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Determination of PCB fluxes from Indiana Harbor and Ship Canal using dual-deployed air and water passive samplers☆

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Abstract

We have developed a method for measuring fluxes of PCBs from natural waters using air and water passive samplers deployed simultaneously in the Indiana Harbor and Ship Canal (IHSC). Net volatilization of Σ PCBs was determined for 2017, and ranged from 1.4 to 2.8 $\mu\text{g m}^{-2} \text{d}^{-1}$, with a median of 2.0 $\mu\text{g m}^{-2} \text{d}^{-1}$. We confirm earlier findings that the IHSC experiences constant release of gas-phase PCBs. Gas-phase and freely-dissolved water Σ PCB samples median were 4.0 ng m^{-3} and 14 ng L^{-1} , both exhibiting increasing concentrations over the year of study, and with a strong positive correlation between them ($R^2 = 0.93$ for Σ PCBs). The relative concentrations of individual PCB congeners were very similar between air and water samples, and resemble Aroclor 1248, a mixture previously reported to contaminate the IHSC sediments. Monthly variability of the volatilization fluxes was primarily driven by the freely-dissolved water concentration changes ($R^2 = 0.87$). Although different sampling methods were performed to estimate air-water fluxes between the month of August of 2006 and 2017, Σ PCB net fluxes have decreased by more than 60%, suggesting that either dredging at IHSC from 2012 to 2017 or reduction of upstream sources have decreased the freely-dissolved water concentrations of PCBs, thus reducing the air-water net volatilization in IHSC. Finally, we have shown that this passive sampling approach represents a simple and cost-effective method to assess the air-water exchange of PCBs, increase analytical sensitivity, enable measurements over time, and reduce uncertainties related to unexpected episodic events.

Keywords

PCB; Air-water flux; IHSC; Volatilization; Passive sampler

1. Introduction

Contaminated waterways are important sources of airborne semi-volatile organic compounds (SVOCs). For example, net volatilization fluxes of polychlorinated biphenyls (PCBs) at the Hudson River Estuary were ~40 times higher than atmospheric deposition, with an annual loss through volatilization of 28 kg yr^{-1} , clearly showing the role of the water as an airborne PCB source (Totten et al., 2001; Yan et al., 2008). Similar results were found for the

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Delaware River, where net volatilization fluxes ranged from 360 to 3000 ng m⁻² d⁻¹ for ΣPCBs (Rowe et al., 2007). Likewise, the contaminated waters from New Bedford Harbor are responsible for most of the airborne PCB concentrations in the surrounding area (Martinez et al., 2017). The air-water exchange process is a crucial component for determining the fate of water-borne SVOCs and airborne exposures to communities living near contaminated waterways. Both spatial and temporal resolution is required to better understand the dynamics of the system.

Passive sampling of SVOCs in air and water is a promising approach to better collect spatial and temporal data (Greenwood et al., 2007). Furthermore, due to longer deployments, which increase the amount of chemical capture, passive sampling improves the sensitivity and accuracy of the analytical methods (Bohlin et al., 2014; Mills et al., 2014).

Increasingly, passive sampling techniques are used to estimate the air-water exchange of SVOCs. For example, air-water exchange of PCBs and PAHs have been determined in the Lower Great Lakes (Liu et al., 2016), the Lower Duwamish waterway, Washington (Apell and Gschwend, 2017), the Gulf of Mexico (Tidwell et al., 2016), and the Willamette River, Oregon (Tidwell et al., 2017). These studies found that a passive sampling approach improves the spatial resolution, as well as allows direct determination of the freely-dissolved phase of the compounds both in the air and water compartments.

Here we report a new passive sampling design to determine the direction and magnitude of PCB air-water fluxes. We developed a dual-sampling system of polyurethane foam passive air (PUF-PAS) and low-density polyethylene (LDPE) water samplers that was deployed in the Indiana Harbor and Ship Canal (IHSC), IN, USA. IHSC is located on the southern shore of Lake Michigan, and it is contaminated with PCBs, PAHs and heavy metals from more than 70 years of industrial operations. We previously reported an annual release from the water to the air of about 7 kg of PCBs, and almost 45 kg were exported to Lake Michigan in 2006 (Martinez et al., 2010b). In 2012, a navigational dredging operation began, and it was not clear if dredging had reduced or increased the fluxes of PCBs. Using a comparable modeling approach to interpret air-water fluxes, we are now able to evaluate the monthly changes in PCB fluxes over the course of 2017 and compare to findings more than a decade earlier.

2. Materials and methods

2.1. Passive sampling device

The passive sampling device consisted of a PUF-PAS set approximately 1 m above the water (see graphical abstract) and 2.5 cm × 30 cm LDPE strips threaded onto solvent-cleaned stainless steel metals rings attached to a long, steel chain with a weight at the bottom. Four depths were measured for the first two deployments (~0.3, 1.5, 3.5 and 5.3 m from the water surface, total depth 5.5 m), but due to little vertical variability found in the freely-dissolved concentration, only the top and bottom depths were measured for the rest of the deployments. The passive sampling device was deployed at IHSC, adjacent to a USGS streamflow-gaging and water monitoring station (USGS 04092750). The device was

deployed for ten consecutive periods, from November 2016 to October 2017, ranging from 21 to 62 days of deployment times, with an average of 35 days.

2.2. Gas-phase PCB measurements

PUF-PAS was used to measure gas-phase PCB concentrations as previously described for other studies (Ampleman et al., 2015; Herkert et al., 2016; Martinez et al., 2017). Prior to deployment, PUF disks were cleaned in an ASE-350 (Dionex™ Accelerated Solvent Extraction), with a mixture of 1:1 (v/v) acetone:hexane solution. PUFs were dried for at least 1 h in a ventilated fume hood, wrapped in combusted aluminum foil, placed individually in plastic Ziploc bags, and stored at 4 °C until deployment. Prior to deployment, PUF disks were spiked with 1000 ng of a mixture of deuration compounds (DCs) or performance reference compounds of PCB9-d₅ (2,5-dichlorobiphenyl-2',3',4',5',6'-d₅, deuterated), PCB22-d₄ (2,3,4'-trichlorobiphenyl-2',3',5',6'-d₄, deuterated), PCB52-d₃ (2,2',5,5'-tetrachlorobiphenyl-3,4,6-d₃, deuterated), PCB116-d₅ (2,3,4,5,6-pentachlorobiphenyl-2',3',4',5',6'-d₅, deuterated) and PCB156-d₃ (2,3,3',4,4',5-hexachlorobiphenyl-2',6,6'-d₃, deuterated), from CDN Isotopes Inc., Canada. We used a previously described method (Persoon et al., 2010).

