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RESEARCH ARTICLE

Distribution, sources, and risk assessment of polychlorinated biphenyls in surface waters and sediments of rivers in Shanghai, China

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Abstract The distribution, sources, and potential risks of polychlorinated biphenyl (PCB) contamination in the rivers of Shanghai, China were investigated. Fourteen PCB congeners in surface waters and sediments, which were collected from 53 sampling sites, were quantified by gas chromatography-mass spectrometer (GC-MS). The total concentrations of PCBs in the dissolved phase, in particulates, and in sediments ranged from not detected (nd) to 34.8 $ng \cdot L^{-1}$, from 0.76 to 39.71 $ng \cdot L^{-1}$, and from 1.46 to 46.11 $ng \cdot g^{-1}$ (dry weight, dw), respectively. The corresponding WHO toxic equivalents (TEQs) of dioxin-like polychlorinated biphenyls (dl-PCBs) ranged between nd–1135.63 pg $TEQ \cdot L^{-1}$, 0.02–605.94 pg $TEQ \cdot L^{-1}$, and 0.05–432.12 pg $TEQ \cdot g^{-1}$ dw, respectively. The *penta*-CBs, especially PCB 118 and PCB 105, were the dominant congeners in all samples. Principle Component Analysis (PCA) indicated that the PCBs were mainly influenced by a historical accumulation of commercial PCB products, the burning of house coal, and emissions from municipal solid waste incineration (MSWI) and secondary metallurgy industries. The center of Shanghai was significantly affected by PCB contamination, followed by the industrial parklands and suburban towns, while the farmland of Chongming Island was the least affected area. Adverse biological and health effects would be likely in the central urban areas, industrial parks, and residential towns of Shanghai.

Keywords PCBs, river water, sediments, sources, biological risk

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1 Introduction

Polychlorinated biphenyls (PCBs) are typical persistent organic pollutants (POPs) with 209 congeners and have been accepted in the list of the "Stockholm Convention on Persistent Organic Pollutants" based on their bioaccumulation properties, their persistence in the environment, their impact on ecosystems, and their wide spectrum of deleterious effects on humans. Among the numerous PCB congeners, the degree of PCB toxicity is related to the substitution pattern of chlorine atoms, and the most toxic group of compounds are dioxin-like PCBs (dl-PCBs), including 12 congeners, which are referred to as the *non-ortho* and *mono-ortho* PCBs (Safe, 1990). PCBs were first synthesized in 1929 and used extensively for different industrial applications until the late 1970s with about 1.3 million tons of PCBs having been discharged into the environment (Breivik et al., 2002). Amongst this, about 8,000 tons of commercial PCBs (1# PCB and 2# PCB) were produced during the 1960s and 1970s in China. 1# PCB (also called PCB 3) was used as a dielectric fluid in electronic capacitors, and is similar to Aroclor 1242. 2# PCB (also called PCB 5) was used as an additive in paints, and is similar to Aroclor 1254 (Jiang et al., 1997; Takasuga et al., 2006).

PCBs have been extensively studied over the past 40–50 years. Much research has focused on the distribution, concentration, and exchange of PCBs in different environmental media, such as the atmosphere, soils, sediments, waters, and organisms. Past pollution from industrial activities has been regarded as the main contribution to the accumulation and distribution characteristics of PCBs (Nhan et al., 2001; Zhang et al., 2004; Colombo et al., 2005; Rowe et al., 2007; Kim et al., 2009). Generally,

PCBs have mainly accumulated in terrestrial and aquatic ecosystems by means of direct dry deposition, runoff, and industrial and municipal waste water discharge (Samara et al., 2006; Totten et al., 2006). In aquatic ecosystems, PCBs have mainly accumulated in suspended particulate matter (SPM), sediments, and sediment-dwelling organisms. In the case of accumulated PCBs in sediments, the compounds would be released to the overlying water, and endanger aquatic ecosystems influenced by human activities such as channel reconstruction, dredging, and resuspension by shipping (Dachs et al., 2002).

Shanghai is located near the Yangtze River estuary. There are about 33,127 rivers and creeks in the Shanghai basin, spanning an area of ca. 24,915 km in length, including the Suzhou River and the Huangpu River, which is the last tributary of the Yangtze River. As one of the largest and most important industrial cities of China, Shanghai has undergone extensive urban expansion and development with a commensurate environmental degradation since the early 1980s (Wang et al., 2008). Large amounts of industrial wastewater and domestic sewage have been discharged into the river network without adoption of any decontamination measures, resulting in serious deterioration of river water quality in the the rivers of Shanghai (Zhang et al., 2014a). In 2012, water quality of the main rivers and lakes in Shanghai varied between Category III to over Category V (Shanghai Environmental Protection Bureau, 2012). Historically, a number of commercial PCBs have been produced in Shanghai and used mostly as paint additives which eventually were mobilized into the environment (Zhang et al., 2009). Wu et al. (1999) reported that the total PCB concentrations in sediments were influenced by the industrial activities in the Yangtze estuary and the Huangpu River. Consequently, some studies had focused on the occurrence and risk assessment of PCBs in the sediments of the Yangtze estuary and its tidal plain (Gao et al., 2013), and the sediments of the Suzhou River (Li et al., 2007). However, little information has been reported on the concentrations and exchange pathways of PCBs, especially dl-PCBs in the waters and sediments of the whole river network of Shanghai. To this end, systematic studies have been performed on the river network system of Shanghai with a view to gaining new information on the spatial distribution, source identification, and risk assessment of PCBs in the different areas, and to better understand how land usage which is influenced by human activities has affected the distribution of PCBs along the river network.

2 Materials and methods

2.1 Sampling and pretreatment

Fifty-three samples of surface water and sediments were collected from the Shanghai river network in April, 2012 (Fig. 1). The 53 sampling sites (SS) were classified into five different areas based on the location of its corresponding land use as follows: industrial parks of industrial area (Area 1, A1), farmland in agricultural area (Area 2, A2), the city center of Shanghai (Area 3, A3), residential areas of suburban towns (Area 4, A4) and farmland in

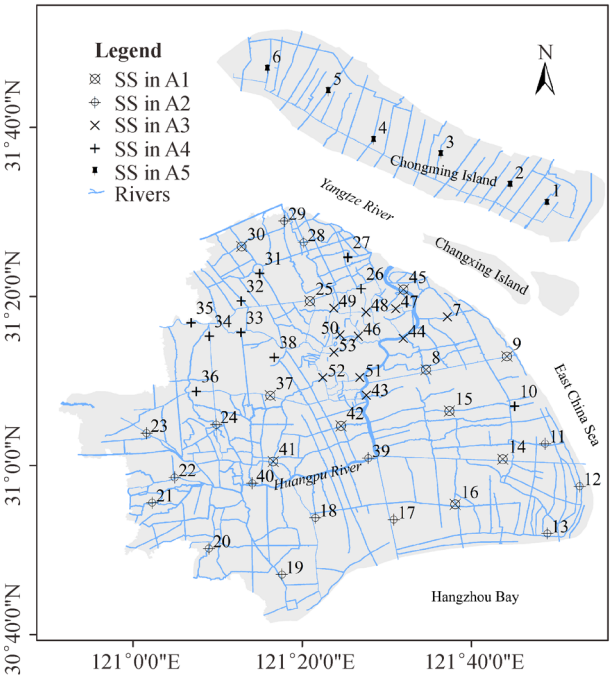

Fig. 1 Sampling sites (SS) of surface water and sediments in the rivers across different areas of Shanghai. A1, industrial parks; A2, farmland; A3, city center; A4, residential area in towns; A5, farmland of Chongming Island.

Chongming Island (Area 5, A5) (Yu et al., 2013). In each site, about 2 L of surface water was collected using a Plexiglas sampler and transferred to a brown glass bottle. Surface sediments were sampled by an Ekman-Birge bottom sampler (HYDRO-BIOS, Germany) and then placed into polyethylene bags. All samples were stored at 4°C in the laboratory.

Water samples were filtered using combustion-cleaned (450°C) glass fiber filters (GF/F, 0.45 μm; Whatman, UK) (Khim et al., 2001). The filtered GF/F and sediment samples were freeze dried in a freezer dryer (Christ, Germany). Then sediment samples were powdered with a mortar and pestle and sieved through a 60 mesh wire screen.

2.2 Extraction

Water samples were extracted by solid phase extraction (SPE) (Supelco, USA). Before extraction, the HLB columns (Waters, USA) were activated by flowing through successively 5 mL *n*-hexane, dichloromethane, methanol, and ultrapure water. Then the filtrate was percolated at a flow rate of 5 $mL \cdot min^{-1}$ under vacuum and the columns were eluted using 10 mL of dichloromethane: *n*-hexane (3:7).

