Polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and dioxin-like polychlorinated biphenyls in sediments from the Yellow and Yangtze Rivers, China

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Abstract Polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are toxic environmental pollutants that are often found in sediments. The Yangtze and Yellow rivers in China are two of the largest rivers in Asia and are therefore important aquatic ecosystems; however, few studies have investigated the PCDD/F and PCB content in the sediments of these rivers. Accordingly, this study was conducted to generate baseline data for future environmental risk assessments. In the present study, 26 surface sediments from the middle reaches of the Yellow and Yangtze rivers were analyzed for PCDD/Fs and dioxin-like (dl) PCBs by high-resolution gas chromatography and high-resolution mass spectrometry. The ranges of PCDD/F, dl-PCB, and WHO-TEQ content in sediments from the Yellow River were 2.1–19.8, 1.11–9.9, and 0.08–0.57 pg/g (dry weight), respectively. The ranges of PCDD/F, dl-PCB, and WHO-TEQ content in sediments from the Yangtze River were 6.1–84.9, 1.8–24.1, and 0.13–0.29 pg/g (dry weight), respectively. Total organic carbon and dl-PCB contents in the Yellow River were significantly correlated (Spearman's correlation coefficient, $r=0.64$, $P<0.05$). It is well known that total organic carbon plays a role in the transport and redistribution of dl-PCB. Principal component analysis indicated that PCDD/Fs may

arise from pentachlorophenol, sodium pentachlorophenate, and atmospheric deposition, while dl-PCBs likely originate from burning of coal and wood for domestic heating. The dioxin levels in the river sediments examined in this study were relatively low. These findings advance our knowledge regarding eco-toxicity and provide useful information regarding contamination sources.

Keywords Polychlorinated dibenzo-*p*-dioxin and dibenzofuran · Dioxin-like polychlorinated biphenyl · Sediment · Middle reach · Yellow River · Yangtze River

Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) are widespread environmental contaminants. Because of their adverse health effects, persistence, bioaccumulation, and ubiquitous presence in the environment (Kannan et al. 2005; Nunes et al. 2014), they are identified as unintentional persistent organic pollutants (POPs) in the Stockholm Convention. POPs can be transferred into aquatic systems via various pathways, including atmospheric deposition, industrial and domestic effluents, storm water, and spills (Buckley-Golder 1999). POPs are hydrophobic compounds that are easily integrated into the particle phase in aqueous systems, where they are ultimately deposited in the sediments by settling (Kim et al. 2009; Montuori et al. 2014). Therefore, sediments are regarded as the main aquatic reservoirs of POPs. However, sediments may also play a role as secondary contamination sources. Bound POPs in the sediments can be rereleased into the water, where they have the potential to affect aquatic organisms (Kim et al. 2009; Montuori et al. 2014). Sediments with bound POPs can pose a further threat

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to humans and wildlife via biogenic accumulation (Neamtu et al. 2009). POPs in the sediments are also known to cause adverse effects including carcinogenicity, reproductive impairment, and endocrine disruption in wildlife and humans (Van den Berg et al. 2006). Consequently, sediment is an important medium for assessing POP levels in aquatic environments.

The Yellow and Yangtze rivers, which are two of the largest freshwater rivers in China, play an important societal role. The Yellow River is the second largest river in China and one of the main water resources of North China. Because of rapid industrialization and urbanization along the river's banks, an increasingly large volume of organic-laden wastewater is discharged into the Yellow River and its tributaries (Wang et al. 2010), which has resulted in environmental stress. Although some studies have investigated organochlorine pesticides in sediments from the Yellow River (Da et al. 2013; Wang et al. 2010), there is little information available regarding the levels of PCDD/Fs and dl-PCBs in sediments from the middle reaches of the Yellow River in China. The Yangtze River originates from the Qinghai–Tibet Plateau and flows into the East China Sea, with a main stream length of over 6300 km. Because of rapid population increases and economic growth in the regions around the river, there are numerous inputs from industrial wastewater, municipal sewage, atmospheric deposition, as well as agricultural soils containing fertilizers, pesticides, herbicides, and heavy metals (Song et al. 2010). While there have been many studies on inorganic and organic matter in sediments from the Yangtze River (Gui et al. 2012; Wen et al. 2013), few have investigated PCDD/F or PCB levels in surface sediments from the Yangtze River (Liu et al. 2003; Wen et al. 2008). PCDD/Fs and dl-PCBs have been detected in sediments from the Yellow and Yangtze estuaries (Hui et al. 2009). Because of rapid economic development along the middle reaches of these rivers, it is important to also carry out studies of these regions. Additionally, investigations of the middle reaches of the Yellow and Yangtze rivers will provide baseline data for future environmental risk assessments.

