Baseline

Characterization of polychlorinated biphenyl congeners in surface sediments of the Changjiang Estuary and adjacent shelf by high-resolution sampling and high-resolution mass spectrometry

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ABSTRACT

Due to limited samples and low-resolution analysis, conflicting findings on major polychlorinated biphenyl (PCB) congeners and their origins remain in the East China Sea (ECS). Based on high-resolution sampling and high-resolution mass spectrometry analysis, 72 surface sediment samples from the Changjiang Estuary and adjacent ECS shelf were determined to characterize 39 PCB congeners. PCBs (Σ_{39} PCBs) ranged from 0.003 to 16.18 ng/g dw, presenting a decreasing seaward trend. Tri-, tetra- and penta-CBs were the main components, accounting for > 64% of Σ_{39} PCBs in most samples. Tetra-CBs were the dominant congeners, corresponding to results of sediments from Changjiang middle reach and soils from Changjiang Delta. Comparison between PCBs and sediment properties indicated there may be a deposition boundary of 30°N. In the north, the spatial distribution of PCBs is controlled by Changjiang input and hydrodynamic conditions, while in the south closely related to combination of local source and riverine input.

Polychlorinated biphenyls (PCBs), one of priority persistent organic pollutants (POPs) in the Stockholm Convention (Stockholm Convention 2015), can often be released into the environment during the processes of production, transportation and usage (Bigus et al. 2014). Although PCBs have been banned legally in China since 1974 (Yang et al. 2011), large amount of e-waste recycling still acts as an important alternative origin of environmental PCBs (Yang et al. 2012). During their life cycles, PCBs have transferred all over the world (Jonsson et al. 2003) and some PCB congeners have been documented to be closely related to severe toxicological effects (Li et al. 2016).

Usually, sediments are considered to be the final sink of PCBs after their transfer, exchange and deposition between soil, water, gas and sediment (Jonsson et al. 2003). The East China Sea (ECS), one of the largest shelf seas in the world, is an important sink of terrigenous matters from Changjiang basin. Every year, Changjiang discharges about 0.5 Gt terrestrial particulate matter to the ECS with 2–5 Mt. being of organic matter which could adsorb POPs (Wang et al. 2008). Large amounts of PCBs emitted from industrial development, sewage discharge and transportation in the Changjiang basin would be transferred into the ECS and buried in the sediments (Liu et al. 2010).

As an important sink of PCBs from Changjiang basin, quite a few

efforts on PCBs in the ECS and its adjacent areas (Table 1) have been performed in recent years (Ono et al. 2012; Yang et al. 2011; Yang et al. 2012; Zhou et al. 2012). Through these productive studies, the pollution levels, spatial distributions, PCBs congeners and origins of these sedimentary PCBs have been clearly revealed. For example, PCBs with low chlorinated PCBs being of the predominated congeners are one of the most common POPs in the ECS and they are proposed to be from PCB products, surface soil, etc. (Wang et al. 2016; Yang et al. 2011). However, the conflicted results on major PCB congeners (tri-CBs, tetra-CBs or penta-CBs) (Lai et al. 2015; Wang et al. 2016; Yang et al. 2011) and ambiguous source analysis on PCBs origins (river input, wastewater discharge or e-waste recycling) (Duan et al. 2013; Fan et al. 2014; Yang et al. 2012) have also been reported because of the limited sampling sites and defective analyzing PCB congeners. By comparison with lipid biomarkers produced from terrestrial plants and marine phytoplankton, Fan et al. have noted that there is a rough boundary (29°N in the inner shelf) for sedimentary PCBs from Changjiang transport and local coastal discharge (Fan et al. 2014).

In this study, sedimentary PCBs in the inner shelf adjacent to Changjiang Delta have been more critically studied via high-resolution sampling and high-resolution mass spectrometry analysis. The purpose

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Table 1
PCBs in the surface sediment samples of Changjiang and the ECS.