Filtered samples and sediments were extracted by accelerated solvent extraction (ASE300, Dionex, USA). Then the extract was purified using a chromatographic column consisting of quartz sand, silica, alumina, and anhydrous Na_2SO_4 (silica, activated at 130°C for > 16 h; silica and alumina drying for 4 h at < 450°C). The analytes were eluted using 70 mL of dichloromethane:n-hexane (3:7). The eluate was transferred into *n*-hexane and enriched to 0.9 mL using a DryVap concentrator (Horizon, USA). Then 0.1 mL of decachlorobiphenyl (Supelco, USA) was added to each eluate to serve as internal standard for GC-MS analysis.

The *n*-hexane, dichloromethane, methanol, and acetone were confirmed to meet the impurity level standard for pesticide analysis grade solvents (Merck and Tedia, USA).

2.3 Analysis

PCBs were determined by GC-MS (Agilent 7890A, equipped with a 30 m × 0.25 mm i.d. × 0.25 μm HP-5MS column; Agilent 5975C, USA) with 1 μL of sample extract being injected by a CTC Combi PAL unit in splitless mode. The carrier gas was He and the flow rate was maintained at 1.2 $mL \cdot min^{-1}$. The temperature of the injection port was 270°C. The GC column oven was set at a temperature of 150°C and held for 3 min, then increased at a rate of $10°C \cdot min^{-1}$ to 300°C and held for 2 min. The mass spectrometer was operated at 280°C and at a resolution of over 10,000 under positive ion mode ionization conditions (70 eV). The data was acquired in selected ion monitoring (SIM) mode.

The PCB-MIX standard solution (14 standards) (O2Si, USA) contained 12 dl-PCBs (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) and PCB 170, 180.

2.4 Quality assurance and quality control (QA/QC)

For each set of 7 samples, a matrix spike sample, a parallel sample, a blank spike sample, and a blank sample were analyzed as part of the QC measures. Samples in duplicate (n = 3) were collected during QA/QC and the relative standard deviations (RSDs) ranged from 8.8% to 13.2%. The spiked recoveries for PCB congeners ranged from 63.8% to 77.8% for the dissolved phase, and from 61.3% to 82.1% for particulates and sediments, respectively. The limit of detection (LOD) was defined as the signal to noise ratio (S/N) > 3 times the average baseline noise level. The LOD values ranged from 0.006 $ng \cdot L^{-1}$ to 0.02 $ng \cdot L^{-1}$ for water samples and 0.009 $ng \cdot g^{-1}$ to 0.08 $ng \cdot g^{-1}$ for sediment samples. All the results were corrected using the recovery ratio data.

2.5 Statistical analyses

Multiple comparisons of the concentrations of the PCBs for the different sampling areas were conducted with the Least Significant Ranges (LSD) test using ANOVA, and differences were considered to be significant if $p < 0.05$. Principle component analysis (PCA) was used to identify the sources influencing the contributions of PCBs in different samples. The principal components were considered if their Eigenvalues were > 1 and the method of Varimax was selected for rotation. Twenty five iterations were performed in the PCA. All of the statistical testing was performed using SPSS version 19.0 (SPSS Inc., USA).

3 Results and discussion

3.1 PCBs concentrations and spatial variation

The concentrations of the $\sum_{14}$PCBs in surface water and sediment samples from the rivers of five different areas of Shanghai are listed in Table A1 and the spatial distributions are shown in Fig. A1, Fig. A2, and Fig. 2. In surface water, the values of the $\sum_{14}$PCBs in the dissolved phase ranged from ND (not detected) to 34.84 $ng \cdot L^{-1}$ with an average value of 8.42 $ng \cdot L^{-1}$. The highest concentrations of the $\sum_{14}$PCBs in the dissolved phase were found in A4, which was significantly higher than A5 ($p < 0.05$). The total $\sum_{14}$PCBs in surface water, including the dissolved phase and particulates, ranged from 2.72 to 53.42 $ng \cdot L^{-1}$, with a mean value of 18.35 $ng \cdot L^{-1}$. The highest concentrations of PCBs were found in A3, which was significantly higher than A5 ($p < 0.05$). In the surface sediments, the concentrations of the $\sum_{14}$PCBs varied between 1.46–46.11 $ng \cdot g^{-1}$ dw, with a mean value of 9.06 $ng \cdot g^{-1}$ dw, and

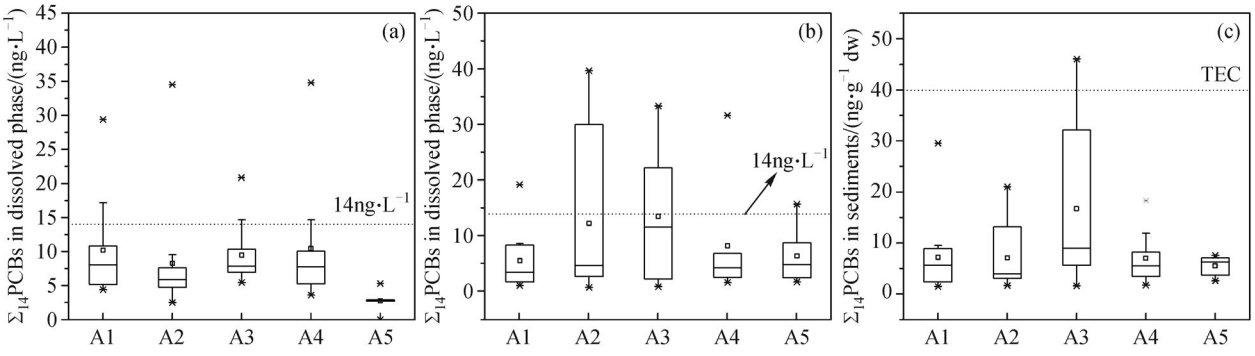

Fig. 2 Distributions of $\sum_{14}$PCBs in surface water and sediments from the rivers in 5 areas of Shanghai. TEC, threshold effect concentration, below which adverse effects of sediment toxicity are unlikely to occur (MacDonald et al., 2000).

the highest concentrations of the $\sum_{14}$PCBs were found in A3, which was significantly higher than those in the other areas ($p < 0.05$).

The average concentrations of the $\sum_{14}$PCBs in the surface water and sediments of the Huangpu River were 25.23 ng·L^{-1} and 5.17 ng·g^{-1} dw, respectively. The mean value of PCBs in the sediments of the Huangpu River was lower than the value for PCBs in the lower urban stream of the Huangpu River reported by Wu et al. (1999) (19.9 ng·g^{-1} dw). The concentrations of the $\sum_{14}$PCBs in the Huangpu River at different areas are shown in Fig. 3. The highest level of PCBs in the surface water of the Huangpu River was observed at SS 39 (A2), while the lowest concentration of $\sum_{14}$PCBs was found at SS 40 (A2). SS 39 was taken near an area of farmland (A2), but there were some shipping companies, shipyards, and building materials industries along the banks near the sampling site, which might be the source of PCB emissions (Gao et al., 2013). In the sediments, the concentration of the $\sum_{14}$PCBs at SS 45 (A1) was the highest, which was sampled at the downstream area of the Huangpu River near the petrochemical and transfer storage zones of New Jiangwan City of Shanghai. The levels of PCBs in the surface sediments increased in going from upstream to downstream along the Huangpu River, but this trend was not observed for PCBs in surface water (Fig. 3).

In general, the total concentrations of the $\sum_{14}$PCBs were higher in A3 and lower in A5 whether for the surface waters or the surface sediments (Fig. 2). A3 was in the center of Shanghai with the greatest industry and population density. Many rivers were black and malodorous, such as SS 46, SS 47, SS 49, and SS 53. Most rivers in A3 had been dammed by floodgates, which would lead to a relative lack of hydrodynamic forces in the water courses. In such a case, the pollutants cannot disperse readily because of the low degradation potential of POPs in urban water systems (Rossi et al., 2004). Furthermore, the untreated industrial, urban runoff, and domestic waste waters in this area would be potential pollution sources

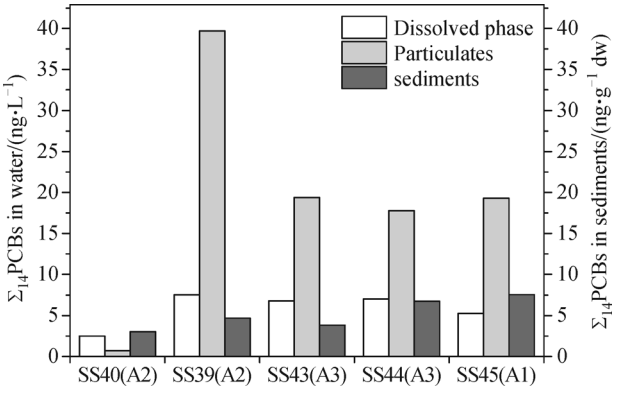

Fig. 3 Concentrations of $\sum_{14}$PCBs in surface water and sediments from Huangpu River. The sampling sites displayed the different places from upstream to downstream relatively with the increase of X-axle run-length.

which may result in higher accumulations of PCBs (Men et al., 2014). The lowest levels of the $\sum_{14}$PCBs in A5 occurred in the farmland of Chongming Island, which is far away from Shanghai city center, and has limited record of pollution due of the presence of fewer industries.