The present study was conducted to investigate the contents of PCDD/Fs and dl-PCBs in sediments from the middle reaches of the Yellow and Yangtze rivers. The distribution status of PCDD/Fs and dl-PCBs in these rivers will help identify pollution sources. Additionally, this study will provide a preliminary ecological risk assessment of the middle reaches of the rivers.

Materials and methods

Sample collection

Surface sediment samples (0–5 cm in depth) were collected from the middle reaches of the Yellow and Yangtze rivers

(China) using stainless steel grab samplers (Ekman Grab Sampler, Wildlife Supply Company, Yulee, FL) from October to November 2010. Sample positions were recorded with a global positioning system. Three to five sediment samples were collected at each sampling site, and all samples taken at a site were combined and homogenized before analysis.

The sampling locations are shown in Fig. 1. Thirteen sediment samples were collected in the Yellow River over approximately 200 km, from Luoyang to Kaifeng in Henan province. The 13 sampling points in the Yangtze River were also distributed over approximately 200 km, from Yichang to Jingzhou in Hubei province. All samples were freeze-dried, ground into powder, homogenized, and stored in amber glass bottles at -20°C until extraction.

Extraction and cleanup

Preparation and analysis of the samples were conducted in accordance with US EPA Method 1613B and 1668A for PCDD/Fs and dl-PCBs, respectively. Before extraction, 10 g of each dried sediment sample was homogenized and spiked with known amounts of $^{13}\text{C}_{12}$ -labeled alternative internal standards (Wellington Laboratories, Guelph, Canada; ^{13}C 1613LCS and ^{13}C 1668LCS). $^{13}\text{C}_{12}$ -labeled alternative internal standards of PCDD/Fs specifically included: $^{13}\text{C}_{12}$ -2,3,7,8-TCDD, $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD, $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDD, $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD, $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD, $^{13}\text{C}_{12}$ -OCDD, $^{13}\text{C}_{12}$ -2,3,7,8-TCDF, $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF, $^{13}\text{C}_{12}$ -2,3,4,7,8-PeCDF, $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF, $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDF, $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDF, $^{13}\text{C}_{12}$ -2,3,4,6,7,8-HxCDF, $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF and $^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF. Additionally, $^{13}\text{C}_{12}$ -labeled alternative internal standards of PCBs specifically included: $^{13}\text{C}_{12}$ -PCB-1, $^{13}\text{C}_{12}$ -PCB-3, $^{13}\text{C}_{12}$ -PCB-4, $^{13}\text{C}_{12}$ -PCB-15, $^{13}\text{C}_{12}$ -PCB-19, $^{13}\text{C}_{12}$ -PCB-37, $^{13}\text{C}_{12}$ -PCB-54, $^{13}\text{C}_{12}$ -PCB-81, $^{13}\text{C}_{12}$ -PCB-77, $^{13}\text{C}_{12}$ -PCB-104, $^{13}\text{C}_{12}$ -PCB-105, $^{13}\text{C}_{12}$ -PCB-114, $^{13}\text{C}_{12}$ -PCB-126, $^{13}\text{C}_{12}$ -PCB-155, $^{13}\text{C}_{12}$ -PCB-156, $^{13}\text{C}_{12}$ -PCB-157, $^{13}\text{C}_{12}$ -PCB-167, $^{13}\text{C}_{12}$ -PCB-169, $^{13}\text{C}_{12}$ -PCB-188, $^{13}\text{C}_{12}$ -PCB-189, $^{13}\text{C}_{12}$ -PCB-202, $^{13}\text{C}_{12}$ -PCB-205, $^{13}\text{C}_{12}$ -PCB-206, $^{13}\text{C}_{12}$ -PCB-208 and $^{13}\text{C}_{12}$ -PCB-209. The sediments were then extracted in an accelerated solvent extractor (Thermo Fisher ASE 350), followed by two successive static extraction cycles using 30–40 mL of hexane/dichloromethane (1:1, v/v) for 15 min at 1.03×10^4 kPa and 150°C .