Concentrations of gas-phase PCB congeners were determined by dividing the mass of each congener collected in the PUF disk by the congener-specific effective sampling volume, as described in equation (1):

$$C_{PCBi a} = m_{PUF PCBi} / V_{eff PCBi} \quad (1)$$

where $C_{PCBi a}$ is the gas-phase concentration for the i th PCB (ng m^{-3}), $m_{PUF PCBi}$ is the mass of the i th PCB on the PUF (ng) and $V_{eff PCBi}$ is the effective sampling volume for the i th PCB (m^3). The effective sampling volumes were obtained from modeled and calculated sampling rates from local meteorology (Herkert et al., 2018) and the spiked deuration compounds. Sampling rates ranged from 2.9 to 8.4 $\text{m}^3 \text{d}^{-1}$, whereas congener specific sampling volumes ranged from 26 to 400 m^3 .

2.3. Freely-dissolved PCB water measurements

Freely-dissolved PCB water measurements were carried out using LDPE (25 μm , Menards®, Iowa City, IA, USA), as others have used (Burgess et al., 2015; Liu et al., 2016). Prior to deployment, the LDPE strips were cleaned with a series of solvent soaks and rinses of dichloromethane, methanol and deionized water, for 24 h each. Clean LDPE strips were stored in deionized water until deployment. To account for non-equilibrium during the field deployment, the same DCs used for the PUF disks were loaded into the LDPE strips following the procedure described by Booij et al. (2002) and others (USEPA/SERDP/ESTCP, 2017). Briefly, 1000 ng of DCs in hexane solution were spiked into a clean 1000 mL Erlenmeyer flask and the hexane was allowed to evaporate in a fume hood for ~20 min. Methanol:deionized water mixture of 80:20 (v/v) was added to the flask, air bubbles were removed to the best of our ability, and the mixture was left to equilibrate for 7 days. Next, LDPE strips were soaked with deionized water for 24 h and subsequently rinsed with

deionized water. Loaded LDPE strips were stored in sealed clean glass containers with deionized water, ready to be deployed in the field.

Freely-dissolved PCB water concentrations were calculated using equation (2):

$$C_{PCBi\ w} = C_{LDPE-PCBi} / (K_{LDPE-wi} \times f_{eqi}) \quad (2)$$

where $C_{PCBi\ w}$ is the freely-dissolved water concentration for the i th PCB (ng L^{-1}), $C_{LDPE-PCBi}$ is the concentration collected in the LDPE strip for the i th PCB (ng kg_{LDPE}^{-1}), $K_{LDPE-wi}$ is the congener specific LDPE-water partition coefficient ($\text{L}_w \text{kg}_{LDPE}^{-1}$), and f_{eqi} is the fraction of equilibrium of the specific congener between the LDPE and the water. The congener specific fraction of equilibrium for native PCBs was computed using a graphical user interface (GUI) for water column samples developed by Apell et al. (2016), Tcaciuc et al. (2015) and Thompson et al. (2015), and implemented by US EPA (USEPA/SERDP/ESTCP, 2017), with the calculated fraction of equilibrium from the depuration compounds as input. Calculated fractions of equilibrium for the native PCB congeners ranged from 0.002 for the highly chlorinated congeners (i.e., octa- to decachlorobiphenyl) to 1.0 for the low chlorinated congeners (mono- to trichlorobiphenyls). Congener specific LDPE-water partition coefficients and water diffusivity were corrected by water temperature from each deployment period (see supplementary data).

2.4. Fugacity ratio calculation

The water-air fugacity ratio (f_w/f_a) was used to assess the air-water exchange direction of the individual PCB congeners, following eq. (3):

$$f_w/f_a = (C_{PCBi\ w} \times K_{PCBi\ a/w}) / (C_{PCBi\ a}) \quad (3)$$

where $K_{PCBi\ a/w}$ is the equilibrium air-water partition constant (nondimensional Henry's Law Constant) for the i th PCB (Dunnivant et al., 1992) corrected by air and water temperatures (Goss, 2006). A ratio equal to 1 represents equilibrium, a ratio >1 volatilization and a ratio <1 adsorption.

2.5. PCB flux calculations

Individual PCB congener fluxes were calculated as the air-water mass transfer coefficient multiplied by the water-air concentration gradient [eq. (4)] (Martinez et al., 2017; Martinez et al., 2010b; Schwarzenbach et al., 2003; Zhang et al., 1999).

$$F_{PCBi\ \frac{a}{w}} = V_{PCBi\ \frac{a}{w}} \times \left(C_{PCBi\ w} - C_{PCBi\ a} / K_{PCBi\ \frac{a}{w}} \right) \quad (4)$$

where $F_{PCBi\ a/w}$ is the flux between the air and the water for the i th PCB ($\text{ngm}^{-2}\ \text{d}^{-1}$) and $V_{PCBi\ a/w}$ is the overall air-water mass transfer coefficient for the i th PCB ($\text{m}\ \text{d}^{-1}$). We calculated the net, gross volatilization (i.e., $C_{PCBi\ a=0}$) and gross absorption (i.e., $C_{PCBi\ w=0}$) fluxes using eq. (4). The mass transfer coefficient was calculated following the Whitman two-film model, where individual velocities across air and water films were calculated to compute the overall air-water mass transfer coefficient [eq. (5)]:

$$\frac{1}{V_{PCBi\ \frac{a}{w}}} = \frac{1}{V_{PCBi\ w}} + \frac{1}{V_{PCBi\ a}} \times K_{PCBi\ \frac{a}{w}} \quad (5)$$

where $V_{PCBi\ w}$ is the water transfer velocity for the i th PCB ($\text{m}\ \text{d}^{-1}$) and $V_{PCBi\ a}$ is the air transfer velocity for the i th PCB ($\text{m}\ \text{d}^{-1}$). All physical and chemical properties of the individual PCB congeners used to calculate these mass transfer coefficients included adjustments for environmental and meteorological conditions including air and water temperatures, wind speed, and water flow. Details of the calculations are shown in the supplementary data.

2.6. Analytical methods

Gas-phase PCBs collected via PUF-PAS were extracted and cleaned as previously described (Ampleman et al., 2015; Marek et al., 2017; Martinez et al., 2017). Briefly, PUF disks were spiked with 50 ng of surrogate standards: PCB14 (3,5-dichlorobiphenyl), PCB65-d5 (2,3,5,6-tetrachlorobiphenyl-d5, deuterated) and PCB166 (2,3,4,4',5,6-hexachlorobiphenyl), and extracted utilizing an ASE-350 with equal parts of acetone and hexane. The extracts were cleaned through a Pasteur pipette filled with 0.1 g of combusted silica gel and 1 g of acidified silica gel (2:1 silica gel:sulfuric acid w/w) and eluted with hexane. The eluates were concentrated to ~0.5 mL and 25 ng of internal standard [PCB30-d5 (2,4,6-trichlorobiphenyl-2',3',4',5',6'-d5, deuterated) and PCB204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl)] was added.

