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CHARACTERIZATION OF A NEW SEDIMENT POREWATER PASSIVE SAMPLER FOR HYDROPHOBIC ORGANIC CONTAMINANTS

Samuel D. Katz
University of Rhode Island, sdkatz@uri.edu

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CHARACTERIZATION OF A NEW SEDIMENT POREWATER PASSIVE SAMPLER FOR HYDROPHOBIC ORGANIC CONTAMINANTS

BY

SAMUEL D. KATZ

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MASTER OF SCIENCE THESIS

OF

SAMUEL KATZ

APPROVED:

Thesis Committee:

Major Professor Rainer Lohmann

Arthur Spivack

Thomas Boving

Brenton DeBoef
DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND
2021

ABSTRACT

Passive samplers have been proven as a useful tool for sampling the bioavailable fraction of hydrophobic organic contaminants (HOCs) in sediment. Polyethylene (PE) sheets used as passive samplers enable the quantification of a wide range of the bioavailable HOCs *in situ* and *ex situ*. The sediment of Newark Bay and Passaic River historically is a source of legacy HOCs such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) as well as emerging contaminates such as organophosphate esters (OPEs). Here we examine the distribution of PCBs, PCDD/Fs, and OPEs in Newark Bay utilizing a new form of passive sampling device based on a Danforth anchor that is not reliant on the use of divers for deployment. In the first sampling campaign in the Passaic River we compared our new anchor sampler to a previously used circular sampler. Minimal differences between the two samplers were found, confirming that the new sampler performed similarly to prior tools. The second campaign focused on Newark Bay, utilizing the anchor samplers for 10 bay sites and the circle samplers for 2 river sites. PCBs in the water column and sediment porewater of Newark Bay were evenly distributed with PCB 18 and 28 the dominant congeners at most sites. At all sites, porewater concentrations inferred from *ex situ* equilibrations exceeded those from the *in situ* passive samplers by 2–3 fold. The difference between the two sampling methods could be due to temperature differences or bioturbation. The concentration gradient between the water column and the sediment porewater implied that the sediment took up PCBs from the water column. OPEs were primarily detected in the lower part of Newark Bay suggesting that the Passaic and Hackensack Rivers were not sources of OPEs. Overall, we demonstrated the ability of

our new sampling device to characterize legacy and emerging HOCs in sediment porewater and the water column and that this type of sampler could be effectively used at other contaminated sites.

ACKNOWLEDGMENTS

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Firstly, I like to thank Rainer Lohmann for his help and support throughout this whole project. From the initial troubles of trying to find a captain for sampling in Newark Bay to my struggles as a coffee shop writer writing during a pandemic, Rainer has helped keep me motivated through it all. Along with him, I like to thank the rest of the Lohmann lab for being an amazing team. You've been great for bouncing ideas off of and always willing to give a helping hand throughout the last 2.5 years. A special thanks to Simon Vojta for accompanying me on my sampling trips to the Passaic and for all the help with the quantification of my samples.

I'd also like to thank my other committee members Arthur Spivack and Thomas Boving. While it might not have seemed like much, your support over the last few months was felt. I also need to thank Marc Reiss (EPA) and Jim Lodge (Hudson River Foundation) for coming to our rescue during our first sampling campaign and providing a boat and diver for our deployments in Newark Bay.

I'd also like to thank Loes van Dam and the Kincaid lab for the use of their drill press and bandsaw. I don't think I would have had 20 samplers built in time for the second sampling trip if it wasn't for you allowing me to use your tools. Along these lines I have to thank my dad for helping me with constructing the initial sampler and teaching me basic anchoring techniques. And of course all my friends, family and the GSO community who have provided support to me either through listening to me complain

about last minute sampling trip cancelations or providing welcome distractions to break up long hours in the lab.

PREFACE

This manuscript was written following the manuscript formatting by the University of Rhode Island's Graduate School prescribed for submission to *Environmental Science and Technology* and in accordance with the margin and font requirements of University of Rhode Island's Graduate School guidelines.

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Characterization of a New Sediment Porewater Passive Sampler for Hydrophobic Organic Contaminants

This manuscript has been prepared for submission to Environmental Science & Technology

Samuel Katz, Rainer Lohmann

Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island, U.S.A.

INTRODUCTION

Over the past three decades remediation attempts of the Passaic River and Newark Bay have been aimed at the high concentrations of hydrophobic organic contaminants (HOCs), specifically polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) (Ehrlich et al., 1994; Friedman et al., 2012; Wenning et al., 1992). The former Diamond Alkali Chemical Company was located in Newark, New Jersey, on the banks of the Passaic River. The Diamond Alkali plant produced pesticides and herbicides, most notably Agent Orange, during the 1950s and 1960s and discharged chlorinated byproducts (including 2,3,7,8 TCDD) directly into the Passaic River, leading to the US EPA designating the Passaic River as a Superfund site in 1984 (Bopp et al., 1998; Rappe et al., 1991). In 2012 a pilot-scale cleanup of the most contaminated parts of the Passaic River was completed, removing 40,000 yd^3 of sediment directly adjacent to the site, with some success in reducing the total load of PCDD/Fs and PCBs in the sediment (EPA, 2017). Yet, high concentrations of PCDD/Fs and PCBs can still be found throughout the Passaic River as sediment beds get uncovered and buried through tidal wave action and sedimentation (Figure 1) (Lambert et al., 2011). HOCs present in the top 6 inches of sediment can leach or be flushed through bioturbation or groundwater flow into the water column (Apell et al., 2018; Khairy et al., 2016).

Passive samplers have become a useful tool for characterizing the freely dissolved fraction of contaminants in the water column and sediment porewater. Passive sampling relies on diffusion from water or air to the sampler. There are two types of passive samplers, one samples in the kinetic uptake regime and the second at equilibrium (Mayer et al., 2003). Passive samplers accumulate the freely dissolved fraction of contaminates in

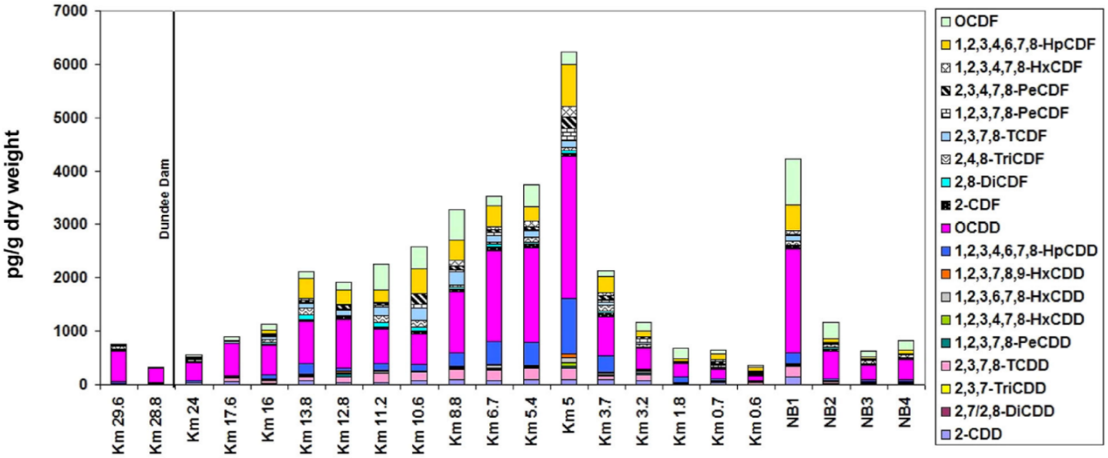

Figure 1: A graph of concentration of PCDD/Fs found in the sediment of the Passaic River and Newark Bay. The Diamond Alkali plant was across the river from river Km 5 (Khairy et al., 2016).

the air, water, or sediment porewater, which represents the mobile fraction of HOCs in sediment (Figure 2) (Di Toro et al., 1991). The equilibrium regime is better understood and equilibrium samplers are typically used when sampling HOCs as concentrations are usually low in the water column and sediment porewater (Gschwend et al., 2011; Mayer et al., 2014). One example of an equilibrium passive sampler material is low density polyethylene (PE), which has been used for air, water, and sediment (Friedman et al., 2012; Lambert et al., 2011). The sampling rate of passive samplers is calculated based on a model of the desorption of performance reference compounds (PRCs) preloaded into the sampler. PRCs are chosen to be physiochemically similar to the range of target compounds in order to mimic the movement of contaminants between the passive sampler and sampling medium (Apell & Gschwend, 2014; Jones et al., 2006).

The calculation of environmental concentrations from passive samplers requires the partitioning constants that define the concentration ratio between two phases at equilibrium. For PE sheets this is defined as

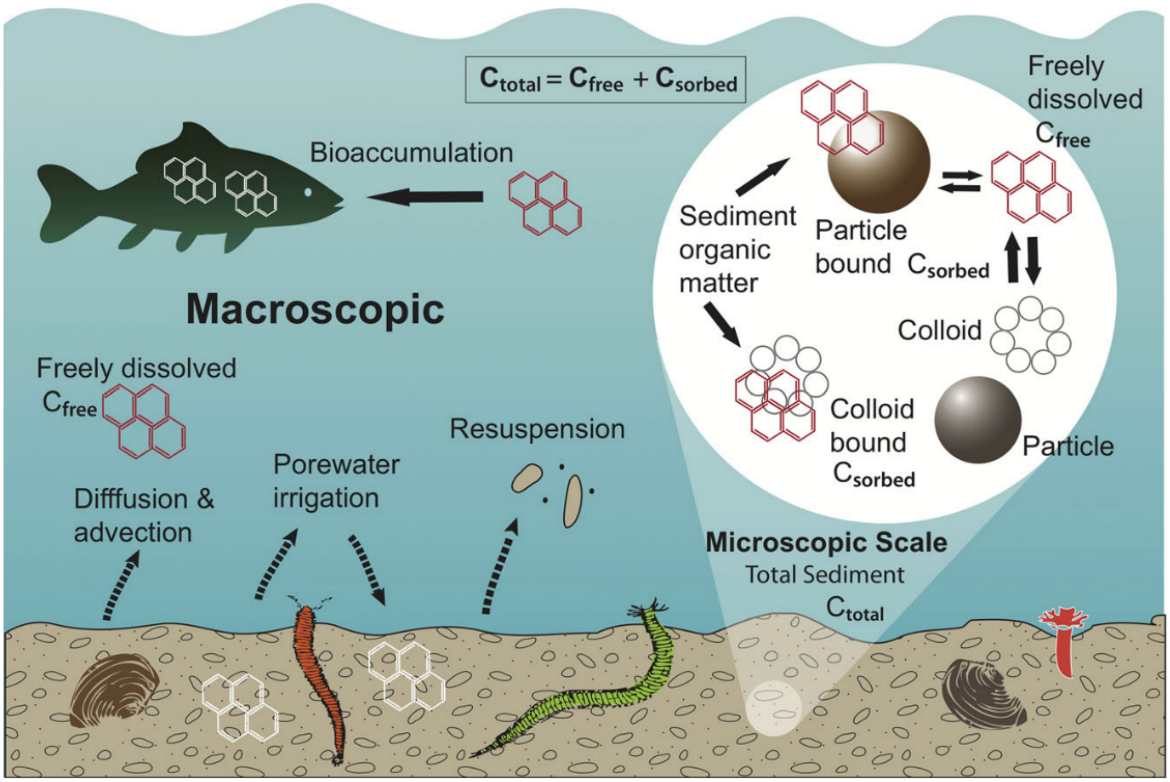

Figure 2: This diagram shows the movement of freely dissolved HOCs between the sediment bed and the overlaying water column (Mayer et al. 2014).

$$K_{PEw} = \frac{C_{PE}}{C_w} \tag{1}$$

where C_{PE} (mol kg^{-1}) is the concentration in the PE and C_w (mol L^{-1}) is the concentration in the water. The same convention is used for HOC partitioning between organic carbon and water (K_{oc}) or octanol and water (K_{ow}) (Schwarzenbach et al., 2016). The partitioning constants of PCBs and PCDD/Fs sorbed to a octanol or organic carbon are proportional to their molecular weight (Schwarzenbach et al., 2016). For example, K_{OC} values increase for PCBs and PCDD/Fs with increasing chlorination (SI Table 1 & 2). This decreases the mobility of these compounds in the environment as they are strongly sorbed to organic and black carbon in the sediment (Lambert et al., 2011).

The Passaic River and Newark Bay are home to many industrial production plants which inevitably release HOCs into the environment and organophosphate esters (OPEs) are of growing concern (Kim & Kannan, 2018). The production of OPEs has increased as a replacement for many brominated flame retardants (BFRs) since their addition to the Stockholm Convention's list of POPs (Salamova et al., 2014). OPEs are used as flame retardants in plastics, furniture, and textiles and are modeled to have similar characteristics to many persistent organic pollutant such as PCBs (Liagkouridis et al., 2015; Reemtsma et al., 2008). Production of OPEs increased by 10% in Europe between 2001 and 2006 and in 2013 of global flame retardants used, OPEs accounted for about 30% (620 kt) (Salamova et al., 2014; Sühring et al., 2016). Away from industrial production sites, and similar to the sources of PCBs, OPEs are mostly released as a non-point source pollutant from industrial products and can be concentrated in wastewater effluent (Ma et al., 2017; Meyer & Bester, 2004). The fate of these compounds in the environment is still being assessed, but they have been found in Arctic air and water and their physicochemical properties suggest they will accumulate in the sediment (McDonough et al., 2018; Stenzel et al., 2013).

In summary, there is a need for monitoring historical contaminants, such as PCBs or PCDD/Fs and determining the fate of emerging compounds, such as OPEs, in the environment. With high sampling rates, ease of use and low cost, passive samplers are a useful tool to use for determining water column and sediment porewater concentrations of these compounds. PCDD/Fs and PCBs in Newark Bay are known to originate from the Passaic River, while the presence and distribution of OPEs is currently unknown. Here we examine the sediment porewater and water column concentrations of OPEs to determine if their distribution is similar to legacy compounds from the Passaic River or if they are introduced from the southern part of Newark Bay, potentially from wastewater treatment plants. Newark Bay is an ideal site for *in situ* examination of OPEs with passive samplers as previous sampling provides historical concentrations of PCBs and PCDD/fs providing context for the interpretation of the distribution of OPEs.

MATERIALS AND METHODS

Sampler Development

Previous studies have relied on divers for the deployment of passive samplers into sediment, increasing the cost and difficulty of deploying samplers. A new sediment passive sampling device was created as a part of this study, designed and modeled on a Danforth anchor to be set from a boat without the use of divers (Figure 3). The PE sheets are placed between an aluminum screen and an external frame bolted together forming the fluke of the anchor. The flukes were designed to slide into the crown of a Fortress Guardian anchor and were attached to the stock with a zip tie at the point away from the crown. The PE sheets were loaded into the frame in the lab and wrapped in combusted aluminum foil 1-2 days before deployment and anchor samplers were assembled on site.

PRC Loading

Preparation of PE sheets followed the method of Booij et al. 2002. 50.8 µm thick PE sheets were cut into 45 cm x 15 cm rectangles; for the anchor samplers these

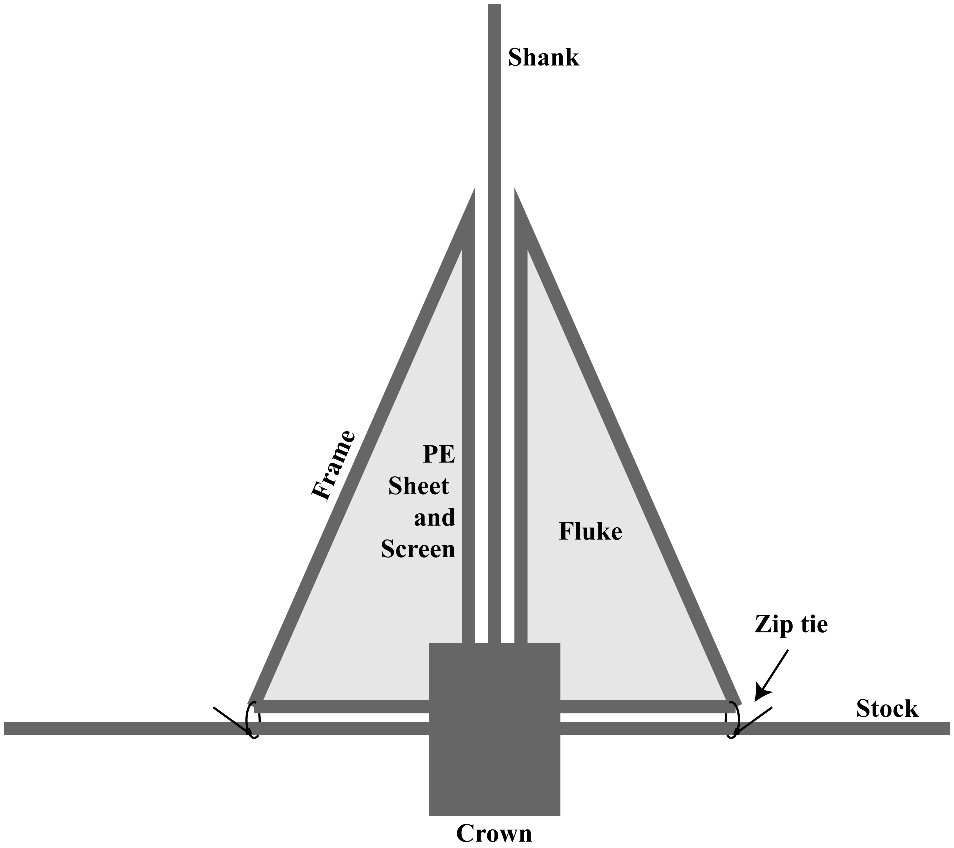

Figure 3: A diagram of our new anchor sampler based on a danforth anchor. The PE sheets pressed between an outer aluminum frame forming the flukes of the anchor.

rectangles were cut diagonally into triangles. Sheets were cleaned overnight in hexane and dichloromethane, before being added to performance reference compound (PRC) loading solution of methanol/water 8:2. The PRC loading solution consisted of 40 µg PAHs (Acenaphthene-d10, Chrysene-d12, Perylene-d12, and Phenanthrene-d10), PCBs (^{12}C PCB 2, PCB 14, PCB 30, PCB 50, PCB 104, PCB 145 and ^{13}C PCB 8, PCB 28, PCB 52, PCB 81, PCB 118, PCB 138, PCB 180, PCB 209), and 45 µg of PCDD/Fs (^{13}C 1,3,6,8-TCDD, 1,2,3,8,9-PeCDD, and 1,2,3,4,6,8-HxCDD) were added to the loading solution. PAHs were used as PRCs for the OPEs, consistent with McDonough et al.,

2018. Sheets were allowed to equilibrate for 30 days before being dried and stored in combusted aluminum foil bags in a ziplock bag until use.

