Quantitative analysis of 209 polychlorinated biphenyl (PCB) congeners in sediments of the Raritan River estuary, USA

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ABSTRACT

This study investigated the distribution of 209 polychlorinated biphenyl (PCB) congeners in sediment samples collected from seven sites in the Raritan River estuary (NJ, USA) using gas chromatography/tandem quadrupole mass spectrometry (GC/MS/MS). Results showed that concentrations of 209 PCB congeners ranged up to 20 ng/g, that total PCB concentrations by homolog groups varied from 9.0 to 327 ng/g, and that total PCB mass ranged from 101.0 to 1,476.3 ng with the order of sites $6 > 7 > 3 > 4 > 2 > 1 > 5$. Furthermore, higher PCB concentrations were detected for homolog groups including hexa- and hepta-PCBs. More PCBs were associated with sediments at downstream sites possibly due to accumulation and deposition in the estuary, as supported by strong correlations of PCB concentrations between different sampling sites ($R^2 \leq 0.96$). Comparisons with prior reports showed that all total PCB concentrations were below those reported by the Contamination Assessment and Reduction Project (CARP) and Delaware River Basin Commission (DRBC), except for sites 6 and 7. Sites 3 and 4 had PCB concentrations exceeding the 22.7 ng/g limit of the Sediment Quality Guidelines (SQGs), whereas sites 6 and 7 exceeded the 180 ng/g limit, indicating potential health hazards from PCBs.

Key words | analytical chemistry, congeners, GC/MS/MS, organic pollutant, polychlorinated biphenyls (PCBs), sediment contamination

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HIGHLIGHTS

- Sediment samples were collected from seven sites along the Raritan River for PCB analysis.
- Concentration and mass of 209 PCB congeners and homologs were analyzed using GC/MS/MS.
- Higher concentrations were found in sediments downstream and for hexa- and hepta-PCBs.
- Most total PCB concentrations at the seven sites were below those reported by CARP and DRBC.
- Sediments at sites 3, 4, 6, and 7 had PCB concentrations exceeding sediment guidelines.

GRAPHICAL ABSTRACT
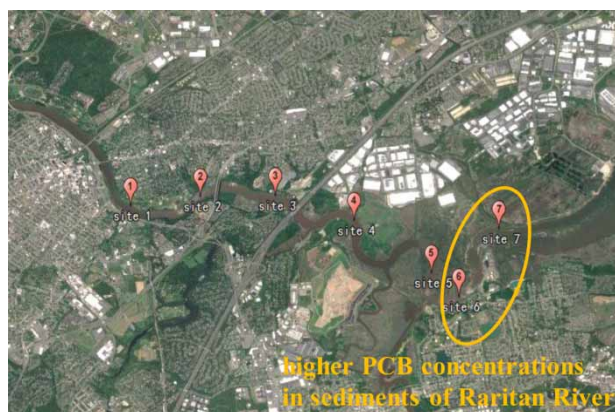
INTRODUCTION

The Raritan River basin is the largest river basin in New Jersey with a total area of 1,100 square miles and is divided into the North and South Branches (Amidon & Cosgrove 2006). It provides over one million people with water supply, recreation, and ways of transportation in seven counties nearby. The Raritan Estuary connects the Raritan Bay and ultimately the Atlantic Ocean. This unique location renders hydrodynamic complexity inherent to an estuary as the Raritan River has various daily tidal formations, continuous mixture of freshwater with seawater, and an average annual water discharge rate of $42.2 \, \text{m}^3/\text{s}$ (Chant 2006). Appropriate management and assessment of the aquatic environments along the Raritan River are necessary for protection of the surrounding ecosystem and human health (Dickerson *et al.* 2019).

Polychlorinated biphenyls (PCBs) had been used as a commercial product in dielectric fluids, flame retardants, and lubricating oils since the 1930s, with about 1.5 million tons of PCBs produced worldwide (Fiedler 2015). Due to their toxicity and persistence, PCBs were later banned in the 1970s (Zani *et al.* 2017). They were classified as probable human carcinogens and can cause non-cancer health effects in animals (EPA 1999a; WHO 2000). PCBs are an important group of persistent organic pollutants (POPs) and tend to accumulate in human organs (Hens & Hens 2018). Studies have shown that a high concentration of PCBs in the uterus is associated with long-term adverse impact on children's intellectual function (Jacobson & Jacobson 1997). PCB congeners may also induce neurodevelopmental changes that increase the risk of becoming addicted to tobacco and alcohol (Dickerson *et al.* 2019).

Most of the 209 congeners of PCBs have strong chemical and physical stability and are semi-volatile or non-volatile, lipophilic, and resistant to biodegradation. Attributed to the above physicochemical properties, PCBs are persistent non-point source (NPS) pollutants detected throughout environmental compartments including water, sediments, and biological tissues (Sapozhnikova *et al.* 2004; Tarola & Preti 2010). Specifically, their lipophilic and persistent properties render them easily adsorbed by sediments in the aquatic environment for decades. Since the Raritan River connects the Raritan Bay and ultimately the Atlantic Ocean, sediments are slowly washed out towards the estuary due to tidal flushing. As a result, PCBs adsorbed onto sediments likely transport with the sediments and accumulate along the estuary. In addition, water in the estuary closer to the ocean contains higher salinity, which induces the salting-out effect that further limits the solubility of PCBs and facilitates their adsorption onto sediments (Turner & Rawling 2001). Therefore, the amounts of PCBs present in the sediments of the Raritan River may be dependent upon the distance towards the estuary, where washouts

occur with tidal formation (Belton & Ruppel 1983). Considering the persistence and toxicity of PCBs as well as their strong tendency of association with sediments in aquatic environments, quantitative measurements for the concentrations of PCBs in sediments along the Raritan River are necessary for assessment of their potential risks.

The objective of this study was to quantify the concentrations of 209 PCB congeners in the sediment samples collected from seven sites in the Raritan River estuary for assessment of their potential environmental risks. The sampling sites were located at about 8 km upstream of Raritan Bay in Middlesex county of New Jersey and were under the influence of tides (Figure 1(a)). Gas chromatography/tandem quadrupole mass spectrometry (GC/MS/MS) was employed for the measurement of 209 PCB congeners, following the standard EPA method 1668A (EPA 1999b). Extraction, volume reduction, Florisil cleanup, and addition of internal standards were performed for the sediment samples before injection into the GC/MS/MS system for analysis. The recoveries of added surrogate standards and blanks were taken into consideration in the analysis. The results on the PCB congener concentrations were compared with the data reported by the Contamination Assessment and Reduction Project (CARP) and the Delaware River Basin Commission (DRBC) as well as sediment guidelines. The results from this study suggested that PCB contamination and accumulation existed in sediments of the Raritan River estuary especially at downstream sections.