The levels of PCBs in the dissolved phase for this study were in the range observed by Li et al. (2012) for middle reaches of the Yangtze River (3.81–46.69 ng·L^{-1}), and the levels of PCBs in particulates were similar to the data of Men et al. (2014) for the Dailiao River estuary (6.78–66.55 ng·L^{-1}) (Table 1). The total concentrations of PCBs in water were similar to those in the Seine River estuary in France (14.1–55.0 ng·L^{-1}) (Cailleaud et al., 2007), and were higher than those in the Delaware River in the USA (Rowe et al., 2007) , but were lower than those in Lake Taihu (Wang et al., 2003), the Hai River (Wang et al., 2007), the Minjiang River estuary (Zhang et al., 2003), the Tonghui River (Zhang et al., 2004), and in the waste water of Qingyuan city in China (Wu et al., 2008), and in the water from Delhi in India (Kumar et al., 2012) (Table 1). In

the sediments, the levels of PCBs in this study were consistent with those in Lake Baiyangdian (5.96–29.61 $ng \cdot g^{-1}$ dw (Dai et al., 2011), and were higher than those in Lake Taihu (Chen et al., 2009), the Tonghui River (Zhang et al., 2004), the Daliao River (Men et al., 2014) in China, and the Han River in Korea (Kim et al., 2009), but were lower than those in the Yangtze River estuary, the Zhujiang River, and the Minjiang River estuary in China (Fu et al., 2003; Zhang et al., 2003; Gao et al., 2013), and in the Houston Ship Channel in the USA (Howell et al., 2008) (Table 1).

3.2 PCB composition and source identification

In the rivers of Shanghai, PCB 118, 105, and PCB 77 accounted for a higher contribution compared with other PCB congeners in the dissolved phase, and in particulates and in sediments as shown in Fig. 4 and Table A1, respectively. In the dissolved phase, the contribution of PCB 105 was the highest, accounting for 37.51% of all PCB congeners, followed by PCB 118 (34.35%) and PCB 77 (11.75%). In particulates, PCB 118 accounted for 24.64% of the $\sum_{14}$PCBs, followed by PCB 105 (13.97%),

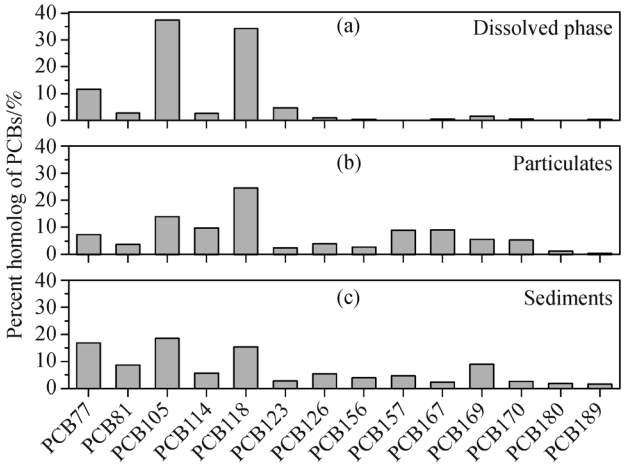

Fig. 4 PCB congener patterns in dissolved phases, particulates and sediments from the rivers of Shanghai, China.

Table 1 Comparison of the concentrations of PCBs in the water and the sediments from other researches

Location	Water		Sediment /($ng \cdot g^{-1}$, dw)	*n*	Reference
	Dissolved/($ng \cdot L^{-1}$)	Particulate/($ng \cdot L^{-1}$)			
River network in Shanghai, China	ND – 34.84 (8.42)	0.76 – 39.71(9.93)	1.46 – 46.11(9.06)	14	This study
Huangpu River, China	2.49 – 7.56 (5.84)	0.76 – 39.71 (19.39)	3.04 – 7.56 (5.17)	14	This study
Daliao River Estuary, China	5.51 – 40.28 (16.91)	6.78 – 66.55 (21.81)	0.83 – 7.29 (1.77)	41	Men et al., 2014
Delaware River, USA	0.42 – 1.65	1.97 – 4.9		116	Rowe et al., 2007
Seine River, Estuary, France	2.0 – 21.2 (7.0)	58 – 463 (227)		8	Cailleaud et al., 2007
Waste water from Qingyuan City, China	196 – 206			44	Wu et al., 2008
Surface water from Delhi, India	14 – 1768 (332)			28	Kumar et al., 2012
Tributaries in Middle Reaches of Yangtze River, China	3.77 – 61.79 (20.71)			28	Li et al., 2012
Mainstream in Middle Reaches of Yangtze River, China	3.81 – 46.69 (13.25)			28	Li et al., 2012
Baiyangdian Lake, China	19.46 – 131.62 (45.35)		5.96 – 29.61 (6.35)	41	Dai et al., 2011
Zhujiang River, China	0.70 – 3.96 (2.3)		12.88 – 65.31(31.52)	209	Nie et al., 2001
Minjiang River Estuary, China	203.9–2473 (985.2)		15.14 – 57.93 (34.49)	21	Zhang et al, 2003
Tonghui River, China	31.58 – 344.9 (105.5)		0.78 – 8.47 (3.29)	12	Zhang et al., 2004
Houston Ship Channel, USA	0.49–12.49 (2.47)		4.18 – 4601 (1168)	209	Howell et al., 2008
Gaoping River, Taiwan, China			0.38 – 5.89(1.43)	42	Doong et al., 2008
Han River, Korea			0.04 – 4.53 (0.55)	12	Kim et al., 2009
Freshwater canals, Hanoi, Vietnam			0.74 – 33.68	13	Nhan et al., 2001
Yangtze Estuary, China			1.86 – 148.22	28	Gao et al., 2013
Taihu Lake, China	70.2 – 827			4	Wang et al., 2003
Taihu Lake, China			1.35 – 13.8 (4.86)	58	Chen et al., 2009
Niagara River, USA			1.70 – 124.60 (24.19)	14	Samara et al., 2006
Yamuna River, India			0.20 – 21.16 (6.63)	28	Kumar et al., 2013
Rio de la Plata Estuary, Argentina			0.04 – 98.5	41	Colombo et al., 2005

n, Number of PCB congeners analyzed in each study.

PCB 167 (9.13%), and PCB 77 (7.25%). In the sediments, the PCB congeners with high contributions were PCB 105 (18.56%), PCB 77 (16.88%), PCB 118 (15.46%), and PCB 169 (9.83%). The contribution of PCB 169 was relatively high (0.82 $ng \cdot g^{-1}$ dw) in the sediments. Men et al. (2014) also reported that PCB 169 was the highest contributor relative to the other 40 PCB congeners, with a concentration of 0.37 $ng \cdot g^{-1}$ dw in the sediments of the Daliao River estuary.

In China, the 1# PCB and 2# PCB have been used extensively and are regarded as potential sources of PCBs in the environment because of the serious local pollution and possible long-term effects (Xing et al., 2005; Zhang et al., 2010). For 1# PCB in this study, only PCB 77, 105, 118, 123, and PCB 126 were detected, and PCB 77 accounted for 80.84% among the 14 PCB congeners examined. For 2# PCB, PCB 77, 105, 114, 118, 123, 126, and PCB 156 were detected, and PCB 105 accounted for 94% of the total PCBs (Jiang et al., 1997). While Huang et al. (2011) reported that only PCB 77, 118, and PCB 105 were detected in insulating oil samples, which were produced by the Xi'an Electrical Capacitor Plant where the 1# PCBs were first produced in China. Some researchers have proposed that emissions from the burning of house coal and hardwood (Lee et al., 2005; Gao et al., 2015), and from industrial activities, such as secondary Al and Cu metallurgy, might be potential sources of PCBs in the environment (Ba et al., 2009; Liu et al., 2016).