Sampling

We conducted two sampling campaigns in the Passaic River and Newark Bay, NJ (Figure 4). The first campaign, designed to validate the new sampler design, was centered around the Passaic river during the summer of 2019. The second campaign focused on the spatial distribution of contaminants in the sediment porewater and water column of

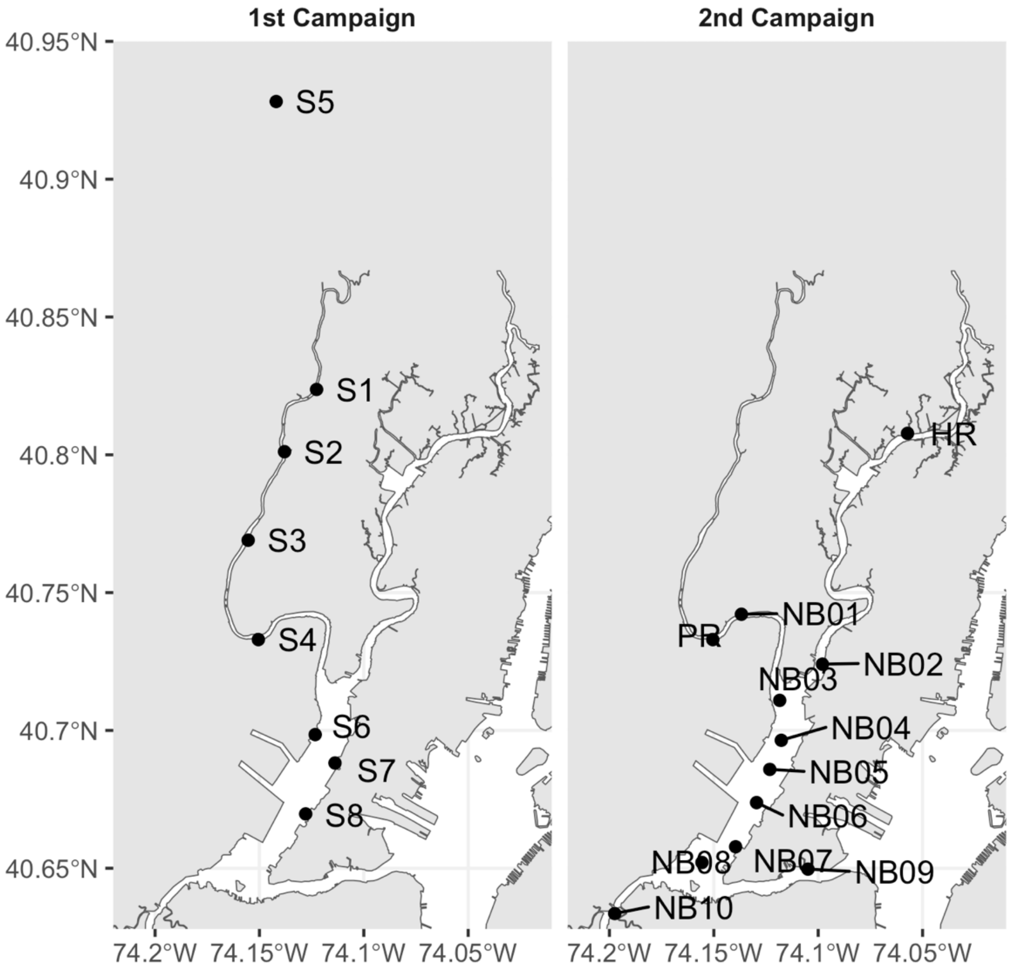

Figure 4: Map of sampling sites for the 2 sampling campaigns.

Newark Bay, during the winter of 2020. Sediment was collected at each site for *ex situ* equilibrium sampling.

During our sampler validation campaign in the Passaic River during the summer of 2019, our new anchor sampler was deployed in the shallow riverbank sites along with previously used PE sediment samplers for 1 month (Khairy et al., 2016). A surface buoy and messenger line to the shore were used as retrieval methods for both samplers. Three samplers were set in Newark Bay to ensure the samplers performed when set from a boat. A diver deployed the other samplers and verified that the anchor samplers had set properly.

Our second campaign, focused on the distribution of contaminants in Newark Bay, was conducted from the beginning of January through February of 2020. Samplers were placed in duplicate at each of the 12 sites, our new anchor samplers used for sites in Newark Bay and the traditional circle samplers used in both the Passaic and the Hackensack Rivers. Water column PE sheet samplers were attached to the surface buoy line with a zip tie. Upon recovery PE sheets were stored in combusted aluminum foil bags inside a ziplock bag and kept cool until returned to the lab where they were stored at -20˚ C. Upon recovery, for a few anchor samplers, the zip ties snapped, resulting in partial recovery of the flukes from some of the sites (Table 1).

Surface sediment was taken with a Van Veen grab sampler from each site and used for *ex situ* equilibration. Following the protocal by Jonker et al. (2020), 250 g ww of sediment and a 150 mg PE sheet were added to a glass jar with a 200 mg L^{-1} sodium azide solution leaving 2-3 cm head space. Jars were sealed and placed horizontally on a shaker table at 100 rpm for 12 weeks.

Table 1 Recoveries from the 2nd sampling campaign. 2 denotes that the sample was recovered completely intact, 1 is where only 1 of the two anchor flukes was recovered, and 0 is where the sampler was not recovered.

Sample	Sediment Sampler a	Sediment Sampler b	Water Sampler
PR	2	0	1
HR	2	2	1
NB01	0	0	0
NB02	2	2	1
NB03	2	2	0
NB04	1	0	1
NB05	1	2	1
NB06	2	1	1
NB07	2	0	1
NB08	1	2	1
NB09	2	2	1
NB10	2	2	1

Ex Situ **Sediment Depletion**

We performed an additional experiment to determine if there was a concentration difference resulting from the depletion of the porewater from the *ex situ* equilibration experiments by exceeding the PE:OC ratio recommended by Jonker et al. (2020). Hackensack River sediment and PE sheets were added to glass jars at varying percentages of PE mass to sediment mass (Table 2). The jars were filled with a 200 mg L^{-1} sodium azide solution, leaving 3-4 cm of head space and placed horizontally on a shaker table at 100 rpm for 8 weeks.

Chemical Analysis

PE sheets were wiped clean to remove biofouling before being placed in glass vials for extraction. 3 µg of PCDD/F (13C12 2378-TCDD, 12378-PeCDD, 123478-HxCDD, 123678-HxCDD, 123789-HxCDD, 1234678-HpCDD, OCDD, 2378-TCDF, 12378-PeCDF, 23478-PeCDF, 123478-HxCDF, 123678-HxCDF, 123789-HxCDF,

Table 2: Mass of organic carbon and PE sheets and Organic Carbon to PE sheet depletion used in our *ex situ* sediment depletion experiment.

Sample	Organic Carbon (g dw)	PE Sheet (g)	Percent PE sheet
250:1a	9.45	0.16194	1.71%
250:1b	9.41	0.14016	1.49%
250:2a	9.63	0.35475	3.69%
250:2b	9.43	0.37315	3.96%
250:3a	9.41	0.43728	4.65%
250:3b	9.45	0.57743	6.11%
250:4a	9.43	0.69568	7.37%
250:4b	9.40	0.60558	6.44%
250:5a	9.40	0.78097	8.31%
250:5b	9.47	0.83316	8.80%
500:1a	19.02	0.17955	0.94%
500:1b	19.05	0.19594	1.03%

234678-HxCDF, 1234678-HpCDF, 1234789-HpCDF, OCDF) and 10 µg of PCBs, PAHs, and OPEs (13C12 PCB 8, PCB 28, PCB 52, PCB 81, PCB 118, PCB 138, PCB 180, PCB 209, HCB, DDT, PBDE 28, PBDE 47, PBDE 99, PBDE 153, PBDE 183; deuterated Acenaphthene-d10, Chrysene-d12, Perylene-d12, Phenanthrene-d10; deuterated TriBR-d27, TPP-d15) surrogate standard were added to each sheet. Sheets were extracted overnight in Hexane and DCM before being concentrated to approximately 1 mL. Samples were cleaned with 4 g silica gel column, eluded with hexane/DCM (9:1) and DCM/acetone (7:3) and blown down to 50 µL.

An Agilent 6890N gas chromatograph coupled to a Waters Quattro Micro tandem quadrupole mass spectrometer optimized for the parent and daughter mass traces of the compounds was used for analysis. A DB-5ms column (60 m x 0.25 mm ID, 0.25µm film thickness) was used for PCB and PAH analysis, while a DB-Dioxin column (60 m x 0.25

mm ID, 0.25µm film thickness) was used for PCDD/F analysis. OPEs were analyzed on an Agilent GC-MS (7980 GC/5977 MSD) with a DB-5ms column (30 m x 0.25 mm ID, 0.25µm film thickness) in SIM mode. Limits of detection are defined as three times the standard deviation of the mean concentrations in the field blanks (SI Table 14 & 15). The average concentration per gram PE of the field blanks per PE sheet batch was subtracted from the mass of contaminant per gram PE.

Deriving Dissolved Concentrations

Environmental concentration from PE sheets were calculated based on the physicochemical properties of PCBs, PCDD/Fs, and OPEs (SI Table 1-3). The concentration of the sediment porewater was calculated from (Equation 2)

$$C_{pw} = \frac{C_{PE}}{f_{eq}\, K_{PEw}} \quad (2)$$

Where C_{PE} is the concentration in the PE sheet (pg/g PE),

K_{PEw} is the PE water partitioning coefficient (L kg^{-1}),

f_{eq} is the fractional equilibrium and,

C_{pw} is the porewater concentration (ng L^{-1}).

Fractional equilibrium is used to account for any compounds not yet at equilibrium with the sampler. For *in situ* sediment samples, the Passive Sampler PRC Calculation Software developed as part of the ESTCP Project ER-200915 was used to derive the fractional equilibrium of the PE sheets. For the *in situ* water samplers the fractional equilibrium was calculated based on Equation 3:

$$f_{eq} = 1 - e^{-\frac{Rs * t}{K_{PEw} * M}} \quad (3)$$

Where Rs is the sampling rate (L day^{-1}), t is the length of deployment (days),

M is the mass of PE sheet (g).

The sampling rate of the *in situ* PE sheet water samplers was calculated through minimizing the root mean square of the difference in f_{eq} of the predicted concentrations of the PRCs to the observed f_{eq}. The PE water partitioning coefficient was adjusted for temperature using the following equation,

$$K_{PEw}(T_2) = K_{PEw}(T_1) * e^{\frac{\Delta H_{sol}}{R} * \left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \tag{4}$$

Where T_1 is the temperature (K) at which K_{PEw} values were measured/derived (SI Table 1 & 2),

T_2 is the mean temperature of the deployment (K),

ΔH_{sol} is the entropy of solvation (kJ/mol) (SI Table 1 & 2),

R is the gas constant (kJ mol^{-1} K^{-1}).

K_{PEw} were derived at derived at 25˚C and the temperature adjustment were just used to correct for the *in situ* samplers where summer water temperatures were 20˚C and winter 5˚C.

No temperature or fractional equilibrium correction were performed for ex situ porewater determinations, as the set-up is designed to achieve equilibrium. Equilibrium is achieved though actively shaking the jars effectively removing the water boundary layer around the PE sheet ensuring that absorption is not slowed and prolong exposure at room temperature.

RESULTS AND DISCUSSIONS

Sampler Validation

Similar porewater concentrations between the previously used circle and our new anchor samplers were obtained for PCBs during the summer sampling campaign in 2019 (Figure 5). Visually there is little difference between both approaches, with most results clustering around the 1-1 line; yet a regression analysis of the porewater concentration

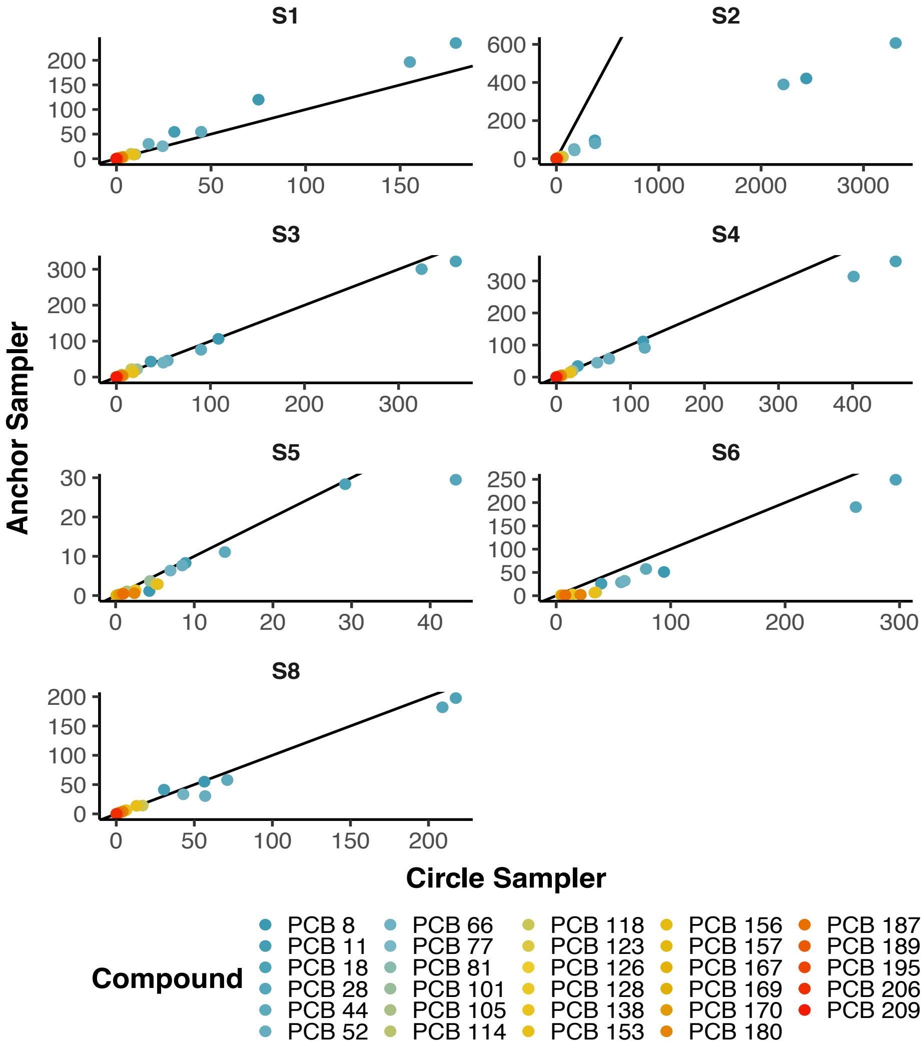

Figure 5: Comparison of previously used circle sampler vs new anchor sampler per PCB congerger for each site. Site 7 was not included as the circle sampler was not recovered.

between the results from the new samplers and the circle sampler found no significant correlation (SI Table 16). However, the lack of a correlation maybe caused by the limited number samples or the error associated with environmental passive sampling. Site S2 is the outlier in the concentration deviation between the two samplers with the concentration of the circle sampler, about 10 times higher than any other site or sampler.

