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

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

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Abstract

Passive sampling has emerged as a promising tool to better assess sediments contaminated with a range of hydrophobic organic contaminants (HOC), such as polychlorinated biphenyls (PCBs) or polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs). Previous work had evaluated the ability of passive samplers to predict bioavailability of sedimentary HOCs in the laboratory, in particular for marine organisms. The focus of the current study was to validate the use of *in situ* passive samplers in porewater and surface water to derive freely dissolved concentrations of PCDD/Fs and PCBs simultaneously. Passive multisamplers were also used to detect spatial trends of these HOCs, and to predict their bioaccumulation by benthic organisms. Low density polyethylene samplers (LDPE) were deployed at four locations along the lower Passaic River (NJ), where sediment and benthic species samples were also collected. Good agreement was generally observed for PCB and PCDD/F concentrations comparing *in situ* and the *ex situ* approaches (within 0.30 – 39%). Including a higher chlorinated $^{13}C_{12}$ PCDD congener as a performance reference compound improved results for PCDD/Fs. Significant linear relationships were observed between log LDPE based –log lipid-based concentrations of PCDD/Fs and PCBs. The *in situ* multisampler showed

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

Introduction

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

To overcome problems associated with direct measurement/prediction of porewater concentrations, passive samplers have been developed to estimate the freely dissolved concentrations of HOCs. Passive samplers such as low density polyethylene (LDPE)[3,8–11], polyoxymethylene (POM)[1,12,13] and/or polydimethylsiloxane (PDMS)[14] has been widely used to estimate porewater and surface water concentrations of HOCs. LDPE have been widely used for monitoring hydrophobic organic compounds (HOCs) in porewater[3,4,8,9,11,15–17] and surface water. [4,8,16] HOCs accumulate in LDPE via diffusion and absorption into the sampler matrix, with a high enrichment in LDPE[16] thus offering lower detection limits. Other advantages of LDPE include simplicity (in its chemical makeup), low cost and ease of deployment[18]. For LDPE, complicated cleanup techniques for extracts are rarely needed (except for PCDD/Fs), and it can be used both in the linear uptake (kinetic) or equilibrium (thermodynamic) sampling mode by varying the thickness of the PE, the use of performance reference compounds (PRCs) and the exposure time (days, weeks and months).

Freely dissolved concentrations of HOCs in porewater have been previously measured either *in situ* (field deployment by inserting samplers in sediments for a sufficient period of time)[11,19–22] or *ex situ* (equilibrating sediment-water slurry with passive sampler in the lab for a period of time usually sufficient to attain equilibrium)[3,4,8,9]. Although the *ex situ* approach is more widely used due to the reduced equilibration time/enhanced mass transfer (continuous agitation of the sediment-water-passive sampler system) and improved precision[23], the *in situ* approach is used when it is required to capture field conditions (refer to Ghosh et al.[2] for more details on criteria for selecting the *in situ* vs the *ex situ* approaches). As the *in situ* deployed passive samplers require longer time to reach equilibrium with sediments, PRCs are needed and crucial for disequilibrium corrections. Alternatively, deployed LDPE passive samplers with vibrating motors were suggested[11,19–22] to disrupt the depletion layer around the passive sampler and thus accelerate the uptake of HOCs.

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

River[3,7,8,24]. LDPE were spiked with PRCs for disequilibrium corrections. Estimated concentrations of all the investigated HOCs were compared with measured concentrations of the same HOCs in fish species and blue crabs. Results indicated that porewater concentrations were the best predictors of tissue concentrations, and both porewater and diet were important uptake sources of HOCs in higher level biota[8].

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

Materials and Methods

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

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

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

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

As a control to the *in situ* porewater sampling system, *ex situ* estimation of porewater concentrations was also performed (using LDPE sheets with 25 and 51 µm thickness) with the same sediments as described previously[4].

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

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

All samples were separately analyzed for mono- through octa-chlorinated dioxins and furans, and 209 PCB congeners using gas chromatography coupled with to a triple quadrupole mass spectrometry. For PCBs, a 30-m long x 0.25-mm I.D. fused silica capillary column with DB-5MS bonded phase, or equivalent was used for GC/MSMS analyses. The analytical method for PCB detection is functionally equivalent to the U.S. EPA method 1668b[26] and the Japanese standard method[25].