Next, extracts were concentrated using a rotary evaporator (Heidolph, Schwabach, Germany), after which the residues were purified on an acidic silica gel column treated with 44 % sulfuric acid (30.0 cm $\times$ 15.0 mm i.d.) and multilayer silica columns (30.0 cm $\times$ 15.0 mm i.d.). The PCDD/Fs and dl-PCBs were fractionated on a basic alumina column (20.0 cm $\times$ 8.0 mm i.d.), then concentrated to about 20 μL by rotary evaporation followed by a gentle stream of nitrogen. Samples were spiked with $^{13}\text{C}_{12}$ -labeled injection internal

Fig. 1 Map of the sampling sites in the middle reaches of the Yellow and Yangtze rivers

standards of PCDD/Fs ($^{13}\text{C}_{12}$ -1,2,3,4-TCDD and $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxDD) and PCBs ($^{13}\text{C}_{12}$ -PCB-9, $^{13}\text{C}_{12}$ -PCB-52, $^{13}\text{C}_{12}$ -PCB-101, $^{13}\text{C}_{12}$ -PCB-138 and $^{13}\text{C}_{12}$ -PCB-194) before extraction for recovery correction. The spiked extracts were subsequently injected into a high-resolution gas chromatograph and high-resolution mass spectrometer for analysis.

Instrumental analysis

PCDD/Fs and dl-PCBs were identified and quantified on a high-resolution gas chromatograph and high-resolution mass spectrometer (AutoSpec Ultima). The HRMS (Waters, Milford, MA) was operated in positive electron ionization mode with selected ion monitoring (SIM), an ionization energy of 35 eV and an ion source temperature of 270 °C at $R \geq 10$, 000.

The high-resolution gas chromatography (HRGC) (Agilent 6890, Agilent Technologies, Santa Clara, CA) was equipped with a DB-5 column (60.0 m $\times$ 0.25 mm, 0.25 μm) and operated in splitless mode. The sample volume was 1 μL and was injected by an auto-sampler (CTC PAL, CTC Switzerland, Zwingen, Switzerland). Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min. To analyze PCDD/Fs, the following GC temperature program was used: (1) 150 °C initial isothermal hold for 3 min, (2) increase at 20 °C/min to an isothermal hold at 230 °C for 18 min, (3) increase at 5 °C/min to an isothermal hold at 235 °C for 10 min, and (4) increase at 4 °C/min to an isothermal hold at 320 °C for 3 min. The temperature program used for dl-PCBs analysis was as follows: (1) 120 °C initial isothermal hold for 1 min, (2) increase at 30 °C/min to 150 °C, and (3) increase at 2.5 °C/min to an isothermal hold for 1 min at 300 °C.

For TOC analysis, freeze-dried and homogenized sediment samples were treated with 5 % phosphoric acid to remove carbonates prior to measurement. The content of total organic carbon (TOC) in the sediment samples was analyzed using a TOC analyzer (O.I. Analyzer, Station, TX).

Quality control and quality assurance

Our laboratory participated in round 10–17 of the international intercalibration of dioxins and dl-PCBs organized by Örebro University in Sweden, and the Biennial Global Interlaboratory Assessment on persistent organic pollutants is organized by the United Nations Environment Programme (UNEP). The results of the analyses performed in our laboratory agreed well with the median of the results produced by all of the participating laboratories around the world. A method blank and a parallel sample were analyzed with each sample batch (six samples). The recovery was obtained by calculating the ratio of the labeled cleanup standard and the labeled injection internal standard. According to $^{13}\text{C}_{12}$ -labeled isotope internal standards, the recovery ranges of the PCDD/Fs and PCBs were

