) and black carbon (BC) content in the sediments were determined as detailed in Gustafsson et al. (1997).

LDPE passive samplers were fastened to an anchored rope and suspended in the water column ~ 1-2 m below the surface at six different locations along the lower Passaic River (Figure S1) to sample the freely dissolved OCPs and PBDEs.

Freely dissolved porewater concentrations were determined by shaking (equilibrating) LDPE passive sampling sheets (25 µm thick) with sediment-water (containing sodium azide as a biocide) slurry for 9 weeks according to the method detailed in Lohmann et al. (2005).

Biota and sediment samples were extracted and subjected to cleanup according to the methods detailed elsewhere (Khairy et al. 2014, 2015). LDPE (both deployed in the river water and porewater) were cold extracted twice (24 hours each) in dichloromethane followed by hexane, concentrated and were not subjected to any further cleanup steps.

Collection of water samples, extraction and analysis of all the samples for PFAAs

We used the same sediment and biota samples that were collected for OCPs and PBDEs. Water samples (~ 20 cm below the surface) were collected in pre-cleaned (inner walls were cleaned with basic methanol followed by methanol and left overnight to dry) one-liter polypropylene bottles with polypropylene lids at 8 different locations along the lower segment of the Passaic River (Figure S3). Samples were kept in an ice bath until preserved in a freezer for analysis. Water samples (400 mL each) were analyzed for PFAAs (PFHxA - PFDoDA, PFBS, PFHxS and PFOS) in the U.S. Food and Drug Administration's (FDA) Laboratory in Maryland (USA) according to the method detailed in Young et al. (2013). Sediments and fish samples were analyzed at

University of Rhode Island (URI), USA. Extraction and cleanup was done according to the U.S. EPA method for the analysis of PFAAs (EPA 2011) (see SI, Tables S2 and S3 for more information). PFAAs were measured in 8 fish species [*Morone saxatilis* (29 – 33 cm), *Anguilla rostrate* (110 cm), *Morone Americana* (8 -16 cm), *Fundulus diaphanous*, *Hybognathus regius*, *Menidia menidia*, *Dorosoma cepedianum*, and *Fundulus heteroclitus*], but not in the blue crabs due to a lack of extra tissue after PBDE and OCP analysis.

Quality assurance

Procedural blanks, field blanks (LDPE), matrix spikes, and duplicate samples (20% of the total samples) were included with each sample batch and were carried throughout the entire analytical procedure in a manner identical to the samples. BDE-47 was detected in the blanks (10-20 % of the least detected concentration in the different matrices). Similarly, detected PFAAs in the blank samples were 12-25 % of the sample concentrations and accordingly, correction of samples for the blank detects was performed.

Recoveries of the surrogate standards in the biota, LDPE and sediment samples generally ranged from 65 - 102% and 72-104 % for OCPs and PBDEs respectively. Matrix spikes recoveries (Table S4) ranged from 94 – 104 % for OCPs and PBDEs with RSD % < 10 %. Reproducibility of the results ranged from 7.0 – 17 % and 5.0 – 18.5 % for OCPs and PBDEs respectively.

Recoveries of PFAAs in the matrix spikes (Table S5) were 87-133% for the majority of the target PFAAs and < 55 % for C_{13} - C_{18}- perfluorocarboxylic acid and C_{10}-perfluorosulfonate. Accordingly, these PFAAs were excluded from the discussion. Recoveries of the surrogate standards ranged from 57 – 120 % (Table S5). Limit of detection (LOD) corresponded to a signal-to-noise ratio of 3 (Table S6). Variability between duplicates was <20%.

Physicochemical properties

Octanol-water partitioning coefficient (K_{ow}) values of OCPs were obtained from Schenker et al. (2005). K_{ow} values for PBDEs were obtained from Yue and Li (2013). Polyethylene-water partitioning coefficients (K_{PE-W}) for OCPs and PBDEs were obtained from Lohmann (2012). Lipid-water partitioning coefficients (K_{lip-w}) were estimated from K_{OW} according to the method of Endo et al. (2011). Organic carbon-water partitioning coefficient (K_{OC}) were calculated as shown in Xia (1998) .