Ex Situ **Polyethene to Organic Carbon**

The passive sampling protocol by Jonker et al. (2020) for *ex situ* passive sampling aims to prevent depletion of the contaminants in the sediment porewater. It is recommended that the amount of passive sampler be 5% or less of the organic carbon, ensuring that the partitioning between the passive sampler and the porewater does not significantly deplete porewater concentrations. To the best of our knowledge, no experiment has been carried out that verified the effects of varying passive sampler mass to organic content of the sediment. Our experiment with PE to OC ratios ranging from 0.94% – 8.80% found little to no statistical correlation between the ratio of PE mass to OC concentration and derived porewater concentration of PCBs (Figure 6 & SI Table 17). In general, no significant correlations between the slope of the linear regression between concentration and OC depletion and K_{OW} or molecular weight was found (SI Figure 1and 2). This implies that exceeding a 5% depletion ration (up to 9%) will only decrease dissolved concentrations by up to 5%. A passive sampler to OC content of greater than 5% might be needed for compounds present at trace levels, such as PCDD/Fs or certain other target analytes.

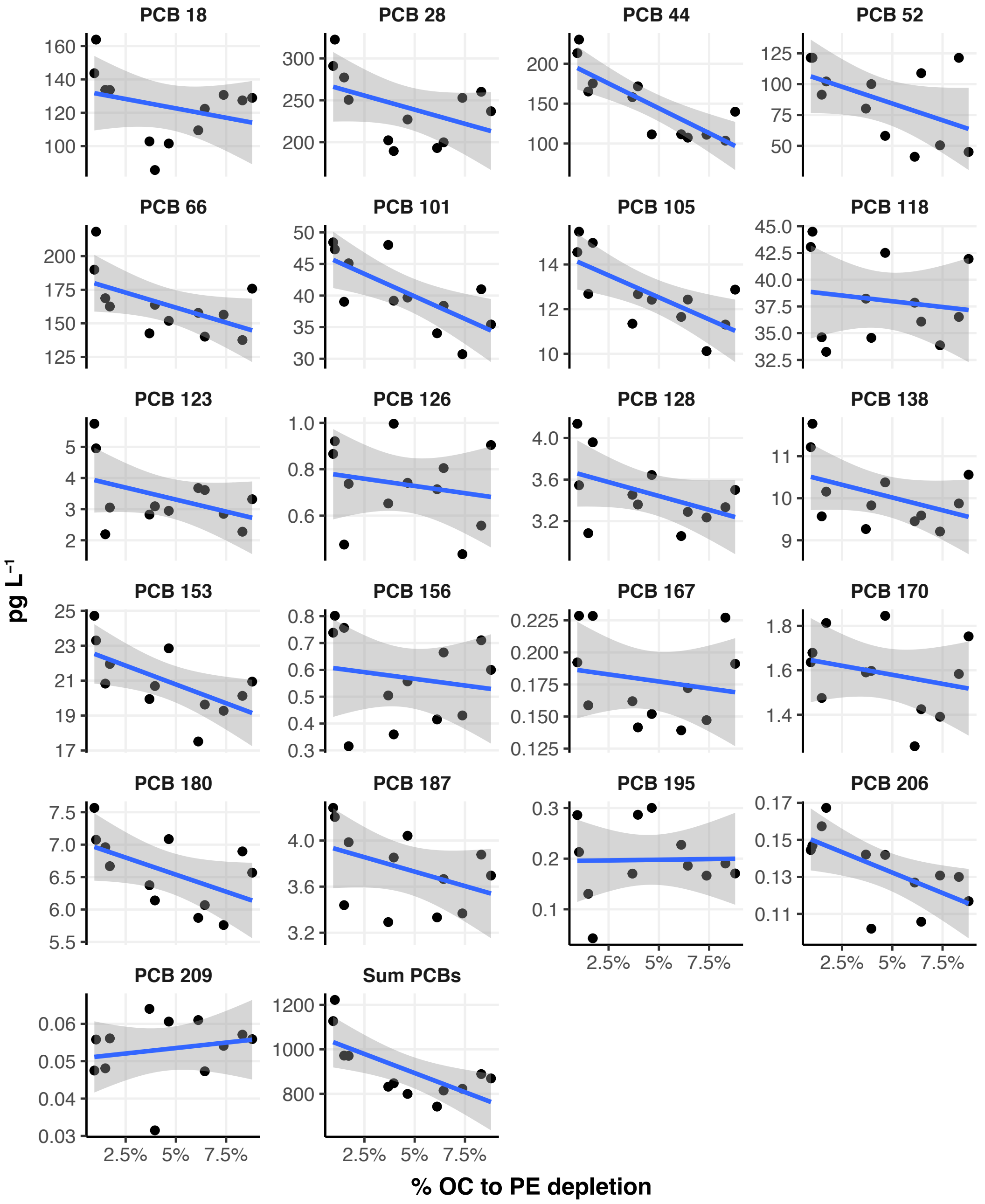

Figure 6: Measured concentration of PCBs with varying porewater depletion ratios. The line is the linear regression and the gray is the 95% confidence interval. PCBs 8, 77, 81, 114, 157, 169, 189 were removed as they were not detected.

Newark Bay Contaminants

PCBs – Porewater Overview

The sediment porewater concentration of PCBs in both the *in situ* and *ex situ* samplers were representative of a well mixed surface sediment in Newark Bay (Figure 7). The $\sum_{29}$ PCBs *in situ* concentrations across all sample sites ranged from 173 - 384 pg L^{-1} with a mean of 233 pg L^{-1}. The $\sum_{29}$ PCBs *ex situ* concentration across all sites ranged from 354 – 2559 pg L^{-1} with a mean 1258 pg L^{-1}. In both the *in situ* and *ex situ* samplers, site NB10 was an outlier with concentrations higher then nearby sites - 384 pg L^{-1} vs 181 pg L^{-1} (NB08). Site NB07 for the *ex situ* sampler results is also an outlier with

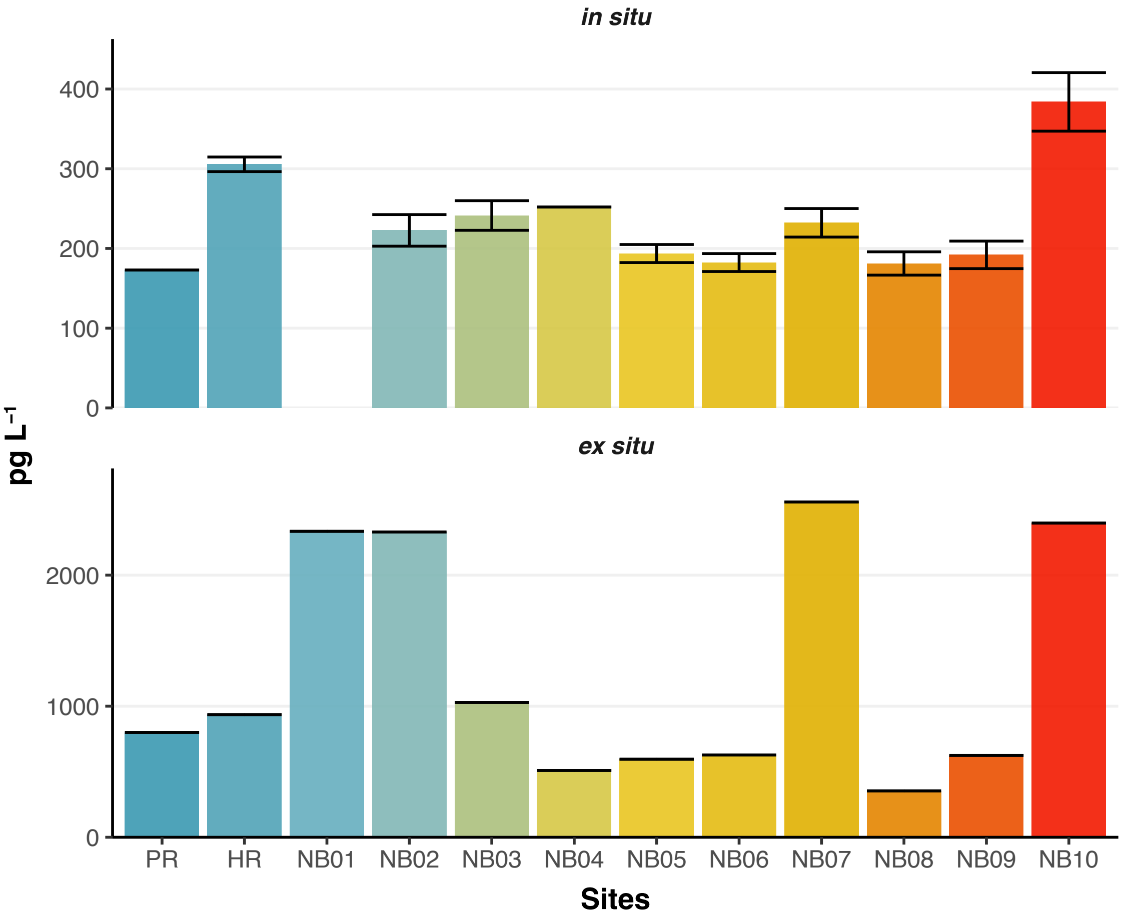

Figure 7: $\sum_{29}$ PCBs from in situ and ex situ samplers.

concentrations about 5 times higher than surrounding sites. This is not seen in the *in situ* samplers and could be an artifact of localized concentrations at the site as targeting a precise location is not attainable with the anchor samplers.

PCB Congener Porewater Profile

Newark Bay *in situ* sediment porewater PCB concentrations showed that the HOCs were similar across the Bay (Figure 8). PCB 18 and 28 were the dominant congeners present with mean concentrations of 50 ± 23 and 56 ± 22 pg L^{-1} respectively. These tri-chlorobiphenyl congeners dominated the porewater concentrations across all sites (Figure 8). Concentrations at site NB10 were slightly higher than at other bay sites, with 384 ± 35 pg L^{-1}, compared to the mean concentration of the bay (Sites NB03-08) with 214 ± 34 pg L^{-1}. This suggested that there could be a second source of PCBs impacting this site.

In situ sampling concentrations consistently showed the same PCB congener profile throughout Newark Bay. These concentrations were similar to the porewater concentrations from our 1st sampling campaign in the summer of 2019 (Figure 9). The two compounds with greatest concentrations at all the sites were PCBs 18 and 28, which were around 4 times higher in our first sampling campaigns. This trend of lighter PCBs being at a higher concentration during our first – summer – sampling campaign probably highlights the importance of temperature on the mobility of HOCs. The 15 ˚C temperature difference in the water column between our two sampling campaigns drives the partitioning towards the water phase during the warm summer months from our first campaign.

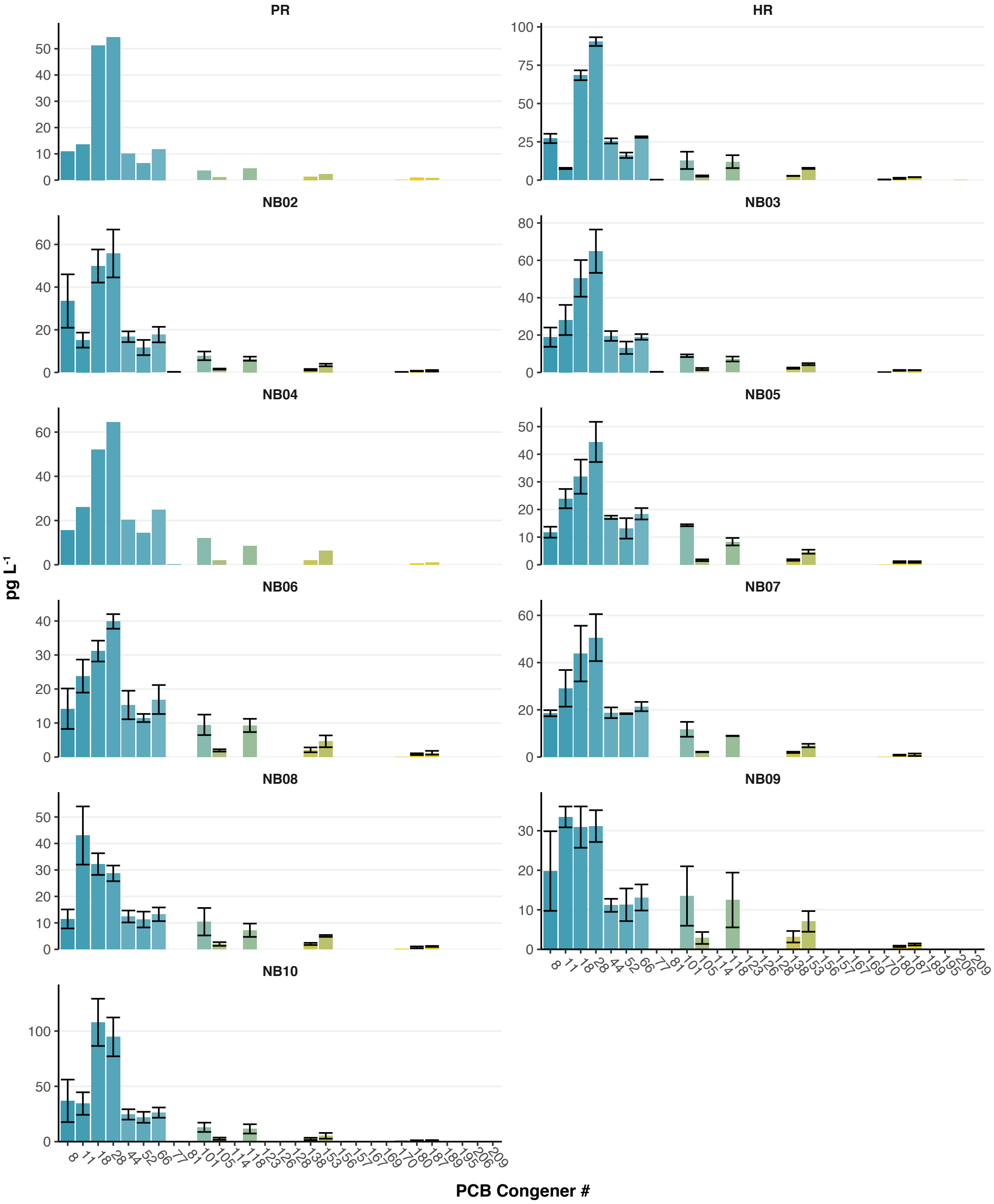

Figure 8: The *in situ* PCB concentration for each of the Newark Bay sites.

