



Patterns and sources of PCDD/Fs and dioxin-like PCBs in surface sediments from the East River, China

Man Ren^{a,b}, Ping'an Peng^{a,*}, Deyi Chen^a, Pei Chen^a, Xiaoming Li^a

^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^b Research Center of the Pearl River Delta Environmental Pollution and Control, Guangzhou 510640, China

ARTICLE INFO

Article history:

Received 23 December 2008

Received in revised form 26 March 2009

Accepted 20 April 2009

Available online 3 May 2009

Keywords:

PCDD/F

Dioxin-like PCB

East River

Sediment

Source

ABSTRACT

The contamination status of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs) was preliminarily investigated in surface sediments collected from the East River during April 2007. The contamination levels of PCDD/Fs and DL-PCBs ranged from 2.1 to 9.8 with mean concentration of 4.5 pg WHO₉₈-TEQ g⁻¹ and ranged from 0.042 to 0.45 with mean concentration of 0.19 pg WHO₉₈-TEQ g⁻¹, respectively. All sediments were characterized by the elevated levels of PCDDs, especially OCDD. Higher concentrations of PCDD/Fs were found in the sediments from Guangzhou and Dongguan. Source analysis revealed that PCDD/Fs in the sediments from Guangzhou were mainly from the secondary copper smelters and steel-making plants, and PCDD/Fs in the sediment from Dongguan were mainly from MSWIs. PCP and paper mills were unlikely to be the main sources.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The East River is the major tributary of the Pearl River, which is the third largest river in China. It originates in Jiangxi Province; flows through several cities in Guangdong Province, including Heyuan, Huizhou and Shenzhen, Dongguan and Guangzhou; and finally enters into the South China Sea. In Guangdong Province, the East River is 435 km long, with a basin of 31,840 km². It is an important source of water for drinking, agricultural and industrial uses since the most drinking water for Hong Kong and Shenzhen are abstracted from the East River. On the other hand, the rapid development of the economy and the explosion in city population has led to water pollution and shortages. From this point of view, the risk assessment of water quality deterioration in the East River had been increasingly paid attention by Chinese public. The water quality and river sediments of the East River have been investigated for heavy metals and organic chemicals, such as PCBs, PAHs, HCHs, PBDEs, linear alkylbenzenes [1–3], yet with few data of other POPs, such as PCDD/Fs and dioxin-like PCBs. In the East River basin, the main industries related to dioxins are the mining industry metallurgy, waste incinerators, electrical and electronics manufacturing, and the paper-making industry.

The present study aims to assess the contamination status of PCDD/Fs and PCBs in surface sediments from the East River, and investigate the main sources of PCDD/Fs.

2. Materials and methods

2.1. Sampling

Sampling locations are shown in Fig. 1. Nine sediments were sampled along the East River in April 2007. Surface sediments (about 5 cm in depth) were collected using a grab sampler (Ekman grab, Wildlife Supply Company, Buffalo, USA) and placed in pre-cleaned glass bottles. The top 5-cm layer of sediments was expected to represent the modern inputs. The samples were stored at –20 °C until analysis.

2.2. Chemicals

All solvents were of pesticide residue grade and purchased from Merck (Germany). Silica gel and glass wool were purchased from Merck (Germany) whereas florasil was purchased from Fluka (USA). All standard solutions of dioxins were purchased from Cambridge Isotope Laboratory Inc. (USA), including ¹³C₁₂-labeled PCDD/Fs (EDF-8999), recovery standards (EDF-5999), and window defining and isomer specificity mixture (EDF-4147). However standard solutions of PCBs were purchased from Wellington Laboratories Inc. (Canada), including ¹³C₁₂-labeled DL-PCBs (WP-LCS), and recovery standards including 2,3',4',5'-TeCB (PCB70), 2,3,3',5,5'-PeCB

* Corresponding author. Tel.: +86 20 85290126; fax: +86 20 85290706.

E-mail address: pinganp@gig.ac.cn (P. Peng).

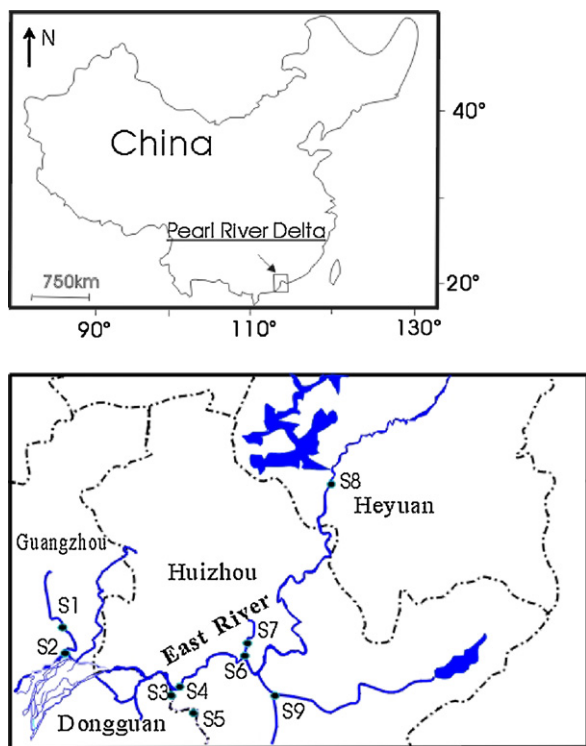


Fig. 1. Sampling stations in the East River, China.