For PFAAs, K_{OC} were obtained from obtained from Higgins and Luthy (2007). Missing values were obtained by correlating the available values against those obtained from Labadie and Chevreuil (2011). Protein-water partitioning coefficients (K_{PW}) were obtained from Kelly et al. (2009). Missing values were obtained from correlating the available values against K_{OC}s (n = 8; R^2 = 0.98); K_{OW} values were obtained from Wang et al. (2011). K_{PW} rather than K_{lip-w} were used with PFAAs as these compounds bind to proteins rather than to general lipids. All the physicochemical properties used in the current study are given in Table S7.

Estimated compound specific metabolic biotransformation rates (K_{mtr}s) normalized to 10 g tissue weight were obtained from the BCFBAF function in EPI Suite 4.11 (US EPA 2016b).

Calculation of BAFs, TMFs and predicting biota concentrations

Bioaccumulation factors (BAFs, L/kg lipid or ww) were calculated as the ratio of lipid normalized tissue concentrations of PBDEs and OCPs (C_{lip}, ng/kg lipid) to the freely dissolved river water concentrations from PE-samplers (C_w, ng/L), or fresh weight concentrations of PFAAs (; ng/kg ww) to grab water sample concentrations (C_w, ng/L) as follows (equation 1) (Schwarzenbach et al. 2005):

$$BAF = \frac{C_{lip(ww)}}{C_w} \quad \textbf{(1)}$$

TMF values were calculated as follows (equation 2):

$$TMF = e^{b} \quad \textbf{(2)}$$

where b is the slope of the linear relationship between the natural log of lipid-normalized tissue concentrations and the trophic position of each species. TMFs >1 indicates that contaminants are biomagnifying whereas values < 1 indicate that contaminants are not taken up by the organism or that they are metabolized (trophic dilution).

Lipid-based concentrations (ng/g) of HOCs were estimated from each sediment's sorbent phase [organic carbon (OC) and black carbon (BC)], porewater LDPE, and riverwater LDPE and compared to those measured in tissues (C_{lip}) as follows: (equation 3-5):

$$C_{lip(OC)} = \frac{C_{sed}}{f_{OC}\ K_{OC}}\ K_{lip\text{-}w} \quad \textbf{(3)}$$

Where, C_{sed} is the sediment concentration (ng/g) and f_{OC} is the fraction of OC in sediments. Similarely, lipid concentrations based on OC + BC ($C_{lip,OC+BC}$) were estimated using a Freundlich coefficient of n = 0.7:

$$C_{lip(OC+BC)} = \frac{C_{sed}}{f_{OC}\ K_{OC} + f_{BC}\ K_{BC}\ C_{PW}^{n-1}}\ K_{lip\text{-}w} \quad \textbf{(4)}$$

where f_{BC} is the fraction of BC in the sediment and K_{BC} is the black carbon-water partitioning coefficient. We used site specific K_{BC} values in the current study.

Lipid concentrations from PE-derived porewater [$C_{lip(PW)}$] and riverwater [$C_{lip,(W)}$] were estimated as follows:

$$C_{lip[PW(W)]} = C_{[PW(W)]} * K_{lip\text{-}w} \quad \textbf{(5)}$$

For PFAAs, protein-based concentrations were predicted only from sediment's OC and from river water using equations 3 and 5. In both equations, $K_{lip\text{-}w}$ was replaced with K_{PW}. Concentrations of PFAAs in the samples were normalized to a generic total protein content (25 %) assigned for fish tissues as shown in Kelly et al. (2009) and references therein.

Statistical Analysis

Statistical tests (ANOVA, t-test and correlations) were performed with SigmaPlot (version 11, Germany); regression analysis with IBM SPSS V25.

RESULTS

Uncertainty analysis

Uncertainties associated with the estimated porewater and river water concentrations (equation S4) from LDPE ranged from 41 – 65 % and 40 – 64 % respectively. Uncertainties associated with predicted tissue concentrations from sediment's OC were the lowest (22 – 58 %) followed by predicted concentrations from porewater (41 – 65 %), river water (40 – 80 %) and sediment's OC + BC (28 - 88 %).