42–120 and 70–123 %, respectively, which are defined as acceptable in method 1613B and 1668A. Five sediment samples of 26 sediment samples were randomly selected to conduct the parallel analysis experiment. The RSD of results was not more than 10 %. Field and laboratory blanks were collected with each set of samples and processed in a manner identical to the samples. The limit of detection (LOD) was defined as three times the signal/noise ratio. The LOD values determined for this study ranged from 0.02 to 0.1 and 0.03 to 0.08 pg/g for PCDD/Fs and dl-PCBs, respectively. When concentrations were below the LOD, a value of half the LOD was used to calculate the total concentrations and toxic equivalents (TEQs). No lower chlorinated congeners were detected in the blanks. Octachlorodibenzo-*p*-dioxin (OCDD) was the most prevalent congener in the blanks. The contents of target compounds in the blanks were less than 5 % of the contents found in the sediment samples. Therefore, OCDD does not affect the experimental results of the sediment samples

Statistical analysis

Principal component analysis (PCA) was performed using the SPSS 22.0 statistical package (SPSS Inc., Chicago, IL, USA). The contents of congeners below the LOD were assumed to be zero. Principal components with eigenvalues greater than 1 were considered. Through factor analysis using SPSS, the data were projected into two dimensions, resulting in generation of a simpler and easier to understand data set. Additionally, potential emission data were provided to recognize the relationship between the sediment receptors and the possible emission sources through groups or cluster characters and distances in output figures. PCA was widely used to compare congener-specific data from the large number of samples in detail to determine the possible sources of PCDD/Fs and PCBs in the samples.

Results and discussion

Contamination levels of PCDD/Fs and dl-PCBs

Content of PCDD/Fs and dl-PCBs

The contents of PCDD/Fs and dl-PCBs found in surface sediment samples from the middle reaches of the Yellow and Yangtze rivers in China are given in Table S1 and Table S2 (see Supplementary material). The contents of Σ_{17} PCDD/Fs in the sediment samples from the Yellow River ranged from 2.10 to 19.80 pg/g dry weight (dw). These contents were much lower than those in the Yellow River estuary (2.30–253 pg/g dw, August 2004) (Hui et al. 2009), which might have been due to implementation of the Stockholm Convention, or to different positions and/or different pollution

Table 1 The PCDD/Fs and dl-PCBs (pg TEQ/g dw) in surface sediments of different regions in the world

Location	PCDD/Fs	dl-PCBs	Reference
The middle reaches of the Yellow River	0.08–0.55	0.001–0.043	This study
The middle reaches of the Yangtze River	0.09–0.46	0.002–0.036	This study
Daliao River Basin	0.28–29.01 (7.45)	ND	(Zhang et al. 2008)
Yangtze Estuary	0.36–0.74	0.001–0.03	(Hui et al. 2009)
East River	2.1–9.8 (4.5)	0.042–0.45 (0.19)	(Ren et al. 2009)
Pearl River Delta	3.1–9.5	ND	(Zhang et al. 2009)
Taihu Lake	0.83–17.72	ND	(Zhang and Jiang 2005)
Tokyo Bay, Japan	0.39–49	0.18–3	(Hosomi et al. 2003)
Toyano lagoon, Japan	0.49–76	ND	(Sakai et al. 2008)
Hyeongsan River, Korea	0.38–1037	0.05–3.37	(Koh et al. 2004)
Lake Maggiore, Italy	0.1–17	0.03–6	(Castro-Jimenez et al. 2008)
Nile River, Egypt	1.8–38.1	0.08–1.3	(El-Kady et al. 2007)
Northwest Mediterranean	0.4–39.24	0.03–24.75	(Eljarrat et al. 2001)
Po River, Italy	1.3–13	ND	(Fattore et al. 2002)

ND not detected

sources. PCDD/F contents in the 13 sediment samples from the Yangtze River ranged from 6.05 to 84.87 pg/g dw (mean 21.78 pg/g dw) and were about three times those in the samples from the Yellow River. The total PCDD/F contents in sediment samples from the Yangtze River were more than 10 times lower than those (0.31 to 51 pg TEQ/g dw, September 2010) collected from the lower Yangtze River basin, Jiangsu, and Shanghai areas of Eastern China (Nie et al. 2013), likely because the lower Yangtze River basin contained more industrial areas than the middle reaches of the Yangtze River.