METHODS

Sample collection

Samples were collected from sediments at seven sites along the Raritan River estuary (New Jersey, USA) The locations and corresponding geographic coordinates for the seven sampling sites are presented in Figure 1. Sediment samples were collected from the research vessel CALETA using a Ponar dredge sampler. This sampler only collected superficial sediment samples dredged up to six inches in depth. The top 2 cm of sediment was removed from the sampler and scooped into clean glass jars covered with aluminum-foil-lined lids.

### Accelerated solvent extraction

The accelerated solvent extraction for PCBs was conducted following the EPA method 3545A (EPA 1995). The sediments were air-dried for 24–48 h in hexane-rinsed aluminum dishes at room temperature. The dry sediment samples were weighed and grounded into fine powder before being loaded into extraction cells. Two PCB surrogates (PCB congeners d65 and d169) were added into each extraction cell before filling the void volume with baked sea sand. The extraction cells were placed into the autosampler tray and a precleaned collection vessel was placed in the instrument for each sample. The extraction of PCBs was carried out at 100 °C and 2,000 psi using a mixture of methylene chloride/hexane (25:75, v/v) as the solvent and a flush volume 60% of the extraction cell volume. Samples were subjected to a 5-min static extraction and two static cycles. The extraction was started and then collected in clean vials.

Volume reduction and solvent exchange

The collected extracts were concentrated from ~30 mL to about 3–5 mL under gentle nitrogen gas flow and then transferred to 10 mL amber vials by rinsing the extract vials with hexane. The extracts were further concentrated to 0.5 mL under gentle nitrogen flow, and 100 mL of deuterated PCB internal standards (200 ng/mL) including d30 and d116 were injected into the samples prior to the instrumental analysis.

Florisil cleanup

Clean Florisil was baked at 550 °C for at least 4 h for activation to burn off contaminating organics and volatiles. The Florisil was placed in a drying oven for ~30 min and then a desiccator, after which it was allowed to cool to room temperature. Then 8.0 g weighed Florisil was added into each screw-top test tube for each sample. For Florisil deactivation, 200 mL (2.5% by weight) Milli-Q water was added to each test tube and shaken for 15 min. The chromatography column with glass wool in the bottom, stopcock, and glass tip was assembled and pre-rinsed by dichloromethane and then by petroleum ether, and 2.5% deactivated Florisil was put into the column and covered with ~1 cm sodium sulfate. The column was eluted with
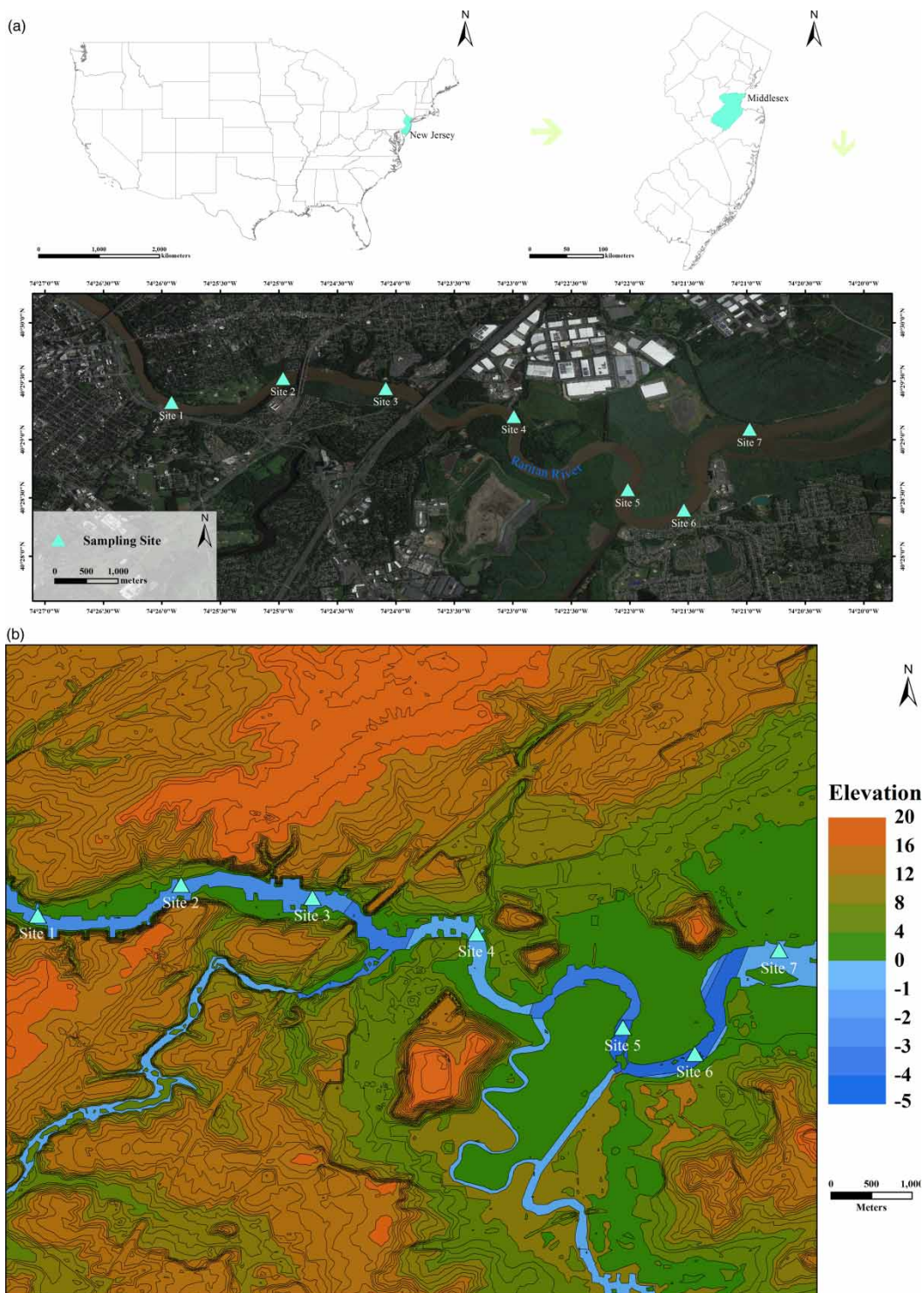
Figure 1 │ (a) Locations of sampling sites 1 to 7 for the collection of sediment samples along the Raritan River (New Jersey, USA). The geographic coordinates of the seven sampling sites are: site 1 (40°29′15.75″ N 74°25′42.33″ W), site 2 (40°29′31.20″ N 74°24′55.98″ W), site 3 (40°29′24.40″ N 74°23′56.66″ W), site 4 (40°29′12.66″ N 74°23′1.65″ W), site 5 (40°28′39.91″ N 74°21′58.00″ W), site 6 (40°28′21.99″ N 74°21′34.52″ W), and site 7 (40°29′5.25″ N 74°21′9.80″ W). (b) Bathymetry chart in the vicinity of the Raritan River based on digital elevation model (DEM) data of Advanced Land Observing Satellite (ALOS) image as generated by cartographic processing. The underwater and ground bathymetry contours were at 1 and 2 m intervals, respectively.