Locations	Time	PCB NO.	Cl no.	Σ PCBs (ng/g dw)	Mean (ng/g dw)	Source	Main composition	Ref.
Wuhan reach of Changjiang	2005	39	3–10	1.2–45.1	9.2	Surface runoff; industrial wastewater; domestic sewage	Tetra-CBs, penta-CBs	Yang et al. (2009)
The coast to the middle shelf of the ECS	2011	24	4–7	0.019–0.496	0.125	Atmospheric deposition; riverine input of the Changjiang; atmospheric deposition	Low chlorinated PCBs	Fan et al. (2014)
Changjiang Estuary and ECS inner shelf	2010–2011	23	2–9	0.024–0.343	0.127	Contaminated soils erosion; surface runoff; wastewater discharge; shipping industry	Tri-CBs, penta-CBs, tetra-CBs	Duan et al. (2013)
Changjiang Estuary and Hangzhou Bay	2007	9	3–7	0.60–63.00	–	E-waste recycling; Changjiang and Qiantang River runoff	Tri-CBs, tetra-CBs, di-CBs	Addeye et al. (2016)
Changjiang Estuary and adjacent ECS	2007	20	2–10	5.08–19.64	10.15	E-waste recycling; intense aquacultural and shipping activities; sediment re-suspension	Tri-CBs > tetra-CBs > di-CBs > penta-CBs > hexa-CBs > hepta-CBs	Yang et al. (2012)
Yueqing Bay, Xiangshan Bay, and Sanmen Bay	2006	20	2–10	9.33–19.60	–	E-waste recycling; landfills pollution; municipal products refuse; sewage sludge incineration	Tri-CBs	Yang et al. (2011)
Zhoushan Archipelago and Xiangshan Harbor, ECS	2014	18	3–7	1.48–7.94	4.20	Atmospheric deposition; paint flaking	Penta-CBs	Wang et al. (2016)
Middle reach of Changjiang, from Yichang to Jingzhou	2010	12	4–7	0.0018–0.0241	–	Burning of domestic coal and wood	Tetra-CBs, penta-CBs	Gao et al. (2015)
Changjiang Delta city cluster	2012	32	2–7	Nd–8.28	1.98	Soil erosion loss; economic development	Hexa-CBs > penta-CBs > tetra-CBs > tri-CBs > hepta-CBs	Zhang et al. (2014)
Changjiang Estuary	2006	–	–	0.6–2.6	1.7	Urban and industrial wastewater	–	An et al. (2009)

is to identify PCBs congeners more distinctly and to further distinguish the location of the boundary describing the characteristics of PCBs distributions.

Surface currents in the ECS shelf consist of the Changjiang diluted freshwater carrying terrestrial organic matter into the ECS, the northward flow of the warm and saline Taiwan Warm Current (TWC), and relatively cold and brackish southward-flowing Jiangsu and Zhejiang–Fujian Coastal Current (ZFCC). The vast majority of the sediments discharged from the Changjiang is ultimately deposited in the Changjiang Estuary and southern inner shelf of the ECS (Milliman et al. 1985). Seventy-two surface sediment samples (depth: 0–3 cm) were collected from the adjacent coastal regions of Changjiang Estuary during a cruise in March 2014 using a stainless steel box-corer (40 cm × 60 cm × 50 cm) from the R/V Runjiang 1. The detailed sampling sites were shown in Fig. 1 and Table S1. All samples were then freeze-dried, homogenized, and stored at –20 °C until analysis.

The sediment sample (5.0 g) was spiked with ¹³C-labeled mono- to deca-CBs (PCB 3, 15, 28, 52, 118, 153, 180, 194, 208, and 209, Cambridge Isotope Laboratories, Inc., Andover, MA, USA), and extracted using an accelerated solvent extraction system (ASE300, Dionex, USA) with dichloromethane/*n*-hexane (1:1, *v/v*). The extract was concentrated with a rotary evaporator after the addition of activated copper powder to remove sulfur and then cleaned using a combination silica column filled with 1 g silica, 4 g basic silica (1.2%, *w/w*), 1 g silica, 8 g acidic silica (30%, *w/w*), 2 g silica, and 4 g anhydrous sodium sulfate from bottom to top. The column was prewashed with 80 mL *n*-hexane. After sample loaded, PCBs were eluted with 100 mL *n*-hexane which was finally concentrated to 100 μ L. The internal standard, ¹³C-labeled PCB standards (PCB 77 and PCB 101) were added before the instrumental analysis.