Ex situ samplers displayed the same profiles as the *in situ* samplers, but at higher

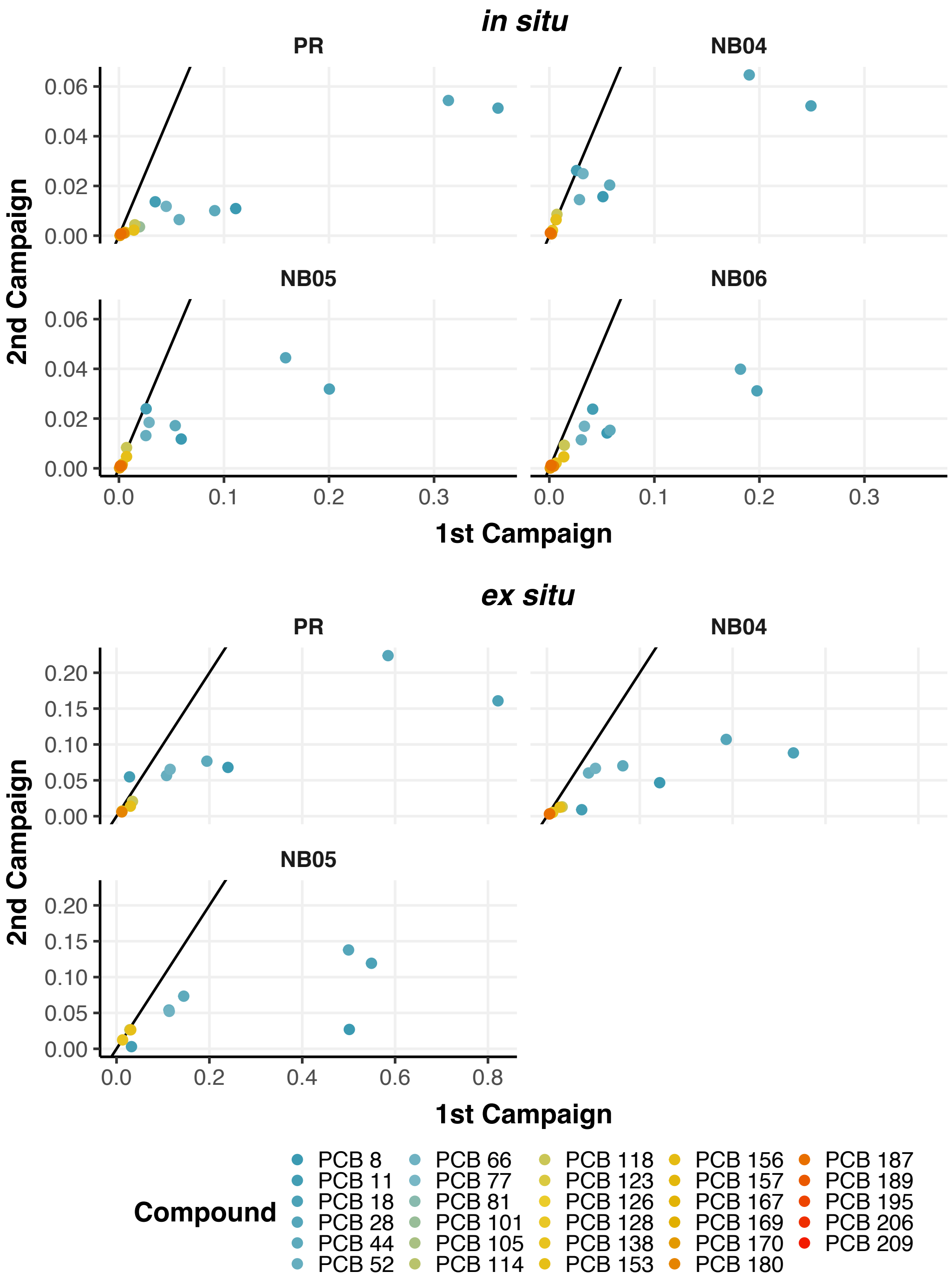

Figure 9: Concentration difference (ng L^{-1}) between our 1st and 2nd sampling campaigns at similar sites for both *in situ* and *ex situ* samplers. The Passaic River site (PR) was the same for both campaigns, S6 was close to NB04, S5 close to NB05, and S6 was close to NB06. The black line represents a 1:1 concentration. Site NB06 is missing from the *ex situ* comparison due to its jar breaking during the 1st campaign equilibration

concentrations (Figure 10). Again, we observe that PCB 18 and 28 were the dominant congeners at most sites with concentrations ranging from 28 – 790 pg L^{-1} and 107 – 664 pg L^{-1} across all sites. The highest concentration of PCBs were found at sites NB01 and

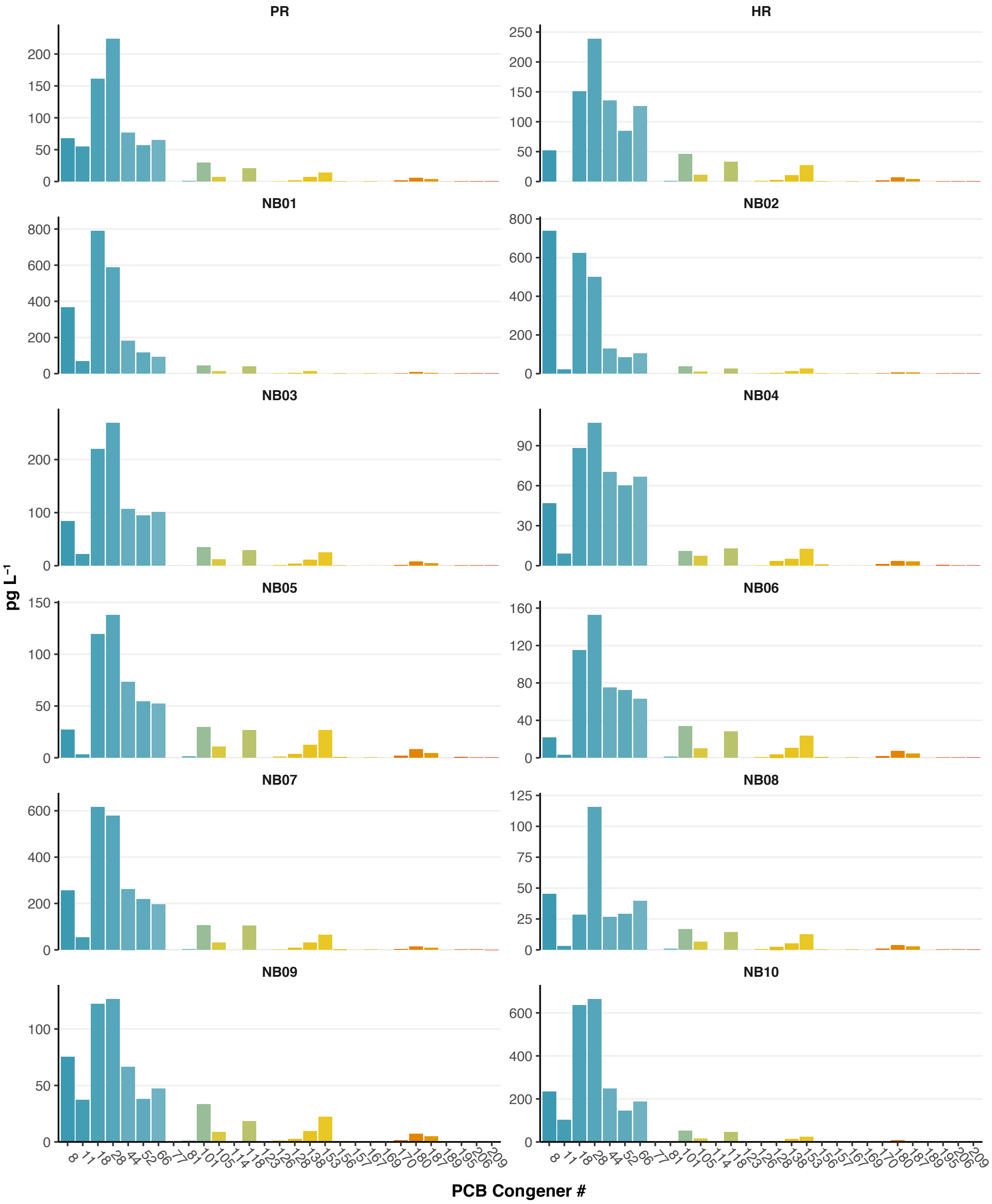

Figure 10: *Ex situ* PCB concentrations at each site.

02 with a total of 2335 pg L^{-1} and 2329 pg L^{-1} dominated by PCB 18 (784 pg L^{-1}) and PCB 2 (738 pg L^{-1}). Similar to the *in situ* samplers, site NB10 was an outlier with 2398 pg L^{-1} compared to most of Newark Bay (excluding NB07) ranging from 354 – 1029 pg L^{-1}, likely due to a second PCB source.

PCBs – Porewater in situ vs ex situ Comparison

Concentration differences between the *in situ* and *ex situ* samplers were seen consistently across all sites (Figure 11). These differences for the $\sum_{29}$ PCBs ranged from 2.0 – 11 times higher in the *ex situ* sampler. Differences were greatest at sites NB02 (the mouth of the Hackensack River) and NB07 (eastern side of the lower extent of Newark Bay), with 10 and 11 times higher. Examining individual PCBs at NB02 PCB 8, 18, and 28 differed by 706, 574, and 444 pg L^{-1}, while all but 3 compounds (PCB 11, 66, 101) were ≥10 times higher than the *in situ* concentration at site NB07. Apell et al. (2018) also observed such differences and suggested that bioirrigation can cause depleted *in situ* porewater (relative to ex situ equilibrations) that can alter porewater concentration and flux calculations by 2-173 times. The increase in site NB10 located in Arthur Kill suggested that there is a second source that could be influencing this concentration. For both the *in situ* and *ex situ* PCBs results, we observed a trend of decreasing *in situ* porewater concentration with increasing K_{ow}, indicating the control of solid-bound PCBs on the partitioning to the dissolved, porewater phase (Figure 12). No such trend was found from the differences between the *ex situ* and *in situ* results (SI Figure 3)

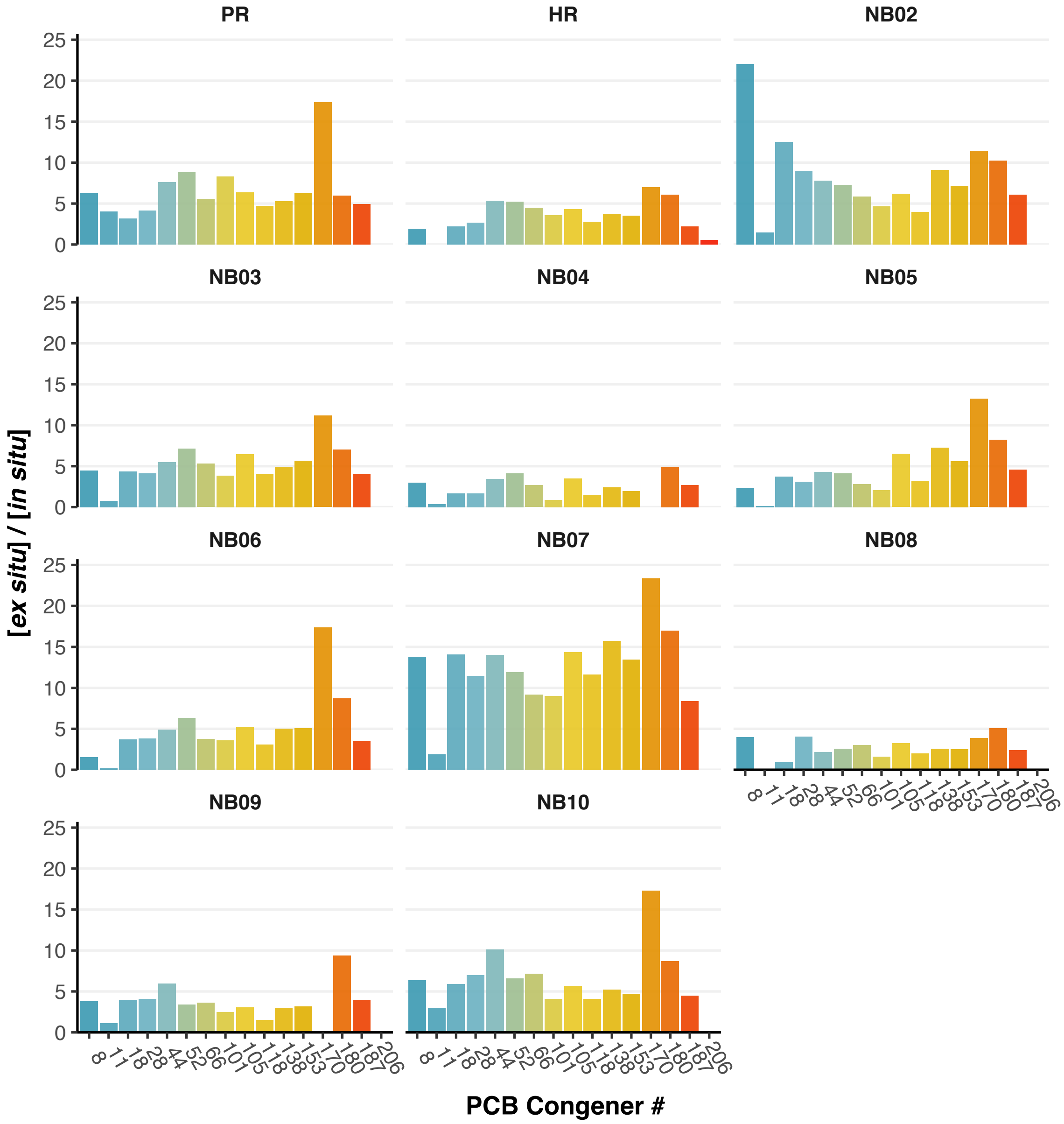

Figure 11: The concentration difference between *ex situ* and *in situ* sampler for PCB congener at each site. Site NB01 was removed as no in situ sample was recovered.

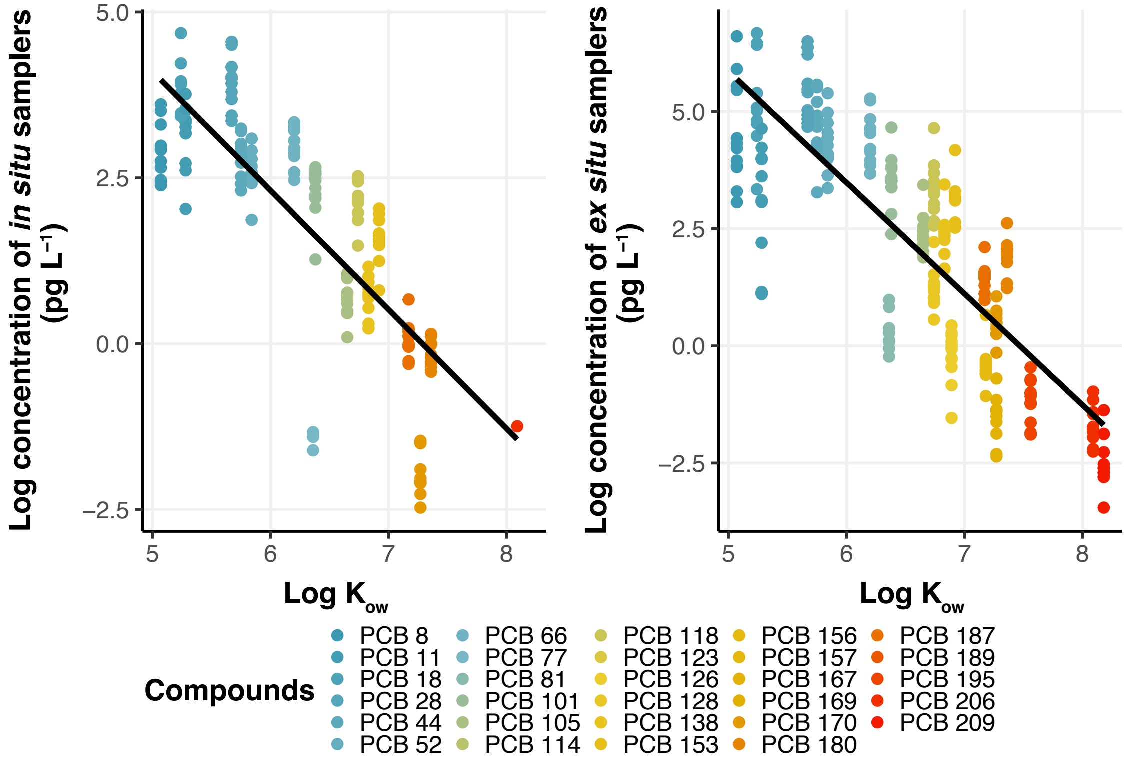

Figure 12: Log K_{OW} value showing the predicted negative trend compared to the log *in situ* (left) and *ex situ* (right) porewater concentrations.

PCBs – Porewater Spatial Trends

Dividing the bay into northern (NB03 and NB04), middle (NB05 and NB06), and southern (NB07 and NB08) parts as well as the inflow from the Passaic River (PR and NB01), Hackensack River (HR and NB02), and outflow (NB09 and NB10) again illustrates that only minor gradients in PCB porewater concentrations existed across Newark Bay (Figure 13). This is likely the result of intense mixing as could be expected for a tidal estuary, with plenty of (human) perturbations, which probably results in many cycles of resuspension and deposition of sediments, causing a well-mixed system (Figure 13). The *in situ* concentrations of tri-chlorinated PCBs (PCB 18 and 28) were about 1.5 times higher in the northern sections of Newark Bay (PCB 18 northern 50 ± 9 pg L^{-1}, middle 32 ± 6 pg L^{-1}, and southern 35 ± 8 pg L^{-1} and PCB 28 northern 65 ± 12 pg L^{-1}, middle 45 ± 7 pg L^{-1}, and southern 38 ± 10 pg L^{-1}). Differences between the concentrations in the Arthur kill and Kill van Kull (192 ± 3 pg L^{-1} and 384 ± 7 pg L^{-1} $\sum_{29}$ PCBs respectively) contribute to the large standard deviation at the outflow of Newark Bay.