(PCB111), 2,2',3,4,4',5'-HxCB (PCB138) and 2,2',3,3',4,4',5'-HpCB (PCB170) ($^{13}\text{C}_{12}$ -labeled, WP-ISS).

2.3. Sample analysis of PCDD/Fs and DL-PCBs

Detailed descriptions of the sample extraction and fractionation procedures have been reported elsewhere [4]. Briefly, sediment samples were freeze-dried and 10–30 g dried samples were spiked with ^{13}C -labeled surrogate standards prior to the 24-h Soxhlet extraction with toluene. All extracts were concentrated to 1 mL with a rotary evaporator. Sample cleanup was accomplished successively with acid silica gel slurry, multi-layer silica gel column. Florisil was used for separating the analytes into two groups. The first fraction contained PCBs; the second fraction contained PCDD/Fs. Recovery standards were added prior to GC injection.

2.4. Instrumentations

Identification and quantification were performed with HRGC/HRMS (Trace GC 2000 and Finnigan MAT 95 XP). A DB-5ms column (J&W Scientific, CA, 60 m, 0.25 mm ID, 0.25 mm film) was used for PCDD/Fs and PCBs. For PCDD/F analysis, the oven temperature program was: 120–160 °C at 20 °C min⁻¹–220 °C (held for 16 min) at 7.5 °C min⁻¹–235 °C (held for 7 min) at 5 °C min⁻¹–320 °C (held for 6 min) at 5 °C min⁻¹. For DL-PCB analysis, the oven temperature program was: 120–160 °C at 20 °C min⁻¹–220 °C at 7.5 °C min⁻¹–300 °C (held for 2.5 min) at 5 °C min⁻¹. Twelve DL-PCB congeners were analyzed, including 3,4,4',5'-TeCB (PCB81), 3,3',4,4'-TeCB (PCB77), 2',3,4,4',5'-PeCB (PCB123), 2,3',4,4',5'-PeCB (PCB118), 2,3,4,4',5'-PeCB (PCB114), 2,3,3',4,4'-PeCB (PCB105), 3,3',4,4',5'-PeCB (PCB126), 2,3',4,4',5,5'-HxCB (PCB167), 2,3,3',4,4',5'-HxCB (PCB156), 2,3,3',4,4',5'-HxCB (PCB157), 3,3',4,4',5,5'-HxCB (PCB169), 2,3,3',4,4',5,5'-HpCB (PCB189).

2.5. Quality assurance

Quality assurance and quality control were conducted with the method blank, the ongoing precise and recovery (OPR), the initial precise and recovery (IPR), and the duplicate sample. There were no detectable PCDD/Fs, yet a small amount of PCB77, 105 and 118 with the average blank of 0.10, 0.13 and 0.60 pg μL^{-1} , respectively (final volume for injection = 20 μL), and the experimental values were corrected by deducting blank values. The recoveries of all the labeled compounds were 50–110%. The detection limits were quantified as three times of the standard deviations for the mean concentration in the blanks, which were 0.1–0.8 pg g⁻¹ for PCDD/Fs and 0.05–0.6 pg g⁻¹ for DL-PCBs, respectively.

3. Results and discussion

3.1. Concentration levels of PCDD/Fs and dioxin-like PCBs in sediments

The concentration levels of PCDD/Fs and dioxin-like PCBs in sediment samples are shown in Table 1. The total concentrations of seventeen 2,3,7,8-substituted PCDD/Fs and twelve dioxin-like PCBs in the surface sediments of the sampling sites were found to range from 1200 to 5300 pg g⁻¹ dw and 48 to 270 pg g⁻¹ dw, respectively. The concentrations of total tetra- to octa-PCDD/Fs ($\Sigma\text{PCDD/Fs}$) were found to be in the range of 1400–5400 pg g⁻¹ dw. The total TEQs of PCDD/Fs and PCBs were respectively in the range of 2.1–9.8 pg g⁻¹ and 0.042–0.45 pg g⁻¹ based on the WHO₉₈-TEFs [5]. PCBs contributed only 2–9% of the total TEQ (PCB + PCDD/F). I-TEQ for PCDD/Fs was also calculated and shown in Table 1. In addition, total WHO₀₅-TEQ for both PCDD/Fs and PCBs calculated based on the updated WHO₀₅-TEF [6] were also listed in Table 1. Higher concentrations of PCDD/Fs were found at sites 1–3, which are located in the downstream of the East River.

The environmental quality guidelines (EQG) in Canada and the USA for dioxins in sediment, quoted as TCDD toxicity equivalents, were 0.85 and 2.5 pg TEQ g⁻¹, respectively [7,8]. Using these guidelines, our sediment samples collected from all sites were found to be higher than EQG established from Canada and the USA and posed a risk of causing deleterious effects to sensitive organisms at all trophic levels. The Canadian guidelines also specified a probable effect level (PEL) of 21.5 pg TEQ g⁻¹, and the American guidelines specified a value that was a 'high risk to sensitive species' of 25 pg TEQ g⁻¹. Using the less stringent American value, no sites were above these guidelines and it can be predicted that adverse biological effects were not likely to occur.