Thirty-nine congeners, PCB 1, 3, 8, 10, 15, 18, 19, 28, 33, 37, 44, 52, 74, 77, 81, 87, 95, 99, 101, 105, 110, 114, 118, 138, 149, 151, 153, 155, 170, 180, 188, 189, 191, 194, 199, 205, 206, 208, 209, numbered according to the IUPAC nomenclature, were analyzed using an Agilent 7200 GC-Q-TOF-MS (Agilent Technologies, Santa Clara, USA) equipped with an electron impact (EI) ion source. A quartz capillary column (DB-5MSUI 30 m × 0.25 mm i.d., 0.25 μ m film thickness) was used for the chromatographic separation. The GC oven temperature program began with 1 min hold at 60 °C followed by heating to 120 °C at 40 °C/min and then to 310 °C at 5 °C/min. The sample (1 μ L) was injected under splitless mode, and the injector temperature was set at 280 °C. Ultrapure helium was used as the carrier gas at a flow rate of 1.0 mL/min. The auxiliary heating and EI source temperatures were set at 280 °C and 250 °C. A solvent delay of 5 min was used to prevent damage in the ion source filament.

Grain-size composition of the surface sediments was measured using a laser Particle Size Analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK) (Yao et al. 2014). Particle sizes < 4 μ m were considered clays, 4 to 63 μ m, silts, and sands were larger than 63 μ m. Total organic carbon (TOC) and total nitrogen (TN) were analyzed using a Vario MICRO cube elemental analyzer (EA) (Elementar, Germany) (Wang et al. 2015). The detailed sediment information, including particle sizes, TOC%, TN% and water depth were shown in Table S1 (Supplementary Data).

All solvents used were of pesticide grade. In order to avoid the cross-contamination, a laboratory blank (anhydrous sodium sulfate) and a surrogate spiking blank sample were treated with each batch (10 samples) of samples. Relative standard deviation of the recoveries for the spiking blank samples ranged from 3% to 10%. The method detection limits ranged from 0.0002 to 0.002 ng/g dw. The average recoveries of the surrogate PCBs ranged from 60% to 110%. All the results were corrected with the internal standards.

SURFER 8.0 was used to plot the sampling map and contour maps. A contour map is a two-dimensional representation of three-dimensional data. The first two dimensions are the X and Y coordinates of the sampled stations. The third dimension (Z, total concentrations of PCBs)

Fig. 1. Sampling sites map. ZFCC, Zhejiang–Fujian Coastal Current; TWC, Taiwan Warm Current; blue area, mud area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is represented by different colors filled in intervals of lines of equal value (lines not show). The Spearman's correlation analysis was done through the software package SPSS Statistics 20.0 (SPSS Inc., Chicago, USA). The ratios for PCB congeners in total PCBs were calculated and plotted by OriginPro 9.0.0 (OriginLab Corporation, USA).

For all the 72 surface sediment samples, 39 PCB congeners with 1–10 Cl atoms were analyzed and the total contents of 39 PCB congeners ($\Sigma_{39}\text{PCBs}$) ranged from 0.003 to 16.18 ng/g dw, with the mean value of 3.41 ng/g dw. The $\Sigma_{39}\text{PCBs}$ level was comparable to some other reports from the ECS (5.08–19.64 ng/g dw) (Yang et al. 2012), including Zhoushan Archipelago and Xiangshan Harbor (1.48–7.94 ng/g dw) (Wang et al. 2016). Compared with the sediments collected from the Wuhan reach (1.2–45.1 ng/g dw) and the soils collected from Changjiang Delta (0.46–116.4 ng/g dw) (Zhang et al. 2011), PCBs contents in the Changjiang Estuary and the inner shelf of the ECS were at lower levels (Yang et al. 2009).