PCA was undertaken in an attempt to give further insight into the sources of PCBs. There were four principal components (PCs), which accounted for 75.43% of the total variance. The first three PCs explained 27.86%, 21.25%, and 15.25% of the total variance, respectively. In PC 1, the factor loading of PCB 105, 123, 126, and PCB 157 was higher than 0.6, and could be classified as a group (Fig. 5), which indicated that the sources of these four congeners might be similar. Because PCB 105 was the dominant congener of the 14 PCB congeners in 2# PCB (Jiang et al., 1997), and PCB 126 accounted for > 84% of the 12 dl-PCB congeners in the emissions from secondary Cu, Al, and Mg metallurgy, respectively (Ba et al., 2009; Nie et al., 2011), PC 1 can be regarded as the historical accumulation of 2# PCB and the emissions of secondary metallurgy activities. In PC 2, the factor loading of PCB 118, 77, and PCB 180 was higher than 0.9 and could be classified into a group (Fig. 5). Thus PC 2 would show the historical accumulation of 1# PCB and emissions of municipal solid waste (MSW) incineration because of the high contributions of PCB 118 and PCB77 in 1# PCB (Huang et al., 2011), and the high contributions of PCB180 from MSW (Ishikawa et al., 2007). PCB 167, 156, and PCB 169 had a high factor loading in PC 3 (Fig. 5), which could be identified as emissions from the metallurgy industry because PCB 169 was the dominant congener in the emissions of secondary metallurgy (Ba et al., 2009; Nie et al., 2011). PCB 170 accounted for about 7% in the emissions from house coal burning (CB) (Lee et al., 2005), therefore, PC4 revealed the possibility of emissions from combustion sources.

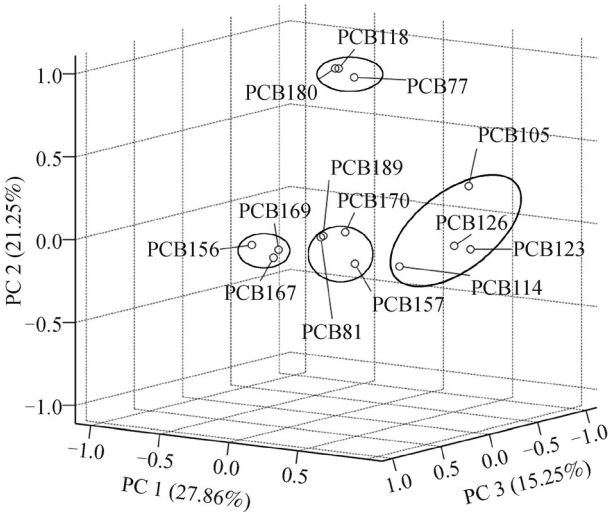

Fig. 5 Component plot in rotated space of 14 PCB congeners in the surface water and sediment from the rivers in Shanghai, China. Four groups of PCB congeners were classified according to their factor loading in the component matrix and their significance in correlation matrix ($P = 0.000$).

The PCA scores of different samples and potential sources are shown in Fig. 6. It is clear that PC1, PC2, and PC3 indicated the sources of 2# PCB, CEC, and CB, respectively. In the PCA scores plot, all of the surface water and sediment samples had similar scores with the potential sources, such as A1242, A1254, SM-Al, SM-Cu, WB, and MSW, which were classified into a group as shown in Fig. 6. Furthermore, the PCB homolog and congener distribution patterns of emission sources which described the above are all listed in Table A2 and shown in Fig. 7 which contrasts with the samples of this study. The PCBs profiles of the surface waters and sediments of the river network of Shanghai were more consistent with A1254 and 2# PCB. In China, 2# PCBs were mainly used in anti-fouling paint, and the compositions were regarded as being similar to A1254 (Jiang et al. 1997). Besides, Fig. 7 showed that the proportion of the *Penta*-CBs dominated the surface water and sediments of the rivers in Shanghai, and the concentration percentages of *Hexa*-CBs and *Hepta*-CBs were in the following order: sediments > particulates > dissolved phase, which indicated that the highly chlorinated PCBs tended to be adsorbed to SPM and deposited in sediments. In general, the mobility of PCB congeners decreases with an increase in the number of chlorine atoms, so the highly chlorinated PCBs might be deposited close to the source, while the lighter PCBs may be transported further from the source (Hong et al., 2003). The differences of the PCB profiles between the surface

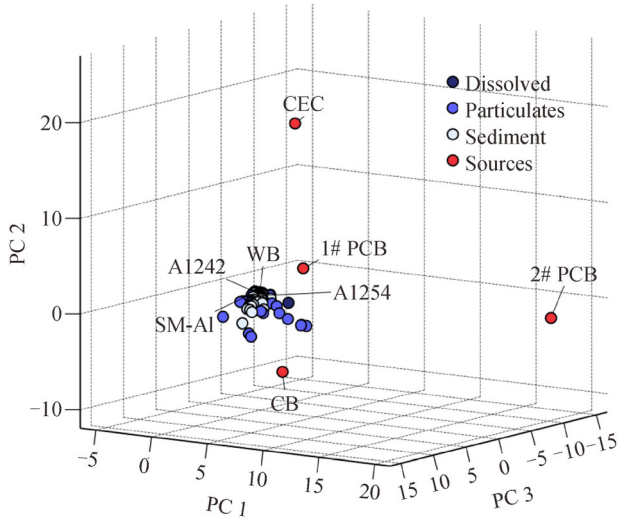

Fig. 6 PCA score plot of PCBs for all samples and potential sources. SM-Al, secondary Al metallurgy; SM-Cu, secondary Cu metallurgy; WB, hardwood buring; CB, housecoal buring; CEC, China electrical capacitors; A1242, Aroclor 1242; A1254, Aroclor 1254; MSW, municipal solid waste incineration.

waters and the sediments of the rivers of Shanghai indicated that the pollutant inputs had changed historically. Gao et al (2013) reported that non-point sources including atmospheric deposition and surface runoff associated with storm water were the major sources of PCBs in the surface sediments of the Yangtze Estuary. While in the surface sediments from the rivers in city clusters in South Jiangsu Province, China, the historical use of technical PCBs products and vessel coatings were suggested as the main PCBs sources (Zhang et al., 2014b). Therefore, according to the PCA results and related research, the sources of PCBs in the surface water and sediments of the rivers in Shanghai were mainly from the historical accumulation of commercial PCB products produced in China, and from combustion sources by means of atmospheric deposition or surface runoff deposition. Moreover, the emissions from secondary metallurgy industries were also potential sources of PCBs in the aquatic environment of Shanghai, China.

3.3 Risk assessment

According to the guidelines of the USEPA standard, the concentrations of PCBs in surface water should be less than 14 $ng \cdot L^{-1}$, a level which is considered to pose no hazard to aquatic or human health. As shown in Fig. 2, there were 7 samples in the dissolved phase that were higher than the USEPA standard. Also there were 14 particulate samples that were higher than the USEPA standard. Generally, 43.4% of all water samples were seriously polluted by PCBs, indicating risk and concern for the aquatic environment and human health. These samples were taken mainly from the city center and the residential areas in towns of Shanghai. In the case of sediment samples, only the concentration of PCBs in SS 51 (A3) was higher than the TEC (40 $ng \cdot g^{-1}$ dw) (Fig. 2), indicating that adverse toxicity effects due to the sediments in the rivers of Shanghai were unlikely to occur (MacDonald et al., 2000).

The WHO_{2005} toxic equivalents (TEQs) were calculated using the 2,3,7,8-TCDD toxic equivalent factors (TEFs), which are listed in Table 2 (Van den Berg et al., 2006). The results (Table 3) revealed that the WHO-TEQ in water samples (dissolved phase plus particulates) ranged between 0.08–1136.56 pg $TEQ \cdot L^{-1}$ with a mean value of 103.9 pg $TEQ \cdot L^{-1}$. The largest WHO-TEQs was found in SS 47 (A3), followed by SS 16 (A1), SS 53 (A4), and SS 35 (A4). In total, A3 had the highest level of WHO-TEQs

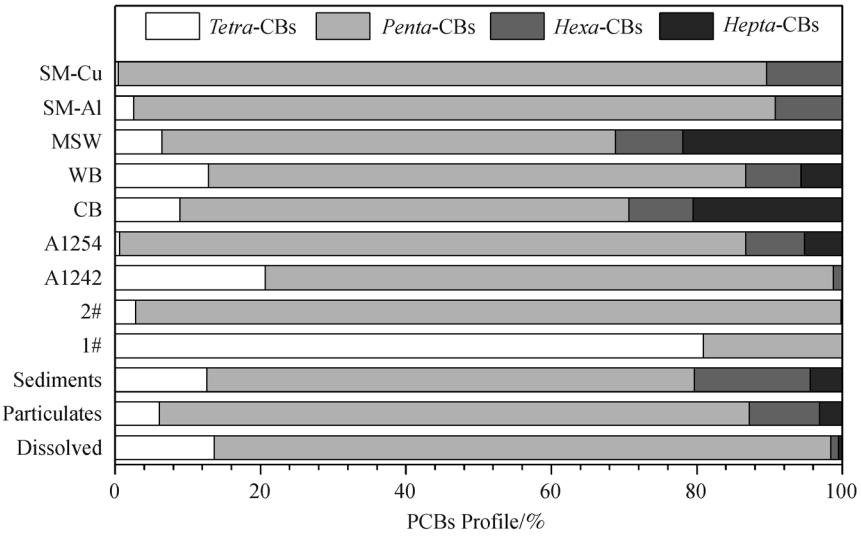

Fig. 7 PCA score plot of PCBs for all samples and potential sources. SM-Al, secondary Al metallurgy; SM-Cu, secondary Cu metallurgy; WB, hardwood burning; CB, housecoal burning; CEC, China electrical capacitors; A1242, Aroclor 1242; A1254, Aroclor 1254; MSW, municipal solid waste incineration.