A comparison between our data and the previous reports about PCDD/Fs and twelve toxic PCBs in other river sediments are listed in Table 2. The levels of PCDD/Fs in the East River were found to be lower than those found in the Haihe River, Hyeongsan River, Nile River in Egypt, Hyeongsan River and southern Mississippi River, yet higher than those found in the Yangtze River and rivers in Akita (Japan). The lowest level of PCDD/Fs detected in this study was relatively higher; possibly indicating the background level in the basin was relatively higher. Although higher concentrations in atmosphere and higher fluxes in atmospheric deposition of PCDD/Fs were found in Guangzhou, Guangdong Province's provincial capital, the level of PCDD/Fs in sediment and soil was not higher [16–18]. DL-PCBs concentrations were found to be not high, which was consistent with the previous study on PCBs in the Pearl River Delta [1,2].

3.2. Profile of PCDD/Fs

Similar congener profiles were found throughout sediments from the East river, in which OCDD was the most abundant con-

Table 1
Concentrations (pg g⁻¹ dw) of PCDD/Fs and dioxin-like PCBs in sediments from the East River, China.

Location	S1	S2	S3	S4	S5	S6	S7	S8	S9
2,3,7,8-TCDF	1.9	2.1	4.9	0.41	0.41	0.50	0.56	0.25	2.4
1,2,3,7,8-PeCDF	2.2	2.8	4.0	0.39	0.51	0.50	0.57	0.30	1.5
2,3,4,7,8-PeCDF	3.0	4.9	6.6	0.58	0.67	0.94	0.90	0.37	1.6
1,2,3,4,7,8-HxCDF	3.8	3.9	5.8	0.70	0.87	0.96	0.99	0.46	1.6
1,2,3,6,7,8-HxCDF	3.6	3.8	4.8	0.57	0.71	0.85	0.82	0.38	1.0
2,3,4,6,7,8-HxCDF	4.4	4.8	5.5	0.73	0.91	1.1	0.96	0.44	1.3
1,2,3,7,8,9-HxCDF	1.3	1.4	2.3	0.18	0.23	0.23	0.24	0.17	0.48
1,2,3,4,6,7,8-HpCDF	18.9	12	17.5	3.8	3.7	4.0	4.0	3.0	4.2
1,2,3,4,7,8,9-HpCDF	2.2	1.7	2.2	0.37	0.35	0.35	0.43	0.32	0.52
OCDF	101	18	61	15	7.8	2.3	3.3	6.0	3.9
2,3,7,8-TCDD	0.16	0.22	0.21	0.065	0.094	0.0	0.038	0.051	0.090
1,2,3,7,8-PeCDD	1.1	1.3	1.8	0.37	0.56	0.51	0.41	0.24	0.60
1,2,3,4,7,8-HxCDD	4.4	1.4	1.3	0.77	1.0	0.61	0.48	0.64	0.72
1,2,3,6,7,8-HxCDD	4.6	2.4	3.0	1.3	2.1	1.2	0.76	1.3	1.4
1,2,3,7,8,9-HxCDD	4.9	2.5	3.8	1.9	5.6	1.9	1.1	1.8	1.9
1,2,3,4,6,7,8-HpCDD	170	54	56	61	69	37	26	55	42
OCDD	3350	1600	3600	3060	2600	5200	2690	4600	2400
Total 2,3,7,8-PCDD/Fs	3700	1700	3800	3150	2700	5300	2730	4700	2500
WHO-TEQ (PCDD/Fs) ^a	8.1	7.2	9.8	2.4	3.2	2.7	2.1	2.1	3.4
WHO-TEQ (PCDD/Fs) ^b	8.1	6.5	9.1	2.8	3.6	3.5	2.4	2.9	3.5
I-TEQ (PCDD/F) ^c	10.6								
	8.0	12.2	4.9	5.3	7.1	4.3	6.1	5.2	
TCDF	51	75	123	9.4	12	20	18	8.8	36
PeCDF	40	67	91	8.7	10	13	12	5.1	31
HxCDF	40	48	57	8.2	9.1	9.9	9.5	5.9	13
HpCDF	43	24	31	10	5.7	6.4	6.9	7.6	7.2
TCDD	22	25	60	6.5	9.6	8.0	6.9	3.7	13
PeCDD	26	29	62	8.1	13	9.5	7.7	4.1	14
HxCDD	68	61	67	30	44	19	17	17	29
HpCDD	330	155	130	144	170	84	58	110	100
ΣPCDD/Fs	4100	2100	4300	3300	2900	5400	2800	4800	2700
ΣPCDDs/ΣPCDFs	14	8	11	63	64	103	56	143	28
PCB 81	0.40	1.9	2.4	0.35	0.38	0.42	1.1	0.52	0.65
PCB 77	20	22	25	5.5	5.8	7.3	11	11	15
PCB 123	7.9	13	15	3.0	6.1	3.1	7.9	3.9	6.9
PCB 118	54	96	110	18	37	25	34	37	69
PCB 114	1.8	4.7	6.0	0.34	1.2	1.3	1.5	1.3	1.8
PCB 105	28	49	55	8.2	16	10	16	17	31
PCB 126	1.4	3.5	4.0	0.35	1.1	1.0	1.9	0.36	1.3
PCB 167	8.4	27	30	8.8	8.3	6.3	13	6.0	6.5
PCB 156	10.6	13	18	2.4	7.5	5.9	11	3.3	9.7
PCB 157	3.0	3.0	4.5	0.63	2.5	1.1	1.9	0.78	3.1
PCB 169	0.31	0.84	1.0	0.13	0.34	0.64	0.40	0	0.39
PCB 189	1.4	1.8	2.2	0.31	1.2	1.1	3.2	0.28	1.1
Total PCBs	140	240	270	48	87	63	100	81	150
TEQ (PCB) ^a	0.16	0.39	0.45	0.042	0.13	0.12	0.21	0.046	0.15
TEQ (PCB) ^b	0.15	0.39	0.44	0.041	0.13	0.12	0.20	0.039	0.15
ΣTEQ (PCB + PCDD/F) ^a	8.3	7.6	10.2	2.4	3.3	2.8	2.3	2.1	3.6
% (TEQ-PCB)	6	5	4	2	4	4	9	2	4