The mean content of Σ_{12} PCBs in the 13 sediment samples from the Yellow River was 2.50 pg/g dw (range 1.12–9.90 pg/g dw), which was three orders of magnitude lower than the dl-PCB contents (range <LOD–5.98 ug/kg dw, June 2004) in surface sediments from the mid- and down-stream regions of the Yellow River (He et al. 2006). The contents of Σ_{12} PCBs in the 13 sediment samples from the Yangtze River ranged from 1.79 to 24.07 pg/g dw and were about three times higher than those in the samples from the Yellow River. Although the

middle reaches of the Yellow River (Henan province) and the Yangtze River (Hubei province) are mainly agricultural, rapid development of industry has made pollution of the middle reaches of the Yangtze River more serious. The total dl-PCB contents (range 5.08–19.64 ng/g dw, October 2007) in sediments from the Yangtze River estuary and East China Sea (Yang et al. 2012) was three orders of magnitude higher than those found in the Yangtze River in the present study. Although the levels of PCDD/Fs and dl-PCBs in the Yangtze River were higher than those in the Yellow River, the levels of PCDD/Fs and dl-PCBs in both rivers were generally low compared with Canadian environmental quality guidelines and the contents in other rivers in China and other countries.

Toxic equivalency factors of PCDD/F and dl-PCB contents

The World Health Organization toxic equivalency factors (WHO-TEFs 2005) (Van den Berg et al. 2006) were used to calculate the toxicity equivalents (TEQs) of the PCDD/Fs and dl-PCBs. The range of the total TEQ values (sum of the

Table 2 Correlations of pollutant contents with total organic carbon in the Yellow and Yangtze rivers

			TOC	PCDD/Fs	dl-PCB	PCDD/Fs TEQ	dl-PCB TEQ
Yellow River	TOC	Spearman Correlation	1	0.140	0.635 ^a	0.230	0.319
		Sig. (2-tailed)		0.648	0.020	0.450	0.289
		N	13	13	13	13	13
Yangtze River	TOC	Spearman Correlation	1	−0.181	0.357	−0.058	0.006
		Sig. (2-tailed)		0.553	0.231	0.851	0.986
		N	13	13	13	13	13

^a Correlation is significant at the 0.05 significance level (two-tailed)

PCDD/F and dl-PCB TEQs) in sediment samples from the Yellow River was 0.08–0.57 pg WHO-TEQ/g dw. For all samples, the PCDD/F TEQ values ranged from 0.08 to 0.55 pg WHO-TEQ/g dw and accounted for 73.6 to 99.3 % of the total TEQ. The dl-PCB TEQ values ranged from 0.001 to 0.043 pg WHO-TEQ/g dw and contributed to 0.7 to 26.4 % of the total TEQ. The total TEQ values from the middle reaches of the Yellow River were comparable to those (0.11 to 1.01 pg WHO-TEQ/g dw) reported for the Yellow Estuary (Hui et al. 2009), much lower than those (0.30–3319 pg WHO-TEQ/g dw) from the lower reaches of the Haihe River basin in China (Li et al. 2013) and lower than those reported in the rivers in China and other countries (Table 1).

The range of the total TEQ values in the sediment samples from the Yangtze River was 0.092–0.474 pg WHO-TEQ/g dw (average 0.223 pg WHO-TEQ/g dw), which was similar to that in the Yellow River in this study. The PCDD/F-TEQ values (range 0.09–0.46 pg WHO-TEQ/g dw) contributed to 87.8 to 98.4 % of the total TEQ values. The dl-PCB TEQ values ranged from 0.002 to 0.036 pg WHO-TEQ/g dw and only contributed to 1.6 to 12.2 % of the total TEQ. The contents of PCDD/Fs and dl-PCBs in the middle reaches of the Yangtze River in China were much lower than or equal to those reported in other rivers in China and in other countries (Table 1).

Overall, the contribution rates of the PCDD/Fs TEQs to the total TEQs in both rivers were higher than those of the dl-PCBs TEQs. These findings imply that toxic effects in these regions will mainly come from PCDD/Fs.