PCBs- Water Column

The water column concentrations of PCBs were dominated by the mono – tetra chlorinated PCBs (Figure 14). Sampling rates of the water passive samplers ranged from 22- 265 L day $^{-1}$ (SI Table 5). The range of the $\sum_{29}$ PCBs in the water column was 120 –

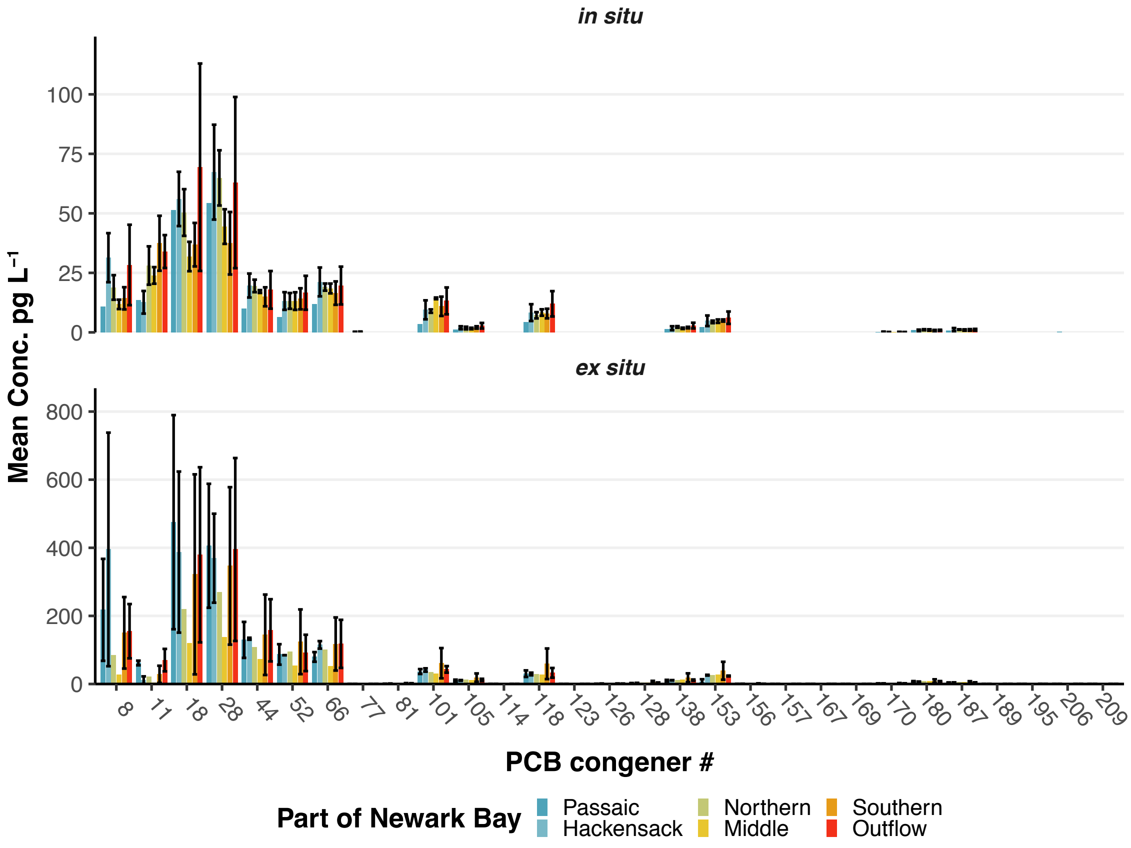

Figure 13: Concentrations divided into sections of the bay: Passaic (PR and NB01), Hackensack (HR and NB02), Northern (NB03&4), Middle (NB05&6), Southern (NB07&8), and Outflow (NB09&10).

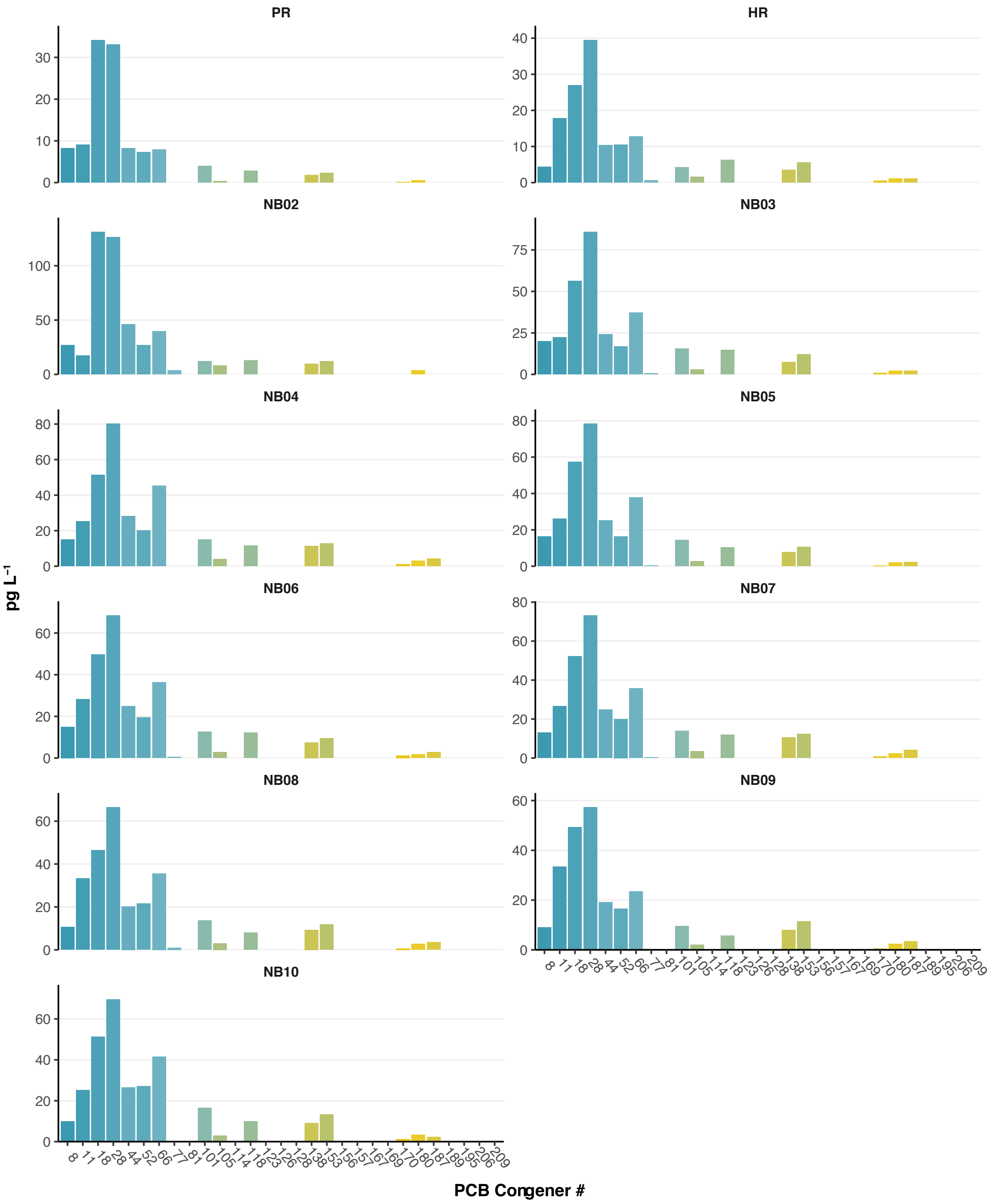

Figure 14: Water column concentration of PCBs in Newark Bay.

477 pg L^{-1}, with a mean concentration in Newark Bay (all sites expect PR and HR) of 321 pg L^{-1}. The Passaic and Hackensack River sites were about 3 times lower with a concentration of 120 pg L^{-1} and 147 pg L^{-1}. The sampling rate at the river sites were also

about 3 times higher than that the samplers from Newark Bay (SI Table 5). We suspect that this was caused by an increase of suspended partials at the river sites, depleting the PRCs. Site NB02 was the highest concentration (477 pg L^{-1}), with most of this sum comprised of PCB 18 and 28 (131 and 126 pg L^{-1}). Similar to porewater concentrations, PCB 18 and 28 were the dominant congeners in the water column, ranging from 27 – 131 pg L^{-1} and 33 – 126 pg L^{-1}.

The concentration gradient of PCBs between the water column and the sediment at each site showed the water column displaying greater PCB concentrations than the sediment porewater (Figure 15). The concentration gradient was derived by dividing the average porewater concentration by the water column concentration, resulting in values >1 representing porewater releases into the water column and values <1 representing the water column concentration being taken up by sediment. At most places in Newark Bay PCBs in the water column display greater concentrations than in porewater, indicating a potential for uptake of PCBs by sediment. The river sites are the exception with porewater concentrations of most PCBs detected 2-3 times higher than the water column. This is consistent with the River sediments harboring strongly contaminated sediment, which continues to impact Newark Bay.

PCDD/Fs

PCDD/Fs were not detected in either the water or porewater *in situ* samplers. Only 1,2,3,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, and OCDD were detected in the fg L^{-1} range in the *ex situ* samplers. This suggest that sedimentation has buried PCDD/Fs effectively, preventing them from being released to the water column. High K_{ow} values (strong sorption to sediment) relative to the K_{PEw} values of PCDD/Fs coupled with cold temperatures (~5 ˚C) during sampling may have limited our ability to detect PCDD/Fs (SI Table 2). Future sampling should aim to conduct sampling campaigns in the summer

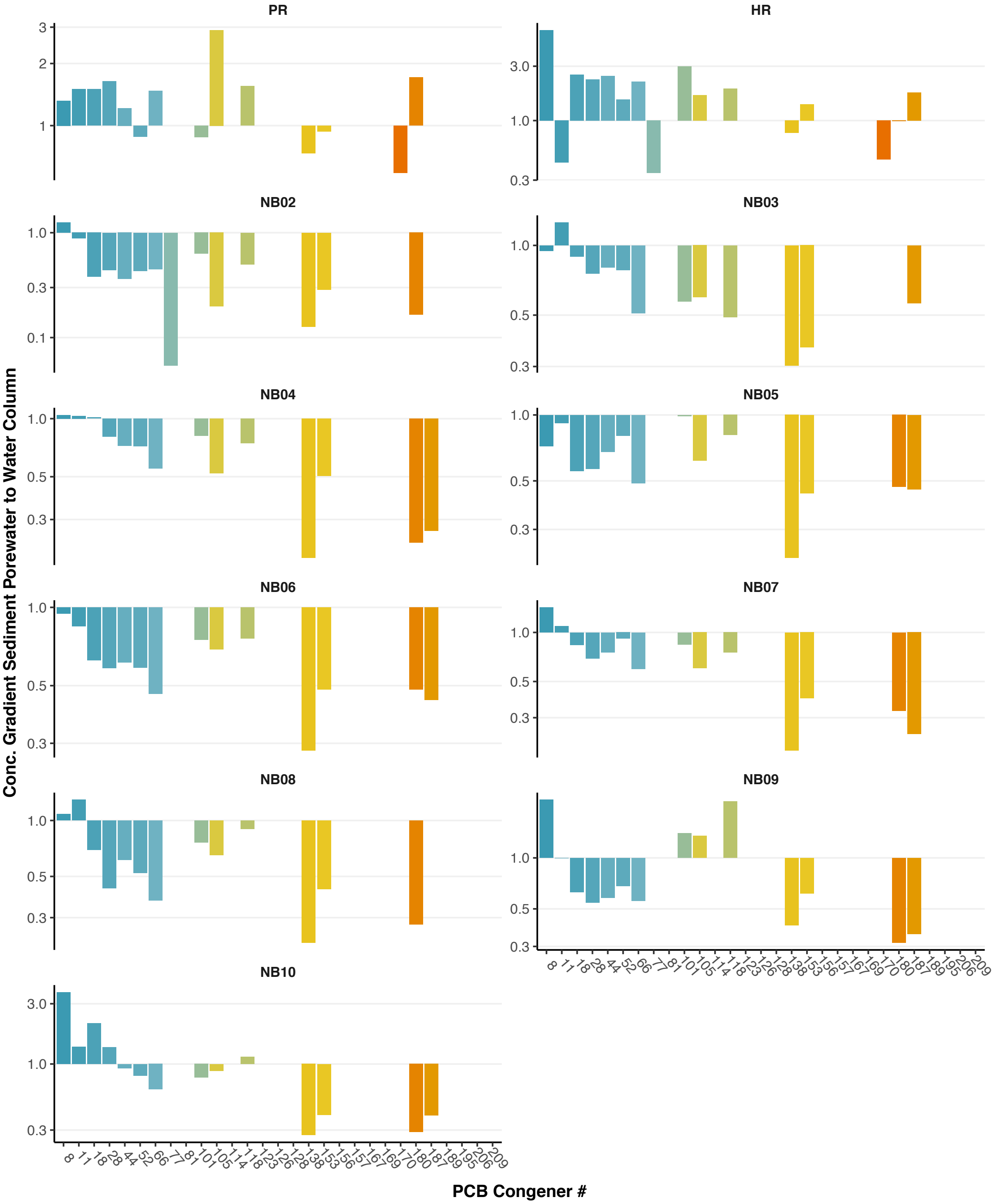

Figure 15: The concentration gradient between the *in situ* sediment sampler and water column sampler ([*in situ*] / [water column]).

when temperatures could increase the mobility of PCDD/Fs

OPEs

Of the ten OPEs screened, 6 were regularly detected in the pasive samplers (Figure 16). In the *in situ* samplers, TnBP was detected at the highest concentrations, 5.41 ± 1.51 ng L^{-1} at NB07, with a mean concentration in the mid, lower, outflows of Newark

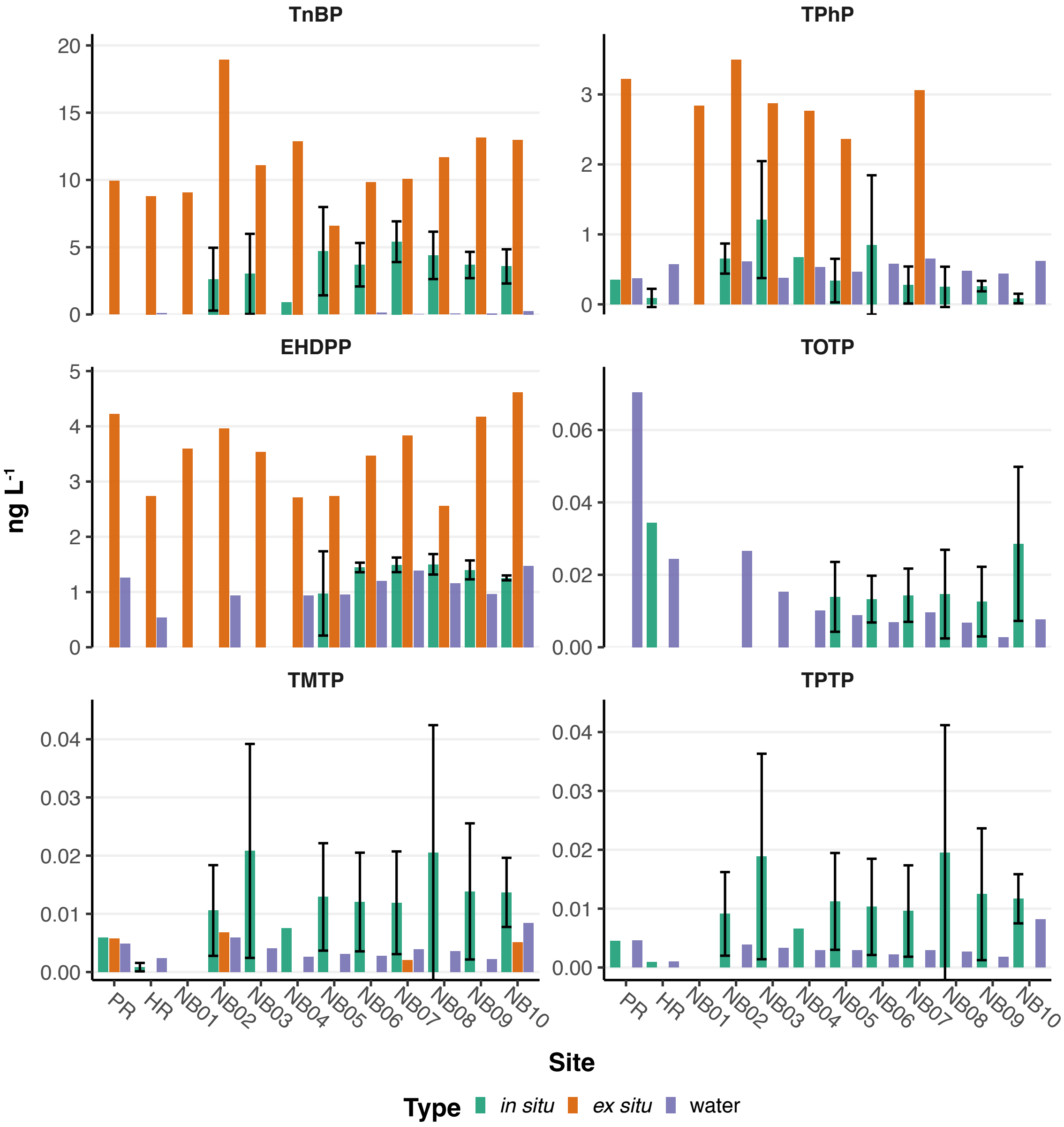

Figure 16: The *in situ*, *ex situ*, and water column OPEs concentrations in Newark Bay

Bay (NB05-10) of 4.24 ± 1.89 ng L^{-1}. TOTP, TMTP, and TPTP, isomers of tris(methylphenyl) phosphate were present in the range of 0.123 – 0.034, 0.001 – 0.021, and 0.001 – 0.020 ng L^{-1} respectively. The *in situ* observed distribution showed OPEs mostly present in the lower section of Newark Bay, with all detected OPEs present at southern sites NB05 – 10. This suggests the source of OPEs is not from the Passaic or Hackensack Rivers but from southern sources, potentially wastewater treatment plants or introduced through tidal transport from Arthur Kill or Kill van Kull.