PCBs collected using LDPE were extracted and cleaned similarly to previously reported methods (Apell and Gschwend, 2017; Fernandez et al., 2014; Fernandez et al., 2012). LDPE strips were rinsed with deionized water, dried with laboratory tissue, and spiked with 50 ng of surrogate standards: PCB14 (3,5-dichlorobiphenyl), PCB65-d5 (2,3,5,6-tetrachlorobiphenyl-d5, deuterated) and PCB166 (2,3,4,4',5,6-hexachlorobiphenyl). The LDPE strips were then transferred to a sealed glass vial with hexane. After equilibration for 24 h, the hexane volumes were reduced to ~0.5 mL and the concentrates were cleaned through Pasteur pi-pettes as described above for the PUF. The eluates were concentrated to ~0.5 mL and 25 ng of internal standard [PCB30-d5 (2,4,6-trichlorobiphenyl-2',3',4',5',6'-d5, deuterated) and PCB204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl)] was added.

PCBs were detected and quantified as previously described (Martinez et al., 2017). Tandem Mass Spectrometry GC-MS/MS (Agilent 7000) in multiple reaction monitoring (MRM) mode was used to quantify all 209 congeners in 171 individual or coeluting congener peaks.

The GC was equipped with a Supelco SBP-Octyl capillary column (30m × 0.25mm ID, 0.25mm film thicknesses) with helium as the carrier gas.

2.7. Quality assurance & quality control (QA/QC)

Surrogate standards, as well as laboratory and field blanks were used to evaluate the quality of our methods. The percentage recoveries of surrogate standards for the air samples were 79 ± 9 , 80 ± 11 and 85 ± 12 for PCB14, PCB65-d5, and PCB166, respectively. The percentage recoveries of surrogate standards for the water samples were 85 ± 19 , 85 ± 18 , and 99 ± 22 for PCB14, PCB65-d5, and PCB166, respectively. Recovery correction was performed on all samples to account for any losses during laboratory processes; PCB1 to 39, PCB40 to 127, and PCB128 to 209 were corrected with recoveries from PCB14, PCB65-d5, and PCB166, respectively. The average Σ PCB mass measured in the PUF-PAS field blanks was 5.6 ± 1.1 ng sample⁻¹ (n = 10) and 8.8 ± 6.3 ng gLDPE⁻¹ for water samples (n = 6). Subsequently, a congener specific limit of quantification (LOQ) was applied to all samples; calculated as the upper limit of the 95% confidence interval of the blanks. Congener masses below the LOQ were assigned a mass of zero. The congener specific LOQ for the air samples ranged from 0.002 to 0.3 ng sample⁻¹ with an average of 0.04 ng sample⁻¹. For the water samples, the congener specific LOQ ranged from 0.003 to 1.2 ng gLDPE⁻¹ with an average of 0.1 ng gLDPE⁻¹.

2.8. Monte Carlo simulations

We used Monte Carlo simulations to assess the uncertainty of the calculated fugacity ratios and air-water fluxes (Martinez et al., 2010b). We considered the distribution for each parameter instead of single variables (see supplementary data). These frequency distributions were obtained of the standard deviations from reported values or calculated from available data of the parameters. For example, standard deviations of environmental conditions such as air and water temperatures were computed from the collected data. Henry's Law Constant error was obtained from its publication (Dunnivant et al., 1992). We assumed normal distribution of all errors and that uncertainty in the chemical measurements was primarily due to chemical analysis (20%). We used RStudio (Version 1.1.442) to perform the simulations, which were repeated 1000 times and provided frequency distribution of the fugacity ratios and fluxes. The RStudio codes are provided in the supplementary data.

2.9. Meteorological data

Meteorological data were used to calculate air and water PCB concentrations, fugacity ratios and fluxes. Air and water temperatures, and water flows were obtained from the USGS monitoring station next to our passive sampling device. Wind speed and atmospheric pressure were reported by the Gary/Chicago International Airport weather station.

All the data generated in this research, i.e., individual congener specific masses captured by the PUFs and LDPEs, LOQ for both PUF and LDPE, effective sampling volumes, fraction of equilibrium, LDPE-water partition coefficient, water-air fugacity ratios, fluxes (net, volatilization and absorption), and the meteorological data, are available at <https://doi.org/10.1594/PANGAEA.894908> (Martinez et al., 2018).

3. Results and discussion

3.1. Gas-phase PCB measurements

Median concentration of gas-phase Σ PCB was 4.0 ng m^{-3} , with an interquartile range (IQR) of $1.6\text{--}5.9 \text{ ng m}^{-3}$. On average, 125 peaks representing individual and coeluting congeners were measured in our samples. Individual congener concentrations are presented in Table S1. Even though the samples were collected at the same location, a factor of eight between the highest and the lowest measurements shows an interesting increasing concentration with time that is well correlated with the freely-dissolved water concentration changes (Fig. 1). More than 90% of the gas-phase concentration variability of Σ PCB was explained by the freely-dissolved water concentration changes ($R^2 = 0.93$) (Fig. 2). This was also true for individual congeners, where 47% of the congeners showed significant correlation ($p < 0.05$) (Fig. 2). This gas-phase PCB trend is consistent with reported airborne PCB concentrations measured by the Army Corps of Engineers at five locations nearby our sampling location (Fig. 3). The five congeners measured by the Army Corps (i.e., PCBs8, 15, 18, 28 and 31) showed a similar temporal trend of increasing concentrations throughout the year.

Our measured concentrations of gas-phase Σ PCB agree with measurements carried out at IHSC above the water using active sampling in August 2006 ($1.9\text{--}8.9 \text{ ng m}^{-3}$) (Martinez et al., 2010b). Using the same passive sampling approach, our values are slightly higher than values reported around 2000 m from our sampling location in East Chicago outdoor schools ($0.03\text{--}3 \text{ ng m}^{-3}$) (Marek et al., 2017) and Chicago and Cleveland ($0.3\text{--}4 \text{ ng m}^{-3}$) (Persoon et al., 2010).

3.2. Freely-dissolved PCB measurements

Over the course of the study, freely-dissolved Σ PCB water concentrations increased from 9 to 18 ng L^{-1} , with a median of 14 ng L^{-1} and an IQR of $11\text{--}16 \text{ ng L}^{-1}$ (Fig. 1). On average, 140 peaks representing individual and coeluting congeners were measured in our samples. Individual congener concentrations are presented in Table S1. LDPE placed simultaneously at four different depths for the first two deployments showed that the system is well mixed at the sampling location (relative standard deviation (RSD) of freely-dissolved Σ PCB concentration $< 7\%$).