Concentration of organic pollutants

*OCPs***:** OCP concentrations in the biota samples are given in Figure 1A-C and Table S8. In all species, the following descending order was observed: DDTs (900 – 21,000 ng/g lipid) > chlordanes (840 – 4,700 µg/g lipid) > hexachlorobenzene (HCB) (11 – 330 ng/g lipid) > α-

endosulfan (<LOD – 290 ng/g lipid) > HCHs (8.0 – 83 ng/g lipid). Concentrations of HCB, α-endosulfan and DDTs were 2.0 – 10 times higher in the blue crab samples (Figure 1A) than the other biota as was previously observed for PAHs, PCBs and PCDD/Fs (Khairy et al. 2014). Average concentrations of HCB in the benthopelagic (including the top predator) and pelagic species (164 and 200 ng/g lipid respectively) were 3.0 fold higher than in the benthic species (70 ng/g lipid). Similarly, average concentration of DDTs in the benthopelagic species (9,000 ng/g lipid) was 3.0-4.0 fold higher than in benthic (3,000 ng/g lipid) and pelagic species (2,000 ng/g lipid; Figure 1A).

DDTs (24-52 ng/g dw) were the dominant pesticide in the sediment samples (Table S9), followed by chlordanes (12-35 ng/g dw) and α-endosulfan (1.0 – 11 ng/g dw). In the porewater (Table S10) and surface water samples (Table S11) HCHs (2.6 – 9.0 and 1.4 – 3.1 ng/L respectively) dominated followed by α-endosulfan (0.20 – 5.7 and <LOD – 0.90 ng/L) and chlordanes (0.30 – 1.1 and 0.16 – 0.48 ng/L).

PBDEs: Σ_{12}PBDEs concentrations ranged from 120 ng/g lipid (*Fundulus heteroclitus*) to 2,500 ng/g lipid (*Callinectes sapidus*) in the biota (Table S12), 1.0-11 ng/g dw in sediments (Table S13), 19 – 40 pg/L in porewater (Table S14) and 12 -31 pg/L in surface water (Table S15). All the biotic, sediment, porewater and surface water samples were dominated by BDE-47 and BDE-99 (Figure 1D-F). Other congeners that were detected included BDE-183 in sediments, and BDE-100 and BDE-49 in the biota, sediments and porewater (estimated by LDPE).

PFAAs: Concentrations of PFAAs ranged from 130 ng/g ww (*Fundulus heteroclitus*) to 350 ng/g ww (*Anguilla rostrata*) (Table S16). All the samples were dominated by PFOS (52 – 76 % of the total PFAA, Figure 1G) followed by PFDoA, PFUnDA, PFOA (4.0 – 10 % each) and PFHxA.

PFBA, PFPeA and PFHpS were below LOD in all the samples. In all samples, concentrations of perfluorinated sulfonic acids (PFSAs) were significantly (t- test, $p < 0.05$) higher than perfluorinated carboxylic acids (PFCAs).

PFAAs in the sediment (Figure 1H) samples ranged from 8.0 ng/g dw (km 3.7) to 15 ng/g dw (km 24) (Table S17). PFOS was the dominant compound (42 % of total concentrations). The longer chain PFCAs (PFDoA: 35 %; PFUnDA:11 %), PFOA (5.0 %) and PFDA (4.0 %) were easily detected in sediment, probably related to their greater affinity for particles and hence accumulation in sediments (sorption to OC) due to increasing hydrophobicity with increasing number of CF_2 groups (Ahrens et al. 2010). PFBA, PFPeA and PFBS were below LOD in all the samples, whereas PFHpA and PFHpS were below LOD in the majority of the samples.

Concentrations of PFAAs in the surface water ranged from 44 ng/L (km 3.7) to 120 ng/L (km 22.4) (Table S17). Similar to results for sediments and biota, PFOS dominated in surface water samples, followed by PFOA and PFHxA (Figure 1I).

Tissue concentrations versus abiotic compartments

LDPE concentrations of HOCs [in riverwater ($C_{PE(RW)}$) and porewater ($C_{PE(PW)}$)] at equilibrium (ng/kg PE), OC-normalized sediment concentrations ($C_{sed(OC)}$; ng/kg OC), BC-normalized sediment concentrations ($C_{sed(BC)}$; ng/kg BC) and OC+BC-normalized sediment concentrations ($C_{sed(OC+BC)}$) were compared with lipid-normalized concentrations (C_{lip}) of the target analytes in the food web of the lower Passaic River (Figure S4). For PFAAs, the comparison was only made with $C_{sed(OC)}$. Significant linear relationships were observed between log measured C_{lip} and log $C_{PE(RW)}$ (Figure S4A), log $C_{PE(PW)}$ (Figure S4B) and log sediment (Figure S4C-E) concentrations

283 (including PFAAs). Coefficient of determinations (R^2) ranged from 0.79 to 0.82 and slopes of the
284 best fits were insignificantly different from 1 (slopes = 1.2-1.3, $p < 0.001$).