addition of 35 mL petroleum ether/dichloromethane (50:50, v/v). As the solvent reached the top of the sodium sulfate, 35 mL petroleum ether was introduced until it reached the top of the sodium sulfate again. A solvent-rinsed 125 mL round-bottom flask labeled as F1 was placed under the column to collect all PCBs. A sample (~1 mL in hexane) was pipetted onto the top of the sodium sulfate and the vial was rinsed three times. As the solvent reached the top of the sodium sulfate, 35 mL petroleum ether was added to the column until it reached the top of the sodium sulfate again. The F1 flask was then removed from beneath the column and capped with a stopper. A solvent-rinsed 125 mL round-bottom flask labeled as F2 was placed under the column and 50 mL petroleum ether/dichloromethane (50:50, v/v) was added. All solvents were allowed to elute before the F2 round-bottom was removed from beneath the column and capped with a stopper. The cleaned Florisil was allowed to dry overnight in the hood.

GC/MS/MS analysis

The extracts were reduced to around 3 mL with a rotary evaporator and were further concentrated to ~0.5 mL under nitrogen gas. Internal standards were injected into the samples. A method similar to EPA method 1668A (EPA 1999b) was used to measure the concentrations of 209 PCB congeners. The quantitative congener-specific PCB analysis was performed for each standard and sample with tandem quadrupole GC/MS/MS (6890 GC/7010B quadrupole MS, Agilent Technologies, USA). In the GC compartment, the sample was vaporized and injected into the chromatographic column and was separated into many components due to the difference in adsorption equilibrium between the gas mobile phase and the stationary phase. The tandem mass spectrometry (MS/MS) then performed multiple steps of mass spectrometry selection based on the mass/charge ratio of the ionized gas molecules of the analytes to detect PCB congeners. The samples were measured with an analytical column (30 ± 5 m, 0.25 ± 0.02 mm, 0.25 μm) with the following consecutive temperature program (Somoano-Blanco et al. 2015): start at 70 °C, then ramp at 7 °C/min to 180 °C, 1.05 °C/min to 225 °C, 5.75 °C/min to 285 °C, and then 11.5 °C/min to 300 °C and hold for 8 min. To achieve a maximum sensitivity, the two most common isotopes (M^+ and $(M + 2)^+$) were quantified via the total ion current; the detection limits were ~80–160 pg per passive sample for a lowest concentration peak with S/N ratio of 3; the detector response range showed linearity with $R^2 > 0.999$, indicating a high level of reproducibility.

The GC/MS/MS operation parameters for the analysis of PCBs are presented in Table 1. The MS operating conditions were as follows: the temperature of the transfer line was held at 250 °C during the chromatographic run. The electron ionization (EI) source was operated at 200 °C with an electron energy of 70 eV and a trap current of 100 A. The multiple reaction monitoring (MRM) mode was operated at an argon collision gas pressure of 3.0×10^{-3} mbar.

Table 1 | GC/MS/MS operation parameters for the analysis of PCBs

Function	PCB homolog	Start time (min)	End time (min)	Parent ion (m/z)	Daughter ion (m/z)	Dwell (s)	Collision energy (eV)
1	mono-	15	32	188 + 190	153	0.05	15
2	di-	15	32	222 + 224	152		
3	tri-	23	42	256 + 258	186		
4	tetra-	32	55	289.9 + 291.9	220		
5	penta-	34	65	323.9 + 325.9	254		
6	hexa-	49	75	359.8 + 361.8	289.90		
7	hepta-	58	75	393.8 + 395.8	323.90		
8	octa-	64	76	429.8 + 431.8	360.0		
9	nona-	69	77	463.7 + 465.7	394.0		
10	deca-	77	90	497.7 + 499.7	428		

Data analysis

The four-point calibration curves were constructed to calculate the relative response factor (RRF). For each PCB congener, a four-point linear calibration curve was plotted using the area and mass for four standards at different concentrations measured in each analytical run, and the slope of the curve was calculated as $RRF_{standard}$ (Equation (1)):

$$RRF_{standard} = \left(\frac{A_{congener}}{A_{IS}}\right)_{standard} \div \left(\frac{m_{congener}}{m_{IS}}\right)_{standard} \tag{1}$$

where $\left(\frac{A_{congener}}{A_{IS}}\right)_{standard}$ is the area ratio between the PCB congener and internal standard in the calibration standard; and $\left(\frac{m_{congener}}{m_{IS}}\right)_{standard}$ is the mass ratio between the PCB congener and internal standard in the calibration standard. Samples with concentration outside the range of calibration standards were diluted or concentrated as needed. The R^2 for the four-point standard calibration curves had an average of 0.99.

The mass of PCB congener in the sample (m_{sample}) was calculated with Equation (2):

$$m_{sample} = (m_{IS})_{sample} \times \left(\frac{A_{congener}}{A_{IS}}\right)_{sample} \div RRF_{standard} \tag{2}$$

where $(m_{IS})_{sample}$ is the mass of internal standard in the sample (ng); and $\left(\frac{A_{congener}}{A_{IS}}\right)_{sample}$ is the area ratio between the PCB congener and internal standard in the sample. For PCB analysis, congeners eluting before PCB d116 were quantified with internal standard PCB d30; whereas congeners eluting after PCB d116 were quantified with internal standard PCB d116.

The surrogate recovery for surrogate 1 (PCB d65) and surrogate 2 (PCB d159) was calculated with Equation (3):

$$\text{surrogate recovery} = (m_{surrogate})_{sample} \div 20 \tag{3}$$

The corrected mass of PCB congener (ng) was calculated by the ratio between the mass of PCB congener in the sample (Equation (2)) and the surrogate recovery (Equation (3)) as shown in Equation (4):

$$\text{corrected mass} = (m_{congener})_{sample} \div \text{surrogate recovery} \tag{4}$$

The corrected concentration of PCB congener (ng/g) was then calculated by dividing the corrected mass of PCB congener (ng) by the dry weight of sediment sample (g) (Equation (5)):

$$\text{corrected concentration} = \frac{\text{corrected mass}}{\text{dry weight}} \tag{5}$$

The sum of corrected mass (ng) for each homolog group of PCB congeners based on the number of chlorine atoms on PCBs was calculated for each sample, which was reported as mono-PCBs to deca-PCBs.

RESULTS AND DISCUSSION

209 PCB congeners in sediment samples

PCBs have been detected in all sediment samples collected at seven sampling sites along the Raritan River estuary. Figure 2 shows the corrected concentrations of 209 PCB congeners in sediment samples collected from sampling sites 1 to 7. The concentrations of 209 PCB congeners ranged up to 1 ng/g for sites 1 and 2, 10 ng/g for site 3, 3 ng/g for site 4, 1 ng/g for site 5, and 20 ng/g for sites 6 and 7. The order of the 209 PCB congener concentrations for the sites generally followed sites 6 > 7 > 3 > 4 > 5 > 1 > 2. In general, this trend suggested that the concentrations of the 209 PCB congeners in sediment samples increased in the direction of the estuary mouth.