The spatial distribution patterns of $\Sigma_{39}\text{PCBs}$ in our study were in accordance with other well known POPs, such as PAHs (Lü and Zhai 2005), SCCPs (Zhao et al. 2013), and OCPs (Yang et al. 2005) in the ECS. POPs are tended to be adsorbed on the fine particles and deposited with them. Sediments from Changjiang are transported to ECS mainly through across-shelf diffusion and a strong along-shelf advection, so that large amounts of Changjiang-derived sediments depositing along the shelf (Liu et al. 2006). Therefore, PCBs mainly accumulated at the coastal areas near the Changjiang Estuary and totally presented a seaward decreasing trend (Fig. 2) (Fan et al. 2014). Take transect of A6 along the direction of Changjiang diluted freshwater for example, PCBs contents decrease remarkably with distance from Changjiang Estuary to the outer shelf (Fig. 3), except for site of A6-1 with few fine particles adsorbing organic matters deposited because of stronger hydrodynamics (Gao et al. 2013). In all, the highest values were located at the Changjiang Estuary (A6-2) and Zhoushan Archipelago (A9-1), corresponding to the direct land-derived discharge and the “marginal filter” effect (Yang et al. 2012). Similar to previous reports on sedimentary PCBs in Changjiang Estuary, the relative lower values at site A3-3 and

A3-4 than other Changjiang Estuary sites could be attributed to the seawater intrusion (Fan et al. 2014; Gao et al. 2013).

The total contents of seven PCB indicators ($\Sigma_7\text{PCBs}$, PCB 28, 52, 101, 118, 138, 153/132 and 180) are often recommended as the ecotoxicological assessment criteria (EAC, 1.0–10.0 ng/g) (OSPAR Commission 2000) to indicate their hazards to ecological system and human health. In this study, for $\Sigma_7\text{PCBs}$ (n.d.–2.78 ng/g), 19 of 72 sediment samples exceed the low end value of EAC (1.0 ng/g), and were much lower than the high end value of 10.0 ng/g, indicating the extremely low ecological risks of PCBs in the ECS. Even so, their ecological risks to high trophic level organisms from the anthropic activities and re-suspension cannot be neglected due to their bioaccumulation and biomagnification via food web (Malisch and Kotz 2014).

The detection frequencies for all PCB congeners ranged from 1.3% to 94.6%, with higher values (18.9%–94.6%) for low chlorinated PCBs (mono- to penta-CBs) than high chlorinated PCBs (hexa- to deca-CBs, 1.3%–56.8%) (Table S2, Supplementary Data). The high detection frequencies of low chlorinated PCBs are consistent to previous reports of PCBs in the surface sediments of the ECS (Yang et al. 2012; Zhou et al. 2012), and typical drinking water in Jiangsu Province which are closely related to Changjiang (Hong et al. 2009). The results can be attributed to the higher utilization frequency and higher proportion of low chlorinated PCBs in China (Jiang et al. 2007). High-chlorinated PCBs were mainly accumulated at the Changjiang Estuary (site A5-2, A5-3, A5-5, A6-2, A6-4) and the inner shelf close to Zhoushan Island (A7-3, A8-2, A8-3, A9-1) (Fig. 2) because of their higher K_{ow} values which can result in their good adsorption onto the suspended particles and then deposition (Hong et al. 2003). Additionally, the lower water solubility and weaker migration ability of high chlorinated PCBs can also lead to their lower contents as well as lower detection frequencies in the off-shore area, thus result in their presentation with high contents at the Changjiang Estuary and the inner shelf.

According to chlorine number of PCB congeners in the ECS, no consensus about primary PCB congeners have been reported. Most reports presented that tri-CBs are the major congeners, explained by the

Fig. 2. Spatial distributions of PCBs and the sediment properties of ECS sediment samples.

PCBs production in China from 1960s to 1970s which were also dominated by the tri-CBs, as well as the global PCB products (Adeleye et al. 2016; Duan et al. 2013; Yang et al. 2011). Although penta-CBs were not the dominated PCB products, they were identified as the main composition in the ECS sediment from developed fishery and shipping industries (Wang et al. 2016). In this study, tetra-CBs (Fig. 4) accounted for the highest proportion in all the sediment samples. It has been reported that tetra-CBs were the predominant composition in the surface sediments of Wuhan reach and other middle reach of the Changjiang which might be from surface runoff, industrial wastewater and domestic sewage (Gao et al. 2015; Yang et al. 2009). Meanwhile, the soil

from Changjiang Delta (241 top soil samples) were also dominated by tetra-CBs (Sun et al. 2016). Based on the predominance of Changjiang on the matters from river into the ECS and the characteristics of PCBs obtained from the high-resolution sampling and high-resolution mass analysis in this study, it can be concluded that tetra-CBs, not tri-CBs, are very likely to be the major PCB congeners in the ECS.