Correlation analysis with TOC

The correlation among PCDD/Fs, dl-PCBs, and TOC in sediments from the Yellow and Yangtze rivers was investigated, and the results are shown in Table 2. Organic matter in sediments is the principal factor controlling the sorption of organic

compounds (Cornelissen et al. 2005). PCDD/Fs and dl-PCBs are lipophilic organic compounds and TOC reflects the amount of organic matter; therefore, TOC might be significantly correlated with PCDD/F and dl-PCB content in sediments. TOC was strongly correlated ($p < 0.001$) with PCBs and co-PCBs, but less so with PCDD/Fs ($p < 0.05$) in European background soils (Nam et al. 2008). For PCDD/Fs, the concentrations were significantly correlated with suspended particulate matter, while no correlation to TOC was observed. In the estuary and sea, PCB concentrations were correlated with TOC (Josefsson et al. 2011).

The TOC in the Yellow River sediments ranged from 2.10–19.20 g/kg, which was higher than that previously reported in Yangtze River sediments (Bouloubassi et al. 2001; Wen et al. 2008). TOC and dl-PCB contents were significantly correlated (Spearman's correlation coefficient, $r = 0.64$, $P < 0.05$), implying that organic carbon is an important factor governing the transport and distribution of dl-PCB in the Yellow River. In the Yangtze River, the TOC range was 8.80–33.60 g/kg. There was no significant correlation between the TOC and dl-PCB levels at the 0.05 significance level (Spearman's correlation coefficient, $r = 0.36$, $P = 0.23$). TOC is one of the possible factors affecting the migration and distribution of PCBs.

In the Yellow and Yangtze rivers, there was no significant correlation between TOC and PCDD/F contents, indicating that PCDD/F contents might be affected by direct anthropogenic inputs.

Distribution of PCDD/Fs and dl-PCBs

The distributions of PCDD/Fs and dl-PCBs in surface sediments from the middle reaches of the Yellow and Yangtze rivers in China are shown in Fig. 2.

In the Yellow River, the highest PCDD/F-TEQ content was measured at site Y6 (0.55 pg WHO-TEQ/g), while the lowest

Fig. 2 Distribution of polychlorinated dibenzodioxins and dibenzofuran (PCDD/F) and dioxin-like polychlorinated biphenyl (dl-PCB) toxic equivalents in surface sediments from the middle reaches of the Yellow and Yangtze rivers

was at site Y8 (0.08 pg WHO-TEQ/g). During industrialization in the 1980s, many chemical plants, thermal power plants, and paper mills were established around Y6 and discharged sewage into the Yellow River without restraint. Additionally, there is still a carton plant in Huayuankou. Therefore, the PCDD/F-TEQ content was very high along this stretch. A similar trend was observed in the Yi Luo River, where PCDD/F-TEQ contents in the lower reaches were higher than those in the upper reaches [content order: Y11 (0.39 pg WHO-TEQ/g) > Y12 (0.27 pg WHO-TEQ/g) > Y13 (0.14 pg WHO-TEQ/g)]. Distribution of dl-PCB differed from that of PCDD/Fs. Compared with other sampling locations, the PCDD/F-TEQ content (0.12 pg WHO-TEQ/g) at site Y3 was low, but dl-PCB-TEQ content (0.043 pg WHO-TEQ/g) at site Y3 was more than twice that at the other sampling locations. Y3 is located below the wastewater outfall of a petrochemical plant at Luoyang, China, and industrial wastewater discharged by this plant may be a major source of dl-PCBs at this site. This hypothesis is consistent with the fact that the dl-PCB-TEQ content (0.001 pg WHO-TEQ/g) at site Y2, which was located above the wastewater outfall, was lower than that at Y3 (0.043 pg WHO-TEQ/g).

In the Yangtze River, the highest PCDD/F-TEQ content was detected at site C9 (0.46 pg WHO-TEQ/g), followed by C3 (0.26 pg WHO-TEQ/g). There are numerous fertilizer plants, cement factories, tea farms, and printing and manufacturing plants located above C9, which would all produce pollution and contribute to the higher PCDD/F content at C9 than at the other sites. Because these factories are all relatively small, the PCDD/F content in C9 was lower than those reported in the rivers in China and other countries (Table 1). The highest dl-PCB-TEQ content was found at site C6 (0.036 pg WHO-TEQ/g), followed by C10 (0.024 pg WHO-TEQ/g).