As the Raritan River flows towards the estuary environment and ultimately the Atlantic Ocean, referring this trend to the sampling locations in Figure 1 indicated that more PCB congeners were present in the downstream sites of the Raritan River estuary. This phenomenon may be attributed to the accumulation of PCBs on the sediments in the downstream sites. As PCBs are highly hydrophobic and persistent against degradation, they tend to associate with
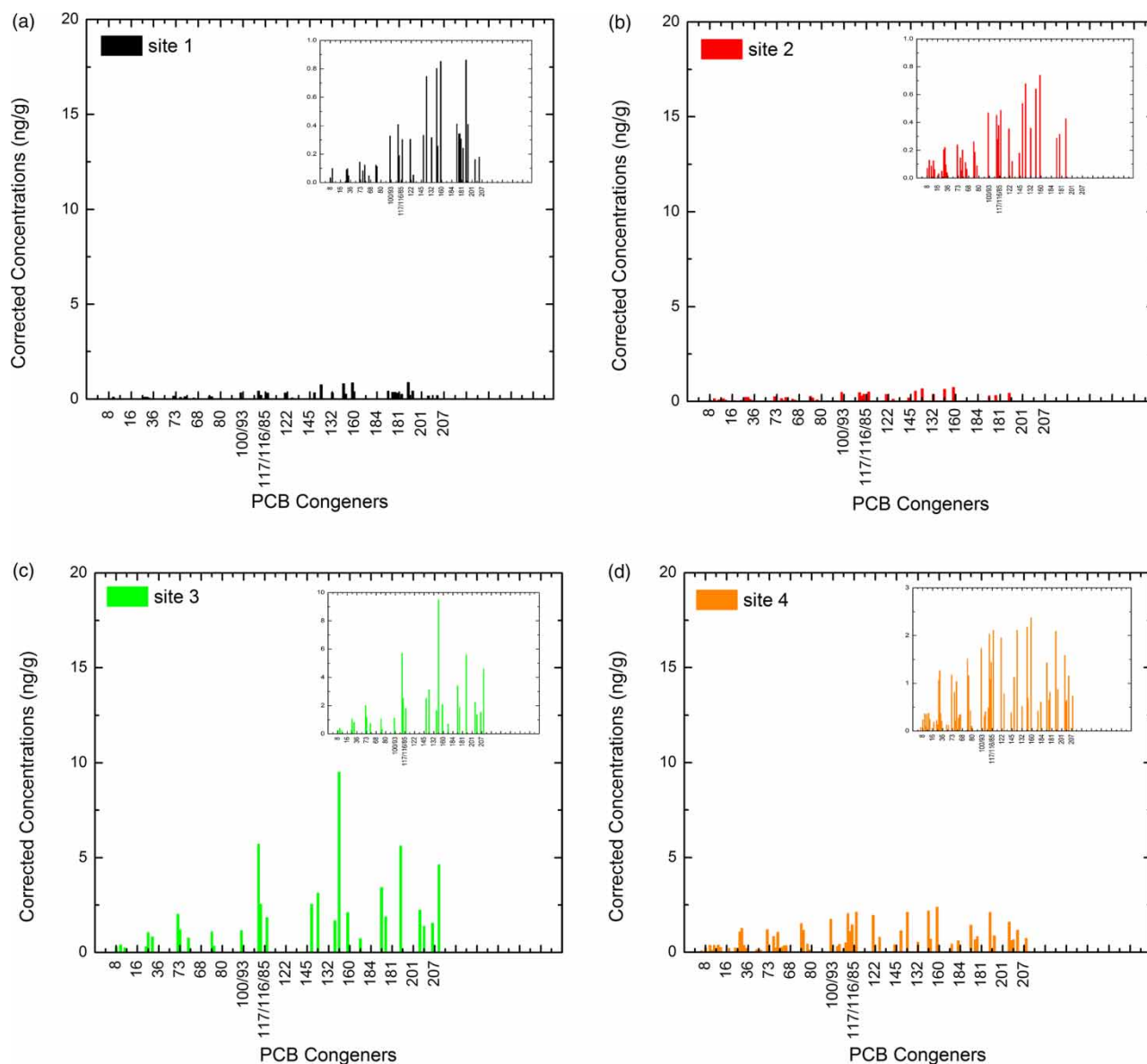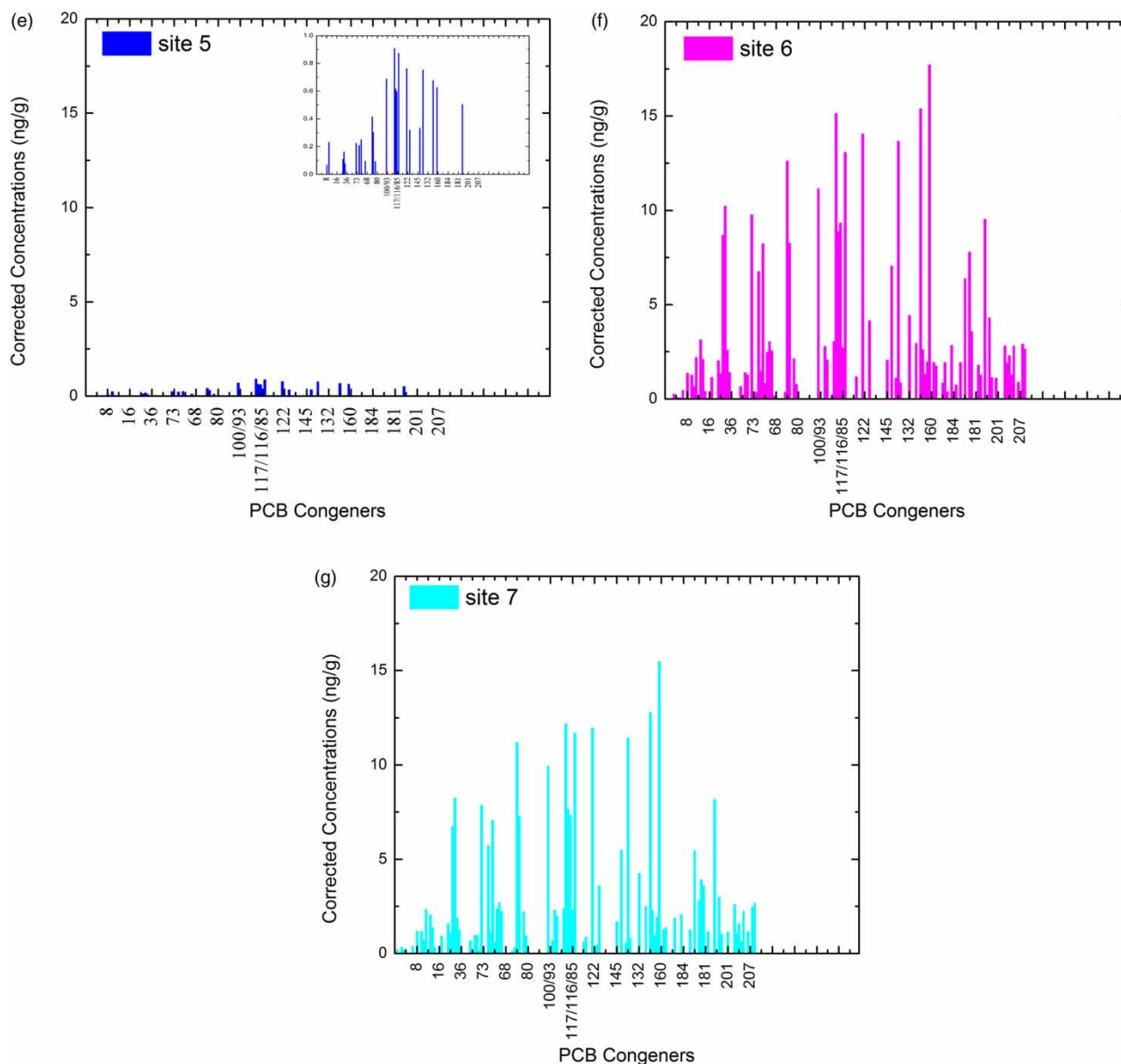
Figure 2 | Corrected concentrations for 209 PCB congeners in sediment samples at sampling sites 1 to 7 along the Raritan River. All *y*-axes are shown with scale up to 20 ng/g for comparison of PCB concentrations, with the insets of some site graphs showing at smaller scales. *(Continued.)*