Table 2 Summary of WHO 1998 and WHO 2005 TEF Values of dl-PCBs (Van den Berg et al., 2006)

Compound	WHO-1998 TEF	WHO-2005 TEF
Non-*ortho*-substituted PCBs		
PCB 77	0.0001	0.0001
PCB 81	0.0001	0.0003
PCB 126	0.1	0.1
PCB 169	0.01	0.03
Mono-*ortho*–substituted PCBs		
PCB 105	0.0001	0.00003
PCB 114	0.0005	0.00003
PCB 118	0.0001	0.00003
PCB 123	0.0001	0.00003
PCB 156	0.0005	0.00003
PCB 157	0.0005	0.00003
PCB 167	0.0001	0.00003
PCB 189	0.0001	0.00003

and was significantly greater than the other four areas ($p < 0.05$).

In the sediments, the WHO-TEQ ranged between 0.05–432.12 pg TEQ·g^{-1} dw with a mean of 74.61 pg TEQ·g^{-1} dw (Table 3). The highest concentrations of WHO-TEQs were in A3, but the differences between the five areas were not significant ($p > 0.05$). The interim sediment quality guidelines (ISQGs) and USEPA guidelines of high risk to sensitive species (HR), based on the 2,3,7,8-TCDD toxic equivalent, were 21.5 and 25 pg TEQ·g^{-1} dw, respectively. Accordingly, there were 23 sampling sites above the ISQGs and HR, accounting for 43.4% of all the sites, which indicated that adverse biological effects would be likely to occur in these sites.

SS 47, SS 16, and SS 53 had higher WHO-TEQs both in the water and in the sediments. SS 47 was located on the Qiujiang River, and the water was malodorous and black. SS 16 was near the Fengxian Industrial Park where chemical and pharmaceutical industries were located. SS 53 was on the Suzhou River which flowed through the west of the central part of Shanghai. High concentrations of PCB 126 were detected in these three sites and hence represents a serious level of biological risk. For all samples, the concentrations of PCB 126, PCB 169, and PCB 77 contributed the most to the WHO-TEQs of the dl-PCBs, so the differences between the levels of these three

Table 3 WHO_{2005}-TEQ of dl-PCBs in the dissolved phase, the particulates and the surface sediments from the rivers in different areas of Shanghai

	Areas	Mean	Standard deviation	Min	Max
Dissolved phase /(pg TEQ·L^{-1})	A1	96.61	286.52	0.09	957.06
	A2	15.34	43.86	ND	161.06
	A3	103.45	342.34	0.13	1135.65
	A4	3.64	10.45	0.10	33.36
	A5	0.08	0.05	ND	0.16
	Total	46.56	202.39	ND	1135.65
Particulates /(pg TEQ·L^{-1})	A1	1.63	4.56	0.03	15.33
	A2	61.23	132.89	0.02	493.30
	A3	124.29	185.95	0.03	605.94
	A4	52.38	164.94	0.05	521.81
	A5	35.27	55.32	0.05	120.82
	Total	57.34	134.47	0.02	605.94
Water /(pg TEQ·L^{-1})	A1	98.24	286.04	0.19	957.32
	A2	76.57	144.66	0.08	493.44
	A3	227.74	351.79	0.22	1136.56
	A4	56.02	175.38	0.20	555.17
	A5	35.35	55.29	0.15	120.90
	Total	103.90	235.02	0.08	1136.56
Sediment /(pg TEQ g^{-1} dw)	A1	65.28	116.12	0.06	378.22
	A2	84.91	129.90	0.05	432.12
	A3	85.51	134.33	0.05	365.81
	A4	60.80	92.19	0.05	236.86
	A5	68.99	81.09	0.08	170.98
	Total	74.61	113.24	0.05	432.12

dominant PCB congeners were the main reason for the different spatial distributions of the WHO-TEQs.

In contrast, The WHO-TEQs for dl-PCBs in the surface water of the river network of Shanghai were similar to the results reported by Khim et al. (2001) for Korean rivers (range: < 0.01–238 pg TEQ·L^{-1} for the dissolved phase and nd–53.2 ng TEQ·g^{-1} for the particulates), and were lower than the levels in the surface waters of the Yamuna River (< 1–1600 pg TEQ·L^{-1}) and the Delhi River (< 1–2314 pg TEQ·L^{-1}) in India (Kumar et al., 2012), but were higher than those in the urban rivers and industrial wastewaters in Japan (Kakimoto et al., 2006) and the Houston Ship Channel in the USA (Howell et al., 2011). In the sediments, the WHO-TEQs for dl-PCBs in this study were similar to the levels of the Venice Lagoon (5–404 pg TEQ·g^{-1}) in Italy (Frignani et al., 2001), were lower than that in the Nanpaiwu River in China (0.1–880 pg TEQ·g^{-1}) (Hu et al., 2005), but were higher than the levels in the Xiangjiang River (Chen et al., 2012), the Hai River, the Dagu River (Liu et al., 2007), the East River (Ren et al., 2009), the Suzhou River (Li et al., 2007), the Huanghe River, and the Yangtze River in China (Gao et al., 2015), and the Han River in Korea (Kim et al., 2009).

4 Conclusions

In this study, the levels of 14 PCB congeners in the surface waters and sediments from rivers in five different areas of Shanghai were investigated. PCB 105, 118, and PCB 77 were the dominant congeners in the $\sum_{14}$PCBs, while PCB 126, 169, and PCB 77 accounted for the most contributions of total WHO-TEQs. The PCA results and the PCBs profiles indicated a historical accumulation of commercial PCB products in China, and the burning of house coal and emissions from municipal solid waste incineration and secondary metallurgy industries were the main sources. The WHO-TEQs of dl-PCBs in surface water of the Shanghai river network were consistent with the findings of moderate risk reported by other researchers. The WHO-TEQs of dl-PCBs in 43.4% of sediment samples were higher than the USEPA guideline for high risk to sensitive species. Most sites with high PCB pollution were located in the center of Shanghai, the industrial parks, and residential areas in towns. Therefore, it is necessary to carry out an overall and thorough monitoring of PCB pollution and perform accurate research of source apportionment ratios for PCBs in the rivers of Shanghai, China.

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References

Ba T, Zheng M, Zhang B, Liu W, Xiao K, Zhang L (2009). Estimation and characterization of PCDD/Fs and dioxin-like PCBs from secondary copper and aluminum metallurgies in China. Chemosphere, 75(9): 1173–1178

Breivik K, Sweetman A, Pacyna J M, Jones K C (2002). Towards a global historical emission inventory for selected PCB congeners-a mass balance approach: 1. Global production and consumption. Sci Total Environ, 290(1−3): 181–198

Cailleaud K, Forget-Leray J, Souissi S, Hilde D, LeMenach K, Budzinski H (2007). Seasonal variations of hydrophobic organic contaminant concentrations in the water-column of the Seine Estuary and their transfer to a planktonic species Eurytemora affinis (Calanoida, copepoda). Part 1: PCBs and PAHs. Chemosphere, 70 (2): 270–280

Chen Y Y, Yin Y, Wang X R, Guo H Y, Chen S J, Mai B X (2009). Polycyclic aromatic hydrocarbons and polychlorinated biphenyl in surface sediments of Taihu Lake: the distribution, sources and risk assessment. China Environ Sci, 29(2): 118–124 (in Chinese)

Chen Z, Yang B, Mengoni A, Dong J, Peng X (2012). Distribution patterns of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in sediments of the Xiangjiang River, China. Environ Monit Assess, 184(12): 7083–7092

Colombo J C, Cappelletti N, Barreda A, Migoya M C, Skorupka C N (2005). Vertical fluxes and accumulation of PCBs in coastal sediments of the Río de la Plata estuary, Argentina. Chemosphere, 61(9): 1345–1357

Dachs J, Lohmann R, Ockenden W A, Méjanelle L, Eisenreich S J, Jones K C (2002). Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. Environ Sci Technol, 36(20): 4229–4237

Dai G, Liu X, Liang G, Han X, Shi L, Cheng D, Gong W (2011). Distribution of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in surface water and sediments from Baiyangdian Lake in North China. J Environ Sci (China), 23(10): 1640–1649