Sources of PCDD/Fs and dl-PCBs in sediments

The congener profiles of PCDD/Fs at the various sampling sites from the Yellow and Yangtze rivers were similar. The dominant congeners were octachlorodibenzo-*p*-dioxin (OCDD), followed by octachlorodibenzofuran (OCDF), 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (1,2,3,4,6,7,8-HpCDD), and 1,2,3,4,6,7,8-heptachlorinateddibenzofuran (1,2,3,4,6,7,8-HpCDF). These findings indicate that the pollution may be from impurities in organochlorine pesticides, such as sodium pentachlorophenate (Na-PCP) and pentachlorophenol (PCP), used in China. The dominant congeners of PCDD/Fs from atmospheric deposition (Ren et al. 2007) were OCDD, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF, indicating that the PCDD/Fs contamination in the Yellow and Yangtze rivers might arise from atmospheric deposition. To further confirm the pollution sources, PCA was conducted for 17 PCDD/F congeners in the sediment samples. Results for

the Yellow River are shown in Fig. 3a, and those for the Yangtze River in Fig. 3b.

For the Yellow River, PCA (Fig. 3a) indicated that PC1 accounted for 89.8 % and PC2 accounted for 6.4 % of the total variability. Therefore, most of the variation in the PCDD/Fs data set could be explained by the first two components. In the score plot, samples Y1–Y11 appeared to cluster together with PCP (Bao et al. 1995), Na-PCP (Bao et al. 1995), and atmospheric deposition (Ren et al. 2007). Y13 was located close to some municipal solid waste incinerators (Shih et al. 2006). The Y12 data point was separated from the other points by a high level of OCDF. The PCDD/F pollution at site Y12 might originate from mixed sources, including thermal electricity generation and wastewater discharges from ferries. None of the sampling sites clustered with an aluminum smelter (Li et al. 2007). PCA of samples from the Yangtze River (Fig. 3b) showed that PC1 and PC2 accounted for 98.3 % of the total variability among samples (PC1, 95.5 %; PC2, 2.8 %). In the score plot, samples C1–C9 and C11–C13 appeared to cluster together with PCP, Na-PCP, and atmospheric deposition. The PCDD/F pollution at site C10 might originate from other sources. Figure 3a, b suggests that PCP or Na-PCP use and atmospheric deposition are the main sources of PCDD/Fs in sediments in the Yellow and Yangtze rivers. Municipal solid waste incinerators could be a source of PCDD/F for the Yellow River, but not for the Yangtze River.

For dl-PCBs, the dominant congeners suggested that pollution in the Yellow and Yangtze rivers originated from coal and wood burning for domestic heating (Lee et al. 2005). Lower chlorinated congeners (CB77, CB118, and CB105) were dominant for the dl-PCBs, while the contents of high chlorinated congeners were substantially lower. Thus, dl-PCBs in the two rivers may have been derived from use or production of Chinese technical products #1PCB (CTP1) and Chinese technical products #2PCB (CTP2) (Jiang et al. 1997). After production and use of these products ceased, new sources of PCBs arose, including electric and electronic waste (Stone 2009). Steel sinter plants (SSP) involve a number of high temperature processes (Aries et al. 2004) that increase the possibility of formation of trace amounts of dioxins (PCDDs, PCDFs, PCBs).

PCA was conducted for 12 dl-PCB congeners in the sediment samples and suspected PCB sources. The results are shown in Fig. 3c for the Yellow River and Fig. 3d for the Yangtze River. For the Yellow River, PC1 accounted for 78.3 %, and PC2 accounted for 11.9 % of total variability. At least two clusters were identified in the score plots. Most samples were grouped with cluster 1 and were separated from CTP1 and CTP2. Y10 was grouped with CTP1 in cluster 2. Therefore, for most samples, dl-PCBs contamination was not correlated with the use and production of CTP1 and CTP2. Based on their proximity in the PCA score plot, domestic coal and wood were the main