The contents of individual $\Sigma_{1Cl}PCBs$, $\Sigma_{2Cl}PCBs$, $\Sigma_{3Cl}PCBs$, $\Sigma_{4Cl}PCBs$, $\Sigma_{5Cl}PCBs$, $\Sigma_{6Cl}PCBs$, $\Sigma_{7Cl}PCBs$, $\Sigma_{10Cl}PCBs$ were significant correlated ($p < 0.01$) with that of $\Sigma_{39}PCBs$, and these factors were also correlated ($p < 0.01$) with each other except $\Sigma_{3Cl}PCBs$ (Table S3, Supplementary Data). High chlorinated PCBs congeners, of which half-lives are often

Fig. 3. Transect contents distribution of PCB congeners.

Fig. 4. PCBs congeners composition ratios in the sediment.

longer than 3 years (Sinkkonen and Paasivirta 2000), are prone to degrade to low chlorinated PCB congeners under anoxic conditions in marine sediments (Matturro et al. 2016). This indicated most of low chlorinated PCB congeners are likely from the similar origins and subsequent degradation from high chlorinated PCB congeners. The significant correlation between $\Sigma_{3\text{Cl}}$ PCBs and $\Sigma_{2\text{Cl}}$ PCBs as well as $\Sigma_{1\text{Cl}}$ PCBs ($p < 0.01$) may be attributed to the dechlorination of tri-CBs to di-CBs and mono-CBs in the sediment (Chang et al. 2001). It has been reported that large amounts of tri-CBs has been produced and utilized from 1960s to 1970s and quite a proportion have been transferred into the ECS (Zhang et al. 2004). Therefore, it is reasonable for the close relationship between these three low chlorinated PCB congeners.

As a mixture of many congeners, the environmental behaviors of commercial PCB products are often different. Based on the Cl content, the application patterns, pollution sources and distribution properties, the PCB congeners were classified as Σ_{39} PCBs, $\Sigma_{1-2\text{Cl}}$ PCBs, $\Sigma_{3-5\text{Cl}}$ PCBs and $\Sigma_{6-10\text{Cl}}$ PCBs to study their deposition characteristics (Fig. 2). Additionally, sediment properties of organic carbon percentage (TOC%), total nitrogen percentage (TN%) and clay percentage (clay%) have also been introduced to investigate the spatial distribution of PCBs.

PCB congener groups, Σ_{39} PCBs, $\Sigma_{1-2\text{Cl}}$ PCBs, $\Sigma_{3-5\text{Cl}}$ PCBs and $\Sigma_{6-10\text{Cl}}$ PCBs, all presented a seaward decreasing trends with highest values located at the Changjiang Estuary and the inner shelf close to Zhoushan Archipelago (Fig. 2). The spatial pattern is largely similar to organic matter index, agreeing well with previous reports on PCBs and other anthropogenic contaminants (Fan et al. 2014). The clay%, TOC% and TN% also presented seaward decreasing trends largely similar to PCBs. $\Sigma_{3-5\text{Cl}}$ PCBs were the representative congeners, accounting for > 64% of Σ_{39} PCBs in 67 of total 72 samples. However, correlation analysis showed that there were relative low correlations ($p > 0.01$)

between the classified PCB groups (including Σ_{39} PCBs and $\Sigma_{3-5\text{Cl}}$ PCBs) and clay%, TOC% and TN%. Generally, the fine particles are prone to adsorb organic matters being of the dominant factor controlling the sorption of hydrophobic organic pollutants (Dunnivant et al. 2005). Thus, the low correlations between these sediment properties and PCBs congeners indicated that there may be other input sources of PCBs into the inner shelf of the ECS.

The Changjiang-derived sediments is mainly deposited in the Changjiang Estuary north of 30°N, accounting for about 40% of the total amount, while 32% is deposited in the Min-Zhe coastal mud area (Lin et al. 2013). In the south of 28°N, it is proposed that there is a natural sedimentation process for OM and PCBs (Duan et al. 2013). Another research on sedimental PCBs in the inner shelf of the ECS studied partly by OM indicators has also revealed the difference on PCBs deposition, with Changjiang input as the main origin in the north of 29°N while both local coastal sources and Changjiang input are the main PCBs origins in the south (Fan et al. 2014). These studies suggest that there may be a boundary for the deposition of organic pollutants in the inner shelf.