Doong R A, Lee S H, Lee C C, Sun Y C, Wu S C (2008). Characterization and composition of heavy metals and persistent organic pollutants in water and estuarine sediments from Gao-ping River, Taiwan. Mar Pollut Bull, 57(6): 846–857

Frignani M, Bellucci L G, Carraro C, Raccanelli S (2001). Polychlorinated biphenyls in sediments of the Venice Lagoon. Chemosphere, 43(4): 567–575

Fu J, Mai B, Sheng G, Zhang G, Wang X, Peng P A, Xiao X M, Ran R, Cheng F Z, Peng X Z, Wang Z S, Tang U W (2003). Persistent organic pollutants in environment of the Pearl River Delta, China: an overview. Chemosphere, 52(9): 1411–1422

Gao L, Huang H, Liu L, Li C, Zhou X, Xia D (2015). Polychlorinated dibenzo-p-dioxins, dibenzofurans, and dioxin-like polychlorinated biphenyls in sediments from the Yellow and Yangtze Rivers, China. Environ Sci Pollut Res Int, 22(24): 1–10

Gao S, Chen J, Shen Z, Liu H, Chen Y (2013). Seasonal and spatial distributions and possible sources of polychlorinated biphenyls in

surface sediments of Yangtze Estuary, China. Chemosphere, 91(6): 809–816

Hong S H, Yim U H, Shim W J, Oh J R, Lee I S (2003). Horizontal and vertical distribution of PCBs and chlorinated pesticides in sediments from Masan Bay, Korea. Mar Pollut Bull, 46(2): 244–253

Howell N L, Rifai H S, Koenig L (2011). Comparative distribution, sourcing, and chemical behavior of PCDD/Fs and PCBs in an estuary environment. Chemosphere, 83(6): 873–881

Howell N L, Suarez M P, Rifai H S, Koenig L (2008). Concentrations of polychlorinated biphenyls (PCBs) in water, sediment, and aquatic biota in the Houston Ship Channel, Texas. Chemosphere, 70(4): 593–606

Hu J, Wan Y, Shao B, Jin X, An W, Jin F, Min Y, Wang X J, Sugisaki M (2005). Occurrence of trace organic contaminants in Bohai Bay and its adjacent Nanpaiwu River, North China. Mar Chem, 95(1): 1–13

Huang J, Matsumura T, Yu G, Deng S, Yamauchi M, Yamazaki N, Weber R (2011). Determination of PCBs, PCDDs and PCDFs in insulating oil samples from stored Chinese electrical capacitors by HRGC/HRMS. Chemosphere, 85(2): 239–246

Ishikawa Y, Noma Y, Mori Y, Sakai S (2007). Congener profiles of PCB and a proposed new set of indicator congeners. Chemosphere, 67(9): 1838–1851

Jiang K, Li L, Chen Y, Jin J (1997). Determination of PCDD/Fs and dioxin-like PCBs in Chinese commercial PCBs and emissions from a testing PCB incinerator. Chemosphere, 34(5): 941–950

Kakimoto H, Oka H, Miyata Y, Yonezawa Y, Niikawa A, Kyudo H, Tang N, Toriba A, Kizu R, Hayakawa K (2006). Homologue and isomer distribution of dioxins observed in water samples collected from Kahokugata Lagoon and inflowing rivers, Japan. Water Res, 40 (10): 1929–1940

Khim J S, Lee K T, Kannan K, Villeneuve D L, Giesy J P, Koh C H (2001). Trace organic contaminants in sediment and water from Ulsan Bay and its vicinity, Korea. Arch Environ Contam Toxicol, 40 (2): 141–150

Kim K S, Lee S C, Kim K H, Shim W J, Hong S H, Choi K H, Yoon J H, Kim J G (2009). Survey on organochlorine pesticides, PCDD/Fs, dioxin-like PCBs and HCB in sediments from the Han river, Korea. Chemosphere, 75(5): 580–587

Kumar B, Kumar S, Sharma C S (2013). Ecotoxicological risk assessment of polychlorinated biphenyls (PCBs) in bank sediments from along the Yamuna River in Delhi, India. Hum Ecol Risk Assess Int J, 19(6): 1477–1487

Kumar B, Singh S K, Mishra M, Kumar S, Sharma C S (2012). Assessment of polychlorinated biphenyls and organochlorine pesticides in water samples from the Yamuna River. J Xenobiotics, 2(1): e6

Lee R G, Coleman P, Jones J L, Jones K C, Lohmann R (2005). Emission factors and importance of PCDD/Fs, PCBs, PCNs, PAHs and PM10 from the domestic burning of coal and wood in the UK. Environ Sci Technol, 39(6): 1436–1447

Li K, Yin H W, Zheng M H, Rong Z Y, Jia L J (2007). Polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxinlike biphenyls in sediments from the Suzhou Creek, China. Bull Environ Contam Toxicol, 79(4): 432–436

Li K, Zhao G F, Zhou H D, Zeng M, Liao B H, Wu Z Y, Zhang P W, Hao H (2012). Distribution characteristics and potential risk of PCBs in surface water from 22 tributaries and mainstream in middle reaches of Yangtze River. Environ Sci, 33(5): 1676–1681

Liu G, Zheng M, Jiang X, Jin R, Zhao Y, Zhan J (2016). Insights into the emission reductions of multiple unintentional persistent organic pollutants from industrial activities. Chemosphere, 144: 420–424

Liu H, Zhang Q, Wang Y, Cai Z, Jiang G (2007). Occurrence of polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls pollution in sediments from the Haihe River and Dagu Drainage River in Tianjin City, China. Chemosphere, 68(9): 1772–1778

MacDonald D D, Dipinto L M, Field J, Ingersoll C G, Lvong E R, Swartz R C (2000). Development and evaluation of consensus-based sediment effect concentrations for polychlorinated biphenyls. Environ Toxicol Chem, 19(5): 1403–1413

Men B, He M, Tan L, Lin C (2014). Distributions of polychlorinated biphenyls in the Daliao River estuary of Liaodong Bay, Bohai Sea (China). Mar Pollut Bull, 78(1): 77–84

Nhan D D, Carvalho F P, Am N M, Tuan N Q, Yen N T H, Villeneuve J P, Cattini C (2001). Chlorinated pesticides and PCBs in sediments and molluscs from freshwater canals in the Hanoi region. Environ Pollut, 112(3): 311–320

Nie X P, Lan C Y, Luan T G, Huang M H, Mai Z Q (2001). Polychlorinated biphenyls in the waters, sediments and benthic organisms from Guangzhou reach of Pearl River. China Environ Sci, 21(5): 417–421 (in Chinese)

Nie Z, Zheng M, Liu W, Zhang B, Liu G, Su G, Lv P, Xiao K (2011). Estimation and characterization of PCDD/Fs, dl-PCBs, PCNs, HxCBz and PeCBz emissions from magnesium metallurgy facilities in China. Chemosphere, 85(11): 1707–1712

Ren M, Peng P A, Chen D, Chen P, Li X (2009). Patterns and sources of PCDD/Fs and dioxin-like PCBs in surface sediments from the East River, China. J Hazard Mater, 170(1): 473–478

Rossi L, de Alencastro L, Kupper T, Tarradellas J (2004). Urban stormwater contamination by polychlorinated biphenyls (PCBs) and its importance for urban water system in switzerland. Sci Total Environ, 322(1−3): 179–189

Rowe A A, Totten L A, Xie M, Fikslin T J, Eisenreich S J (2007). Air-water exchange of polychlorinated biphenyls in the Delaware River. Environ Sci Technol, 41(4): 1152–1158

Safe S (1990). Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). CRC Crit Rev Toxicol, 21 (1): 51–88

Samara F, Tsai C W, Aga D S (2006). Determination of potential sources of PCBs and PBDEs in sediments of the Niagara River. Environ Pollut, 139(3): 489–497

Shanghai Environmental Protection Bureau (2012). Shanghai Environmental Bulletin 2010. http://www.envir.gov.cn/law/bulletin/2012/

Takasuga T, Senthilkumar K, Matsumura T, Shiozaki K, Sakai S I (2006). Isotope dilution analysis of polychlorinated biphenyls (PCBs) in transformer oil and global commercial PCB formulations by high resolution gas chromatography-high resolution mass spectrometry. Chemosphere, 62(3): 469–484

Totten L A, Panangadan M, Eisenreich S J, Cavallo G J, Fikslin T J (2006). Direct and indirect atmospheric deposition of PCBs to the

Delaware River watershed. Environ Sci Technol, 40(7): 2171–2176

Van den Berg M, Birnbaum L S, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L, Rose M, Safe S, Schrenk D, Tohyama C, Tritscher A, Tuomisto J, Tysklind M, Walker N, Peterson R E (2006). The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol Sci, 93(2): 223–241