285 C_{lip} for all HOCs were predicted from equations 3-5 using the OC ($C_{lip(OC)}$) and the OC + BC
286 models ($C_{lip(OC+BC)}$), porewater ($C_{lip(PW)}$) and riverwater ($C_{lip(RW)}$) LDPE (Figure 2) and compared
287 to measured concentrations. Similarly, protein-based tissue concentrations of PFAAs were
288 predicted from $C_{lip(OC)}$ and $C_{lip(RW)}$ based on measured riverwater concentrations. To facilitate the
289 comparison between HOCs and PFAAs, measured (in biota) and predicted protein-based
290 concentrations of PFAAs from sediment and riverwater were normalized to the lipid content. This
291 step was done by converting the predicted protein-based concentrations (from abiotic
292 compartments) to equivalent wet weight concentrations and then normalizing to the measured lipid
293 content in tissues. In addition to the regression lines, a factor difference of $\pm$ 10 (represented by
294 the dashed red lines) was used to evaluate the predictive ability of the abiotic compartments. This
295 factor was previously used to evaluate the ability of using passive samplers as a surrogate for
296 bioaccumulation of HOCs (Joyce et al. 2016). When points occur within the dashed lines, it
297 indicated similarities in the affinities of geochemical natural sorbents (OC and BC), lipid and
298 LDPE to the organic pollutants. Mono-through tri-chlorinated dioxins and furans and HCHs were
299 excluded from the comparison because of their high biotransformation potential and/or
300 uncertainties in the physicochemical properties.

301 Highly significant linear relationships (all regression parameters are shown in Figure 2) were
302 observed between log measured C_{lip} and predicted log $C_{lip(OC)}$ (Figure 2A) , $C_{lip(OC+BC)}$ (Figure 2B)
303 and $C_{lip(PW)}$ for HOCs only (Figure 2C) and $C_{lip(RW)}$ (Figure 2D) for all species. In general,
304 PCDD/Fs were less well predicted than other classes of pollutants.

Jahnke et al. (Jahnke et al. 2014) used passive samplers to derive the chemical activity of several PCBs and HCB in sediment and biota and to investigate the possibility of using passive samplers as a metric for the thermodynamical potential for the bioaccumulation of HOCs. According to their results and other cited studies, measured C_{lip}/predicted C_{lip} from porewater were either below or near their equilibrium benchmark values (0.5 – 2.0). In the current study, 2,3,7,78-TCDD, 2,3,7,8-TCDF, PCB 52, 101, 105, 118, 128, 138, 153, 180 and 187, BDE-28, 49, 47, 100, 154, HCB, chlordanes and DDTs in the majority of the fish and blue crab samples showed values greater than the equilibrium benchmark based on porewater (> 2).

Bioaccumulation and biomagnification of HOCs and PFAAs

Calculated BAFs for OCPs, PBDEs (both in L/kg lipids) and PFAAs (in L/kg PW) are given in Tables (S18 – S20). Average BAFs ranged from 4.1×10^3 (α-HCH) – 7.7×10^7 (o,p'-DDE), 7.1×10^5 (BDE-2) – 5.3×10^8 (BDE-154) and 4.8×10^2 (PFBS) – 1.1×10^5 (PFDoA) for OCPs, PBDEs and PFAAs respectively. Calculated BAFs for PBDEs were the highest (Table S18) followed by OCPs (Table S19) and PFAAs (Table S20). Additionally, PBDE BAFs were higher than those previously calculated for PAHs in the same samples (Khairy et al. 2014) but lower than BAFs previously calculated for PCDD/Fs (4.0×10^3 – 6.0×10^8) (Khairy et al. 2014) and PCBs (2.0×10^3 – 2.0×10^9) (Khairy et al. 2014). Reported BAF values for OCPs and PBDEs in the current study were higher than values previously reported for freshwater fish from China (2.0×10^3 – 8.0×10^5 and 2.0×10^2 – 3.2×10^6 for OCPs and PBDEs respectively) (Wu et al. 2008; Wang et al. 2012) and for Lake Trout in Lake Michigan (Streets et al. 2006). Calculated BAFs for PFAAs were within the range of values calculated for PFAAs in literature (1.2×10^1 - 1.0×10^5) (Kwadijk et al. 2010; Labadie and Chevreuil 2011).

