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Polychlorinated Dibenzo-p-dioxins, Dibenzofurans and Dioxinlike Biphenyls in Sediments from the Suzhou Creek, China

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Abstract Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs) were detected in sediments from Suzhou Creek with mean concentrations of 478.1, 245.1, and 4727.6 pg/g dw, respectively. WHO–TEQ concentrations of PCDD/Fs in sediments ranged from 2.90 to 13.96 pg/g dw, while TEQ concentrations of PCBs varied from 0.27 to 1.41 pg/g dw. OCDD or HpCDD were the dominant congeners but PeCDF or HpCDD was the major contributor to PCDD/Fs-TEQ in all the sites. For dioxinlike biphenyls, PCB 118 was the major congener while PCB-TEQ was attributable to PCB 126 in all the samples.

Keywords Suzhou Creek · PCDD/Fs · PCBs · Sediment

Polychlorinated dibenzo-p-dioxins (PCDDs) and furans (PCDFs) and dioxinlike polychlorinated biphenyls (DL-PCBs) are highly toxic contaminants mainly originating from anthropogenic activities. For these poorly soluble pollutants, they accumulate in bottom sediments and reach much higher concentrations than in the upper water column. Aquatic animals, such as fish, can be exposed to the pollutants coming from contaminated sediments through the aquatic food chain (Menone et al. 2000; Vigano et al. 2000).

Suzhou Creek is a major natural waterway that passes through Shanghai, the largest city in the east of China. It is running approximately 125 km from Taihu Lake to the Huangpu River, of which about 53 km passes through the administrative area of the municipal government and about 24 km of downstream section passes through the highly urbanized part, including important financial, commercial, industrial, and residential districts. In past decades, tons of domestic sewage and industrial wastewater flowed into the river every day, so it was the most severely polluted river in the city. To recover the ecological functions of the natural waterway, a project "Suzhou Creek Rehabilitation Plan" was carried out in 1998 to improve water quality. Thenceforth, several researches have been carried on about ecological structure, bio-toxicity of the sediments and the water and concentrations of heavy metals and pesticides in the sediments (Hu et al. 2005). However, to our knowledge, the data of PCDDs, PCDFs and DL-PCBs in this river is lacking. As a step towards a broader study on the effective of Rehabilitation Plan, we report herein the levels of the dioxinlike chemicals in bottom sediments along the course of the river.

Materials and Methods

Sediment samples were collected from six sites (SS1–SS6) in the Suzhou Creek (Fig. 1). Surface sediment (0–10 cm) samples were collected using a sampler (Eijkelkamp Agrisearch Equipment) and blocks were removed. Each sediment sample was freeze-dried and sieved, and the fine fractions were stored in sealed glass bottles until analyzed for the contents of PCDD/Fs and PCBs.

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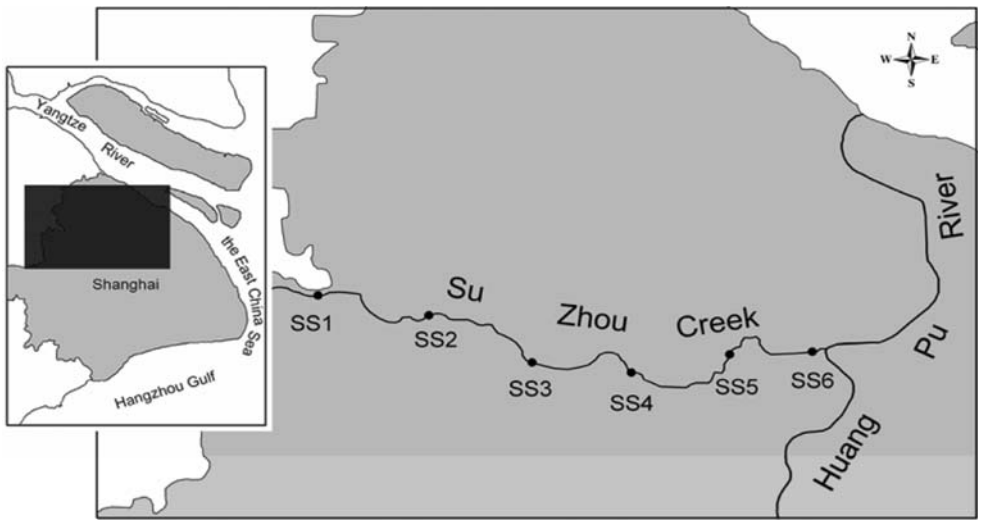