Combined with sedimentary features of matters transported by Changjiang and the spatial distribution characteristics of PCBs, the sampling sites are classified into two parts along the extension of Hangzhou Bay to investigate the existence of the boundary (Fig. 2). The two parts are the combinations of transects of A1–A7 (37 sites) and that of A8–A13 (35 sites) (Fig. 1) respectively and the boundary locates about at 30°N. In the north of 30°N, the spatial distributions of PCBs were in high accordance with clay%, TOC% and TN% (Fig. 3) and there were significant correlations between these factors and all PCBs congener groups ($p < 0.01$) (Fig. 5, Table S4, Supplementary Data). The results agreed well with previous reports of the deposition of riverine input PCBs in the Changjiang Estuary and its adjacent regions (Lin et al. 2013) which are closely related to the intensified flocculation and gravitational sedimentation of suspended particulate matter (SPM) indicated by clay and terrestrial organic matters (Fan et al. 2014). In the south of 30°N, the spatial distributions of Σ_{39} PCBs, $\Sigma_{3-5\text{Cl}}$ PCBs and Σ_{71} PCBs are dramatically different from that of clay%, TOC% and TN%, while $\Sigma_{1-2\text{Cl}}$ PCBs and $\Sigma_{6-10\text{Cl}}$ PCBs are largely similar to the latter (Fig. 5). Correlation analysis also presented stronger correlations of $\Sigma_{1-2\text{Cl}}$ PCBs and $\Sigma_{6-10\text{Cl}}$ PCBs with clay%, TOC% and TN% than Σ_{39} PCBs, $\Sigma_{3-5\text{Cl}}$ PCBs and Σ_{71} PCBs (Fig. 5). As for $\Sigma_{1-2\text{Cl}}$ PCBs, their stronger migration ability (Hong et al. 2003; Zhou et al. 2012) and coastal discharge source may lead to their spread and similar distribution to clay %, TOC% and TN% in the south of 30°N. For $\Sigma_{6-10\text{Cl}}$ PCBs (Fig. 5), the good agreement with these sediment factors in the south of 30°N can be attributed to their weaker migration ability and lower contents as well as lower detection frequencies (Yang et al. 2011). The dramatical difference on the relationships between sediment properties and Σ_{39} PCBs, $\Sigma_{3-5\text{Cl}}$ PCBs being of dominant congener groups and Σ_{71} PCBs being of PCB indicator in the north and south of 30°N suggested that there is indeed a clear boundary and the deposition of PCBs on both sides of the

Fig. 5. Correlation coefficients of PCBs with the sediment properties of sediment. A means all the samples; N means samples in the north of 30°N (A1–A7); S means samples in the south of 30°N (A8–A13).

boundary are controlled by their terrestrial sources and hydrodynamic conditions. In the north of 30°N, PCB distribution is controlled by Changjiang input and deposition of SPM, while in the south of 30°N it might be more closely related to the local coastal source (Fan et al. 2014).

Based on high-resolution sampling and high-resolution mass spectrometry analysis, the homolog and congener patterns of PCBs as well as their spatial patterns in the inner shelf adjacent to Changjiang Delta have been critically studied in this paper. The spatial distributions of Σ_{39} PCBs covering 1Cl to 10Cl PCB and the congener groups based on chlorine numbers all presented a seaward decreasing trend, comparable to previous reports in the ECS. Tetra-CBs were the dominant congeners and low chlorinated PCBs ($\Sigma_{3-5\text{Cl}}$ PCBs) were the predominated compositions. There might be a deposition boundary of 30°N for PCBs in ECS and adjacent shelf. In the north of 30°N, PCBs deposition was controlled by riverine input of Changjiang and hydrodynamic conditions while in the south PCBs were closely related to local coastal source. In all, the combination of high-resolution sampling and high-resolution mass spectrometry analysis provide us a novel protocol for identifying the environmental behaviors of POPs more precisely.

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