Four of the 10 OPEs TnBP, TPhP, EHDPP, and TMTP were detected in the *ex situ* samplers. TnBP was the highest at site NB02 (the mouth of Hackensack River) at 18.9 ng L^{-1} and mean of 10.4 ng L^{-1} (range 6.57 – 12.9 ng L^{-1}) throughout Newark Bay (NB03 – 8). The second highest detected OPE was EHDPP at 6.51 ng L^{-1} at NB10 (Arthur Kill). The concentration in Newark Bay ranged from 2.56 – 3.83 ng L^{-1} with a mean of 3.14 ng L^{-1}. TPhP was detected in the Passaic River and at sites NB01 – 5 and NB07 with mean of 2.95 ng L^{-1} (range 2.37 – 3.50 ng L^{-1}). Of the three tris(methylphenyl) phosphate isomers only tris(3-methylphenyl) phosphate (TMTP) was detected at 0.006 ng L^{-1} at PR, 0.007 ng L^{-1} at NB02, 0.002 ng L^{-1} at NB07, and 0.005 ng L^{-1} at NB10.

The *ex situ* concentrations were consistently a few ng L^{-1} higher than the *in situ* samplers. This is a product of the small mass PE sheet used for the *ex situ* sampling coupled with the low K_{PEw} values of OPEs. To our knowledge this is the first time PE sheets have been used for OPE sampling in the sediment porewater.

Six of the 10 OPEs were detected in the water column of Newark Bay (Figure 16). Sampling rates of the water passive samplers ranged from 16 – 432 L day $^{-1}$ (SI

Table 5). EHDPP was detected at all sites except for NB03 at concentrations ranging from 0.537 – 1.47 ng L^{-1} with a mean concentration of 1.08 ± 0.27 ng L^{-1}. TPhP was detected at all sites with concentrations ranging from 0.370 – 0.656 ng L^{-1} with a mean concentration of 0.518 ± 0.09 ng L^{-1}. TnBP was only detected in the mid to southern parts of Newark Bay (NB06 – 10) and the Hackensack River at concentrations ranging from 0.033 – 0.249 ng L^{-1}. All three isomers TOTP, TMTP, and TPTP were detected at low concentrations ranging from 0.003 – 0.070, 0.002 – 0.008, and 0.001 – 0.008 ng L^{-1}.

The concentration gradient between the *in situ* sediment porewater and the water column was the inverse of the PCB gradient, with most compounds being released to the water column from the porewater (Figure 17). TnBP was the highest gradient from the porewater to the water column and found only in the southern part of the bay as water concentrations were not found at sites north of NB06. In contract to the other OPEs, TPhP was being up taken by the sediment mostly in the southern part of the bay (NB07 – 10) and released in the northern part (NB02 – 06). This suggest that there is a northern source of TPhP in Newark Bay and it is being transported to the southern sites. EHDPP is being released from the sediment porewater at sites NB05 – 09 and being taken up at site NB10 (Arthur kill). The three tris(methylphenyl) phosphate isomers gradient is are similar with them being released from the porewater to the water column. TOTP was only detected in the porewater at sites NB05 – 10 and the Hackensack river resulting in a gradient only at these sites.

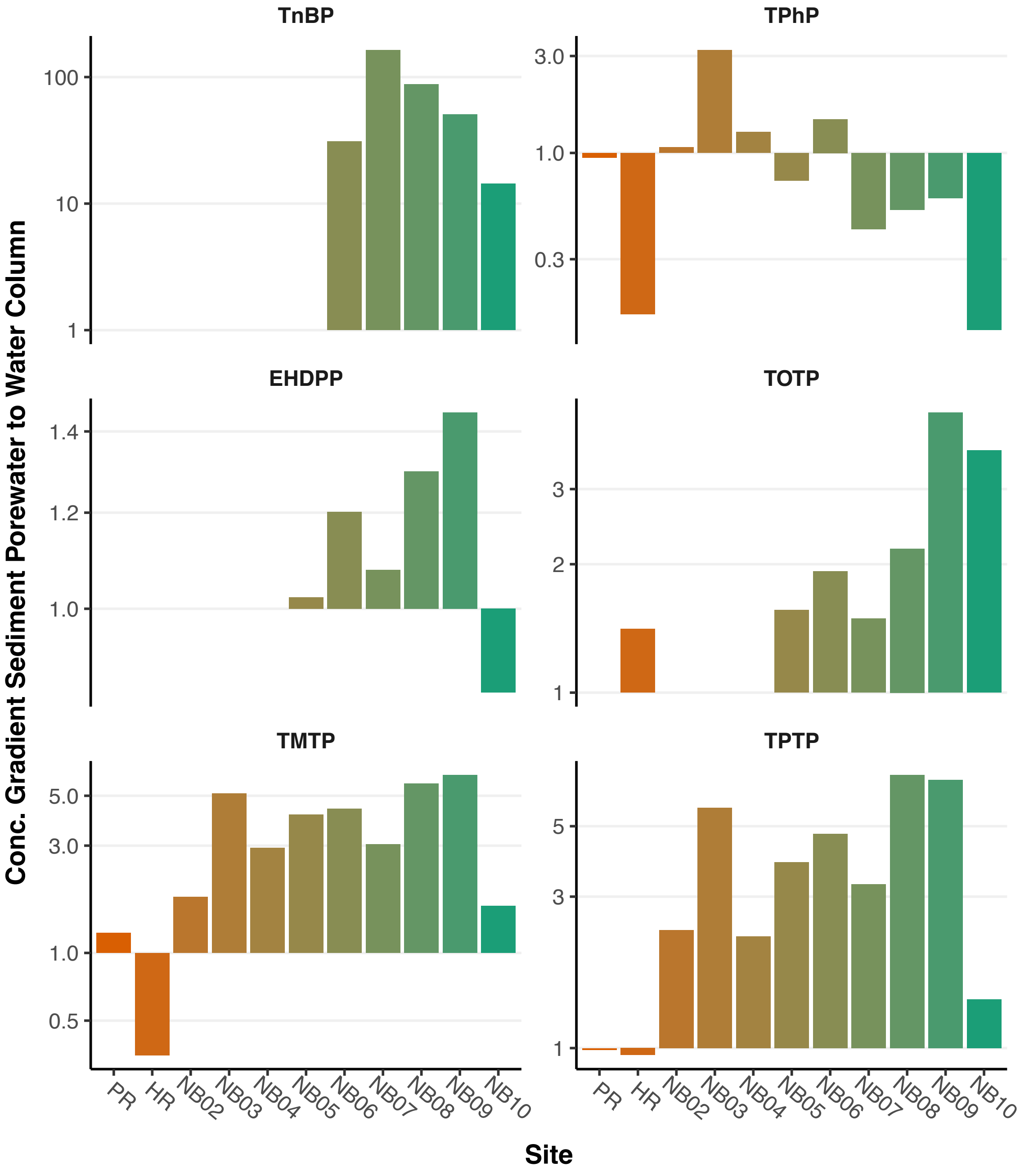

Figure 17: The OPE concentration gradient between the sediment porewater and water column.

CONCLUSIONS

Newark Bay provided an ideal location for testing a new passive sampling device and characterizing PCBs and OPEs in the water column and sediment porewater. Our new anchor sampler performed similar to a previously used sediment porewater sampler for detecting PCBs in the Passaic River, but did not require divers for deployment. Newark Bay PCB concentrations were consistent throughout Newark with tri-chlorinated PCBs dominating the porewater concentrations in both *in situ* and *ex situ* samplers. The *ex situ* concentrations were between 1.96 – 11.02 times higher than the *in situ* samplers but no difference between the profile of PCBs was observed, comparable to previously reported results. Water column concentrations of the PCBs were approximately 2 – 3 times higher than the porewater concentrations resulting in a gradient into the sediment at most sites in Newark Bay. OPEs did not mimic PCBs in the sediment with the majority being detected in the outflows, southern and some middle of Newark Bay, suggesting wastewater treatment plants in the southern part of the bay are the source of OPEs to Newark Bay and not the Passaic River that is the source for legacy compounds. By demonstrating the effectiveness of this new passive sampling device in the characterization and distribution of legacy and emerging HOCs, we hope this will be a potential tool for future studies at contaminated sites such as the Lower Willamette River (WA), sites in the Great Lakes, and Newark Bay (NY/NJ).

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SUPPORTING INFORMATION

Tables

SI Table 1: Physiochemical properties used for PCBs.

Compound	Log K_{ow} [a]	Log D_{pe} [b]	Log K_{PEw} (L/kg) [c]	ΔH_{sol} (kj/mol) [d]
PCB 8	5.07	-8.64	4.76	32
PCB 11	5.28	-8.64	4.99	32
PCB 18	5.24	-8.81	4.95	35.3
PCB 28	5.67	-8.81	5.39	35.3
PCB 44	5.75	-8.98	5.46	38.3
PCB 52	5.84	-8.98	5.55	38.3
PCB 66	6.2	-8.98	5.91	38.3
PCB 77	6.36	-8.98	6.07	38.3
PCB 81	6.36	-8.98	6.07	38.3
PCB 101	6.38	-9.16	6.09	41.3
PCB 105	6.65	-9.16	6.36	41.3
PCB 114	6.65	-9.16	6.36	41.3
PCB 118	6.74	-9.16	6.45	41.3
PCB 123	6.74	-9.16	6.45	41.3
PCB 126	6.89	-9.16	6.6	41.3
PCB 128	6.74	-9.33	6.45	44.1
PCB 138	6.83	-9.33	6.54	44.1
PCB 153	6.92	-9.33	6.64	44.1
PCB 156	7.18	-9.33	6.89	44.1
PCB 157	7.18	-9.33	6.89	44.1
PCB 167	7.27	-9.33	6.98	44.1
PCB 169	7.42	-9.33	7.13	44.1
PCB 170	7.27	-9.4	6.98	46.9
PCB 180	7.36	-9.4	7.07	46.9
PCB 187	7.17	-9.4	6.88	46.9
PCB 189	7.71	-9.4	7.42	46.9
PCB 195	7.56	-9.66	7.27	49.6
PCB 206	8.09	-9.83	7.8	52.2
PCB 209	8.18	-10	7.89	54.7

a: (Hawker & Connell, 1988)
b: Calc: Log D_{pe}= -(0.0145*V_m + 6.1) V_m: SPARC
c: (Lohmann, 2012)
d: A linear relationship with MW was created to estimate based on (Shiu & Ma, 2000)

SI Table 2: Physiochemical properties used for PCDD/Fs.

Compound	**Log Kow** [a]	**Log D_{pe}** [b]	**Log K_{PEw} (L/kg)** [c]	**ΔH_{sol} (kj/mol)** [d]
2,3,7,8-TCDD	6.67	-8.74	6.33	45.8
1,2,3,7,8-PeCDD	6.67 *	-8.92	6.34	45.8
1,2,3,4,7,8-HxCDD	7.56 *	-9.45	6.92	45.8
1,2,3,6,7,8-HxCDD	7.56	-9.45	6.95	45.8
1,2,3,7,8,9-HxCDD	7.56 *	-9.45	6.95	45.8
1,2,3,4,6,7,8-HpCDD	8.17	-9.62	7.14	45.8
OCDD	8.64	-9.80	7.89	45.8
2,3,7,8-TCDF	6.13	-8.99	6.07	39.1
1,2,3,7,8-PeCDF	6.56 *	-9.17	6.48	39.1
2,3,4,7,8-PeCDF	6.56	-9.17	6.65	39.1
1,2,3,4,7,8-HxCDF	6.92	-9.35	7.55	39.1
1,2,3,6,7,8-HxCDF	6.92 *	-9.35	7.55	39.1
2,3,4,6,7,8-HxCDF	6.92 *	-9.35	7.55	39.1
1,2,3,7,8,9-HxCDF	6.92 *	-9.35	7.55	39.1
1,2,3,4,6,7,8-HpCDF	7.37 *	-9.52	8.19	39.1
1,2,3,4,7,8,9-HpCDF	7.37	-9.52	8.19	39.1
OCDF	8.03	-9.70	9.15	39.1

a: (Åberg et al., 2008), * Used value of compound of similar chlorination
b: Calc: Log $D_{pe} = -(0.0145*V_m + 6.1)$ V_m: McGowan
c: (Lohmann, 2012)
d: (Friedman et al., 2012)

SI Table 3: Physiochemical properties used for OPEs.

Compound	**Name**	**Log K_{ow}** [*a*]	**Log D_{pe}** [b]	**Log K_{PEw} (L/kg)** [a]
TnBP	tributyl phosphate	4	-9.35	3.28
TCEP	tris(2-chloroethyl) phosphate	1.44	-8.65	2.48
TCPP	tris(1-chloropropan-2-yl) phosphate	2.59	-9.27	2.71
TDCPP	tris(1,3-dichloropropan-2-yl) phosphate	3.8	-9.80	2.35
TPhP	triphenyl phosphate	4.59	-9.54	3.72
EHDPP	2-ethylhexyl diphenyl phosphate	5.37	-10.29	4.21
TEHP	tris(2-ethylhexyl) phosphate	9.49	-11.32	6.87
TOTP	tris(2-methylphenyl) phosphate	6.3	-10.15	5.5
TMTP	tris(3-methylphenyl) phosphate	6.3	-10.15	5.77
TPTP	tris(4-methylphenyl) phosphate	6.3	-10.15	5.85

a: (McDonough et al., 2018)

b: Calc: Log $D_{pe} = -(0.0145 * V_m + 6.1)$ V_m: McGowan

SI Table 4: Site PE sheet IDs

	PE Sheet ID
PR	204-04, 205-05
HR	204-05, 204-06, 205-06
NB02	204-07a, 204-07b, 204-08a, 204-08b, 205-07
NB03	204-09a, 204-09b, 204-10a, 204-10b, 205-08
NB04	204-11, 205-09
NB05	210-05, 210-06a, 210-06b, 205-10
NB06	210-07a, 210-07b, 210-08, 205-11
NB07	210-09a, 210-09b, 205-12
NB08	210-10, 210-11a, 210-11b, 205-13
NB09	210-12a, 210-12b, 210-13a, 210-13b, 205-14
NB10	210-14a, 210-14b, 210-15a, 210-15b, 205-15

SI Table 5: Calculated sampling rate from water column PE sheets.