328 Trophic levels of the fish species were calculated here based on the levels of nitrogen isotopes in
329 the tissues (Khairy et al. 2014). Blue crabs were excluded because of their relatively high detected
330 concentrations of OCPs and PBDEs despite of their low trophic position, which is probably due to
331 accidental sediment ingestion. Calculated TMFs were significantly greater than 1 ($p < 0.05$) for
332 o,p'-DDD (4.1), HCB (3.9), o,p'-DDE (3.6). p,p'-DDE (3.1), p,p'-DDT (2.1), heptachlor (2.0),
333 oxychlordane (1.8), BDE-47 (3.1), BDE-154 (2.5), Σ_{12}PBDEs (2.4), and BDE-100 (2.1) (Table
334 S21).
335
336 **DISCUSSION**

337 *Comparing tissue concentrations to sediment, riverwater and porewater concentrations*

338 In this study, significant linear relationships were observed between log $C_{PE(PW)}$, $C_{PE(RW)}$, $C_{sed(OC)}$
339 and $C_{sed(OC+BC)}$ and log C_{lip} in biota. Similar relationships were previously observed for PCBs
340 (Friedman et al. 2009; Joyce et al. 2015; Joyce et al. 2016) and PBDEs (Joyce et al. 2015) when
341 tissue concentrations were compared to LDPE concentrations adjusted for equilibrium.
342 Coefficients of determination (R^2) reported in the current study (for all classes of HOCs + PFAAs
343 in sediments) were within the range previously observed for PCBs (0.59-0.94) (Friedman et al.
344 2009; Joyce et al. 2015; Joyce et al. 2016) and DDTs (0.72) but higher than for PBDEs (0.59)
345 (Joyce et al. 2015).

346 In contrast, slopes of the regression lines in the current study (1.2 – 1.3, $p < 0.001$) were higher
347 than those observed in the previous studies for PCBs, PBDEs and DDTs (0.74 – 1.0) (Friedman et
348 al. 2009; Joyce et al. 2015; Joyce et al. 2016). The slopes we observed indicated that accumulated
349 amounts of HOCs in tissues exceeded those predicted from LDPE or sediment geochemistry. This
350 implies that biotransformation of most HOCs did not play a significant role in the fish samples

collected from the lower Passaic River. These results suggest that the linear relationships with abiotic compartments could be used to predict the bioaccumulation potential in the fish. Best predictions of C_{lip} for HOCs and PFAAs were obtained from either $C_{sed(OC+BC)}$ and/or $C_{PE(PW)}$ (Figure 2), as demonstrated by higher R^2, lower SE and slopes closer to 1.

All the OCPs, PFAAs and the majority of PBDE, PCDD/F and PCB congeners occurred within a factor of 10 of measurements, although lipid-based concentrations were overestimated for many congeners. Importantly, PFAAs were not separated from the other HOCs and the regression parameters with and without PFAAS did not differ (Figure 2). This possibly implies a similar affinity of HOCs and PFAAs to OC. Moreover, tissue concentrations of PFOA through PFDoA, PFOS and PBDEs were well predicted from $C_{sed(OC)}$within a factor difference ranging from 1.0 to 2.8 (Figure 2A).

Lipid-normalized concentrations of OCPs and PCBs were similarly better predicted using the $C_{PE(PW)}$ and $C_{sed(OC+BC)}$ models (Figure 2B, C) within a factor difference of 1.0 – 4.0. Higher factor differences (measured /predicted > 2.0) was observed for some PCB congeners (PCB 28, 52, 101, 153, 138, 180, which are known to be strong bioaccumulative) and OCPs such as chlordanes and DDTs. presumably due to their uptake from food and their biomagnification potential (see below). As for OCs, regression parameters for the measured versus predicted tissue concentrations from riverwater were similar with and without adding PFAAs (Figure 2D), which again indicates a similar lipid-water partitioning behavior for HOCs and the more polar PFAAs. However, many PFAAs were underestimated by riverwater, with factor differences (measured/predicted) > 10. Only the more soluble PFHxA and PFHpA were better predicted from riverwater (factor difference: 1.5 – 2.5) than sedimentary OC, $C_{sed(OC)}$. Unfortunately, concentrations of PFAAs were not measured in porewater and the predictive ability of $C_{PE(PW)}$ and $C_{sed(OC+BC)}$ cannot be examined.