Fig. 1 Study area, showing the six sampling sites in the Suzhou Creek

PCDD/Fs and PCBs in sediment samples were quantified by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) using EPA Method 1613B and Method 1668A, respectively. The condition of the analysis was based on the method that is described in detail elsewhere (Zhang and Jiang 2005). Briefly, the samples were well homogenized, spiked with ^{13}C-labeled surrogate standards (Cambridge Isotopes Laboratories, Andover, MA, USA) and 1–2 g sediments were extracted with toluene in a Soxhlet apparatus. The extract was sequentially subjected to multilayered silica gel, acid alumina and florisil chromatographic columns cleanup procedures to remove interferences from the extracts. Before instrumental analysis, ^{13}C-labeled injection standards for dioxin analysis (Cambridge Isotopes Laboratories, Andover, MA, USA) and for PCBs analysis (Weillington Laboratories, Guelph, Canada) were added. The quantification of PCDD/Fs and PCBs homologues was performed by HRGC/HRMS on an Agilent 6890 gas chromatography coupled with an Autospec Ultima mass spectrometer (Waters Micromass, Manchester, UK). Chromatographic separation was achieved with a DB-5 MS fused silica capillary column (60 m × 250 μm i.d. × 0.25 μm film thickness).

Results and Discussion

Seventeen 2378-substituted chlorinated congeners of PCDD/Fs in the sediments were quantitatively determined (Table 1). The sum of PCDD and PCDF concentrations, and the WHO–TEQ values for the sites ranged from 365 to 1,307 and from 2.9 to 14 pg g^{-1} dry weight sediment, respectively. The recoveries of the samples are in the range from 54% to 94%, and the limit of determination for 2378-TCDD is 0.5 pg/g dw.

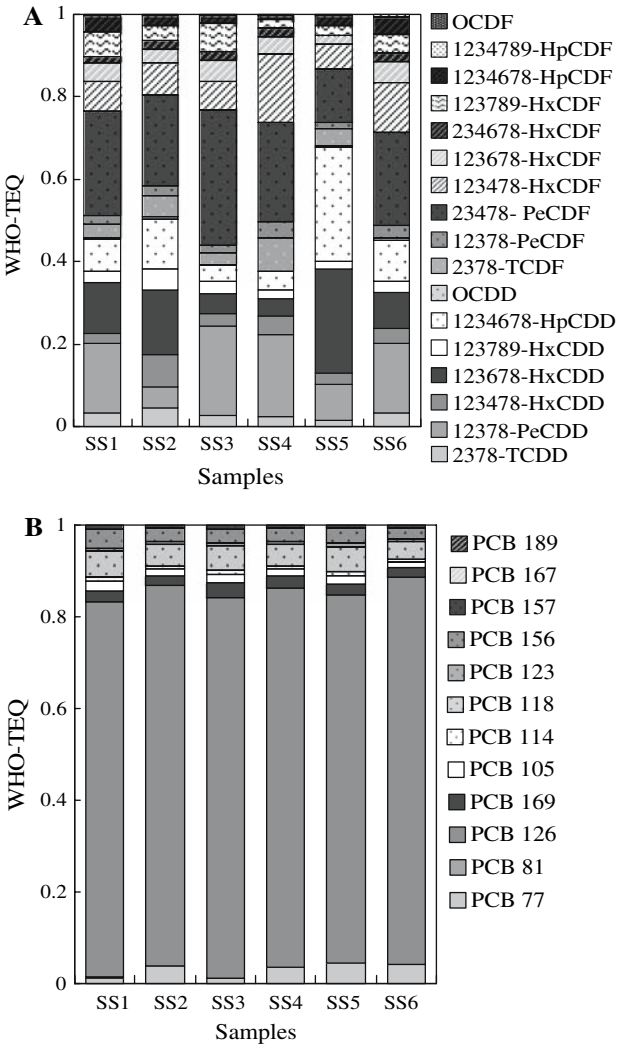

Fig. 2 Congeners contribution of PCDD/Fs (**a**) and PCBs (**b**) to the WHO-TEQ in sediment samples from Suzhou Creek

The total of PCDD and PCDF concentrations in this study were comparable to those reported by Koh et al. (2004) in sediments from Hyeongsan River in Korea, and to those in sediments of the other rivers in China (Zheng et al. 2001; Hu et al. 2005). But the concentrations of PCDD/Fs is higher than other studies on the Yangtze estuary nearby, which can due to the dilution of an amount of water from upper reaches (Sun et al. 2005).