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

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

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

Estimation of Freely Dissolved Concentrations from LDPE: PRCs were used to gauge whether target analytes had achieved equilibrium and to adjust for disequilibrium in polyethylene (C_{LDPE}) assuming that uptake and elimination rates are equivalent[27]. Sampling rates were calculated using the PRCs according to the method of Booij and Smedes[28]. For porewater LDPE, PRCs were used to correct for disequilibrium using the PRC calculator developed by Gschwend et al.[15] for sediment's deployed LDPE by applying a fixed-bed diffusive mass transfer model[29].

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

Results

Sediment Concentrations

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

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

PCDD/Fs: Σ_{27} PCDD/Fs ranged from 1.7 ng/g dw (S4) to 4.6 ng/g dw (S2) with an average concentration of 3.0 ng/g dw. As for PCBs, detected concentrations of PCDD/Fs at S2 were higher than concentrations observed at the other locations, but it was not statistically significant. Detected concentrations were within the same range as previously observed in sediments of the lower Passaic River in 2011[3]. Sediments were dominated by 1,2,3,4,6,7,8,9-CDD comprising on average 53 % of the total detected concentrations followed by 1,2,3,4,6,7,8,9-CDF (11 %) (Figure S5). In terms of the WHO toxic equivalents[30], concentrations ranged from 56 pg TEQ/g dw to 211 pg TEQ/g dw with an average concentration of 147 pg TEQ/g dw. In all the samples 2,3,7,8-TCDD dominated the total WHO-TEQ with contributions ranging from 71 – 81 % followed by hexa-chlorinated furans (5.0 – 9.0 %).

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

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

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

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

PRCs and Adjustment for Disequilibrium

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

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

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

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

Porewater concentrations

Good agreement was generally observed for PCBs congeners measured with the tumbling experiment using two different thicknesses and the *in situ* sampler (Figures 1d and S8 and Tables S3- S6) with relative standard deviation % (RSD) ranging from 0.3 – 39 % in the four samples. Our results contrast with those reported by Appell and Gschwend[31], in which the authors observed significantly lower *in situ* concentrations, presumably driven by bioirrigation.

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

Deuterated PAHs vs $^{13}C_{12}$ PCDDs as PRCs: To investigate whether generic PRCs (d-PAHs) were adequate for the accurate estimation of porewater concentrations of PCDD/Fs compared to $^{13}C_{12}$-PCDDs, we performed an additional field deployment (last deployment period) with LDPE that were spiked with deuterated PAHs and one of each of $^{13}C_{12}$ di-, tetra- and hexa-chlorinated dibenzo-p-dioxins (Figure 3a). These PRCs were also used in the accompanying *ex situ* tumbling experiment, which represented the ‘true’ porewater concentrations (Figure 3b).

Slightly different results are obtained whether d-PAHs or $^{13}C_{12}$-PCDDs were used as PRCs in the *in situ* (or the *ex situ* approaches). For the *in situ* samplers, relative percent difference (RPD %) for PCDD/Fs in the four locations ranged from 1.0 % to 35 % for all PCDD/F congeners except for 2,7/2,8-CDD, 2,3,7,8-CDF and 2,3,7,8-CDD at Passaic Avenue station (41 – 42 %) and 1,2,3,6,7,8-CDD at Doremous Street sampling site (52 %). For the *ex situ* samplers, lower differences were observed (RPD %: 0.0 – 35 %) than in the *in situ* samplers. These calculated % differences are within the estimated uncertainties for estimating porewater concentrations from LDPE. Based on the obtained results, we conclude that d-PAHs could successfully be used as PRCs for PCDD/Fs to correct for disequilibrium. We consider the use of $^{13}C_{12}$ PCDD/Fs as optional, depending on budget constraints and needed certainty.