PE Sheet	PCBs Rs (L/day)	OPEs Rs (L/day)
205-05	265.75	432.00
205-06	157.71	232.81
205-07	22.24	16.42
205-08	69.54	114.96
205-09	44.35	35.20
205-10	58.50	41.20
205-11	54.06	82.63
205-12	51.50	42.17
205-13	38.85	29.92
205-14	48.30	39.66
205-15	48.61	46.80

SI Table 6: Water samplers fractional equilibrium for PCBs

	205-05	**205-06**	**205-07**	**205-08**	**205-09**	**205-10**	**205-11**	**205-12**	**205-13**	**205-14**	**205-15**
PCB 8	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
PCB 11	1.00	1.00	0.94	0.99	0.96	0.98	0.98	0.97	0.93	0.96	0.97
PCB 18	1.00	1.00	0.95	0.99	0.97	0.99	0.99	0.98	0.94	0.97	0.98
PCB 28	1.00	0.97	0.60	0.77	0.65	0.73	0.73	0.68	0.57	0.65	0.69
PCB 52	0.99	0.82	0.36	0.51	0.40	0.47	0.47	0.43	0.34	0.40	0.44
PCB 44	1.00	0.95	0.53	0.70	0.58	0.66	0.66	0.61	0.51	0.58	0.62
PCB 66	0.93	0.60	0.21	0.32	0.24	0.29	0.29	0.26	0.20	0.24	0.26
PCB 81	0.83	0.47	0.15	0.23	0.17	0.21	0.21	0.18	0.14	0.17	0.19
PCB 77	0.83	0.47	0.15	0.23	0.17	0.21	0.21	0.18	0.14	0.17	0.19
PCB 101	0.79	0.42	0.13	0.20	0.15	0.18	0.18	0.16	0.12	0.15	0.17
PCB 123	0.48	0.20	0.06	0.09	0.06	0.08	0.08	0.07	0.05	0.07	0.07
PCB 118	0.66	0.31	0.09	0.14	0.10	0.13	0.13	0.11	0.09	0.11	0.12
PCB 114	0.56	0.25	0.07	0.11	0.08	0.10	0.10	0.09	0.07	0.08	0.09
PCB 105	0.66	0.31	0.09	0.14	0.10	0.13	0.13	0.11	0.09	0.11	0.12
PCB 126	0.36	0.14	0.04	0.06	0.04	0.05	0.06	0.05	0.04	0.04	0.05
PCB 153	0.33	0.13	0.04	0.06	0.04	0.05	0.05	0.04	0.03	0.04	0.05
PCB 138	0.25	0.10	0.03	0.04	0.03	0.04	0.04	0.03	0.02	0.03	0.03
PCB 128	0.49	0.21	0.06	0.09	0.07	0.08	0.08	0.07	0.05	0.07	0.07
PCB 167	0.15	0.05	0.01	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.02
PCB 156	0.15	0.06	0.01	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.02
PCB 157	0.19	0.07	0.02	0.03	0.02	0.03	0.03	0.02	0.02	0.02	0.02
PCB 169	0.10	0.04	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
PCB 187	0.18	0.07	0.02	0.03	0.02	0.03	0.03	0.02	0.02	0.02	0.02
PCB 180	0.19	0.07	0.02	0.03	0.02	0.03	0.03	0.02	0.02	0.02	0.02
PCB 170	0.12	0.05	0.01	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.02
PCB 189	0.05	0.02	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01
PCB 195	0.07	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
PCB 206	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 209	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SI Table 7: Sediment porewater samplers fractional equilibrium for PCBs

	204-04	**204-05**	**204-06**	**204-07a**	**204-07b**	**204-08a**	**204-08b**	**204-09a**	**204-09b**	**204-10a**	**204-10b**	**204-11**
PCB 8	0.96	0.82	0.88	0.79	0.87	0.68	0.88	0.80	0.91	0.69	0.88	0.93
PCB 11	0.94	0.76	0.84	0.74	0.83	0.63	0.84	0.74	0.88	0.65	0.84	0.90
PCB 18	0.94	0.76	0.84	0.74	0.83	0.63	0.84	0.75	0.88	0.64	0.84	0.90
PCB 28	0.87	0.59	0.74	0.62	0.70	0.50	0.70	0.59	0.74	0.54	0.69	0.81
PCB 52	0.82	0.51	0.69	0.57	0.64	0.45	0.62	0.51	0.66	0.49	0.61	0.75
PCB 44	0.85	0.55	0.72	0.60	0.67	0.47	0.66	0.55	0.70	0.51	0.65	0.78
PCB 66	0.69	0.36	0.58	0.46	0.50	0.35	0.46	0.37	0.48	0.41	0.45	0.61
PCB 81	0.62	0.31	0.53	0.42	0.43	0.32	0.38	0.31	0.40	0.37	0.38	0.54
PCB 77	0.62	0.31	0.53	0.42	0.43	0.32	0.38	0.31	0.40	0.37	0.38	0.54
PCB 101	0.60	0.29	0.51	0.40	0.42	0.30	0.37	0.30	0.38	0.36	0.36	0.52
PCB 123	0.43	0.18	0.39	0.31	0.29	0.23	0.23	0.20	0.23	0.28	0.23	0.36
PCB 118	0.43	0.18	0.39	0.31	0.29	0.23	0.23	0.20	0.23	0.28	0.23	0.36
PCB 114	0.47	0.21	0.42	0.33	0.32	0.24	0.26	0.22	0.26	0.30	0.26	0.40
PCB 105	0.47	0.21	0.42	0.33	0.32	0.24	0.26	0.22	0.26	0.30	0.26	0.40
PCB 126	0.36	0.15	0.35	0.27	0.24	0.20	0.19	0.16	0.18	0.26	0.18	0.30
PCB 153	0.34	0.14	0.32	0.25	0.22	0.19	0.17	0.15	0.16	0.24	0.17	0.28
PCB 138	0.38	0.16	0.36	0.28	0.25	0.20	0.20	0.17	0.19	0.26	0.19	0.32
PCB 128	0.42	0.18	0.38	0.30	0.28	0.22	0.23	0.19	0.22	0.28	0.22	0.35
PCB 167	0.21	0.09	0.24	0.19	0.15	0.14	0.10	0.10	0.09	0.19	0.10	0.18
PCB 156	0.24	0.10	0.26	0.21	0.17	0.15	0.12	0.11	0.11	0.20	0.12	0.20
PCB 157	0.24	0.10	0.26	0.21	0.17	0.15	0.12	0.11	0.11	0.20	0.12	0.20
PCB 169	0.17	0.07	0.21	0.17	0.12	0.12	0.08	0.08	0.07	0.17	0.08	0.15
PCB 187	0.24	0.10	0.26	0.20	0.16	0.15	0.12	0.11	0.11	0.20	0.11	0.20
PCB 180	0.18	0.07	0.21	0.17	0.13	0.12	0.09	0.08	0.08	0.17	0.09	0.15
PCB 170	0.21	0.08	0.23	0.19	0.15	0.14	0.10	0.09	0.09	0.19	0.10	0.18
PCB 189	0.10	0.04	0.15	0.12	0.08	0.09	0.05	0.05	0.04	0.13	0.05	0.09
PCB 195	0.13	0.05	0.17	0.14	0.10	0.10	0.06	0.06	0.05	0.15	0.06	0.11
PCB 206	0.05	0.02	0.09	0.08	0.05	0.06	0.03	0.03	0.02	0.09	0.02	0.05
PCB 209	0.04	0.02	0.08	0.07	0.04	0.05	0.02	0.02	0.02	0.08	0.02	0.04

SI Table 8: Sediment porewater fractional equilibrium for PCBs

	210-05	**210-06a**	**210-06b**	**210-07a**	**210-07b**	**210-08**	**210-09a**	**210-09b**	**210-10**	**210-11a**	**210-11b**	**210-12a**	**210-12b**	**210-13a**	**210-13b**	**210-14a**	**210-14b**	**210-15a**	**210-15b**
PCB 8	0.92	0.89	0.92	0.74	0.87	0.91	0.87	0.94	0.87	0.69	0.80	0.68	0.82	0.74	0.83	0.79	0.88	0.78	0.89
PCB 11	0.89	0.85	0.88	0.68	0.83	0.88	0.83	0.92	0.81	0.64	0.73	0.63	0.76	0.68	0.79	0.75	0.84	0.73	0.85
PCB 18	0.90	0.86	0.89	0.68	0.83	0.88	0.83	0.92	0.82	0.63	0.74	0.62	0.76	0.68	0.79	0.74	0.84	0.72	0.85
PCB 28	0.79	0.73	0.77	0.54	0.70	0.76	0.71	0.81	0.65	0.50	0.56	0.51	0.59	0.55	0.65	0.62	0.71	0.59	0.74
PCB 52	0.73	0.66	0.70	0.48	0.63	0.68	0.65	0.74	0.57	0.45	0.48	0.46	0.51	0.49	0.58	0.56	0.64	0.52	0.68
PCB 44	0.76	0.70	0.73	0.50	0.66	0.72	0.68	0.78	0.61	0.47	0.52	0.48	0.55	0.52	0.61	0.59	0.67	0.55	0.71
PCB 66	0.58	0.51	0.53	0.36	0.48	0.52	0.52	0.56	0.39	0.35	0.33	0.37	0.36	0.38	0.44	0.44	0.48	0.40	0.55
PCB 81	0.50	0.44	0.45	0.32	0.42	0.44	0.46	0.48	0.32	0.31	0.27	0.33	0.30	0.34	0.39	0.39	0.41	0.35	0.48
PCB 77	0.50	0.44	0.45	0.32	0.42	0.44	0.46	0.48	0.32	0.31	0.27	0.33	0.30	0.34	0.39	0.39	0.41	0.35	0.48
PCB 101	0.48	0.42	0.43	0.30	0.40	0.42	0.44	0.45	0.31	0.29	0.26	0.32	0.28	0.32	0.37	0.38	0.39	0.34	0.46
PCB 123	0.33	0.29	0.28	0.22	0.27	0.27	0.32	0.28	0.19	0.22	0.16	0.25	0.18	0.24	0.26	0.28	0.26	0.24	0.33
PCB 118	0.33	0.29	0.28	0.22	0.27	0.27	0.32	0.28	0.19	0.22	0.16	0.25	0.18	0.24	0.26	0.28	0.26	0.24	0.33
PCB 114	0.36	0.32	0.31	0.23	0.30	0.31	0.35	0.32	0.21	0.23	0.18	0.26	0.20	0.26	0.28	0.30	0.29	0.26	0.36
PCB 105	0.36	0.32	0.31	0.23	0.30	0.31	0.35	0.32	0.21	0.23	0.18	0.26	0.20	0.26	0.28	0.30	0.29	0.26	0.36
PCB 126	0.27	0.24	0.23	0.19	0.23	0.22	0.28	0.22	0.15	0.19	0.13	0.22	0.15	0.21	0.22	0.24	0.22	0.21	0.28
PCB 153	0.25	0.22	0.21	0.17	0.21	0.20	0.26	0.20	0.13	0.17	0.12	0.20	0.13	0.19	0.20	0.22	0.20	0.19	0.26
PCB 138	0.28	0.25	0.24	0.19	0.24	0.23	0.29	0.23	0.16	0.19	0.14	0.22	0.15	0.21	0.23	0.25	0.23	0.22	0.30
PCB 128	0.32	0.28	0.27	0.21	0.27	0.26	0.31	0.27	0.18	0.21	0.16	0.24	0.17	0.23	0.25	0.27	0.25	0.24	0.32
PCB 167	0.16	0.14	0.12	0.12	0.14	0.12	0.18	0.11	0.08	0.13	0.07	0.16	0.08	0.14	0.13	0.16	0.12	0.14	0.18
PCB 156	0.18	0.16	0.14	0.13	0.15	0.14	0.20	0.13	0.09	0.14	0.08	0.17	0.09	0.15	0.15	0.18	0.14	0.15	0.20
PCB 157	0.18	0.16	0.14	0.13	0.15	0.14	0.20	0.13	0.09	0.14	0.08	0.17	0.09	0.15	0.15	0.18	0.14	0.15	0.20
PCB 169	0.12	0.11	0.10	0.10	0.11	0.10	0.15	0.08	0.06	0.11	0.06	0.14	0.06	0.12	0.11	0.14	0.10	0.11	0.15
PCB 187	0.17	0.15	0.14	0.13	0.15	0.14	0.19	0.13	0.09	0.14	0.08	0.17	0.09	0.15	0.15	0.17	0.14	0.15	0.20
PCB 180	0.13	0.12	0.10	0.11	0.12	0.10	0.16	0.09	0.07	0.11	0.06	0.14	0.07	0.12	0.12	0.14	0.11	0.12	0.16
PCB 170	0.15	0.13	0.12	0.12	0.13	0.12	0.17	0.11	0.08	0.12	0.07	0.15	0.08	0.14	0.13	0.16	0.12	0.13	0.17
PCB 189	0.08	0.07	0.06	0.07	0.07	0.06	0.10	0.05	0.04	0.08	0.04	0.11	0.04	0.09	0.07	0.10	0.06	0.08	0.10
PCB 195	0.09	0.09	0.07	0.08	0.09	0.07	0.12	0.06	0.05	0.09	0.04	0.12	0.05	0.10	0.09	0.11	0.08	0.09	0.12
PCB 206	0.04	0.04	0.03	0.04	0.04	0.03	0.06	0.02	0.02	0.05	0.02	0.07	0.02	0.06	0.04	0.06	0.03	0.05	0.06
PCB 209	0.03	0.03	0.02	0.04	0.03	0.02	0.05	0.02	0.02	0.05	0.02	0.06	0.02	0.05	0.04	0.05	0.03	0.04	0.05

SI Table 9: Sediment porewater fractional equilibrium for PCDD/Fs

	204-04	**204-05**	**204-06**	**204-07**	**204-08**	**204-09**	**204-10**	**204-11**
2,3,7,8-TCDF	0.70	0.30	0.32	0.36	0.31	0.22	0.31	0.35
2,3,7,8-TCDD	0.59	0.24	0.27	0.29	0.25	0.20	0.25	0.31
1,2,3,7,8-PeCDF	0.37	0.12	0.13	0.15	0.13	0.09	0.12	0.16
2,3,4,7,8-PeCDF	0.37	0.12	0.13	0.15	0.13	0.09	0.12	0.16
1,2,3,7,8-PeCDD	0.57	0.23	0.26	0.28	0.24	0.19	0.24	0.30
1,2,3,4,7,8-HxCDF	0.07	0.02	0.02	0.02	0.02	0.02	0.02	0.03
1,2,3,6,7,8-HxCDF	0.07	0.02	0.02	0.02	0.02	0.02	0.02	0.03
2,3,4,6,7,8-HxCDF	0.07	0.02	0.02	0.02	0.02	0.02	0.02	0.03
1,2,3,7,8,9-HxCDF	0.07	0.02	0.02	0.02	0.02	0.02	0.02	0.03
1,2,3,4,7,8-HxCDD	0.28	0.11	0.12	0.13	0.12	0.11	0.11	0.17
1,2,3,6,7,8-HxCDD	0.28	0.11	0.12	0.13	0.12	0.11	0.11	0.17
1,2,3,7,8,9-HxCDD	0.28	0.11	0.12	0.13	0.12	0.11	0.11	0.17
1,2,3,4,6,7,8-HpCDF	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
1,2,3,4,6,7,8-HpCDD	0.23	0.10	0.12	0.12	0.11	0.12	0.10	0.18
OCDD	0.06	0.02	0.03	0.03	0.03	0.03	0.03	0.05
OCDF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SI Table 10: Sediment porewater fractional equilibrium for PCDD/Fs

	210-05	210-06	210-07	210-08	210-09	210-10	210-11	210-12	210-13	210-14	210-15
2,3,7,8-TCDF	0.33	0.08	0.37	0.29	0.20	0.34	0.32	0.32	0.35	0.34	0.47
2,3,7,8-TCDD	0.25	0.15	0.27	0.22	0.16	0.23	0.21	0.23	0.29	0.26	0.37
1,2,3,7,8-PeCDF	0.13	0.06	0.14	0.11	0.08	0.12	0.11	0.12	0.15	0.13	0.20
2,3,4,7,8-PeCDF	0.13	0.06	0.14	0.11	0.08	0.12	0.11	0.12	0.15	0.13	0.20
1,2,3,7,8-PeCDD	0.24	0.15	0.26	0.21	0.15	0.22	0.20	0.22	0.27	0.25	0.35
1,2,3,4,7,8-HxCDF	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.03
1,2,3,6,7,8-HxCDF	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.03
2,3,4,6,7,8-HxCDF	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.03
1,2,3,7,8,9-HxCDF	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.03
1,2,3,4,7,8-HxCDD	0.11	0.30	0.10	0.08	0.07	0.07	0.06	0.08	0.13	0.10	0.14
1,2,3,6,7,8-HxCDD	0.11	0.30	0.10	0.08	0.07	0.07	0.06	0.08	0.13	0.10	0.14
1,2,3,7,8,9-HxCDD	0.11	0.30	0.10	0.08	0.07	0.07	0.06	0.08	0.13	0.10	0.14
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01
1,2,3,4,6,7,8-HpCDD	0.09	0.60	0.08	0.07	0.07	0.05	0.05	0.07	0.13	0.09	0.12
OCDD	0.02	0.45	0.02	0.01	0.02	0.01	0.01	0.01	0.03	0.02	0.03
OCDF	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SI Table 11: Water column fractional equilibrium for OPEs

	205-05	205-06	205-07	205-08	205-09	205-10	205-11	205-12	205-13	205-14	205-15
TnBP	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
TCEP	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
TCPP	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
TDCPP	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
TBEP	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
TPhP	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
EHDPP	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
TEHP	0.70	0.32	0.03	0.16	0.06	0.06	0.14	0.07	0.05	0.06	0.08
TOTP	1.00	1.00	0.45	0.98	0.76	0.79	0.97	0.80	0.68	0.77	0.86
TMTP	1.00	0.99	0.28	0.89	0.53	0.57	0.84	0.58	0.45	0.55	0.65
TPTP	1.00	0.98	0.24	0.84	0.47	0.50	0.78	0.51	0.40	0.48	0.58

SI Table 12: Sediment porewater fractional equilibrium for OPEs

	204-04	204-05	204-06	204-07a	204-07b	204-08a	204-08b	204-09a	204-09b	204-10a	204-10b	204-11
TnBP	1.00	0.98	0.99	1.00	0.99	0.99	0.99	1.00	1.00	1.00	0.99	1.00
TCEP	1.00	0.94	0.97	1.00	0.99	0.98	0.99	1.00	1.00	1.00	0.99	1.00
TCPP	1.00	0.97	0.98	1.00	0.99	0.99	0.99	1.00	1.00	1.00	0.99	1.00
TDCPP	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
TBEP	0.99	0.59	0.74	1.00	0.87	0.81	0.86	1.00	0.93	1.00	0.84	0.97
TPhP	1.00	0.96	0.98	1.00	0.99	0.98	0.99	1.00	0.99	1.00	0.99	1.00
EHDPP	1.00	0.94	0.97	0.99	0.98	0.98	0.98	0.99	0.99	1.00	0.98	0.99
TEHP	0.42	0.65	0.71	0.00	0.60	0.75	0.57	0.00	0.72	0.00	0.66	0.60
TOTP	0.95	0.65	0.76	0.63	0.79	0.81	0.78	0.62	0.89	0.65	0.79	0.91
TMTP	0.90	0.48	0.61	0.46	0.65	0.68	0.64	0.45	0.80	0.48	0.66	0.83
TPTP	0.88	0.43	0.56	0.41	0.61	0.63	0.59	0.40	0.76	0.43	0.61	0.80