^a WHO₉₈-TEF [5].^b WHO₂₀₀₅-TEF [6].^c I-TEF.**Table 2**
Comparison of the concentrations (pg TEQ g⁻¹) of PCDD/Fs and dioxin-like PCBs in sediments from some rivers of the world.

Location	PCDD/F range (mean)	DL-PCBs range (mean)	References
Dongjiang River, China	2.1–9.8 (4.5) ^a 3.5–12.2 (7.1) ^b	0.042–0.45 (0.19) ^a	This study
Haihe River, China	1.4–19 (8.3) ^a 1.3–26 (8.6) ^b	0.07–0.53 (0.27) ^a	[9]
Yangtze River estuary, China	0.29–0.78 (0.54) ^b		[10]
Pearl River Delta, China	0.6–17.5 (6.4) ^b		[11]
River Nile in the Cairo region, Egypt	1.8–38.1 (9.1) ^a 1.8–35.4 (8.6) ^b	0.08–1.3 (0.34) ^a	[12]
Rivers in Akita, Japan	0.022–5.3 (0.81) ^b		[13]
Hyeongsan River, Korea	0.38–1037 (222) ^a	0.05–3.7 (1.4) ^a	[14]
Southern Mississippi, USA.	0.41–33.3 (10.5) ^b		[15]

^a WHO₉₈-TEQ [5].^b I-TEQ.

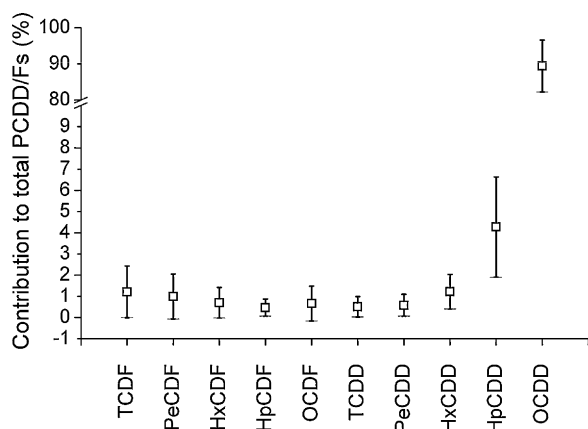


Fig. 2. Homologue profile of PCDD/Fs in sediments from the East River, China.

gener, which constituted 91–99% of the total concentrations of seventeen 2,3,7,8-PCDD/Fs, followed by 1,2,3,4,6,7,8-HpCDD, OCDF, and 1,2,3,4,6,7,8-HpCDF. The congener profiles of PCDD/Fs in the East River were in accordance with the profiles reported the sediments and soils from the Pearl River Delta [11,17] and in Lake Erie sediments [19]. The main contributors to WHO₉₈-TEQ (PCDD/F) were 2,3,4,7,8-PeCDF (range: 9–34%, mean: 20%), 1,2,3,7,8-PeCDD (range: 12–19%, mean: 17%), 1,2,3,4,6,7,8-HpCDD (range: 6–26%, mean: 16%) and OCDD (range: 2–22%, mean: 10%).

Furthermore, OCDD was predominant in the homologue profiles in sediments from the East river, which constituted 76–97% of the total amount of tetra–octa PCDD/Fs (Σ PCDD/Fs), followed by HpCDD (Fig. 2).