We know of two possible explanations for the increasing trend in the freely-dissolved water concentrations: (i) change in equilibrium and biological processes driven by an increase in water temperature; and (ii) effluent discharge from an upstream confined disposal facility (CDF). We considered the effect of temperature because we recorded a steady increase in the monthly average water temperature over our study period (from 8 to 21°C). Warmer water enhances sediment-water exchange of SVOCs such as PCBs and DDTs through increasing growth and activity of benthic organisms, diagenesis, gas ebullition and bioturbation (Connolly et al., 2000; Erickson et al., 2005; Sethajintanin and Anderson, 2006). Two studies found a significant positive correlation between chemical water concentration and water temperature. Bremle and Larsson concluded that increasing temperature promoted desorption of PCBs from sediment (Bremle and Larsson, 1997). Sthajintanin and Anderson suggested that increasing water temperature spurred biological activity and subsequent PCB

release at the sediment-water interface (Sethajintanin and Anderson, 2006). Our measurements show the same outcome: concentrations of freely-dissolved PCBs ($R^2 = 0.71$) and 44% of individual congeners exhibit significant correlation with water temperature ($p < 0.05$). The majority of these PCB congeners (80%) were also significantly correlated between the gas-phase and the freely-dissolved concentrations. Additionally, treated effluent from the CDF was discharged from March to September of 2017 (Thai, 2018), after which we observed an increasing trend in our concentrations of freely-dissolved PCBs (Fig. 1). Dredged sediment from the IHSC is disposed in the CDF next to the Lake George Branch, located up-stream of our sampling location. It is possible that both water temperature increase and the CDF discharges explain the trend in freely-dissolved water concentration. However, during our last deployment, we observed the highest measurement of freely-dissolved water concentration (Fig. 1), which is coincident with nearby dredging operations at the end of September of 2017 (Thai, 2018). Indeed, the concentration of freely-dissolved PCBs measured in the last deployment is 30% more than predicted from the temperature correlation of the remaining measurements. Although we cannot definitively conclude if the increasing trend of freely-dissolved PCBs is due to natural processes or activities associated with the navigational dredging, this trend drives an increase in gas-phase concentrations from the system over the course of the study year (Figs. 1 and 2).

Our 2006 measurements of the dissolved water phase of Σ PCB using active sampling (i.e., collected from pumping filtered water through XAD) were higher than our 2017 water measurements, ranging from 21 to 70 ng L⁻¹ (Martinez et al., 2010b). It is likely that the two sampling methods are not directly comparable because our passive sampling method using LDPE does not capture PCBs bound to DOC, whereas water samples collected from active sampling do. To account for this difference, we calculated the freely-dissolved phase obtained from the active sampling via XAD-2 resin from 2006 by subtracting the amount of PCBs bound to DOC, using a two-phase partitioning model [eq. (6)]:

$$C_{PCBi\ w} = C_{PCBi\ w^*} / (1 + [DOC] \times K_{PCBi\ DOC}) \quad (6)$$

where $C_{PCBi\ w^*}$ is the dissolved-phase concentration for the i th PCB (ng L⁻¹) measured using the active sampling (Martinez et al., 2010b), [DOC] is the water concentration of DOC (3.9 ± 1.0 mg L⁻¹) from Risch (2006), and $K_{PCBi\ DOC}$ is the partition coefficient between dissolved organic carbon and the freely-dissolved phase for the i th PCB ($K_{PCBi\ DOC} = 0.06 \times$ octanol-water partition coefficient for the i th PCB corrected by water temperature) from Burkhard (2006). Details of the calculations are presented in the supplementary data. We found a 20% reduction in the water measurements from the active samples from August 2006 when PCBs bound to DOC were removed, i.e., from 40 to 34 ng L⁻¹. We conclude that the difference is not an artifact of our sampling methods: The dissolved-phase concentrations are nearly 50% lower in 2017 than in 2006. This reduction suggests that sediment dredging from 2012 to 2017, control of upstream sources (Martinez et al., 2010b), or a combination of the two has effectively reduced the freely-dissolved water concentrations of PCBs in IHSC.

3.3. PCB congener profiles

As previously reported, the PCB congener distribution present in IHSC resembles the commercial mixture Aroclor 1248 (Martinez and Hornbuckle, 2011; Martinez et al., 2010a; Martinez et al., 2010b). The former refinery Atlantic Richfield CO, located next to the canal, discharged at least 1000 kg of Aroclor 1248 into the sewer system and directly into the environment in the early 1970s (Waller, 1971). More than 40 years later, our 2017 air and water samples still capture the Aroclor 1248 signature, with very small variability between individual air and water samples, and also high similarity between matrices (Fig. 4). To quantitatively estimate similarities between PCB congener profiles, we used $\cos \theta$. This metric uses the cosine of the angle between two multivariable vectors (the profiles) where a value of 1.0 describes two identical vectors and 0.0 describes two completely different (Magar et al., 2005). The average $\cos \theta$ between all the gas-phase and freely-dissolved samples yielded 0.9 ± 0.04 , whereas all the samples versus Aroclor 1248 yielded a $\cos \theta$ of 0.8 ± 0.05 . These results show the similarities between the sample profiles and Aroclor 1248.

3.4. PCB fugacity ratios

Individual PCB congener fugacity ratios indicate a tendency of the PCB congeners to volatilize from the water. The ratios (f_w/f_a) ranged from 0.8 to 850 for all the deployment times, with 99.9% of the (f_w/f_a) > 1. However, if the uncertainty of the air and water temperatures, Henry's Law Constant and analytical error are included into the Monte Carlo simulation, the outcome is different. Here, the fugacity ratio was >1 within a 95% confidence interval (95% CI) only 33% of the time, and 67% of the time it was not possible to determine if the (f_w/f_a) were above, below or equal to 1 with a 95% CI. For example, within the 95% CI, PCB18 always showed (f_w/f_a) > 1 for all the deployment times, PCB84 resulted in six deployments > 1, PCB144 had only two deployments > 1 and PCB203 never showed values > 1 (Fig. S2). Since both gas-phase and freely-dissolved concentrations exhibited a similar trend (Fig. 2), the fugacity ratios were generally constant and thus, no temporal trend was found for these ratios (Fig. S2).

3.5. PCB fluxes

Gross volatilization fluxes were at least 10 times higher than gross absorption fluxes of Σ PCBs, resulting in net volatilization fluxes of PCBs from IHSC (Fig. 5). Total PCB net fluxes ranged from 1.4 ± 0.2 to 2.8 ± 0.3 $\text{mgm}^{-2} \text{d}^{-1}$, with a median of $2.0 \mu\text{g m}^{-2} \text{d}^{-1}$ and an IQR of $1.5\text{--}2.1 \mu\text{g m}^{-2} \text{d}^{-1}$ (Fig. 5). Further, net volatilization fluxes doubled over the course of our study. This increase in fluxes was mostly due to the trend in the freely-dissolved water concentration (Fig. 1), which explained 87% of the variability of Σ PCB fluxes ($p < 0.0003$) (Fig. S3). Gas-phase and air and water temperatures also showed significant correlations with the net fluxes, but to a lesser extent (Fig. S3).

Individual congeners showed the same tendency towards volatilization as Σ PCBs, 90% of the time yielding net volatilization (>0) and only 10% of the time yielding net absorption (<0). Individual PCB congener net fluxes ranged from $-9.2 \times 10^{-5} \pm 7.9 \times 10^{-5}$ to $0.2 \pm 0.1 \mu\text{g m}^{-2} \text{d}^{-1}$ for PCB3 and PCBs18 + 30, respectively. On average, 30 individual PCB congeners contributed to more than 90% of the fluxes, mostly tri-, tetra- and

pentachlorobiphenyls (Fig. S4, b). Within a 95% CI, PCB congener fluxes yielded net volatilization 44% of the time, net absorption only 3% of the time, and 53% of the time it was not possible to determine the direction of the flux with certainty, i.e., the 2.5th and the 97.5th percentiles had a different sign for the same congener. As expected, these results are similar to what the fugacity ratios yielded. For example, PCBs18 + 30 always exhibited a net volatilization within a 95% CI, whereas PCB84 exhibited volatilization 56% of the time, but it was not possible to determine the direction of the fluxes 44% of the time. PCB144 yielded net volatilization flux only 11% of the time, but it was not possible to determine the direction of the fluxes 89% of the time. For PCB203, it was never possible to determine the direction of the fluxes (Fig. 6). Further, individual congener net fluxes yielded different temporal results. For example, PCBs18 + 30 and PCB144 did not show any temporal net flux trends, whereas PCB84 showed an increase in the fluxes and PCB203 a slight decrease with time (Fig. 6).