sediments in surface water instead of the water column (EPA 1999b). The wider opening of the stream as well as more tidal formation along the Raritan River would wash the sediments downstream. The older sediments flowing from upstream to downstream likely attached and accumulated more PCBs. In addition, in estuarine environments where salinity and ionic strength increase compared with freshwater, the hydrophobic PCBs would more likely precipitate on sediments than stay in the hydrophilic water

column (Pavlou & Dexter 1979; Fikslin & Suk 2003). As a result, this study detected more PCBs in sediment samples in the downstream of the Raritan River.

Another trend can be observed from Figure 2, that higher concentrations for the 209 PCB congeners generally appeared in the middle of the congener numbers for sediment samples collected at all seven sites. In addition, lower PCB congeners mostly showed the lowest PCB concentrations in sediments. For further investigation, the

Figure 2 | Continued.

PCB concentrations were reported according to the homolog groups of PCBs, as demonstrated next.

PCB homologs in sediment samples

Table 2 presents the corrected concentrations of homolog PCBs from mono-PCBs to deca-PCBs at the seven sampling sites, with the corresponding average and total concentrations reported. Comparisons of the total PCB concentrations among the seven sampling sites showed that sediments at sites 6 and 7 were the most seriously contaminated with PCBs, which is consistent with the results observed earlier in Figure 2. The total PCB concentrations in sediment samples ranged from 9.0 ng/g at site 1 to 327 ng/g at site 6. The flow rate slowed down from site 2 to site 3 as the river gradually broadened (Figure 1(a)), which likely caused an increase of PCB concentrations from 9.2 to 60.2 ng/g (Table 2) (Zhao et al. 2016). Similarly,

Table 2 │ Corrected concentration, total corrected mass, and surrogate recovery of PCBs for sediment samples collected at the seven sampling sites and data reported by the Contamination Assessment and Reduction Project (CARP) and Delaware River Basin Commission (DRBC)

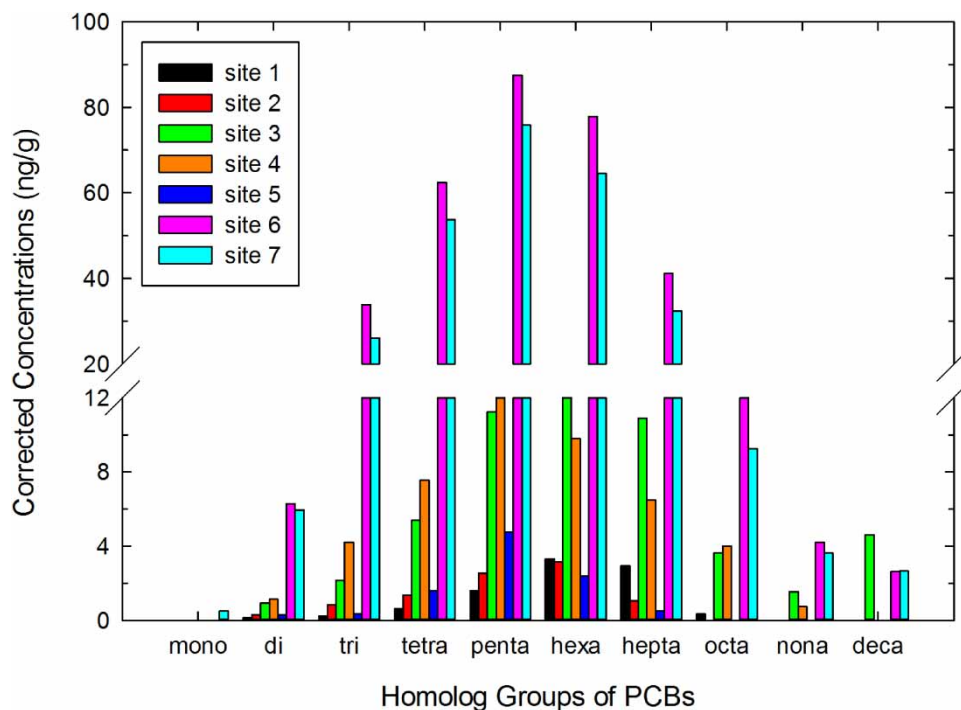| | | Sampling site | | | | | | | | | |
	PCBs	1	2	3	4	5	6	7	Average	CARP[a]	DRBC[b]
Corrected concentration (ng/g)	mono-	0	0	0	0	0	0	0.5	0.071	1.5	
	di-	0.1	0.3	0.9	1.1	0.3	6.3	6.0	2.1	17	
	tri-	0.2	0.8	2.2	4.2	0.4	34	26	9.7	63	
	tetra-	0.6	1.4	5.4	7.5	1.6	62	54	19	130	
	penta-	1.6	2.6	11	12	4.8	87	76	28	99	
	hexa-	3.3	3.1	20	9.8	2.4	78	65	26	73	
	hepta-	2.9	1.0	11	6.5	0.5	41	32	14	37	
	octa-	0.3	0	3.6	4.0	0	12	9.2	4.2	11	
	nona-	0	0	1.5	0.7	0	4.2	3.6	1.4	3.3	
	deca-	0	0	4.6	0	0	2.6	2.7	1.4	2.3	
	Total	9.0	9.2	60.2	45.8	10.0	327	275	105	437	120
	PCB 11	0.10	0.13	0.40	0.36	0.23	1.3	1.2	0.52	2.9	0.12
Total corrected mass (ng)		110.4	119.2	333.2	290.4	101.0	1,476.3	1,208.4			
Surrogate recovery (%)	PCB d65	57	61	54	60	65	76	67	63		
	PCB d159	84	71	55	77	57	69	73	69		