The levels of contamination appear the lowest in the upper reach of the creek, and the increased levels can detected in the downstream flowing through the urban districts (Table 1). Marked increases in PCDD/Fs concentrations were observed in the sample from the SS3, and the maximum concentration (1,307 pg g^{-1} dw) was revealed at SS5. The concentration decreased in the sample collected from SS6, in where the river goes into the HuangPu River. Due to its sensitive to the tide change, reversing current of the river mouth can carried some pollutant away.

The TEQs of PCDD/Fs presented the same pattern with the concentrations of PCDD/Fs around the sample sites. Except for SS5, 2378-TCDF is the most responsible for TEQs calculated for PCDD/Fs in all sediments. On the other hand, 123678-HxCDD and 1234678-HpCDD are the dominant congeners contributing to the TEQs of PCDD/Fs in SS5 (Fig. 2).

Table 1 PCDD/F concentrations in sediment samples from Suzhou Creek

Sampling points	Surface sediments (pg g^{-1} dry sediment)					
	SS1	SS2	SS3	SS4	SS5	SS6
2378-TCDD	0.10	0.13	0.38	0.33	0.19	0.17
12378-PeCDD	0.50	<0.149	3.02	2.63	1.04	0.87
123478-HxCDD	0.70	2.27	4.15	5.65	3.04	1.86
123678-HxCDD	3.60	4.55	6.93	5.72	30.01	4.54
123789-HxCDD	0.80	1.44	4.15	2.8	2.26	1.26
1234678-HpCDD	22.9	35.39	52.25	57.64	329.15	51.31
OCDD	136.00	159.42	206.35	189.13	390.57	300.4
2378-TCDF	1.00	1.48	4.13	10.61	5.01	0.03
12378-PeCDF	1.20	1.42	5.58	10.33	3.72	3.17
23478-PeCDF	1.50	1.27	9.15	6.4	3.07	2.32
123478-HxCDF	2.10	2.27	9.61	21.99	7.29	6.24
123678-HxCDF	1.30	1.03	7.31	5.54	2.28	2.6
234678-HxCDF	0.50	0.55	2.88	2.66	<0.026	1.14
123789-HxCDF	1.80	1.04	9.40	2.64	3.00	2.36
1234678-HpCDF	10.80	7.27	27.05	13.78	26.89	20.34
1234789-HpCDF	1.00	0.68	3.30	3.16	4.37	3.22
OCDF	31.2	22.08	39.72	43.05	77.86	60.90
Sum of 17 congeners	217.00	242.44	395.36	384.06	889.78	462.73
TCDD	14.10	19.11	43.94	34.75	19.88	16.19
PeCDD	12.40	14.47	64.74	42.40	25.12	17.26
HxCDD	21.70	35.75	88.83	57.82	89.40	31.16
HpCDD	42.70	64.01	99.50	96.90	446.57	88.18
OCDD	136.00	159.42	206.35	189.13	390.57	300.40
TCDF	28.80	30.68	85.56	88.33	57.49	60.80
PeCDF	36.70	25.23	111.06	74.66	50.45	53.09
HxCDF	19.30	15.86	75.72	50.37	47.20	31.46
HpCDF	21.90	17.91	44.24	25.38	102.68	40.92
OCDF	31.20	22.08	39.72	43.05	77.86	60.90
$\sum$PCDD	226.90	292.76	503.36	421.00	971.54	453.19
$\sum$PCDF	137.90	111.76	356.3	281.79	335.68	247.17
$\sum$PCDD/Fs	364.80	404.52	859.66	702.79	1307.22	700.36
I-TEQ	2.85	3.00	12.67	12.1	11.79	5.04
WHO-TEQ	2.95	2.90	13.96	13.21	11.89	5.15

Relative high concentrations of OCDD observed at all sites indicated that the likely sources of PCDD in the Suzhou Creek were primarily due to atmospheric input from industrial complexes or combustion related sources in this area. On the other hand, HpCDDs were found to be the dominant congener in the sample collected in the SS5. The pattern of PCDD/Fs in the sediments characterized by high OCDD and HpCDDs could also be related to use of sodium pentachlorophenate to control *snailborne schistosomiasis* for decades in these rivers drainage basins (Zheng et al. 2001; Sun et al. 2005).

From the samples analyzed in our study, SS5 presented a $R_{TEQ\ PCDD/TEQ\ PCDF}$ value of 2.1. Generally, sewage sludge samples and sediment samples collected in the surroundings of the sewage sludge disposal site are characterized by a $R_{TEQPCDD/TEQ\ PCDF} > 1$ (Eljarrat et al. 2001). On the other hand, Koh et al. (2004) found that the total concentrations of PCDDs was threefold greater than that of PCDFs in sediment from a reservoir receiving the wastewater from the industrial complex. The ratio PCDD/PCDF value of 2.9 indicated that the sediment collected from SS5 were relative to the municipal wastewater. Although the sewage discharged into the river has been reduced in recent years, the wastewater outlet near this site would be expected.