PCB net air-water fluxes from IHSC show a decrease since 2006. Net fluxes were recalculated using air and water samples collected in August 2006 nearby our 2017 sampling location (Martinez et al., 2010b). Because the 2006 water samples were collected via active sampling, a DOC correction to water samples was performed for a direct comparison with this study (see eq. (6)). Further, and as performed with our 2017 estimations, a Monte Carlo simulation was used to recalculate the net flux from August 2006. We found a reduction of ~60% of net Σ PCB fluxes from 5.0 ± 0.6 to $2.0 \pm 0.3 \mu\text{g m}^{-2} \text{d}^{-1}$ between August 2006 and 2017, which is in agreement with the calculated reduction in the freely-dissolved water concentration of PCBs from 2006 to 2017. As observed with the water concentration reduction, the sediment dredging from 2012 to 2017, the control of upstream sources (Martinez et al., 2010b), or a combination of the two has effectively reduced the net air-water PCB fluxes. We noticed that air and water temperatures and wind speed were very similar in August of 2006 and 2017, reducing the effect of these environmental conditions in the air-water exchange calculations and comparison.

Although the fluxes have decreased in the last decade, the area-normalized release of PCBs from the IHSC is still higher than has been reported elsewhere. For example, net fluxes from the Lower Duwamish Waterway, Washington, ranged from 0.06 to $0.09 \mu\text{g m}^{-2} \text{d}^{-1}$ (Σ_{27} PCBs) (Apell and Gschwend, 2017) and open waters from Lake Erie and Lake Ontario ranged from 0.002 to $0.009 \text{mg m}^{-2} \text{d}^{-1}$ (Σ_{29} PCBs) (Liu et al., 2016). Freely-dissolved Σ PCBs are lower in these systems than in the IHSC, and hence experience lower air to water fluxes.

4. Implications

Advantages of using a passive sampling approach compared to active sampling include: (i) increased mass collected to improve detection; (ii) reduced extraction and cleanup analytical steps; (iii) direct measurement of the freely-dissolved water concentrations, i.e., no correction of PCBs bound to DOC is needed; (iv) longer temporal measurements, which reduce the risk of missing episodic events and eliminate the need to extrapolate concentrations to estimate longer time period fluxes (Martinez et al., 2010b; Yan et al., 2008); and (v) eliminate the need for electrical power and specialized personnel to perform

the sampling. However, prudence should be taken when environmental concentrations are calculated from the mass of the chemical collected from passive sampler devices. Fortunately, existing web-based and GUI mathematical models are available to back-calculate environmental concentrations from masses collected from passive sampling devices (Apell et al., 2016; Herkert et al., 2018; Tcaciuc et al., 2015; Thompson et al., 2015). Currently, water passive sampling media such as LDPE still needs to be spiked with DCs; for PUF-PAS, if the sampling location is not common, e.g., above water or the location presents unusual high wind speed ($>10 \text{ m s}^{-1}$), DCs should also be spiked to verify/calculate sampling rates.

Although we did not set up our sampling campaign to evaluate air-water PCB fluxes changes due to sediment dredging and related activities, our results suggest a possible effect on the fluxes due to these activities. Therefore, more monitoring is needed, and a passive sampling approach is the most appropriate and efficient option.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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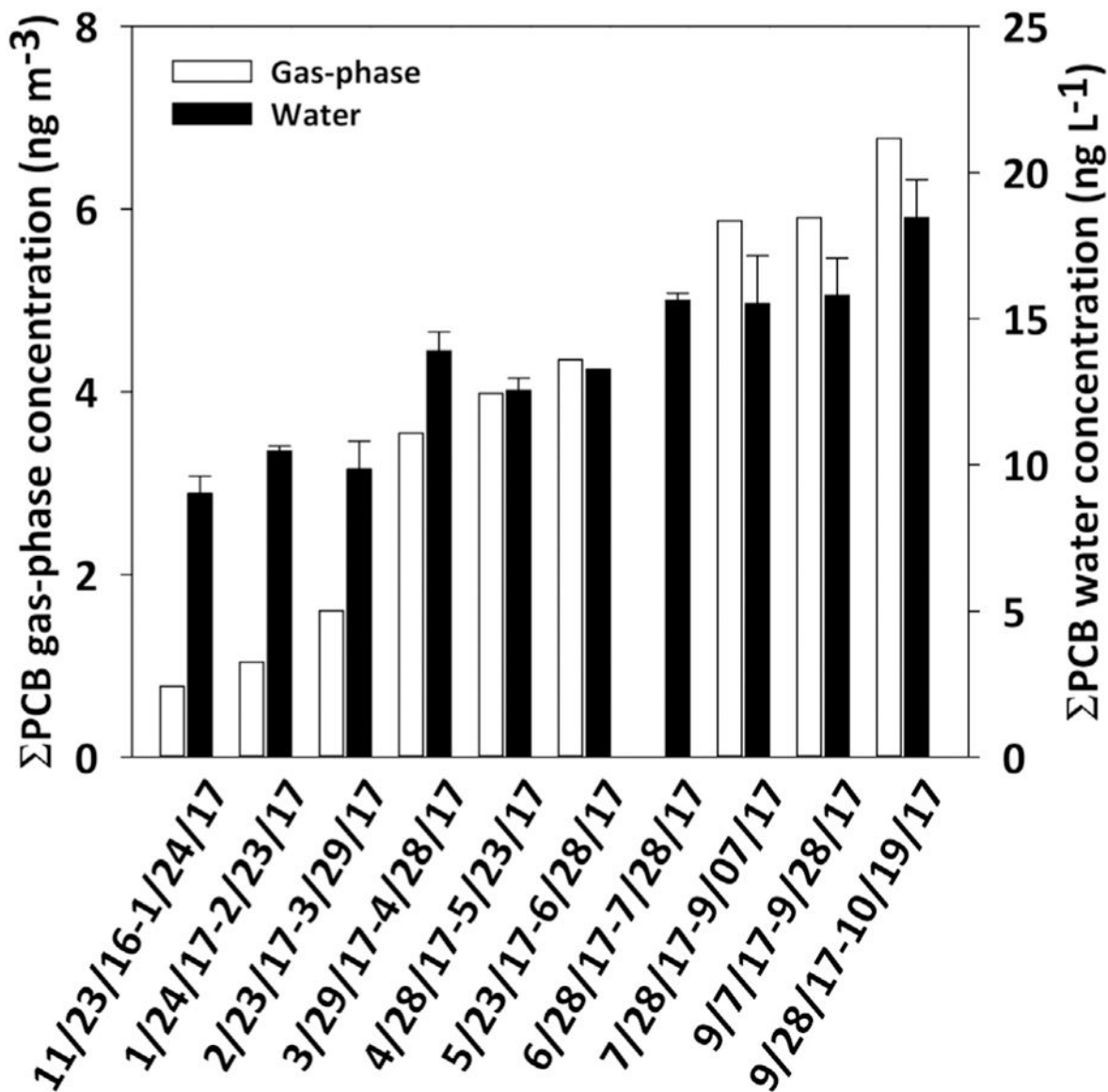