Trends of Porewater concentrations

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

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

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

Riverwater concentrations

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

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

PCDD/Fs: Estimated freely dissolved concentrations of PCDD/Fs at the three sampling sites (samplers from one site were lost) are given in Table S12. Concentrations generally ranged from 19 pg/L (S1) to 39 pg/L (S4) with an average concentration of 25 pg/L. All the samples were dominated by the lower chlorinated congeners (mono- through tri-chlorinated furans and di-chlorinated dioxins) comprising > 93 % of the total concentrations (Figure S11). In terms of TEQ, concentrations ranged from 0.16 pg TEQ/L to 0.33 pg TEQ/L. 2,3,7,8-TCDD was the dominant congener comprising 27 – 82 % of the total TEQ concentrations.

Porewater vs River water Concentrations and Profiles

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

Biota Concentrations

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

Variance on Ranks, $p < 0.001$). Similar PCB profiles were observed in all the investigated benthic species, where PCBs were dominated by tri- through hepta-chlorinated homologous groups (like sediments) comprising 83 – 94 % of the total lipid normalized PCB concentrations (Figure S13).

PCDD/Fs: Concentrations of $\sum_{26}$ PCDD/Fs in the benthic species ranged from 12 ng/g lipids (shrimp) to 34 ng/g (clams) lipid with an average concentration of 23 ng/g lipid (Table S14). No statistical significant difference was observed for the detected PCDD/F concentrations in the different investigated benthic species. Unlike for PCBs, different patterns were observed in the benthic species (see Figure S14). Concentrations of the most toxic 2,3,7,8-CDD congener ranged from 0.70 ng/g lipid (tube worms at S1) to 2.0 ng/g lipid (mud crab at S1) comprising 2.0 – 9.0 % of the total lipid normalized PCDD/F concentrations.

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

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

To investigate the similarities/dissimilarities in the observed profiles of PCBs and PCDD/Fs in sediments, porewater, biota and river water, factor analysis was performed. The factor analysis (Tables S15-S17) generated 3 factors that explained 96 % of the total variability in the data. Factor 1 explained 42 % of the total variability and was heavily loaded on all the porewater and riverwater profiles at all the sampling sites (> 0.95). This is a reflection of the similar freely dissolved profiles of OCBs and PCDD/Fs (dominance of the lower chlorinated congeners). Factor 2 explained 29 % of the total variability and was heavily loaded (> 0.90) on all the sediment samples and moderately loaded (0.54 – 0.63) on some of the benthic species. This explains some of the similarities in the profiles of HOCs in the sediments and the benthic species (abundance of the higher chlorinated PCB and PCDD/F congeners). Factor 3 explained 25 % of the total variability in the data and was loaded on the biota samples. Although biota samples had high contributions from 1,2,3,4,6,7,8,9-CDD, tetra- and penta-chlorinated PCBs like in sediments, they also showed significant contributions from the lower chlorinated PCDD/F congeners and less contribution of the hexa- and hepta-chlorinated PCBs compared to sediments and accordingly, they were heavily loaded on a separate factor than sediments.

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

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

In our previous work[7], LDPE concentrations of HOCs (PCBs, PCDD/Fs, PBDEs and organochlorine pesticides) obtained from the *ex situ* approach also displayed significant log-log linear relationship with their corresponding lipid-based concentrations in various fish species ($R^2 = 0.79$, SE = 0.62, slope = 1.2, $p < 0.001$) of the lower Passaic River. Lipid based concentrations were higher than LDPE concentrations as was also observed in the current and other studies (see Figure 4). Coefficient of determinations (R^2) for the regression analysis in the current study (0.81 – 0.91) were among the highest observed in previous studies. [19,36–43]

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

Influence of lipophilicity on the affinities of HOCs to LDPE and lipids: Log ($C_{lip}/C_{passive}$) was calculated and plotted against log $K_{lip\text{-}w}$ as a surrogate for lipophilicity (Figure 5). Log ($C_{lip}/C_{passive}$) values ranged from -0.37 ± 0.37 to 1.6 ± 0.50 with an average value of 0.51 ± 0.33. The average value of the current study was similar to that calculated for DDTs and PCBs using various passive samplers in Joyce et al.[40], albeit with a lower standard deviation in our work (0.52 ± 0.49). Calculated $C_{lip}/C_{passive}$ decreased with the increase in $K_{lip\text{-}w}$ indicating that the affinity of HOCs to lipids and LDPE becomes more similar with the increase in hydrophobicity. Future work should measure the exact difference between animal lipids and LDPE to be able to correct for this divergence, as far as it is caused by physico-chemical partitioning differences.