374 However, based on regression output of $C_{sed(OC)}$ and $C_{PE(RW)}$, we assume that the uptake of PFAAs
375 probably occurred from porewater and diet similar to HOCs.

376 When comparing measured to predicted concentrations of the legacy pollutants, we did not account
377 for the biotransformation rates in the biota. We assumed biotransformation was negligible for
378 several reasons: First, significant linear relationships were observed between calculated log
379 bioaccumulation factors (BAFs) and log K_{OW}s (Figure 3) indicating either equilibrium or steady
380 state for the HOCs. Second, as shown in Figure 3, log BAFs for all the analytes (except BDE-99)
381 were above the 1:1 line. In other words, calculated log BAFs were higher than their corresponding
382 log K_{OW}s, which is an indicative of low/non-biotransformation except for BDE-99. Third, lipid-
383 based concentrations of HOCs were higher than sediment concentrations (normalized to OC, BC
384 and OC + BC) and LDPE concentrations (ng/kg PE) (Figure S4). Finally, Wirgin et al. (2011)
385 indicated that fish in the Hudson River, which is located in the same region of the Passaic River,
386 have developed a mechanism to resist biotransformation due to evolutionary changes from the
387 exposure to legacy pollutants.

388 *Comparison of porewater and foodweb chemical activities*

389 In contrast to other studies [25 and references therein], measured C_{lip} of the majority of the HOCs
390 in the current study were higher than the porewater's equilibrium benchmark set by Jahnke et al
391 (2014). The benchmark value was derived as a factor of 2 of the chemicals' activites in porewater
392 as estimated by passive samplers in sediment and biota directly. Possible reasons for these
393 divergent results in our study include (i) the structure of the foodwebs, (ii) the relative importance
394 of pelagic vs trophic coupling, and (iii) relying on a different approach of comparing chemical
395 activities in biota relative to abiotic compartments.

We rule out metabolism having a significant influence on these persistent chemicals as we mentioned in the previous section. Similarly, trophic levels in the Swedish lake's food-chain were even greater (assumed to reach a TL of up to 4.4), than in the Passaic River, where the top predator was at a TL of 4.0 (Khairy et al. 2014).

We argue that the exceedance of porewater chemical benchmark observed in biota of the Passaic River is due to the strong benthic coupling, as we described previously (Khairy et al. 2014; Khairy and Lohmann 2017). In other words, the fish in the Swedish lake were likely strongly affected by water column concentrations (not measured), which we assume were much below porewater concentrations. In the Passaic River, differences between porewater and water column were only 0.6 - 11. Lastly, we inferred chemical activities in biota by lipid-normalizing HOC concentrations, while we used passive samplers in porewater and water column. This introduces more uncertainty, but the good agreement observed by numerous studies between lipid-normalized and passive sampler-derived HOC concentrations implies this is of minor importance (Friedman et al. 2009; Friedman and Lohmann 2014; Joyce et al. 2016). Overall, our results suggest that predicting the ecological risk to aquatic biota using measurements of porewater concentrations is not sufficient unless adjusted by the calculated BAFs in benthically-coupled system.

Bioaccumulation of the organic pollutants

Significant log BAFs – log K_{OW} (R^2 = 0.80 - 0.91; $p < 0.001$) and log BAFs – log $K_{lip\text{-}w}$ (R^2 = 0.87 - 0.94; $p < 0.001$) linear relationships were observed for PBDEs and OCPs in the biota using both riverwater (BAF^{RW}; Figures 3A, S5A) and porewater (BAF^{PW}; Figures 3B, S5B) for calculating BAFs, indicating that the observed partitioning between lipids (in biota) and water can be approximated from the octanol – water equilibrium partitioning. In our previous work, we indicated and quantified diffusive fluxes of PBDEs from the porewater to the overlying riverwater,