[a]Litten (2003).
[b]Fikslin & Suk (2003).

the sharp increase of PCB concentrations from site 5 (10.0 ng/g) to site 6 (327 ng/g) may be related to the morphodynamics of the estuary. As shown in the bathymetry chart (Figure 1(b)), the water depths at these two sites increased dramatically compared with nearby environments. Meanwhile, the transition of river flow direction at site 6 likely induced deposition of sediments and thus accumulation of PCBs (Figure 1(a)). The comparisons of the average PCB concentrations by homolog groups indicated that the congeners including tetra-, penta-, hexa-, and hepta-PCBs accounted for higher PCB concentrations than other homolog groups. Specifically, the penta- and hexa-PCBs generally accounted for the highest PCB concentrations in sediment samples collected from all sites.

The concentration distributions for PCB homologs among the seven sites are plotted in Figure 3. Similar trends were observed that sites 6 and 7 contained the greatest concentrations of PCBs, except that site 3 contained the greatest PCB concentration (deca-PCBs). Consistent with Figure 2 and Table 2, the PCB concentrations also increased towards the homolog groups in the middle, with the greatest concentration observed for penta-PCBs at site 6 (87 ng/g). Note that no mono-PCBs were detected

in sediment samples at sites 1–6 and that site 7 also only contained 0.5 ng/g, which could be because lower PCB congeners were less hydrophobic, less persistent, and more volatile so that they were less likely to be attached to sediments (Fiedler 2015).

Table 2 also shows that the total corrected mass of PCBs in sediment samples at the seven sites ranged from 101.0 to 1,476.3 ng. Generally consistent with the order of 209 PCB congener concentrations among the seven sites as described in the last section, here the order of total corrected mass of PCBs followed the order of sites 6 > 7 > 3 > 4 > 2 > 1 > 5. Only the orders between sites 2 and 5 were switched comparing with the orders of congener concentrations above. This should be attributed to the difference in mass of sediments as the corrected concentration was normalized from corrected mass by dry weight of sediments (Equation (5)). The ratio between the highest mass (site 6) to the lowest mass (site 5) was 14.6, which was slightly higher than the ratio between the highest concentration (site 6) to the smallest concentration (site 1) of 13.0. Nevertheless, both the concentration and mass results indicated that sites 6 and 7 had the most serious contamination of PCBs in sediments of the Raritan River estuary.

Figure 3 | Distribution of corrected concentrations (ng/g) of PCBs by homologs in sediment samples collected at seven sampling sites along the Raritan River.

Comparison with reports and guidelines

Table 2 shows the comparison of the measured concentrations for PCB homolog groups in the Raritan River sediments with previous reports, including the CARP (Litten 2003) data for PCB concentrations in the New York/New Jersey Harbor Estuary and the DRBC (Fikslin & Suk 2003) data for PCB concentrations in the Delaware River. All average concentrations among the seven sampling sites for PCB homolog groups were lower than the CARP data. However, eight PCB homolog concentrations have exceeded the CARP data: hexa-, hepta-, and octa-PCBs at site 6, nona-PCBs at sites 6 and 7, and deca-PCBs at sites 3, 6, and 7. It can be seen that among all sampling sites, site 6 contained the most PCB homologs with concentrations greater than the CARP data. This result also corresponds to previous sections in this study that site 6 had the greatest PCB contamination.

The total concentrations of all PCB congeners at each sampling site could be compared with those reported by CARP and DRBC (Table 2). All these values at the seven sampling sites were lower than the total PCB concentrations reported by CARP. However, the total PCB concentrations

at sites 6 (327 ng/g) and 7 (275 ng/g) exceeded the DRBC value (120 ng/g), while other sites had total PCB concentrations below that reported by DRBC. The average value for the total PCB concentrations at the seven sampling sites was 105 ng/g, which was four times lower than the data reported by CARP (437 ng/g) but was close to that reported by DRBC (120 ng/g). Both the Raritan River and the Delaware River are connected to the ocean and have a downstream estuary section, where river discharges and tides influence the hydrodynamics and sediment transport. Therefore, the similarity of PCB concentrations in these two estuaries may be attributed to the proximity between the basins and eventually to the pollutant sources (Fikslin & Suk 2003). The observed PCB concentration gradients, once PCBs are adsorbed to sediments, should be related mainly to sediment dynamics. Sediment transport patterns in an estuarine system are very complex with a succession of depositional areas and erosional areas. As shown in Figure 1(a), site 7 is located near an estuarine section where deposition dominates with the presence of islands. Comparing the bathymetry chart (Figure 1(b)) with the sampling site map (Figure 1(a)) further confirms the greatest water depth at sites 6 and 7 where deposition most likely

occurs, resulting in the differences between the PCB concentrations detected along the sampling sites (Chant 2020).

Other than PCB homolog groups, the concentrations of PCB 11 detected at the seven sampling sites could be compared with those reported by CARP and DRBC (Table 2). Consistent with the above comparison results, the PCB 11 concentrations in sediments collected from all seven sites were lower than the corresponding CARP data (2.9 ng/g). However, only the sediments at site 1 had slightly lower PCB 11 concentration than the DRBC level, while the other six sites had up to ~10 times more serious contamination by PCB 11 compared with the Delaware River.

According to the Sediment Quality Guidelines (SQGs) (Burton 2002), 18.5%, 40.8%, and 51% of people may experience adverse health effects from PCBs if the concentrations in sediments are above 22.7 ng/g, up to 180 ng/g, and above 180 ng/g. Comparison of the analysis results for PCB concentrations in the Raritan River estuary (Table 2) with this guideline shows that sites 3 and 4 had PCB concentrations exceeding the 22.7 ng/g limit, whereas sites 6 and 7 exceeded the 180 ng/g limit, which are indicative of potential health hazards from PCBs.