The lower chlorinated PCBs (1- and 2-Cl) had a higher affinity towards lipids, which could possibly be attributed to their higher solubilities, and thus more uptake from porewater and riverwater. In the study performed by Joyce et al.[40], a completely different pattern was observed, where higher ratio values were observed for analytes with higher log K_{OW} values. This observed variation could also be attributed to the differences in the passive samplers used, differences in the investigated species and accordingly their metabolic rates and differences in the level of contamination of the sediments with HOCs among the different studies.

Implications

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

Our study indicated that *in situ* porewater passive samplers are good predictors of lipid-based concentrations in freshwater aquatic organisms and that the predictive ability of the passive samplers was better than sediments using the common equilibrium partitioning theory. Additionally, the current results indicated the good agreement between estimated porewater concentrations using both the *in situ* and *ex situ* approaches. We therefore suggest that the *ex situ* laboratory approach, while easier, is not necessarily superior or needed[2,36]. By and large, we report similar results for PCDD/Fs and PCBs both *in situ* and *ex situ* for 2 key groups of HOCs. These results also indicate the absence of significant bioirrigation at those sites[31]. It remains important to select representative PRCs that covers the entire range of analytes investigated. In our previous work[3,7,8,24], we indicated that (*ex situ*) porewater was a better predictor of the bioaccumulation of various HOCs in fish of different trophic levels. An *in situ* comparison might yield more representative results but should also include the analysis of trophic status of benthic biota to better explain the observed results.

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

Future work should then concentrate on studying the ability the proposed *in situ* sampler to predict the bioaccumulation potential in an entire food web and that whether one regression equation could be used as a representative of the entire foodweb or not. Given the recent diverging results from a porewater interlaboratory comparison[44], performing field-based comparisons of different passive sampling approaches will be needed to further increase the confidence in their results.

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Supplementary Information:

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

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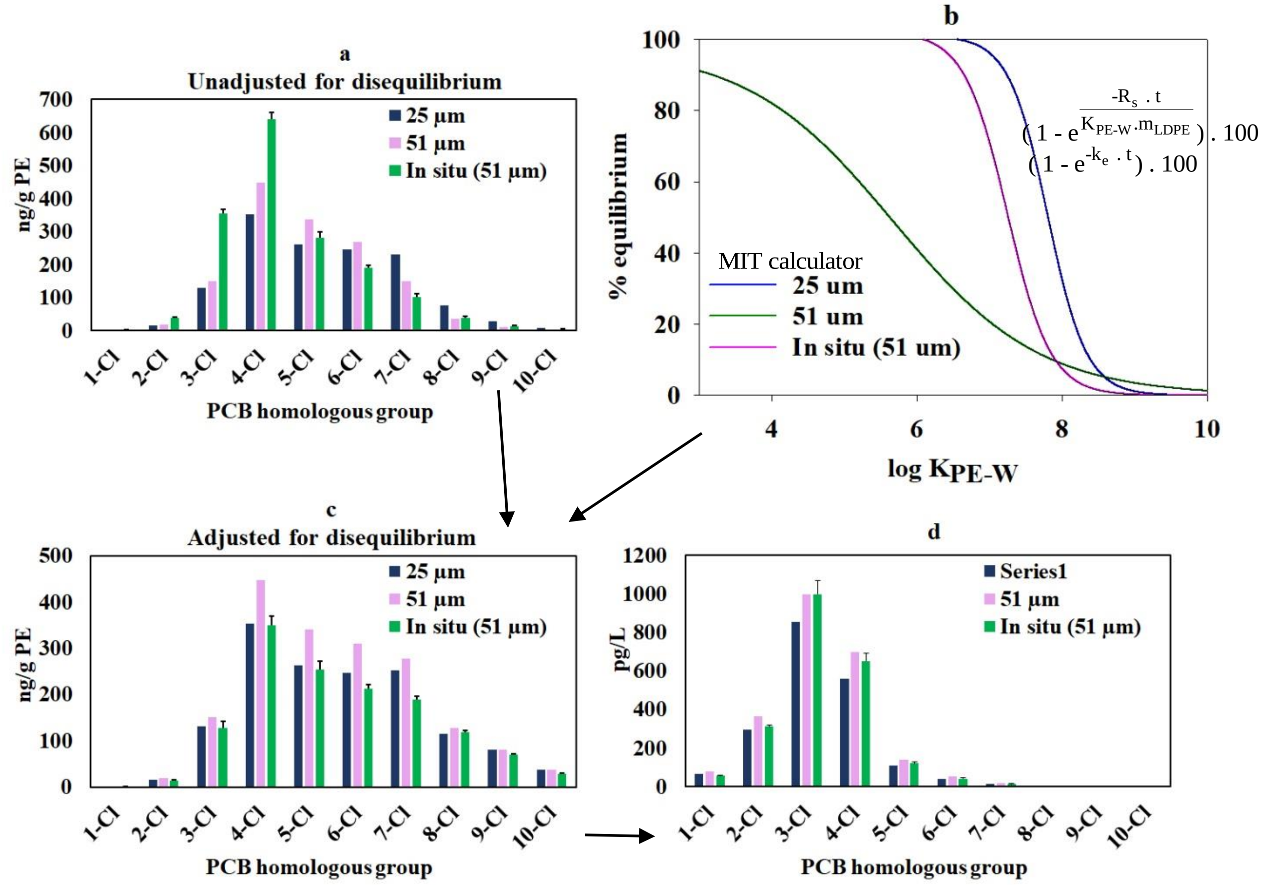