which could explain the tight coupling of HOC concentrations and profiles in porewater and riverwater (Figure 1). Lower log $BAFs^{RW}$ were generally observed for BDE-99 than for the tri- through hepta-brominated congeners (Figure 3A) possibly due to its biotransformation (metabolism) in fish species (Hu et al. 2010). Similar findings were previously observed in aquatic species collected from China (Wu et al. 2008) and in Lake Michigan's trout (Streets et al. 2006). BDE-183 also showed lower BAF values compared to penta- and hexa-congeners, probably due to the limited uptake induced by its large molecular size. However, calculated log $BAFs^{RW}$ and $BAFs^{PW}$ for the majority of the fish samples were higher than their corresponding log K_{OW}s (Figure 3) and log $K_{lip\text{-}w}$ (Figure S5) indicating a possible dietary uptake. We argue that the exceedance of K_{OW}-predicted $BAFs^{RW}$ and $BAFs^{PW}$ is the result of the influence of the porewater on riverwater (via diffusive fluxes).

Calculated BAFs for PFAA increased significantly with increasing log K_{OW} (Figure 3C) and alkyl chain length (Figure 4D; $R^2 = 0.60 – 0.65$; SE = 0.42 – 0.45; $p < 0.01$). Log BAF of the longer chain PFUNDA, PFDoDA and PFOS (average: 4.1, 4.4 and 3.7 respectively) were generally higher than the shorter chain PFAAs. Additionally, values for PFOS were higher than all the PFAAs other than the above-mentioned long chain ones indicating a possible higher bioaccumulation potential for PFOS. Based on the TSCA bioaccumulation criteria (Hong et al. 2015), only the longer chain PFAAs and PFOS appear to be bioaccumulative to very bioaccumulative in the fish species. ($3 \leq \log BAF < 5$), which agrees well with other studies (Hong et al. 2015).

Biomagnification of pollutants in the food web

All the HOCs (DDTs, HCB, oxychlordane, BDE-47, 100, 154, some PCB and PCDD/F congeners) that showed significant trophic magnification potential (TMF > 1, $p < 0.05$) were the analytes that exceeded the equilibrium porewater benchmark value set by Jahnke et al. (2014) indicating the importance of the dietary intake and strong benthic coupling in the Passaic River. All the other investigated OCPs and PBDEs showed either insignificant trophic dilution (γ- and δ-HCH) or trophic magnification. For PFAAs (Table S22), significant trophic magnification was only observed for PFUnDA (1.9), PFOS (1.8), PFDA (1.6) and PFDoA (1.5), as was observed in previous studies (Fang et al. 2014; Xu et al. 2014). However, calculated TMFs for PFAAs were generally lower than values calculated for OCPs and PBDEs.

For PFCAs, TMF values were relatively stable for C_5 - C_8 perfluorinated acids, then increased for C_8 - C_{10}, but decreased again for PFDoA, which is probably due its molecular size, limiting its uptake. For PFSAs, PFOS showed the highest TMF value among all the PFAAs, which agrees well with previous findings in other food webs worldwide (Conder et al. 2008).

Role of metabolic transformation

To investigate the relationships between hydrophobicity, metabolic transformation (k_{mtr}) and TMFs, a conditional probability table was computed using TMFs and presented graphically in Figure (4) based on cumulative frequencies. The figure indicated that the maximum probability of obtaining a TMF > 1 were observed for HOCs having log K_{OW} > 7.5 and characterized by low metabolic transformation rates ($k_{mtr} \leq 0.01$ day^{-1}). Starting from log K_{OW} > 6.5, high probability rates of TMFs > 1 were observed. This range included dioxins, PCBs, PBDEs, OCPs and the longer alkyl chain PFAAs (> C_8). Exceptions were observed at lower log K_{OW}s (4.5 – 6.5) for some OCPs and higher molecular weight PAHs, but still at low metabolic transformation rates (log $k_{mtr} \leq 1.25$