Fig. 3 Principal component analysis score plot of the PCDD/Fs and dl-PCBs in sediment samples from the Yellow and Yangtze rivers. **a** PCA score plot of the PCDD/Fs in sediment samples from the Yellow River. **b** PCA score plot of the PCDD/Fs in sediment samples from the Yangtze River. **c** PCA score plot of the dl-PCBs in sediment samples from the Yellow River. **d** PCA score plot of the dl-PCBs in sediment samples from

the Yangtze River. AD: atmospheric deposition, MSWI: municipal solid waste incinerators, ALS: aluminum ingot 9 smelter, BDC: burning of coal for domestic heating, BDW: burning of wood for domestic heating, CTP1: Chinese technical product #1PCB, CTP2: Chinese technical product #2PCB, SSP: steel sinter plant

sources of PCBs. For the Yangtze River, PC1 accounted for 77.0 %, and PC2 accounted for 9.0 % of total variability. C11 was grouped with CTP2 in cluster 2. In addition to C11, the other samples were grouped in cluster 1 and were separated from CTP1, CTP2, and SSP, indicating that burning of domestic coal and wood was the main sources of dl-PCBs. Figure 3c, d suggested that burning of coal and wood for domestic heating were the main dl-PCB sources for sediment samples for the Yellow and Yangtze rivers.

Risk assessment of PCDD/Fs and dl-PCBs

The potential risk posed by PCDD/Fs and PCBs was evaluated using Canadian environmental quality guidelines for freshwater sediments (Environment 2001). These guidelines include the interim sediment quality guidelines (ISQG) and probable effect levels (PEL). The ISQG is the chemical content below which an adverse effect would rarely be observed, whereas the PEL is the content above which an

adverse effect would be expected to occur frequently. The ISQG and PEL for PCDD/Fs, based on the tetrachlorodibenzo-*p*-dioxin (TCDD) toxicity equivalents, were 0.85 and 21.50 ng TEQ/kg dw, respectively. Additionally, the ISQG and PEL for total PCBs were 21.5 and 189 µg/kg, respectively.

The PCDD/F TEQ values from the Yellow River ranged from 0.08 to 0.55 pg TEQ/g dw, which were lower than the ISQG. The PCDD/F TEQ values in the Yangtze River ranged from 0.09 to 0.47 pg WHO-TEQ/g dw, which were also lower than the ISQG. The content of dl-PCBs in sediments from the Yellow and Yangtze rivers ranged from 1.1 to 9.9 and 1.8 to 24.1 pg/g, respectively, which were much lower than the ISQG and the PEL. These results indicate that contamination of the middle reaches of these rivers is relatively low based on the aforementioned standard (Environment 2001). However, in view of future economic development and tightening environmental standards, further investigation of sediments, water, and animal species should be carried out in the future.

Conclusions

Dioxins were detected in sediments from the middle reach of the Yangtze and Yellow rivers. The dominant congeners of Σ_{17} PCDD/Fs were OCDD, OCDF, 1,2,3,4,6,7,8-HpCDD, and 1,2,3,4,6,7,8-HpCDF. Lower chlorinated congeners (CB77, CB118, and CB105) dominated the dl-PCBs. The levels of PCDD/Fs and dl-PCBs in the Yangtze River sediments were higher than those in the Yellow River sediments. Compared with Canadian environmental quality guidelines and the contents in other rivers in China and other countries, PCDD/F and dl-PCB contents in both rivers were relatively low. Additionally, the TOC and dl-PCB contents in the Yellow River were significantly correlated, but there was no significant correlation between TOC and PCDD/F content in the Yellow and Yangtze rivers. TOC may be influencing the migration and distribution of PCBs, while PCDD/F contents might be influenced by direct anthropogenic inputs. PCA indicated that the potential main sources of PCDD/Fs were PCP, Na-PCP, and atmospheric deposition. PCA of the dl-PCBs profiles suggested that burning of domestic coal and wood was the main sources. The results presented herein advance our knowledge regarding eco-toxicity, provide useful information regarding contamination sources, and provide baseline data for future environmental risk assessments in the study area. Although assessment showed that the risk was low for these pollutants, the rapid development of the Chinese economy could create new sources of pollution. Therefore, regular monitoring of dioxins in this region is important.

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