Wang H, Wang C, Wu W, Mo Z, Wang Z (2003). Persistent organic pollutants in water and surface sediments of Taihu Lake, China and risk assessment. Chemosphere, 50(4): 557–562

Wang J, Da L, Song K, Li B L (2008). Temporal variations of surface water quality in urban, suburban and rural areas during rapid urbanization in Shanghai, China. Environ Pollut, 152(2): 387–393

Wang T, Zhang Z L, Huang J, Hu H Y, Yu G, Li F S (2007). Occurrence of dissolved polychlorinated biphenyls and organic chlorinated pesticides in the surface water of Haihe River and Bohai Bay. China Environ Sci, 28(4): 730–735 (in Chinese)

Wu J P, Luo X J, Zhang Y, Luo Y, Chen S J, Mai B X, Yang Z Y (2008). Bioaccumulation of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in wild aquatic species from an electronic waste (e-waste) recycling site in South China. Environ Int, 34(8): 1109–1113

Wu Y, Zhang J, Zhou Q (1999). Persistent organochlorine residues in sediments from Chinese river/estuary systems. Environ Pollut, 105 (1): 143–150

Xing Y, Lu Y, Dawson R W, Shi Y, Zhang H, Wang T, Liu W B, Ren H (2005). A spatial temporal assessment of pollution from PCBs in China. Chemosphere, 60(6): 731–739

Yu Z J, Deng H G, Wang D Q, Ye M W, Tan Y J, Li Y J, Chen Z L, Xu S Y (2013). Nitrous oxide emissions in the Shanghai river network: implications for the effects of urban sewage and IPCC methodology. Glob Change Biol, 19(10): 2999–3010

Zhang A, Li Y, Chen L (2014a). Distribution and seasonal variation of estrogenic endocrine disrupting compounds, N-nitrosodimethylamine, and N-nitrosodimethylamine formation potential in the Huangpu River, China. J Environ Sci (China), 26(5): 1023–1033

Zhang H J, Zhao X F, Ni Y W, Lu X B, Chen J P, Su F, Zhao L, Zhang L, Zhang X P (2010). PCDD/Fs and PCBs in sediments of the Liaohe River, China: levels, distribution, and possible sources. Chemosphere, 79(7): 754–762

Zhang T, Chen S J, Li N, Liu A M, Zhang L F, Shi D L, Zheng S, Zhao H, Qi L, Mai B X, Huang Y R, Dong L (2014b). Occurrence, sources and ecological risks of PCDD/Fs and dl-PCBs in surface sediments from rivers in city cluster in South Jiangsu Province, China. Environ Chem, 33(9): 1445–1455 (in Chinese)

Zhang Z, Huang J, Yu G, Hong H (2004). Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. Environ Pollut, 130(2): 249–261

Zhang Z L, Hong H S, Zhou J L, Huang J, Yu G (2003). Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China. Chemosphere, 52(9): 1423–1430

Zhang Z, Qi H, Liu Y L, Yang M, Li Y F (2009). Congener and homologue profiles of Polychlorinated Biphenyls (PCBs) produced in China. J Heilongjiang Univ, 26(6): 809–815 (in Chinese)

Appendix

Table A1 Concentrations of PCBs in the dissolved phase ($ng \cdot L^{-1}$), the particulates ($ng \cdot L^{-1}$) and surface sediments ($ng \cdot g^{-1}dw$) from the rivers in different regions of Shanghai

IUPAC#	A1			A2			A3			A4			A5			Total		
	d [a)]	*p* [b)]	*s* [c)]	*d*	*p*	*s*	*d*	*p*	*s*	*d*	*p*	*s*	*d*	*p*	*s*	*d*	*p*	*s*
PCB 77	1.48	0.58	1.02	0.48	1.33	1.02	2.07	0.62	3.99	0.73	0.51	0.95	ND	ND	0.20	1.01	0.72	1.53
PCB 81	0.49	0.19	0.60	ND	0.52	0.50	0.54	0.84	2.50	0.12	0.14	ND	ND	ND	ND	0.24	0.39	0.79
PCB 105	3.30	1.37	1.50	2.26	1.75	1.49	2.88	0.57	2.03	6.78	1.51	1.73	0.18	1.82	1.77	3.22	1.39	1.68
PCB 114	0.28	0.69	0.51	0.55	0.93	0.38	0.06	1.55	0.77	ND	0.96	0.37	0.04	0.58	0.67	0.23	0.98	0.52
PCB 118	3.24	2.07	1.04	3.21	2.44	1.14	2.84	3.05	2.88	2.68	2.19	0.82	2.40	2.48	0.97	2.95	2.45	1.40
PCB 123	0.55	ND	0.19	0.92	0.65	0.05	0.13	0.13	0.98	ND	ND	ND	0.11	0.36	ND	0.41	0.25	0.26
PCB 126	0.14	0.01	0.36	0.11	0.40	0.64	0.08	0.86	0.48	ND	0.42	0.33	ND	0.24	0.69	0.07	0.40	0.50
PCB 156	0.09	ND	0.19	ND	0.49	0.17	ND	0.68	0.70	ND	ND	0.57	ND	ND	0.20	0.02	0.28	0.36
PCB 157	0.01	ND	0.37	ND	1.19	0.32	ND	1.90	0.58	ND	0.44	0.41	ND	0.57	0.53	0.002	0.88	0.43
PCB 167	0.17	ND	0.15	ND	0.96	0.20	ND	2.43	0.27	ND	0.70	0.26	ND	ND	0.20	0.04	0.91	0.21
PCB 169	0.20	ND	0.97	0.15	0.69	0.68	0.16	1.27	1.22	0.11	0.33	0.91	ND	0.37	ND	0.14	0.56	0.82
PCB 170	0.14	0.67	0.09	ND	0.47	0.14	0.11	0.64	0.58	ND	0.72	0.30	ND	ND	0.14	0.05	0.54	0.25
PCB 180	0.02	ND	0.05	ND	0.47	0.21	0.02	ND	0.33	ND	ND	0.17	ND	ND	ND	0.01	0.13	0.17
PCB 189	0.08	ND	0.09	ND	ND	0.13	0.09	ND	0.19	ND	0.30	0.14	ND	ND	0.18	0.03	0.06	0.14
∑dl-PCBs	10.03	4.90	7.00	7.66	11.36	6.72	8.85	13.89	16.58	10.43	7.50	6.49	2.72	6.42	5.42	8.36	9.26	8.64
∑PCBs	10.19	5.58	7.15	7.66	12.29	7.08	8.98	14.53	17.49	10.43	8.21	6.97	2.72	6.42	5.56	8.42	9.93	9.06

a) dissolved phases; b) particulates; c) sediments; ND, not detected.

Table A2 Emissions factors of PCBs from possible sources

	China electrical capacitors [a] (CEC) /(μg·g^{-1})	1# PCB [b] /(μg·g^{-1})	2# PCB [b] /(μg·g^{-1})	Housecoal burning (CB) [c] /(ng·kg^{-1})	Hardwood burning (WB) [c] /(ng·kg^{-1})	Ar1242 [d] /%	Ar1254 [d] /%	Gaseous emission from secondary Al metallurg (SM-Al) [e] /(ng·m^{-3} N)	Gaseous emission from secondary Cu metal-lurg (SM-Cu) [e] /(ng·m^{-3} N)	Gaseous emission from iron ore sintering plant (IOS) [f] /(ng·m^{-3} N)	Municipal solid waster incineration facility (MSW) [g] /(ng·g^{-1})	Gaseous emission from cement plan (CP) [g] /(ng·m^{-3} N)
PCB77	3900	2098	194	21	2.7	0.310	0.098	0.0017	0.0004	2.0	0.043	0.543
PCB81	ND	NA	NA	NA	NA	ND	ND	0.0038	0.0007	0.4	0.004	0.108
PCB105	2500	482	6529	40	5.3	0.410	2.600	0.0016	0.0002	2.5	0.120	0.403
PCB114	ND	0	8.38	2.3	0.3	0.057	0.160	0.0002	0.0001	0.3	0.028	0.055
PCB118	3500	2.63	59.7	96	8.5	0.590	6.900	0.0038	0.0007	6.6	0.292	1.351
PCB123	ND	2.63	59.7	6.6	1.2	0.029	0.260	0.0006	0.0001	0.4	0.008	0.074
PCB126	ND	10	20.87	1.8	0.2	0.008	ND	0.1879	0.2273	0.7	0.004	0.035
PCB156	ND	ND	11.8	13	0.9	0.019	0.910	0.0003	0.0001	0.6	0.041	0.063
PCB157	ND	NA	NA	2.5	0.2	0.005	0.180	0.0001	0	0.3	0.010	0.028
PCB167	ND	ND	ND	5.2	0.4	0.008	0.320	0.0002	0	0.4	0.015	0.048
PCB169	ND	ND	ND	0.2	0.1	ND	ND	0.0197	0.0266	0.1	0.002	0.007
PCB170	ND	ND	ND	17	1.2	0.005	0.560	NA	NA	NA	0.043	0.111
PCB180	490	ND	ND	31	ND	0.011	0.950	NA	NA	NA	0.111	0.184
PCB189	ND	NA	NA	0.9	ND	ND	0.032	0.0001	0.0001	0.2	0.005	0.007

References: a) Huang et al., 2011, Chemosphere 85, 239−246; b) Jiang et al., 1997, Chemosphere 34, 941−950; c) Lee et al., 2005, Environ. Sci. Technol. 39, 1436−1447; d) Takasuga et al., 2006, Chemosphere 62, 469−484; e) Ba et al,. 2009. Chemosphere 75, 1173−1178; f) Aries et al., 2006. Chemosphere 65, 1470−1480; g) Ishikawa et al., 2007, Chemosphere 67, 1838−1851. NA: missing data.