Fig. 1. Concentrations of gas-phase (white bars) and mean freely-dissolved water (black bars) of Σ PCBs at IHSC. X-axis indicates the deployment time. Errors bars from the freely-dissolved water bar plots represent the standard deviation of at least two samples collected at the same time. PUF-PAS from 6/28/17e7/28/17 was lost.

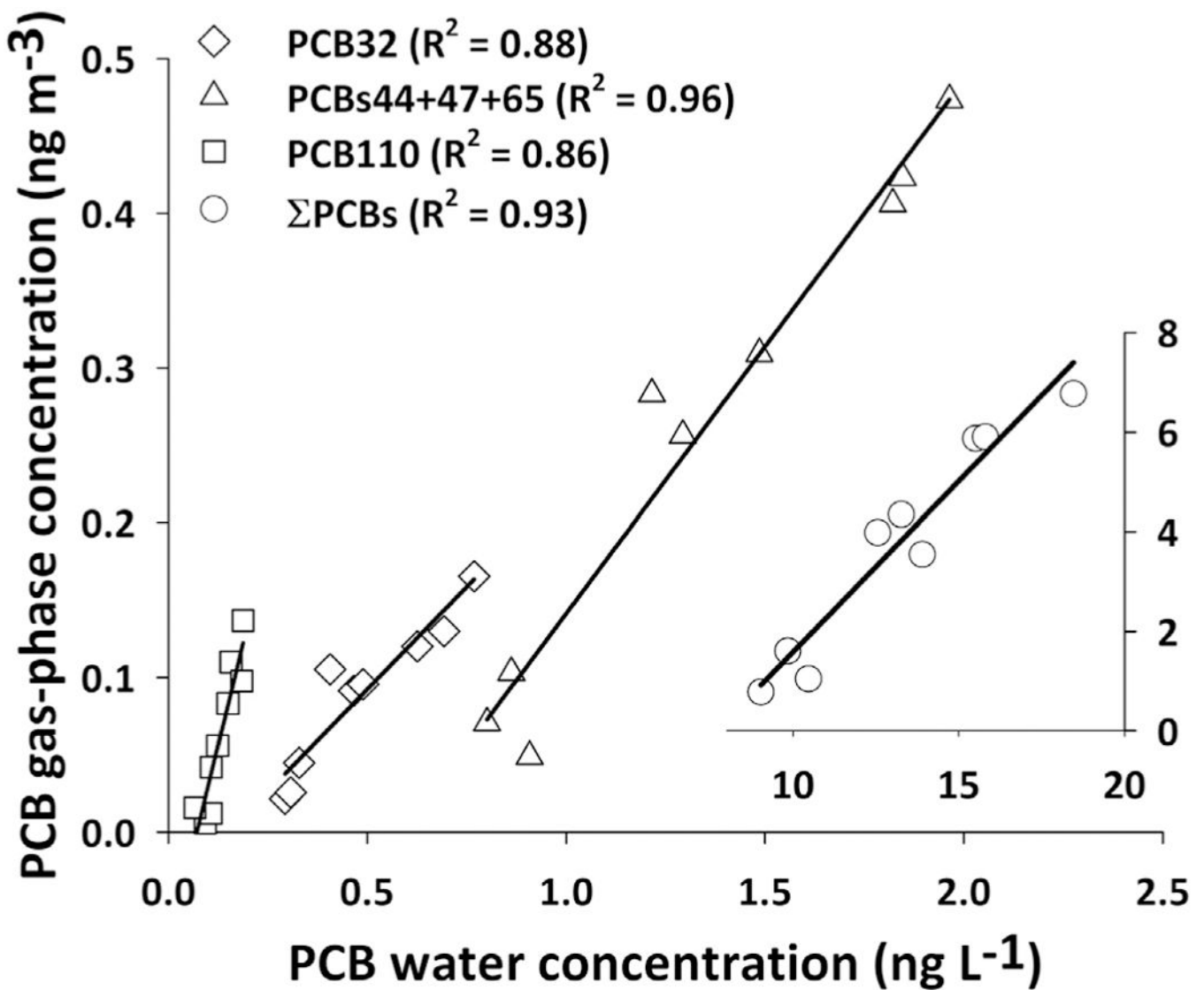


Fig. 2. Gas-phase and freely-dissolved water concentrations for Σ PCBs and selected congeners. Insert plot represents Σ PCBs. Data are from the nine deployments. All correlations are statistically significant ($p < 0.05$).