Figure 1: Concentrations of PCBs (ng/g PE) in the LDPE of the proposed *in situ* porewater sampler before (a) and after (c) correction for disequilibrium using PRCs (b) and the estimated porewater concentrations (d) at S1 (Riverbank Park).

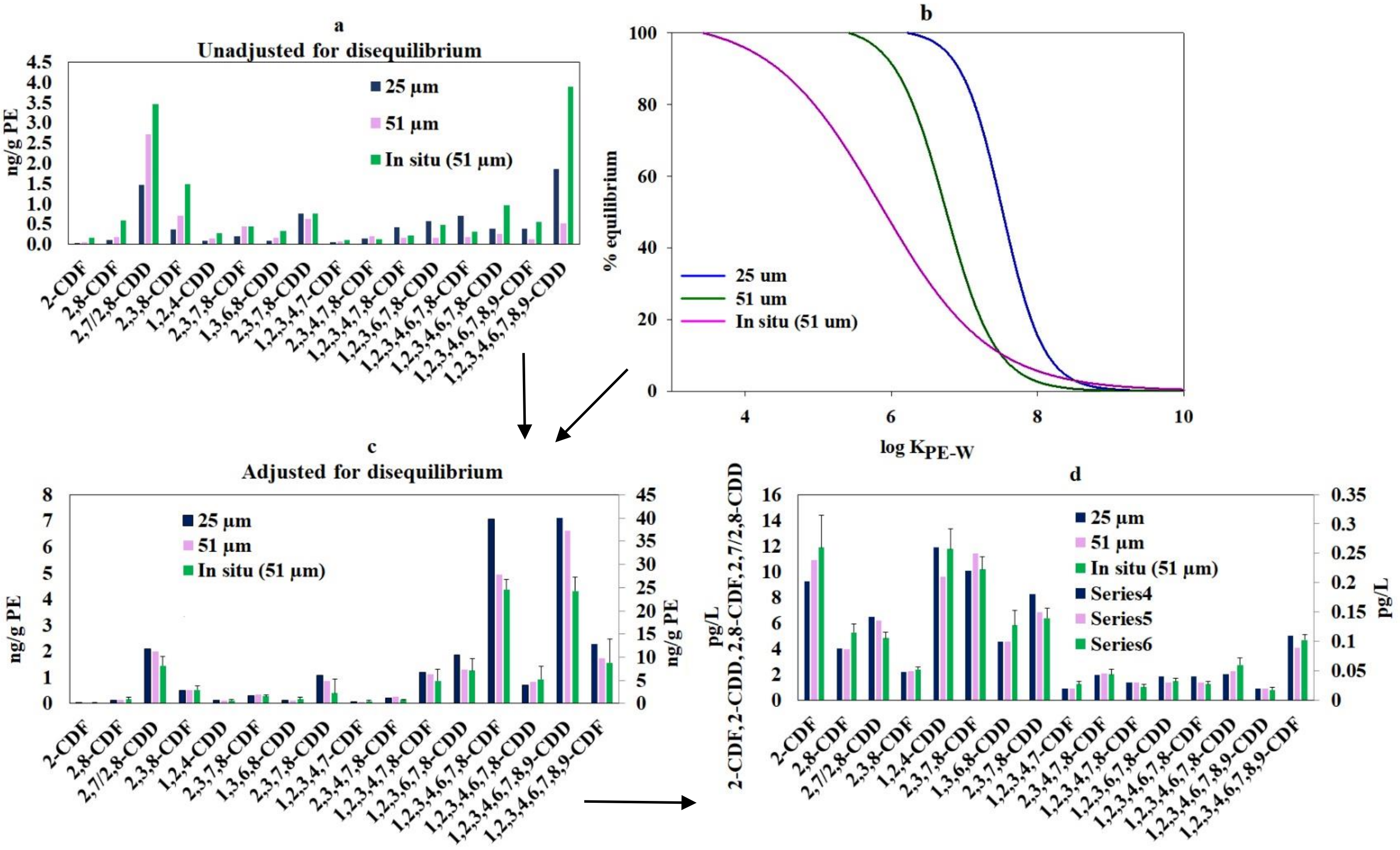


Figure 2: Concentrations of PCDD/Fs (ng/g PE) in the LDPE of the proposed *in situ* porewater sampler before (a) and after (c) correction for disequilibrium using PRCs (b) and the estimated porewater concentrations (d) at S1 (Riverbank Park).