The ratio of Σ PCDDs/ Σ PCDFs was a valuable parameter for source identification. The ratio was lower (generally, <1) for industrial and combustion sources, including secondary aluminum smelters, secondary copper smelters, electronic waste dismantling, municipal solid waste incinerators (MSWIs), medical waste incinerators (MWIs), industrial furnaces, burning hazardous waste, and

coal-fueled combustors [18,20,21]. The ratio was high in some chemicals; it was in the range of 2–83 (mean 24) in PCP and 30–590 (mean 270) in CNP [22]. The ratio was also very high when PCDD/Fs formed naturally in ball clay [23,24]. The ratios in this study were in the range of 8–143 (mean 54). It is interesting that the ratios were relatively low (8–14) and the concentrations of PCDD/Fs were higher at sites 1–2 in Guangzhou, and at site 3 in Dongguan, which is consistent with the high level of industrialization at these sites.

3.3. Source analysis

Generally speaking, there are two categories of PCDD/Fs sources, e.g., byproducts of chlorinated chemicals and combustion, such as PCP, CNP, MSWIs, IWIs, and MWIs. Congener profiles of the seventeen 2,3,7,8-PCDD/Fs and homologue profiles of PCDD/Fs were usually adopted to identify the sources. However, for homologues have different physical properties, the profiles will change when photodegradation, biodegradation, phase partition, sorption/desorption, dry/wet deposition and other processes occur. On the other hand, as isomers of the same degree of chlorination have similar physiochemical properties and therefore they transport in a similar manner. Thus isomer composition was suggested to be used as the basis for source identification [25], although the isomer composition may also change when biodegradation is involved.

3.3.1. Isomer profiles

The isomer profiles of PCDD/Fs in the sediments were not completely similar. The sediments from sites 1 to 3 with higher level PCDD/Fs were selected to identify sources with the isomer profiles. Although many kinds of sources were reported to be characterized by congener profiles and homologue profiles, yet the isomer profiles were scarcely reported. Thus the influence of the combustion sources on the sediments was illustrated by comparing the isomer profiles of PCDFs in the sediments and the ambient atmospheric deposition and air (Fig. 3), for PCDD/Fs from combustion sources

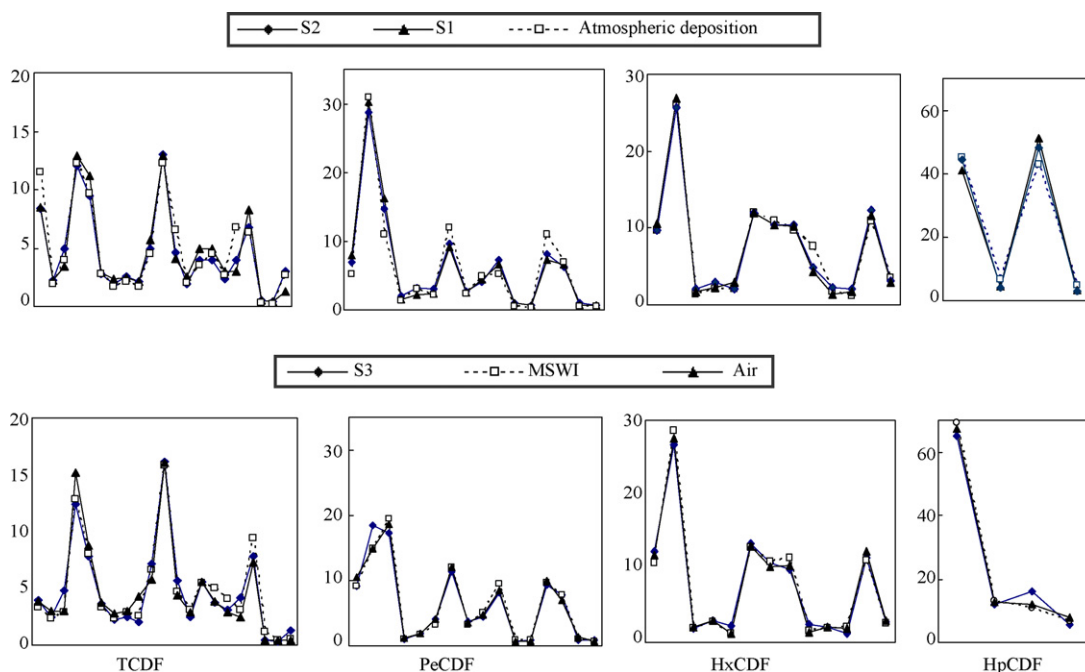


Fig. 3. Dioxin isomer profiles for different environmental media from the East River basin (isomer profiles are shown in percentage composition in each homologue. S1–3: sites 1–3; atmospheric deposition: 13 atmospheric deposition samples from Guangzhou [17]; air: 6 air samples from Dongguan; MSWI: 17 flue gas samples of the municipal solid waste incinerators).

were diffused easily and transported via ambient air. Atmospheric deposition of PCDD/Fs in Guangzhou has been studied in the previous study [17]. The profiles of PCDD/Fs from four districts were very similar ever spatially or temporally, indicating that the sources of PCDD/Fs in atmospheric deposition in Guangzhou were very similar [17]. The average isomer profiles of PCDFs in atmospheric deposition in Guangzhou were compared with those in these sediments from sites 1 to 2, which were located in the east of Guangzhou. Air samples from two northeast towns in Dongguan were collected in January, July and December in 2007. Flue gas samples were collected from MSWIs in Guangdong Province. The average profiles of PCDFs in air and MSWI flue gas were compared with that in the sediment from site 3, which was located in the north of Dongguan.