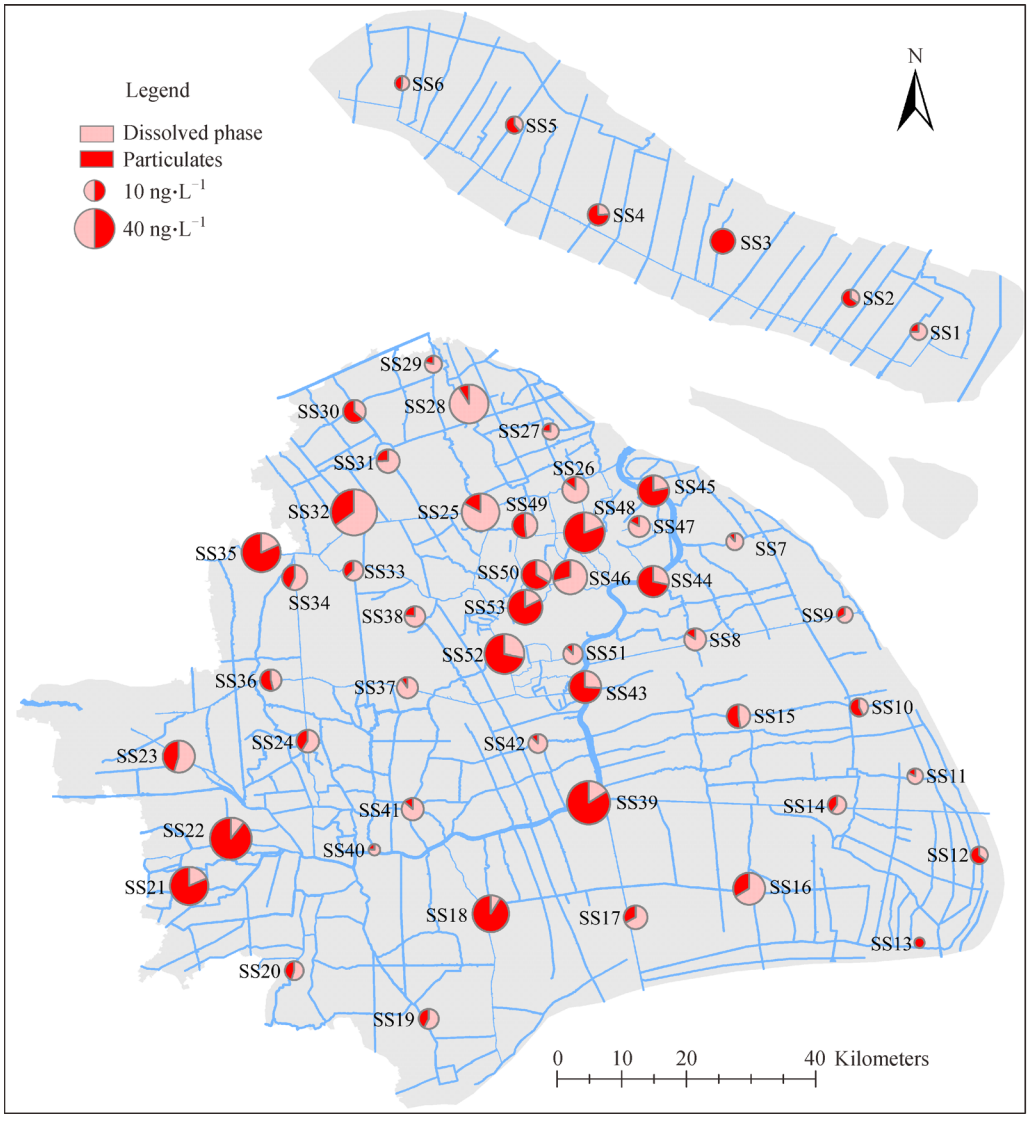

Fig. A1 Spatial distribution of PCBs in the dissolved phase (ng·L^{-1}) and the particulates (ng·L^{-1}) from the rivers in different areas of Shanghai.

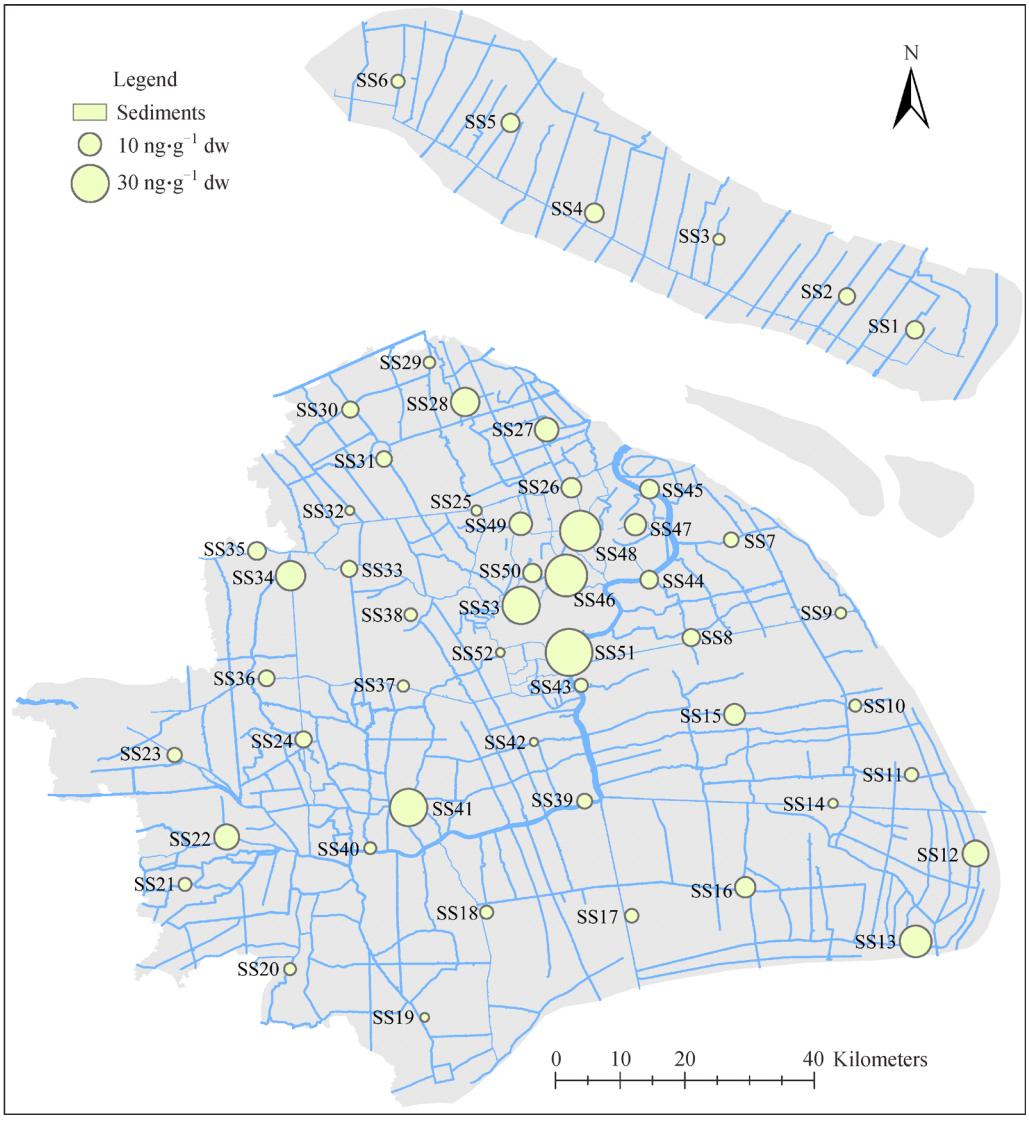

Fig. A2 Spatial distribution of PCBs in surface sediments (ng·g^{-1}dw) from the rivers in different areas of Shangha