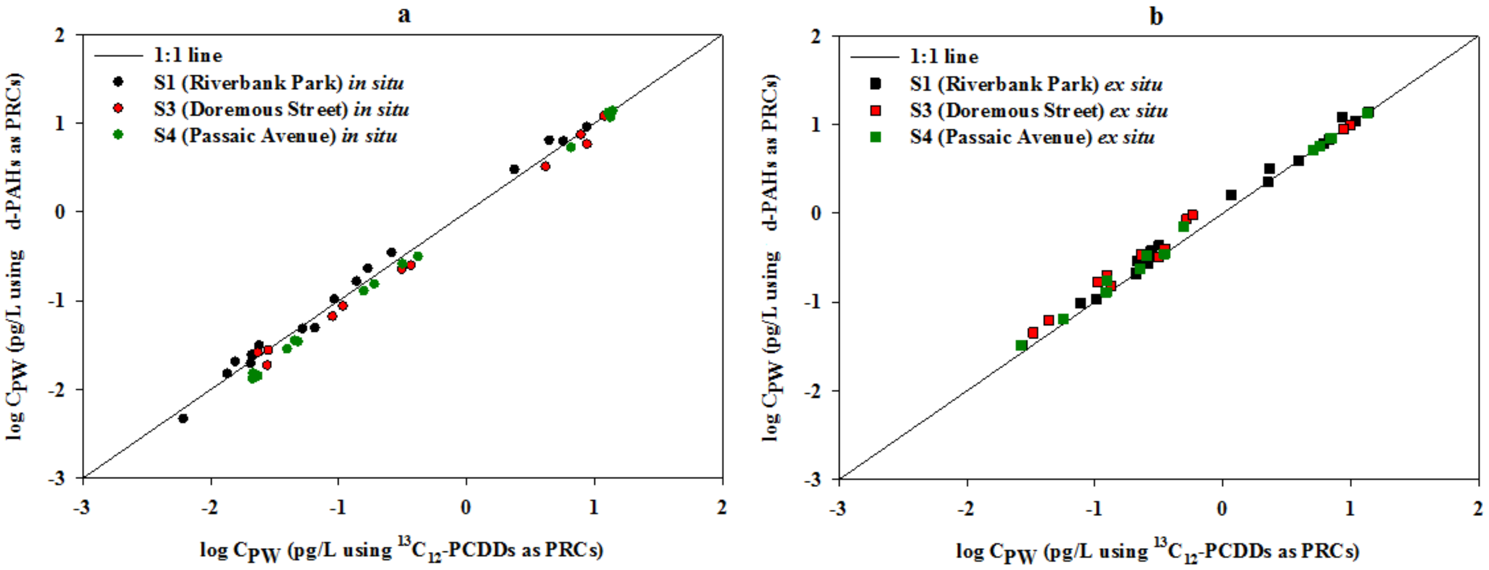


Figure 3: Comparison between using either d-PAHs or ^{13}C -PCDDs as PRCs for correcting porewater passive samplers for non-equilibrium using *in situ* (a) and *ex situ* (b) approaches at the sampling sites.