As shown in Fig. 3, the isomer profiles of PCDFs in the sediments from site 1 and site 2 were very similar to each other and to those in the atmospheric deposition, indicating the PCDD/Fs in the sediments were mainly from combustion sources. The isomer profiles of PCDFs in the sediment from site 3 were very similar to those in the air and MSWI flue gas, indicating the PCDD/Fs in the sediment were mainly from MSWIs. Furthermore, the profiles of TCDF, PeCDF and HpCDF from site 1 were different to those from site 3, indicating the combustion sources were different. The profiles of HxCDF were less variable in all samples in the study.

In Guangzhou, PCDD/F concentrations in air (total suspended particles) were found to range from 0.10 to 0.77 (mean 0.37) pg I-TEQ m⁻³ [16], and the deposition fluxes of PCDD/Fs were 2.1–41 (mean: 20) WHO-TEQ m⁻² day⁻¹ [17], indicating that the contamination level was a bit serious. A survey project to obtain the dioxin emission inventory in Guangdong Province in 2006 was conducted jointly by Guangdong Environmental Protection Bureau and Guangzhou Institute of Geochemistry. TEQs were measured based on the throughputs and the emission factors reported [26]. The survey results showed that the total PCDD/F TEQ in Guangzhou was 131 g in 2006, and the secondary copper smelters and steel-making plants were the main sources, contributing 38% and 28% of the total PCDD/F TEQ, respectively. Sites 1 and 2 were located in the east of Guangzhou, where there were several large steel-making plants and secondary copper smelters. These industries might emit quite a bit of PCDD/Fs, for scrap steel and copper were the main materials [21]. Higher PCDD/F level was found in the metallurgical industrial park (including sinter plants, electric arc furnaces and secondary copper smelters) [21]. Both from the comparison of isomer profiles and from the result of the dioxin source inventory, it was shown that the secondary copper smelters and steel-making plants were the main sources of PCDD/Fs for the sediments from sites 1 to 2 in Guangzhou.

In Dongguan, the PCDD/F TEQs in air were 0.11–2.3 (mean: 0.97, $n=6$) pg WHO₉₈-TEQ/m³, which showed the pollution level of dioxins in the air was high. The dioxin emission source inventory showed that the total PCDD/F TEQ in Dongguan was 18 g in 2006. In addition, the main sources in Dongguan were the paper mills and MSWIs, accounting for 68% and 21% of the total TEQ, respectively. Most of PCDD/Fs from the paper mills exist in wastewater effluent and pulp and paper sludge. In sludge and effluent, 2,3,7,8-TCDD and 2,3,7,8-TCDF were the main congeners of seventeen toxic PCDD/Fs, beside OCDD, 1,2,3,4,6,7,8-HpCDD and OCDF, other congeners were nearly absent [20]. However, the percents of 2,3,7,8-TCDD and 2,3,7,8-TCDF in the sediment were not higher compared with other 2,3,7,8-PCDD/Fs (Table 1). So it would seem that the paper-making industry was unlikely to be the main source. Both from the comparison of isomer profiles and from the result of the dioxin source inventory, it was shown that the main source in the sediment from site 3 was from MSWIs. PCDD/Fs from combustion sources are diffused easily and transported via ambient air, and are suggested to be the major source of non-point environmental contamination; PCDD/Fs from chemical sources such as PCP

and paper mills were relatively difficult to spread, and can cause point-pollution.

3.3.2. The predominant of OCDD

However, the combustion sources cannot explain the predominant OCDD in the sediments. PCDD/Fs in PCP were characteristically dominated by OCDD, and PCP was reported to be the main source of PCDD/Fs in sediments from Tokyo Bay Basin [25], Dongting Lake [27], and Gwangyang Bay, South Korea [28]. In Guangdong Province, 1500 tons of PCP-Na was used to control *Ampullaria gigas* in Guangdong Province, mainly in the North River basin, between 1960 and 1985. Although the profiles of PCDD/Fs in the tested sediments were similar to the profile of the dominant congeners of impurities (OCDD (76%), OCDF (10%) and 1,2,3,4,6,7,8-HpCDD (10%)) in PCP and PCP-Na [29]. However, PCP was possibly not the main source in this study. The reasons are as follows: (1) in PCP, 1,2,3,6,7,8-HxCDD and 1,2,3,4,7,8-HxCDF were respectively the main isomer of the toxic HxCDDs and HxCDF [22]. However, in these sediments these two isomers were not the main ones. (2) According to TCDD isomers, 1,3,6,8-TCDD and 1,3,7,9-TCDD were the indicators for PCP [22]. They contributed on average 58% and 38% of TCDD in PCP, yet they contributed 18–38% (mean: 30%) and 11–25% (mean: 19%) in sediments in this study, respectively. (3) Averagely, HpCDD contained 25% and 75% of 1,2,3,4,6,7,9-HpCDD and 1,2,3,4,6,7,8-HpCDD in PCP respectively [22], yet 60% (range: 48–65%) and 40% (range: 35–52%) in the sediments. In summary, PCDD/Fs in the East River sediments were not mainly from PCP.