Correlation of PCB concentrations between sampling sites

The linear correlations of PCB concentrations between different sampling sites were examined, with those having $R^2 > 0.6$ plotted in Figure 4. Among the 21 total correlations between two sites, 13 correlations were found that had relatively strong linear correlations with $R^2 > 0.6$ as shown in Figure 4. The strongest correlation was observed between sites 6 and 7 with R^2 of 0.96 (Figure 4(h)). It
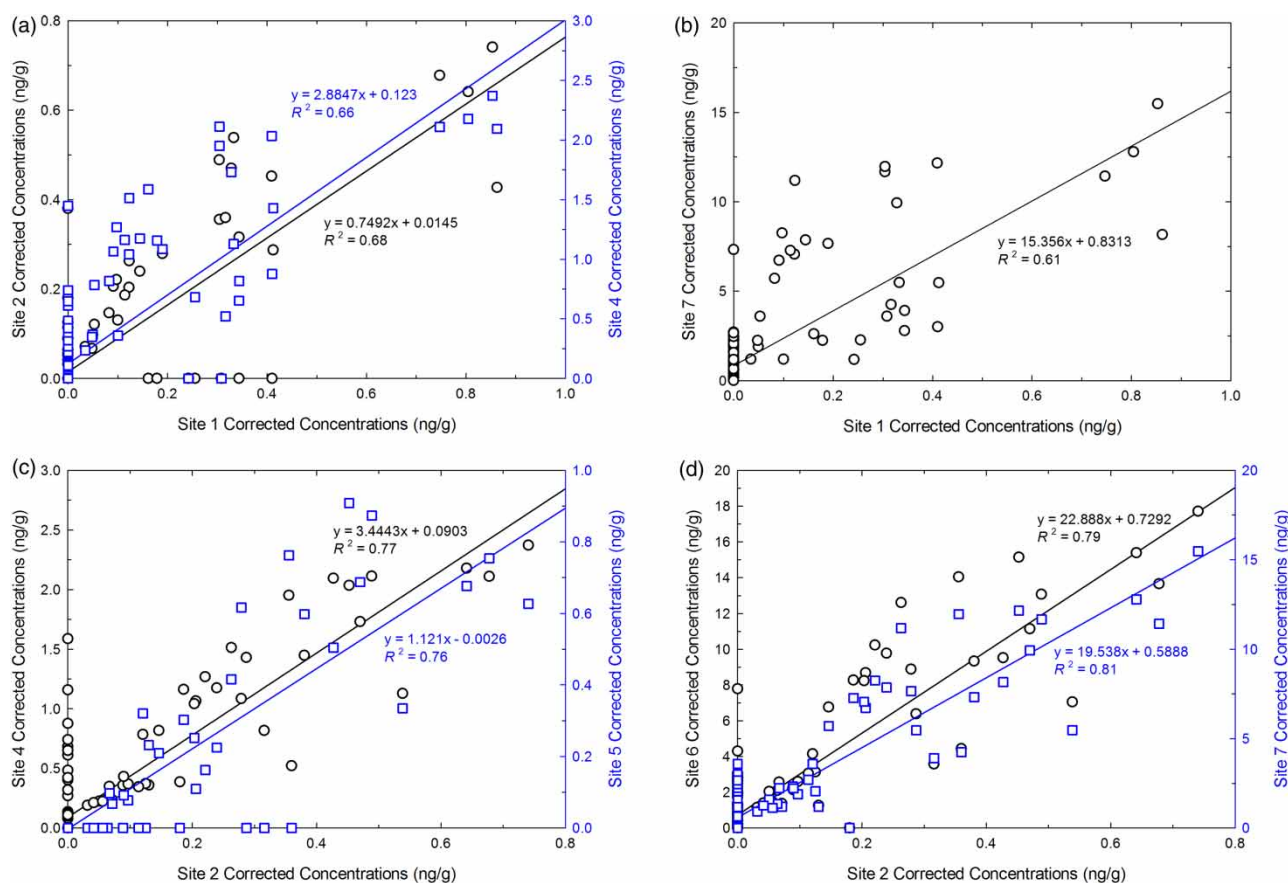
Figure 4 | Linear correlation of PCB concentrations between different sampling sites with $R^2 > 0.6$: (a) site 1 vs sites 2 and 4, (b) site 1 vs site 7, (c) site 2 vs sites 4 and 5, (d) site 2 vs sites 6 and 7, (e) site 4 vs sites 5 and 6, (f) site 4 vs site 7, (g) site 5 vs sites 6 and 7, and (h) site 6 vs site 7. *(Continued.)*
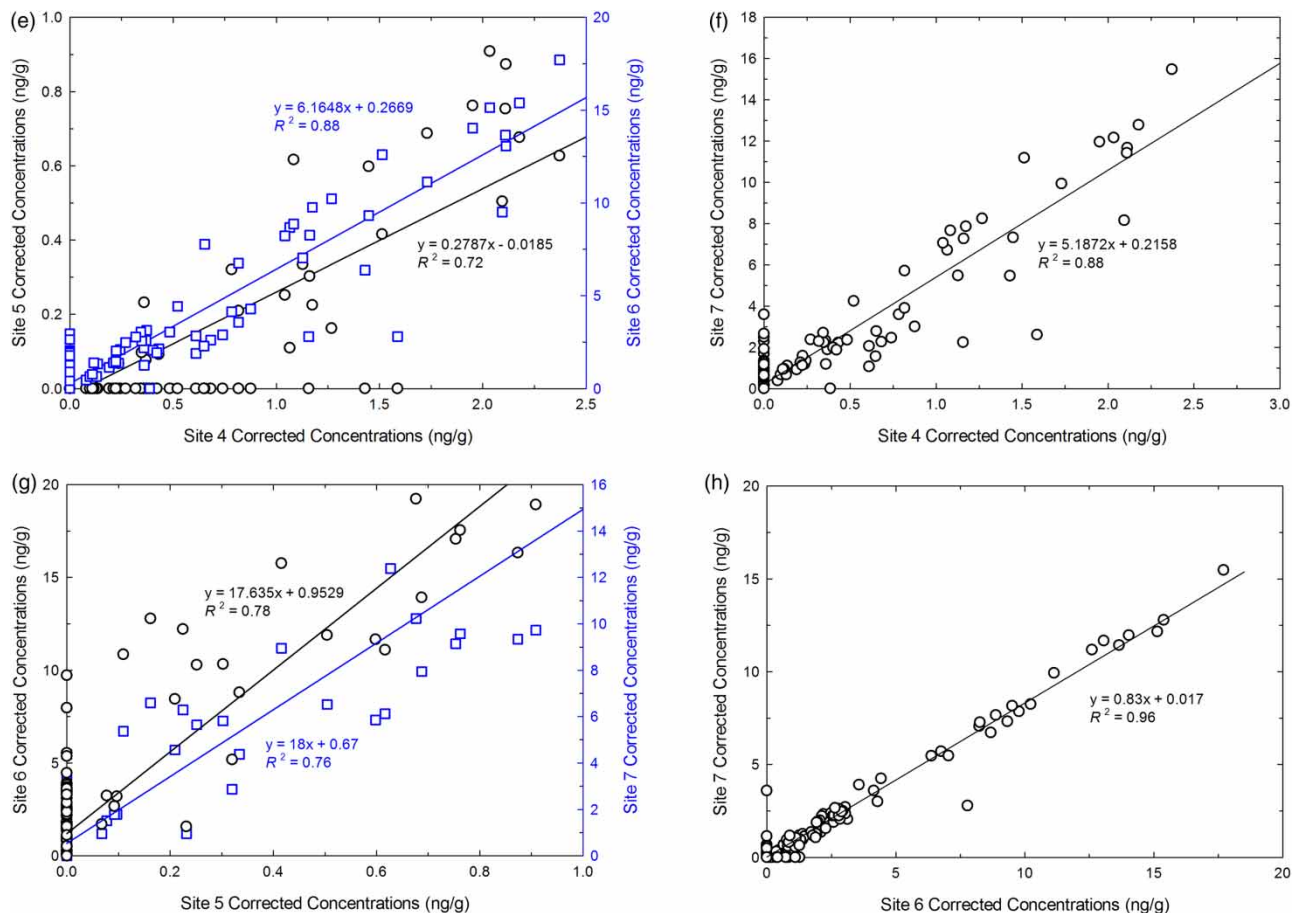
Figure 4 | Continued.