The levels of PCBs in sediments samples are shown in Table 2. The recoveries of the samples are in the range from 51% to 76%, and the limit of determination for PCB 126 is 0.2 pg/g dw. The concentrations of PCBs in the sediments ranged from 1083.0 to 7823.4 pg g^{-1} dry weight sediment. As PCDD/Fs, site SS1 was the least polluted area for PCBs, while site SS5 has the highest concentration of PCBs. Compared with PCDD/Fs, the levels of PCBs are higher and all of the target congeners can be detected. The result of indicator PCBs shows that PCB 28 is the most abundant congener and followed by PCB 138 and PCB 153. Among WHO toxic congeners, PCB 118 was the highest one and the mean concentration

Table 2 PCBs concentrations in sediment samples from Suzhou Creek

Sampling points	Surface sediments (pg g^{-1} dry sediment)					
	SS1	SS2	SS3	SS4	SS5	SS6
Non-ortho PCB						
PCB 77	36	221.9	159.5	511	425.7	388.5
PCB 81	2.4	4.0	12.2	7.9	2.5	5.4
PCB 126	2.2	4.7	11.6	11.7	7.6	7.9
PCB 169	0.6	1.3	4.5	3.5	2.2	1.9
Mono-ortho PCB						
PCB 105	60.3	86.7	263.9	217.1	174.7	116.1
PCB 114	4.6	6.2	20.3	19.8	14.2	10.4
PCB 118	151.1	272.5	764.2	684.9	512.5	362.8
PCB 123	17.4	31.0	70.1	88.4	70.7	50.4
PCB 156	22.1	33.3	90.2	79.2	62.4	44.3
PCB 157	4.5	6.3	19.1	16.9	11.8	10.1
PCB 167	6.5	15.3	37.6	52.2	34.0	18.6
PCB 189	1.7	2.5	7.8	5.9	4.0	4.2
Ballschmiter PCB						
PCB 28	259.6	549.2	1198.2	3285.8	2583.2	1533.7
PCB 52	79.8	122.5	385.8	419.3	454.2	318.1
PCB 101	83.5	167.5	618.5	483.5	514.8	327.9
PCB 138	168.6	228.4	1039.4	659.9	615.8	398.2
PCB 153	125.8	284.9	773.5	670.4	606.5	363.5
PCB 180	27.6	44.3	135.9	131.2	131.4	69.5
PCB 209	28.7	242.4	203.9	474.8	641.7	416.8
Non-ortho PCB	41.2	231.9	187.8	534.1	438	403.7
Mono-ortho PCB	268.2	453.8	1273.2	1164.4	884.3	616.9
Ballschmiter PCB	773.6	1639.2	4355.2	6124.9	5547.6	3427.7
$\sum$PCBs	1083.0	2324.9	5816.2	7823.4	6869.9	4448.3
WHO-TEQ	0.27	0.57	1.40	1.41	0.95	0.93

is 458 pg g^{-1} dw, followed by PCB 77 and PCB 105 which could be detected at 290.4 and 153.0 pg g^{-1} dw, respectively. Although the most toxic PCB 126 is very low, it was responsible for greater than 80% of TEQs calculated for DL-PCBs (Fig. 2). For all sediments samples, PCB 126 is the most responsible for TEQs calculated for DL-PCBs and followed by PCB 118, PCB 77 and PCB 156. The WHO-TEQ varied between 0.27 and 1.41 pg g^{-1} dw.

In general, the overall levels of PCBs appear lower compared to other rivers (Kannan et al. 2001; Zhang and Jiang 2005; Hu et al. 2005). PCB homologue profiles as well as the congener profiles are overwhelmingly dominated by lower chlorinated congeners and homologues (TriCB to PentaCB), which contribute between 60% and 73% of the total PCBs concentrations. This contamination pattern would ascribe to the historical production activities of these kinds of PCBs. The further studies on the pattern of PCBs and PCDD/Fs in the sediment core would provide the information of historical pollute.

Overall, the total of PCDD/Fs and PCBs concentrations of the Suzhou Creek are comparable to those of other rivers in China. But the levels of contamination appear higher than the Yangtze estuary nearby. The PCDD/Fs homologue profiles in the sediments were different among the sampling sites, suggesting complicated origins contributed to the contamination in the Suzhou Creek.

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