466 equivalent to $k_{mtr} \leq 0.06$ day^{-1}) indicating that at these lower K_{OW} ranges, there is an increase in
467 the importance of k_{mtr} in controlling trophic magnification. Additionally, calculated TMFs for PCB
468 189, 195, 206 and 209 (1.4 – 1.97) were higher than TMF values calculated for OCDD, OCDF
469 and BDE-183 (0.70 – 1.72) although all have log K_{OW} values > 8.0 (8.02 – 8.79). This can be
470 explained knowing that the latter group has higher biotransformation rates (log k_{mtr}s: -1.96 to -
471 1.46) than the former group (logk_{mtr}s: -3.04 to -3.30). From all the investigated HOCs with TMFs
472 > 1 (n = 59), only four had log k_{mtr} > -1.5 (K_{mtr} > 0.032 day^{-1}). All these findings suggest that k_{mtr}
473 values are probably more important than hydrophobicity in explaining the biomagnification of
474 HOCs. The uncertainty related to the estimated k_{mtr} values could be substantial, however.

475
476 **CONCLUSIONS**

477 Although banned decades ago, the contamination by legacy pollutants is widespread in the aquatic
478 environment of the lower Passaic River. Our results indicate that $C_{PE(PW)}$ and $C_{PE(RW)}$ of HOCs and
479 - for some HOCs and PFAAs - $C_{sed(OC)}$ can be used to estimate C_{lip} in biota. In contrast to previous
480 results, though, measured C_{lip} in the current study were above the porewater equilibrium
481 benchmark concentration (0.5-2). Our results imply that in systems with strong benthic coupling,
482 bioaccumulation needs to be considered to predict HOC and PFAA concentrations in top predators.
483 Measured tissue concentrations of PFOA, PFNA, PFUnDA, PFDoA and PFOS were 1.4 – 2.7
484 times higher than predicted tissue concentrations from sediment OC. This agrees well with their
485 bioaccumulative nature as suggested by TSCA bioaccumulation criteria (Hong et al. 2015) and
486 suggests dietary uptake. Both hydrophobicity and metabolic transformations are needed to assess
487 the biomagnification potential for both the lipophilic contaminants and PFAAs. Future work
488 should confirm how useful chemical acitivities in sediment are for being able to predict the
489 chemicals' body burden in a given foodweb. This will always depend on the specifics of the

ecosystem under consideration, including variations in the environmental conditions, foodweb characteristics and the physicochemical properties of sediments in the area under investigation. Yet our study indicated that porewater concentrations from passive sampling for HOCs and/or sediment geochemistry for PDBEs and PFAAs were good predictors of lipid-normalized concentrations. There are additional factors, though, that will influence this predictive ability between sites and methods: first, variabilities arising from using different passive samplers and/or using unstandardized methods for the same passive sampler (Jonker et al. 2018); second, uncertainties associated with the use of partitioning coefficients in particular for compounds such as PFAAs that bind to proteins; and finally, expected differences from estimating porewater concentrations using *in situ* vs *ex situ* samplers. Accordingly, these factors should be addressed in future research.

SUPPLEMENTAL DATA

Supplemental Data on sampling, chemical analysis, physicochemical properties, spatial distribution, BAFs and TMFs are available on the Wiley Online Library at DOI: 10.1002/etc.xxxx.

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Data availability statement:

Data pertaining to this manuscript are available in the Supplemental Data.

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Figure captions

Figure 1: Concentrations of OCPs, PBDEs and PFAAs in fish/blue crabs (A, D, G), sediments (B, E, H) and porewater/riverwater (C, F, I) of the lower Passaic River.

Figure 2: Measured versus model-predicted lipid-based concentrations of OCPs, PCBs, PCDD/Fs, PFAAs and PBDEs in fish/blue crabs based on partitioning from (A) sediment OC, (B) sediment OC + BC, (C) porewater, and (D) riverwater in the lower Passaic River. Points represent the average values for all fish/blue crabs; error bars represent the standard deviation; dashed red lines represent the 95 % prediction intervals.

Figure 3: Linear regression relationships between log K_{OW} and log BAFs calculated for OCPs and PBDEs based on riverwater (A), porewater (B), for PFAAs based on riverwater (C), and log BAFs against number of fluorinated carbons for PFAAs (D). TSCA: toxic substance control act.

Figure 4: 3D plot showing the probability of having a trophic magnification factor (TMF) value > 1 based on the values of both metabolism (log k_{mtr}) and octanol-water partitioning (log K_{OW}). Blue color represents the greatest probability (100 %) and the dark orange color represent the least probability.