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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.	ΣPCBs (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	Adeleye 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 ^{13}C-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 μL. The internal standard, ^{13}C-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 μm 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 μL) 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, Malven Instruments Ltd., UK) (Yao et al. 2014). Particle sizes < 4 μm were considered clays, 4 to 63 μm, silts, and sands were larger than 63 μm. 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)