“OCDD abnormality” was found in soils and sediments from many sites. To date, the sources of the elevated OCDD in sediments and soils from Hong Kong [30], Mississippi [15] and a range of other sites remain unclear. But some evidences indicate there were some nonanthropogenic sources. Natural formation of PCDD/Fs was found in American ball clay and in kaolin clay from Germany and Spain [23]. The isotopic signatures of OCDD and the occurrence of OCDD in ancient ball clays deposited in Tertiary Era provide evidences for the *in situ* formation of dioxins [31]. Baker and Hites [32] suggested that the photochemical synthesis of OCDD from PCP in atmospheric condensed water was the most important source of OCDD to the environment. The elevated OCDD and PCDD concentrations in sediments from Hong Kong were supposed to be attributed to the nonanthropogenic sources [30]. Considering that the predominant OCDD was found in many sediments and soils in the Pearl River Delta, we suppose that the predominant OCDD in sediments from the East River is attributed to the nonanthropogenic sources. Further research is needed to focus on the evidences of natural formation and the formation mechanism.

4. Conclusion

The concentrations of PCDD/Fs and DL-PCBs in sediments from the East River were found to be not very high. The profiles of PCDD/Fs were characterized by the predominant OCDD and elevated PCDDs. Source analysis revealed that the higher concentrations of PCDD/Fs in the sediments from Guangzhou were mainly from the secondary copper smelters and steel-making plants, the higher concentrations of PCDD/Fs in the sediments from Dongguan were mainly from MSWIs, and PCP and paper mill were unlikely to be the main sources.

Acknowledgements

This research was financially supported by National Natural Sciences Foundation of China (No. 40803028), Guangdong Province Natural Sciences Foundation (No. 8451064004000324)

and Guangzhou Institute of Geochemistry (No. GIGCX-07-14). This is contribution No. IS-1075 from GIGCAS.