should be noted that these two sites were located next to each other at the downstream of the estuary and were subjected to tidal actions (Figure 1). The great transition of river flow directions occurred from sites 5 to 7. Meanwhile, the river became broadened from sites 6 to 7. Therefore, the rapid water flow turning from sites 5 to 6 with tidal action likely flushed sediments associated with PCBs to deposit at site 6 (Cailleaud *et al.* 2009). Furthermore, the decrease in water flow velocity from sites 6 to 7 as well as the presence of islands at site 7 would facilitate the deposition of sediments at site 7. As a result, the sediments collected at sites 6 and 7 were found to contain the most serious PCB contamination and had a strong correlation between their PCB concentrations (Table 2). The results also suggested that the PCBs attached to sediments at these two sites were likely emitted from the same source that travelled with water and precipitated with the sediments due to

change in hydrodynamics and morphodynamics of the estuary (Pavlou & Dexter 1979).

The other three strong correlations ($R^2 > 0.8$) were found between sites 2 and 7, sites 4 and 6, and sites 4 and 7. Correlations with R^2 of $0.7 \sim 0.8$ were identified between sites 2 and 4, sites 2 and 5, sites 2 and 6, sites 4 and 5, sites 5 and 6, and sites 5 and 7. Lower correlations (R^2 of $0.6 \sim 0.7$) were observed between sites 1 and 2 and sites 1 and 4. The above results showed that sites 6 and 7 had the strongest correlations of PCB concentrations with other sampling sites, which was likely due to their location being at the downstream that accumulated the PCB-associated sediments from other sites. Except for site 3, all other sites exhibited significant correlations with each other, indicating that the PCBs should come from the same source. Site 1 only showed correlations with sites 2 and 4, possibly due to its location being at the most upstream among all the sampling sites.

Quality assurance and quality control (QA/AC)

The surrogate recoveries for PCB d65 and PCB d159 added to the sediment samples from the seven sampling sites are presented in Table 2. The surrogate recovery for PCB d65 varied from 54% to 76% for sediment samples taken from sites 1–7, with an average value of 63%. This recovery level was slightly lower than that for PCB d159, which ranged from 55% to 84% with a mean of 69%. The lower recovery of PCB d65 than PCB d159 may be because the former PCB congener was relatively more volatile and more easily broken down during rotary evaporation, nitrogen blowdown, and cleanup procedures.

The lowest and highest recovery levels for PCB d65 were found in samples from sites 3 and 6, respectively, whereas those respective levels for PCB d159 were detected in samples collected from sites 3 and 1. It can be seen that the samples at site 3 had the least surrogate recovery for both PCB surrogates, while other samples generally showed acceptable recovery levels. As surrogates are typically added to samples for analysis of their recovery for assessing the effectiveness of measurement procedures for the target samples (Mellin *et al.* 2011), the recovery levels for these two surrogates in samples collected from the seven sites were used to calculate for the corrected mass and corrected concentration for PCBs in the samples.

The background contamination of PCBs was examined with the two blank samples as shown in Table 3. The

corrected mass of PCB homologs was detected for di-, penta-, hexa-, and hepta-PCBs for blank 1, and only di-PCB was detected for blank 2. The mass for all PCB homologs was below 3 ng. The total mass of PCBs for blank 1 and blank 2 was 5.3 and 2.8 ng, respectively. In comparison, the total mass of PCBs detected in the sediment samples at all sampling sites was above 100 ng (Table 2), indicating that blank contamination was relatively negligible. In addition, the surrogate recoveries for PCB d65 and PCB d159 in the blank samples were above 60% and 70% (Table 3). Therefore, the analysis for corrected mass and concentration of PCBs in sediment samples should yield reliable results.

CONCLUSIONS

PCBs have been detected in sediment samples collected at all seven sampling sites along the Raritan River. The corrected concentrations for 209 PCB congeners ranged up to 20 ng/g, with the values following the order of sites 6 > 7 > 3 > 4 > 5 > 1 > 2. The total corrected PCB concentrations by homolog groups in the sediment samples varied from 9.0 (site 1) to 327 ng/g (site 6), whereas the total corrected mass of PCBs in the sediment samples ranged from 101.0 (site 5) to 1,476.3 ng (site 6), following the order of sites 6 > 7 > 3 > 4 > 2 > 1 > 5. The greatest PCB contamination was found at sites 6 and 7, indicating that more PCBs were associated with sediments at the downstream of the Raritan River estuary. This may be an accumulation process attributed to the wider opening with more tidal formation that washed sediments downstream, as shown by the morphodynamic and hydrodynamic characterizations of the sampling sites. This was also supported by the strong correlations of PCB concentrations found between sampling sites especially for sites 6 and 7 ($R^2 = 0.96$). Furthermore, higher PCB concentrations were observed for the homolog groups of tetra-, penta-, hexa-, and hepta-PCBs at all sampling sites. Comparisons with prior reports showed that all total PCB concentrations at the seven sampling sites were below those reported by CARP and DRBC, except that sites 6 (327 ng/g) and 7 (275 ng/g) exceeded the DRBC value (120 ng/g). Comparison with guidelines

Table 3 | Corrected mass and surrogate recovery of PCBs for blank samples

	PCBs	Blank 1	Blank 2
Corrected mass (ng)	mono-	0	0
	di-	1.7	2.8
	tri-	0	0
	tetra-	0	0
	penta-	1.1	0
	hexa-	1.2	0
	hepta-	1.3	0
	octa-	0	0
	nona-	0	0
	deca-	0	0
	Total	5.3	2.8
Surrogate recovery (%)	PCB d65	67	64
	PCB d159	75	72

showed that sites 3 and 4 had PCB concentrations exceeding the 22.7 ng/g limit, whereas sites 6 and 7 exceeded the 180 ng/g limit, indicating potential health hazards from PCBs. Therefore, continuous monitoring and proper remediation of PCBs in the Raritan River estuary especially at the downstream may be necessary.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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