SI Table 13: Sediment porewater fractional equilibrium for OPEs

	210-05	**210-06a**	**210-06b**	**210-07a**	**210-07b**	**210-08**	**210-09a**	**210-09b**	**210-10**	**210-11a**	**210-11b**	**210-12a**	**210-12b**	**210-13a**	**210-13b**	**210-14a**	**210-14b**	**210-15a**	**210-15b**
TnBP	0.99	0.99	0.99	0.99	0.99	0.98	0.99	1.00	0.99	1.00	0.99	0.98	0.99	1.00	0.99	0.99	0.99	0.98	0.99
TCEP	0.99	1.00	0.99	0.99	0.99	0.97	0.99	1.00	1.00	1.00	0.99	0.95	0.99	1.00	0.97	0.99	0.99	0.97	1.00
TCPP	1.00	1.00	1.00	0.99	1.00	0.98	0.99	1.00	1.00	1.00	0.99	0.97	0.99	1.00	0.98	0.99	0.99	0.98	1.00
TDCPP	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
TBEP	0.89	0.90	0.88	0.79	0.88	0.69	0.88	1.00	0.90	0.99	0.84	0.63	0.78	0.99	0.72	0.82	0.84	0.70	0.90
TPhP	0.99	0.99	0.99	0.98	0.99	0.97	0.99	1.00	0.99	1.00	0.98	0.97	0.98	1.00	0.98	0.98	0.98	0.97	0.99
EHDPP	0.98	0.98	0.97	0.96	0.98	0.95	0.98	1.00	0.97	0.98	0.96	0.95	0.96	0.98	0.96	0.97	0.97	0.96	0.98
TEHP	0.52	0.49	0.43	0.53	0.46	0.58	0.60	0.03	0.29	0.00	0.29	0.73	0.40	0.00	0.67	0.64	0.59	0.59	0.57
TOTP	0.79	0.79	0.75	0.71	0.76	0.67	0.80	0.91	0.72	0.45	0.64	0.71	0.65	0.46	0.73	0.77	0.77	0.68	0.81
TMTP	0.65	0.65	0.59	0.55	0.61	0.51	0.67	0.83	0.56	0.29	0.47	0.55	0.48	0.31	0.57	0.63	0.62	0.52	0.69
TPTP	0.60	0.60	0.54	0.50	0.56	0.46	0.62	0.80	0.51	0.25	0.42	0.50	0.43	0.27	0.52	0.58	0.57	0.47	0.64

SI Table 14: Limit of Detection for PCBs (pg g_{PE}^{-1})

	204	**205**	**210**
PCB 8	284.08	302.33	258.61
PCB 11	0	0	0
PCB 18	0	0	0
PCB 28	0	0	0
PCB 52	839.10	784.84	800.13
PCB 44	0	0	0
PCB 66	504.40	126.90	447.42
PCB 81	0	0	0
PCB 77	0	0	0
PCB 101	1260.44	0	841.67
PCB 123	0	0	0
PCB 118	531.63	0	558.50
PCB 114	0	0	0
PCB 105	347.64	0	0
PCB 126	0	0	0
PCB 153	1661.71	0	339.72
PCB 138	1333.01	0	386.11
PCB 128	0	0	0
PCB 167	0	0	0
PCB 156	0	0	0
PCB 157	0	0	0
PCB 169	0	0	0
PCB 187	0	0	0
PCB 180	0	0	0
PCB 170	0	0	0
PCB 189	0	0	0
PCB 195	0	0	0
PCB 206	0	0	0
PCB 209	0	0	0

SI Table 15: Limit of Detection for OPEs (ng g_{PE}^{-1})

	205	**204**	**210**
TnBP	3939.95	4129.19	3558.05
TCEP	2788.04	2228.05	4075.40
TCPP	5051.77	3920.42	13973.19
TDCPP	0.00	0.00	0.00
TBEP	0.00	0.00	0.00
TPhP	0.00	0.00	2837.96
EHDPP	0.00	0.00	0.00
TEHP	18354.54	27060.79	3528.37
TOTP	1311.34	16112.34	3462.82
TMTP	1929.14	1892.17	1767.98
TPTP	1994.14	1933.09	1809.25

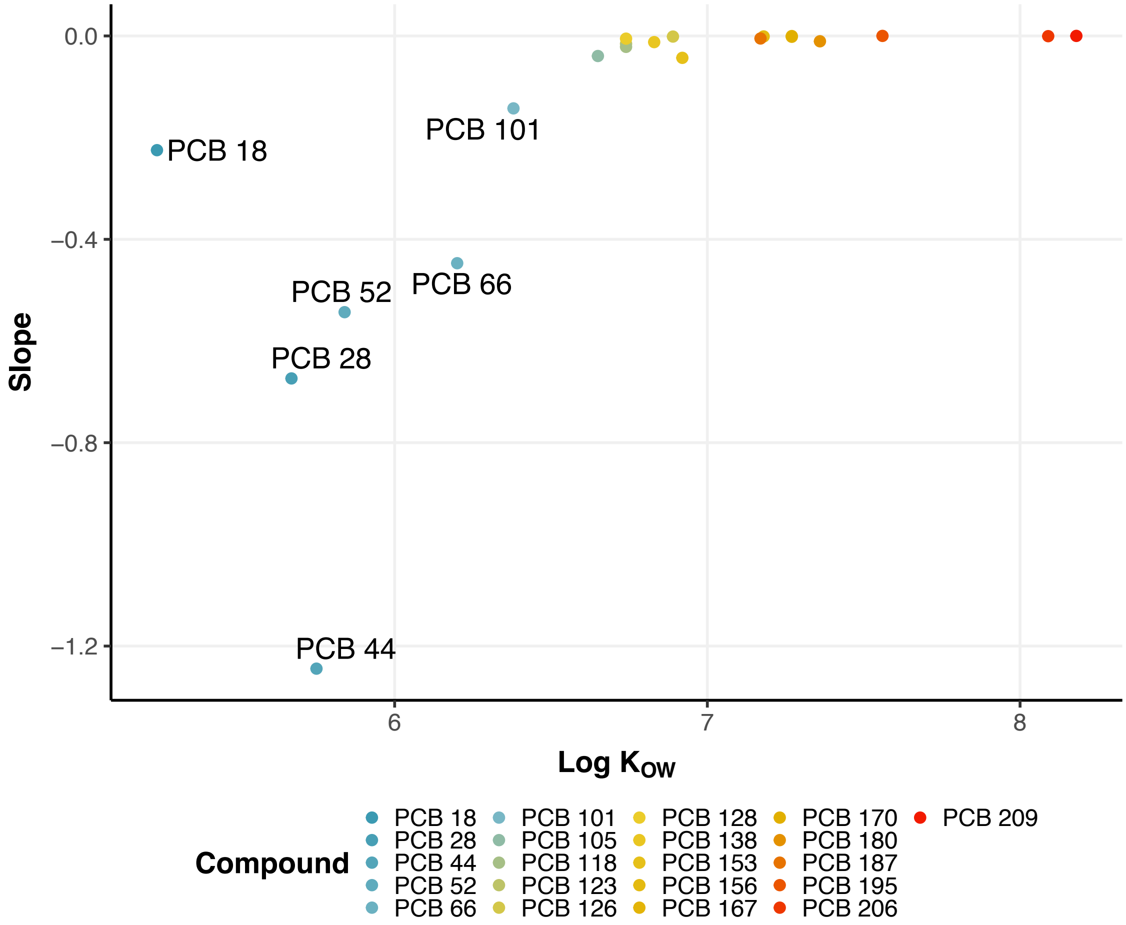
SI Table 16: Regression statistics of circle vs anchor sampler from the first sampling campaign.

Site	**Slope**	**R2**	**P-value**
S1	0.32101617	0.88637836	9.45E-15
S2	-0.8204882	0.99986125	4.05E-38
S3	-0.0917011	0.85483923	7.86E-10
S4	-0.208961	0.97187502	3.38E-16
S5	-0.2247512	0.72136077	4.22E-06
S6	-0.2449878	0.81505371	4.08E-06
S8	-0.1192302	0.67858977	8.76E-05

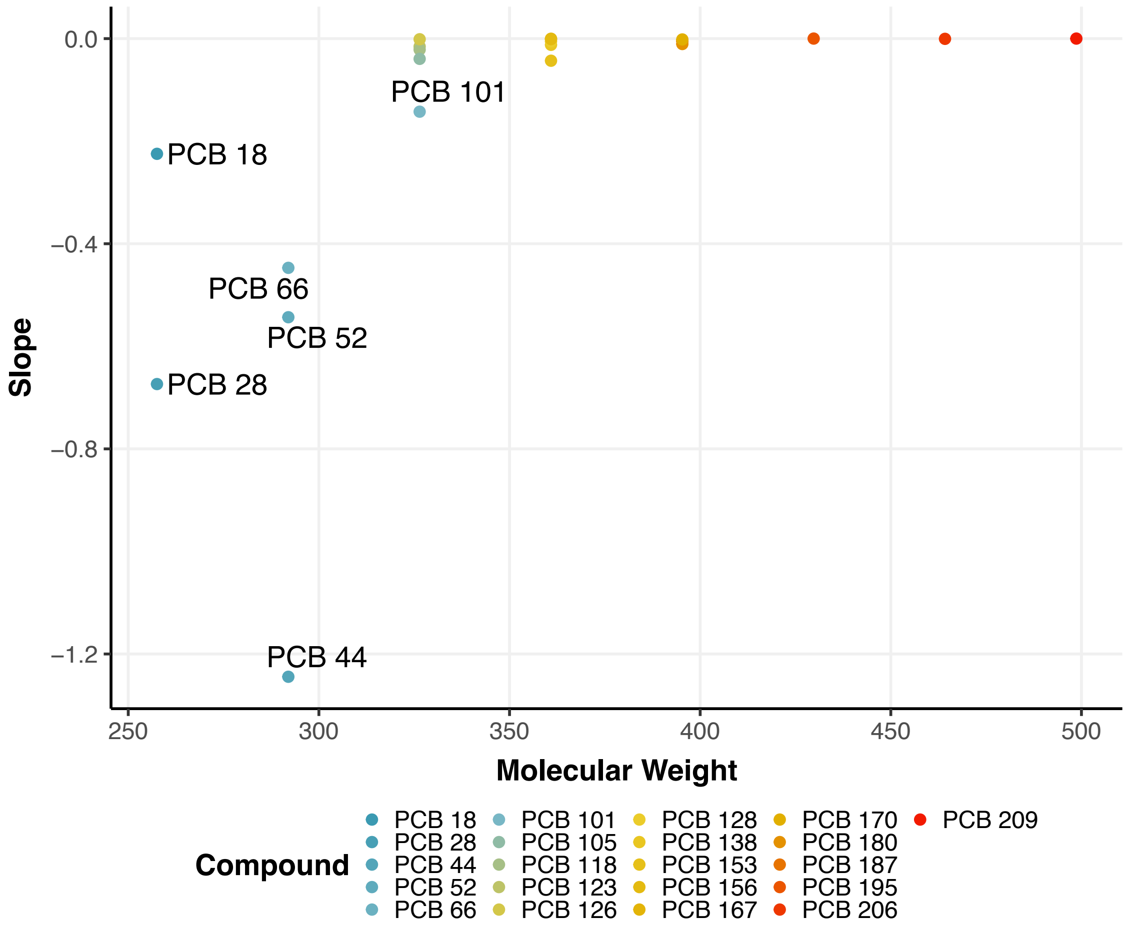
SI Table 17: The polyethylene sheet to organic carbon linear regression statistics for each PCB.

Compound	**Slope**	**Intercept**	**R^2**	**P-value**
PCB-18	-0.22	0.13	0.09	0.33
PCB-28	-0.67	0.27	0.21	0.13
PCB-52	-0.54	0.11	0.25	0.10
PCB-44	-1.24	0.21	0.68	0.00
PCB-66	-0.45	0.18	0.31	0.06
PCB-101	-0.14	0.05	0.51	0.01
PCB-123	-0.02	0.00	0.18	0.17
PCB-118	-0.02	0.04	0.02	0.63
PCB-105	-0.04	0.01	0.50	0.01
PCB-126	0.00	0.00	0.04	0.53
PCB-153	-0.04	0.02	0.39	0.03
PCB-138	-0.01	0.01	0.19	0.15
PCB-128	-0.01	0.00	0.22	0.12
PCB-167	0.00	0.00	0.03	0.57
PCB-156	0.00	0.00	0.03	0.60
PCB-187	-0.01	0.00	0.17	0.18
PCB-180	-0.01	0.01	0.29	0.07
PCB-170	0.00	0.00	0.07	0.41
PCB-195	0.00	0.00	0.00	0.95
PCB-206	0.00	0.00	0.41	0.02
PCB-209	0.00	0.00	0.04	0.55
Sum PCBs	-3.43	1.06	0.48	0.01

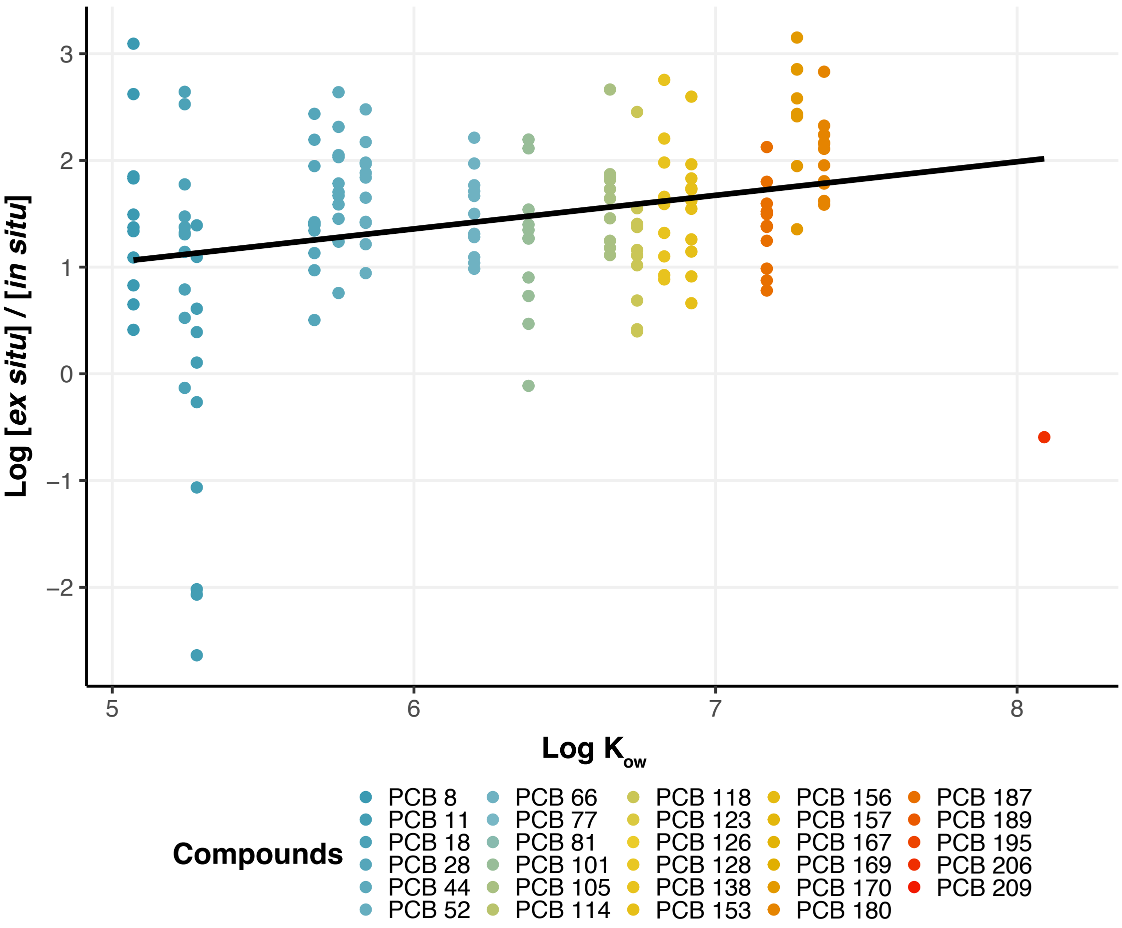
Figures



SI Figure 1: Log K$_{OW}$ vs the slope of the linear regression between PE to OC % and concentration of PCBs.



SI Figure 2: Molecular weight vs the slope of the linear regression between PE to OC % and concentration of PCBs



SI Figure 3: Log KOW value showing no trend compared to the differences between *ex situ* and *in situ* porewater concentrations.