References

- [1] K.C. Ho, K.C.C. Hui, Chemical contamination of the East River (Dongjiang) and its implication on sustainable development in the Pearl River Delta, *Environ. Int.* 26 (2001) 303–308.
- [2] B.X. Mai, S.J. Chen, X.J. Luo, L.G. Chen, Q.S. Yang, G.Y. Sheng, P.A. Peng, J.M. Fu, E.Y. Zeng, Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea, *Environ. Sci. Technol.* 39 (2005) 3521–3527.
- [3] X.J. Luo, S.J. Chen, H.G. Ni, M. Yu, B.X. Mai, Tracing sewage pollution in the Pearl River Delta and its adjacent coastal area of South China Sea using linear alkylbenzenes (LABs), *Mar. Pollut. Bull.* 56 (2008) 158–162.
- [4] M. Ren, P.A. Peng, S.K. Zhang, Y.Y. Deng, B.X. Mai, G.Y. Sheng, J.M. Fu, Determination of 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins-dibenzofurans and dioxin-like polychlorinated biphenyls in environmental samples by gas chromatography/high resolution mass spectrometry, *Chinese J. Anal. Chem.* 35 (2007) 176–180.
- [5] M. van den Berg, L. Birnbaum, A.T.C. Bosveld, B. Brunström, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S.W. Kennedy, T. Kubiak, J.C. Larsen, F.X. Rolaf van Leeuwen, A.K. Djien Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern, T. Zacharewski, Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife, *Environ. Health Persp.* 106 (1998) 775–792.
- [6] M. Van den Berg, L. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritscher, J. Tuomisto, M. Tysklind, N. Walker, R. Peterson, The 2005 WHO reevaluation of human and mammalian toxic equivalency factors for dioxin and dioxin-like compounds, *Toxicol. Sci.* 93 (2006) 223–241.
- [7] CCME (Canadian Council of Ministers of the Environment), Canadian environmental quality guidelines for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), 2002.
- [8] US EPA, Interim report on data and methods for assessment of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin risks to aquatic life and associated wildlife, EPA/600/R-93/055, 1993.
- [9] H.X. Liu, Q.H. Zhang, Y.W. Wang, Z.W. Cai, G.B. Jiang, Occurrence of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and biphenyls pollution in sediments from the Haihe River and Dagou drainage river in Tianjin City, China, *Chemosphere* 68 (2007) 1772–1778.
- [10] Y.Z. Sun, B. Zhang, L.R. Gao, Z.T. Liu, M.H. Zheng, Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in surface sediments from the estuary area of Yangtze River, People's Republic of China, *B. Environ. Contam. Tox.* 75 (2005) 910–914.
- [11] M.H. Zheng, S.G. Chu, G.Y. Sheng, Y.S. Min, Z.C. Bao, X.B. Xu, Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in surface sediments from the Pearl River Delta in China, *B. Environ. Contam. Tox.* 66 (2001) 504–507.
- [12] A.A. El-Kady, M.A. Abdel-Wahhab, B. Henkelmann, M.H. Belal, M.K.S. Morsi, S.M. Galal, K.W. Schramm, Polychlorinated biphenyl, polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran residues in sediments and fish of the River Nile in the Cairo region, *Chemosphere* 68 (2007) 1660–1668.
- [13] O. Kiguchi, T. Kobayashi, Y. Wada, K. Saitoh, N. Ogawa, Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in paddy soils and river sediments in Akita, Japan, *Chemosphere* 67 (2007) 557–573.
- [14] C.H. Koh, J.S. Khim, K. Kannan, D.L. Villeneuve, K. Senthilkumar, J.P. Giesy, Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) and 2,3,7,8-TCDD equivalents (TEQs) in sediment from the Hyeongsan River, Korea, *Environ. Pollut.* 132 (2004) 489–501.
- [15] C. Rappe, R. Andersson, M. Bonner, K. Cooper, H. Fiedler, F. Howell, S.E. Kulp, C. Lau, PCDDs and PCDFs in soil and river sediment samples from a rural area in the United States of America, *Chemosphere* 34 (1997) 1297–1314.
- [16] L.P. Yu, B.X. Mai, X.Z. Meng, X.H. Bi, G.Y. Sheng, J.M. Fu, P.A. Peng, Particle-bound polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the atmosphere of Guangzhou, China, *Atmos. Environ.* 40 (2006) 96–108.
- [17] M. Ren, P.A. Peng, S.K. Zhang, L.P. Yu, G. Zhang, B.X. Mai, G.Y. Sheng, J.M. Fu, Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in Guangzhou, *Atmos. Environ.* 41 (2007) 592–605.
- [18] H.R. Li, L.P. Yu, G.Y. Sheng, J.M. Fu, P.A. Peng, The severe PCDD/Fs and PBDD/Fs pollution in air of electronic wastes dismantling area, *Environ. Sci. Technol.* 41 (2007) 5641–5646.
- [19] S. Li, S.B. Gewurtz, E.J. Reiner, K.A. MacPherson, T.M. Kolic, P.A. Helm, I.D. Brindle, C.H. Marvin, Patterns and sources of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in surficial sediments of Lakes Erie and Ontario, *Environ. Pollut.* 156 (2008) 515–525.
- [20] US EPA, An inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000, EPA/600/P-03/002F, 2006.
- [21] J.B. Wang, C.H. Hung, C.H. Hung, G.P. Chang-Chien, Polychlorinated dibenzo-*p*-dioxin and dibenzofuran emissions from an industrial park clustered with metallurgical industries, *J. Hazard. Mater.* 161 (2009) 800–807.
- [22] S. Masunaga, T. Takasuga, J. Nakanishi, Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations, *Chemosphere* 44 (2001) 873–885.
- [23] C. Rappe, M. Tysklind, R. Andersson, P.C. Bruns, R.L. Irvine, Dioxin in ball clay and kaolin, *Organohal. Compd.* 51 (2001) 259–263.
- [24] H. Holmstrand, D. Gadomski, M. Mandalakis, M. Tysklind, R. Irvine, P. Andersson, Ö. Gustafsson, Origin of PCDDs in ball clay assessed with compound-specific chlorine isotope analysis and radiocarbon dating, *Environ. Sci. Technol.* 40 (2006) 3730–3735.
- [25] S. Masunaga, Y. Yao, I. Ogura, T. Sakurai, J. Nakanishi, Source and behavior analyses of dioxins based on congener-specific information and their application to Tokyo Bay Basin, *Chemosphere* 53 (2003) 315–324.
- [26] UNEP (United Nations Environment Programme) Chemicals, Standardized toolkit for identification and quantification of dioxin and furan releases, 2005.
- [27] M. Zheng, Z. Bao, H. Yang, X. Xu, Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in lake sediments from Chinese schistosomiasis areas, *B. Environ. Contam. Tox.* 59 (1997) 653–656.
- [28] Y.S. Kim, H. Eun, H.S. Cho, K.S. Kim, E. Watanabe, K. Baba, T. Katase, The characterization of PCDDs, PCDFs and coplanar PCBs during the past 50 years in Gwangyang Bay, South Korea, *J. Hazard. Mater.* 154 (2008) 756–765.
- [29] Z.C. Bao, K.O. Wang, J.X. Kang, L.W. Zhao, Analysis of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in pentachlorophenol and sodium pentachlorophenate, *Chinese J. Environ. Chem.* (in Chinese) 14 (1995) 317–321.
- [30] J.F. Müller, C. Gaus, J.A. Prange, O. Pöpke, K.F. Poon, M.H.W. Lam, P.K.S. Lam, Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in sediments from Hong Kong, *Mar. Pollut. Bull.* 45 (2002) 372–378.
- [31] Y. Horii, B. van Bavel, K. Kannan, G. Petrick, K. Nachtigall, N. Yamashita, Novel evidence for natural formation of dioxins in ball clay, *Chemosphere* 70 (2008) 1280–1289.
- [32] J.I. Baker, R.A. Hites, Is combustion the major source of polychlorinated dibenzo-*p*-dioxins and dibenzofurans to the environment? A mass balance investigation, *Environ. Sci. Technol.* 34 (2000) 2879–2886.