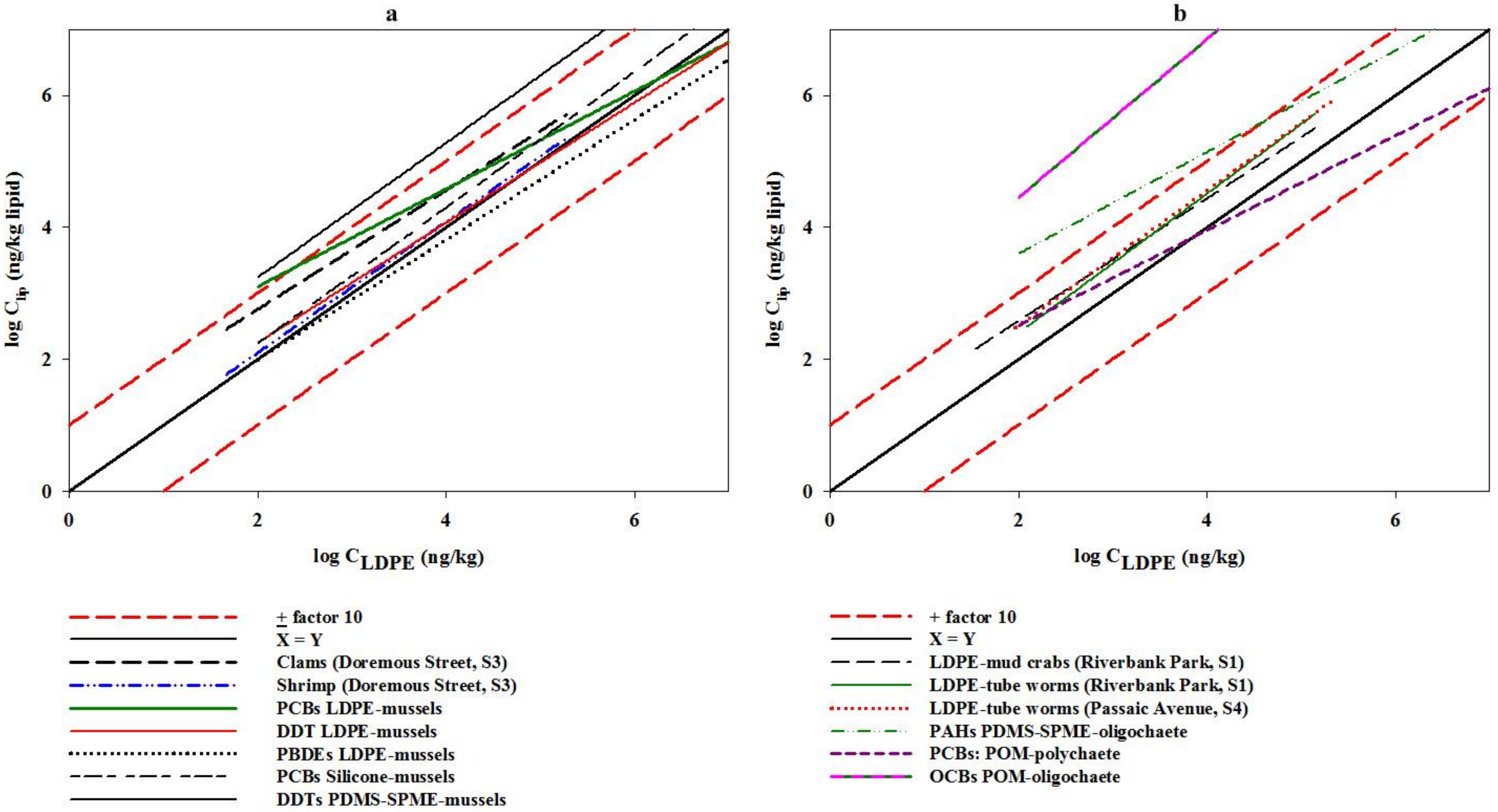


Figure 4. Log-log linear relationships between lipid-based tissue concentrations (C_{lip}) in clams and mussels (a) and in crabs, oligochaete and polychaetes (b) vs passive sampler's concentrations in the current and previous studies. The continuous black line represents a 1:1 correlation. The two dashed red lines represent plus or minus a factor of 10. PCBs LDPE-mussels relationship from Burgess et al.[38]; DDT-LDPE and PBDE-LDPE relationships from Joyce et al.[40]; PCBs silicone-mussels relationship from Smedes[45]; DDTs PDMS-SPME relationship from Pirogovsky[42]; PCBs POM-polychaete relationship from Janssen et al.