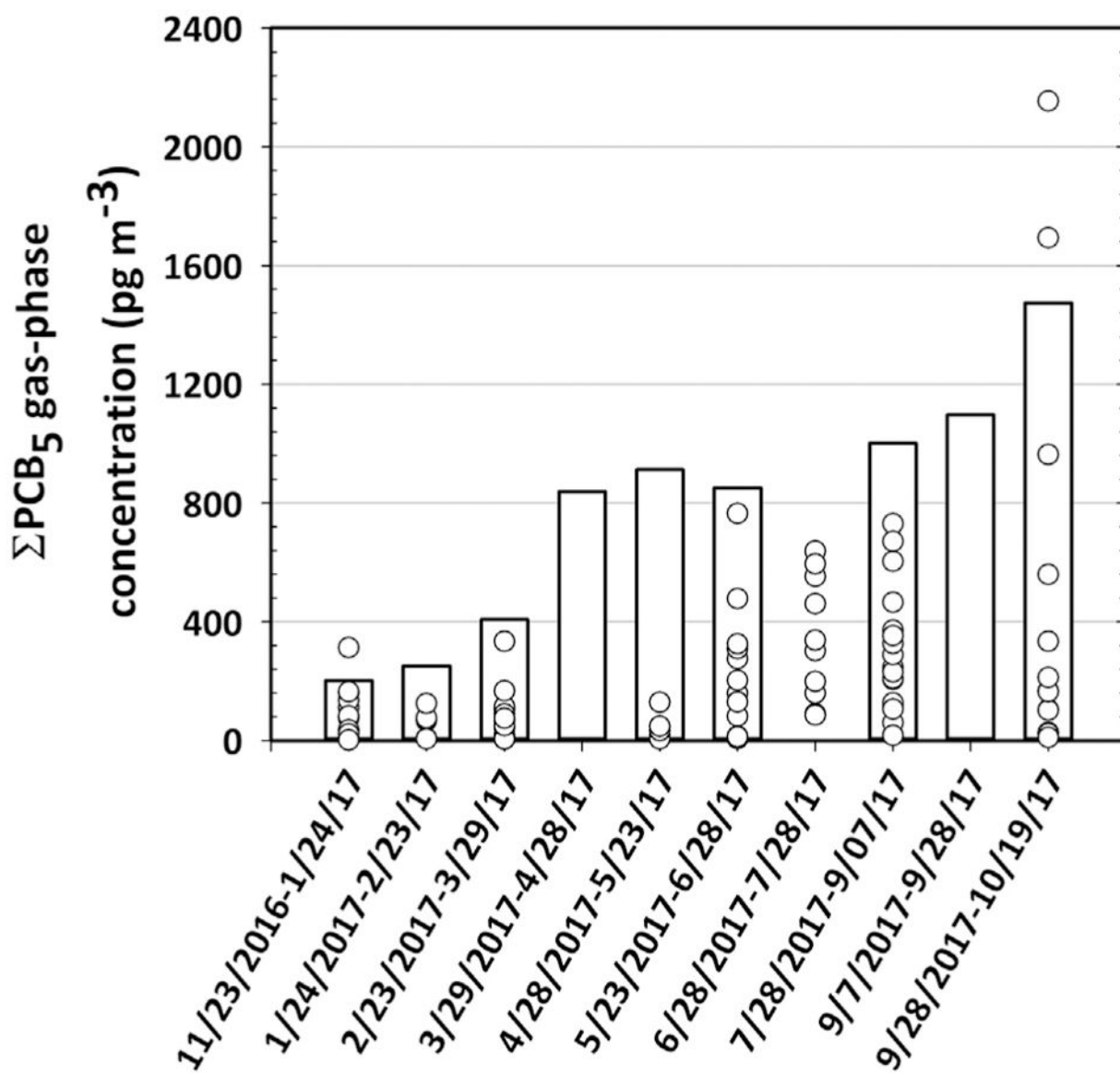


Fig. 3. Concentrations of gas-phase of ΣPCB_5 (i.e., PCBs8, 15, 18, 28 and 31) from our PUF-PAS samples (cyan bars) and active sampling from the Army Corps of Engineers (void circles). The active samplers were obtained from five locations nearby our sampling location. Source: <http://web.ead.anl.gov/inharbor/data/analysis/publicTables/index.cfm>.

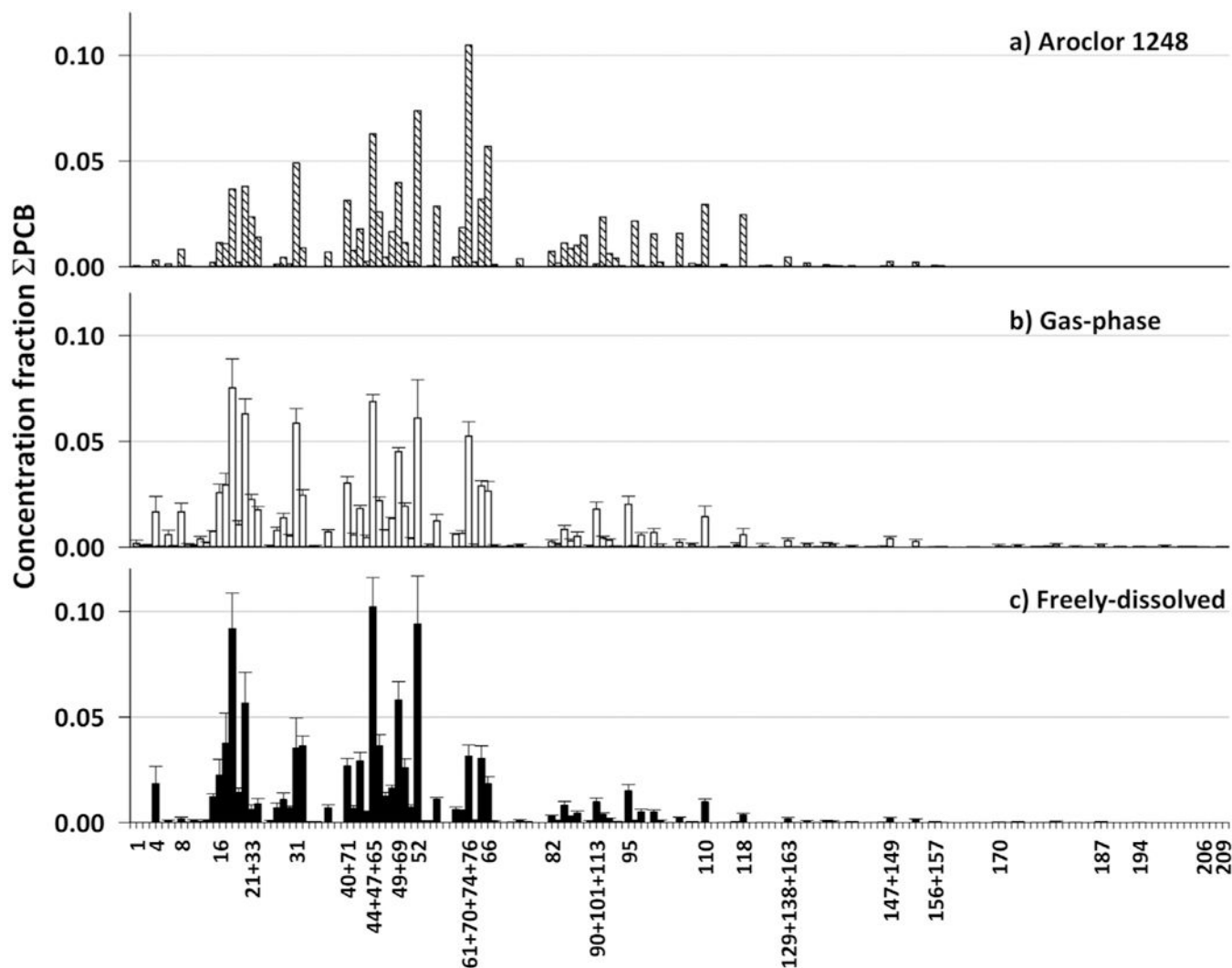


Fig. 4. Mean individual PCB congener profile of (a) Aroclor 1248, (b) gas-phase ($n = 9$) and (c) freely-dissolved samples ($n = 23$). Each congener was normalized to the total concentration of PCBs in the sample. The error bars represent one standard deviation above the mean.