[46]; PCBs POM-oligochaete relationship from Beckingham and Ghosh[19]. Regression parameters are given in Table S18.

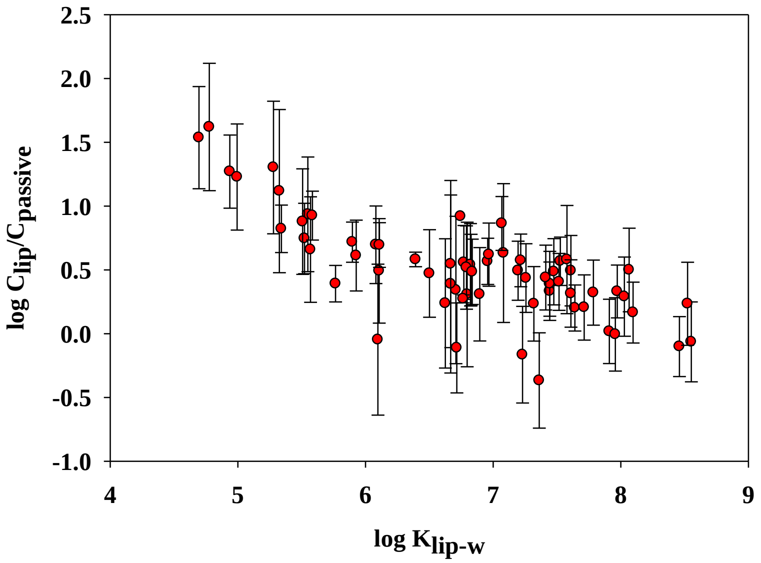
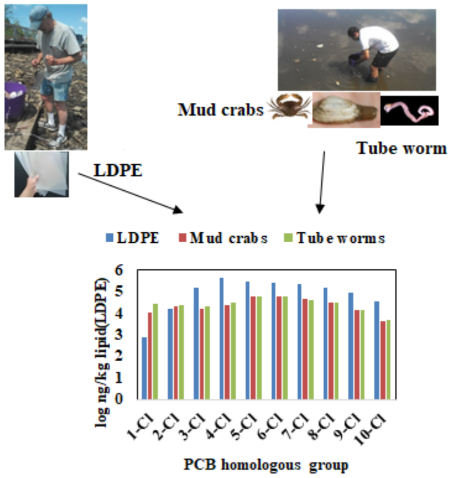


Figure 5: Ratio of lipid normalized concentrations to LDPE-based concentrations plotted against lipid-water partitioning coefficient ($K_{lip\text{-}w}$). Circles represent average values of all the investigated species and the error bars represent the standard deviation.


Mud crabs
Tube worm
LDPE
LDPE
Mud crabs
Tube worms
log ng/kg lipid(LDPE)
6
5
4
3
2
1
0
1-Cl
2-Cl
3-Cl
4-Cl
5-Cl
6-Cl
7-Cl
8-Cl
9-Cl
10-Cl
PCB homologous group

TOC art