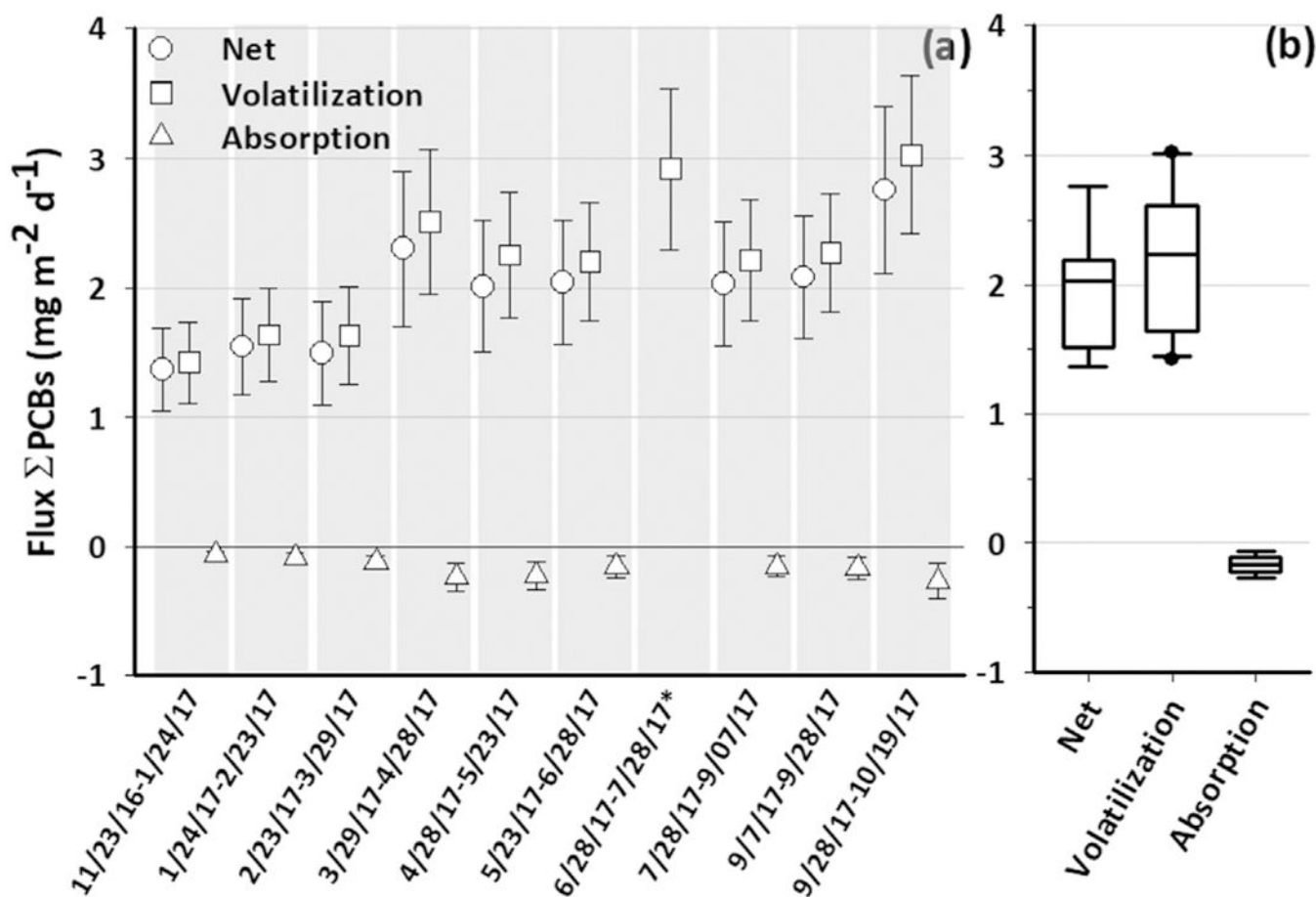


Fig. 5. Average net fluxes (grey circles), volatilization (cyan circles) and absorption (blue circles) of ΣPCBs in $\mu\text{g m}^{-2} \text{d}^{-1}$ for the sampling periods (a). Error bars in plot (a) represent the 2.5th and 97.5th percentiles calculated from the Monte Carlo simulations. Net and absorption from 6/28/17–7/28/17* were not calculated due to loss of air sample. Plot (b) summarizes the average net, volatilization and absorption fluxes for the ten sampling periods via box plots, describing from top to bottom the maximum, 75th percentile, median, 25th percentile and the minimum value.

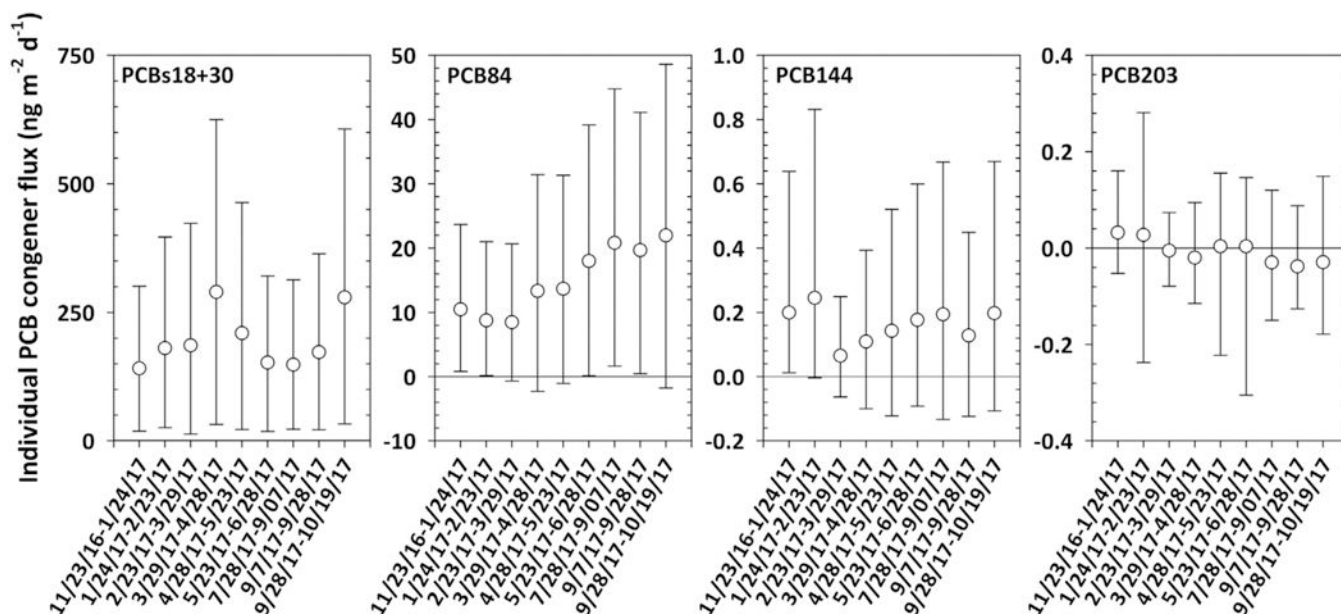


Fig. 6. Selected PCB congeners net fluxes (PCBs18 + 30, 84, 144 and 203) for the nine deployments. Void circles represent the measure values and the error bars represent the 2.5th and 97.5th percentiles (i.e., 95% confidence interval). Monte Carlo simulations were run 1000 times. Net flux from deployment 6/28/17–7/28/17 was not calculated due to loss of PUF sample. Please note the difference in the y-axis scales.