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Distribution Pattern of Dioxins in Sediment Cores from the Xiangxi River, a Tributary of Three Gorges Reservoir, China

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Abstract: Sediment cores were collected from the Xiangxi River, a tributary of the Three Gorges Reservoir, the deposition time in the longest sediment core (90 cm) was measured by radiometry (^{137}Cs, ^{210}Pb) activities and polychlorinated dibenzo-p-dioxins/furan (PCDD/F) concentrations in different depths of the sediment core were measured. The results indicated that the mean deposition rate was 1.01 cm/a. The total PCDD/F concentrations ranged from 19.28 to 70.07 pg/g d.w. with a mean of 35.06 pg/g d.w. PCDD/Fs in the 1960–1990s were higher than others, which were significantly different in the various layers and cores ($p < 0.05$). PCDD occupied 63.42–87.33% of PCDD/Fs, and octachlorianted debenzo-p-dioxin (OCDD) was the predominant congener. The ratio of PCDD to PCDF was 2.26–8.08. PCDD/Fs significantly correlated with total organic carbon (TOC) ($p < 0.01$). The toxic equivalent (TEQ) ranged from 0.15 to 0.98 pg/g d.w. No significant difference was found in TEQ ($p > 0.05$). It was concluded that the spatio-temporal heterogeneity determined by hydrodynamics and total organic carbon (TOC) was the distribution pattern of PCDD/Fs in the sediment cores of Xiangxi River, the concentrations of PCDD/Fs were low, with a low environmental pollution risk, and by-products of sodium pentachlorophenate might be the main source.

Keywords: polychlorinated dibenzo-p-dioxins; polychlorinated dibenzo-p-furans; sediment; environmental pollution risk; three gorges reservoir (TGR)

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1. Introduction

Dioxin is typical of persistent organic pollutants; polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two groups of dioxin compounds including 22 pollutants recognized under the Stockholm Convention. No PCDD/F is produced intentionally; they are formed as halogenated aromatic by-products in a variety of industrial activities and combustion processes [1]. The most important sources of PCDD/F are the organochlorine industries, the incineration of mixed waste, metal smelting, refining and the chlorine bleaching of pulp; they present a threat to animal and human health with their persistence and toxicity [2]. In aquatic ecosystems, PCDD/Fs are particle-associated in abiotic compartments, but for biota, they are primarily associated with lipids due to the hydrophobic/lipophilic properties, which lead to the tendency of PCDD/Fs to accumulate in sediments [3]; consequently, the sediment becomes an important secondary emission source, which constitutes a particular threat to the associated biota and other organisms throughout the food web. The contamination status of PCDD/F in sediment is important for the environmental safety of aquatic ecosystems.

Three Gorges Reservoir (TGR) is the largest river-type reservoir with many tributaries in the world, playing an important role in water resource exploitation and economic development in China, which is highly concerned with ecological and health risks. Pollutants in the TGR, such as organic pollutants, microplastics, heavy metals (Cr, Cd, Cu, Hg, As and Zn) and so on, have been addressed [4–6]. Tributaries carry the runoff and bring nutrients/pollutants into the TGR, all of which affect the TGR's environmental safety and sustainable utilization; so, water environment safety in tributaries is very important. Information on nutrient loading, dissolved organic matters and heavy metal in some tributaries of TGR has been reported [5,7–10]. Although PCDD/Fs are a particular threat, to date, there are few documents on the water environmental safety assessment based on PCDD/Fs data.

The Xiangxi River originates from the Shennongjia Forest Region, with a length of 94 km and a watershed area of 3099 km^2. It is the largest tributary of the Three Gorges Reservoir (TGR) in Hubei and the closest tributary to the Three Gorges Dam (the distance is 38 km). As a typical tributary of TGR, its environmental safety is concerned. Investigations were conducted on microplastics, nutrient distribution, greenhouse gases and pollutant transport in Xiangxi River [5,11–13]. Though all the results indicated that the ecological and environmental problems in the Xiangxi River were serious, no data on persistent organic pollutants could be found. In this study, our hypothesis was that the distribution pattern of dioxins in sediment cores from tributaries of TGR was heterogeneous due to the long-term environment variation. The Xiangxi River was selected as the delegate of the tributary, and PCDD/Fs in sediment cores were screened. The data of PCDD/Fs in different depths of sediment filled the knowledge gaps in the tributaries of TGR. The environmental risk based on PCDD/Fs was evaluated using the toxic equivalent (TEQ) from the world health Organization (WHO) [14]. It is the first report on the dioxins in sediment cores from the tributaries of TGR.

2. Materials and Methods

2.1. Sample Site and Sampling Methods

Three sediment cores were obtained from the XX, XK and PYK sample stations in June, 2010, which represented the downstream, midstream and upstream of this river, respectively (Figure 1). The distance between every two stations was about 10 km.

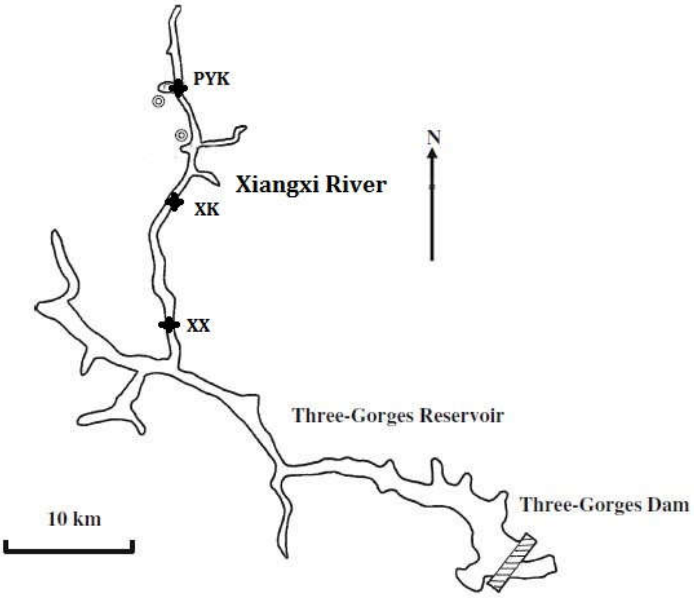

Figure 1. Sketch map of the sample stations in the Xiangxi River (three sample stations: XX, XK and PYK, located at the upstream, midstream and downstream).

Before the sample collection, all glassware for the collection and storage of samples was thoroughly cleaned with 10% HNO_3 and rinsed with double-distilled water three times before use. Sediment cores were collected by a stainless gravity sampler (100 cm length and 2.5 cm diameter; 100 L, Hubei Xiakoushegtai Ltd, Yichang, China). Samples were obtained by direct extrusion, capped, and frozen immediately before the samples were transferred to the laboratory. Each core was sliced into 10 cm fractions (samples) with a spatula from the bottom to the top layers; the samples were mixed and stored at −20 °C for analysis after they were dried with a freeze-dryer at 0 °C (CTFD-12S, Qingdao Yonghe Ltd., Qingdao, China).

2.2. Sediment Rate Measurement

The radiometry activities of ^{210}Pb, ^{226}Ra and ^{137}Cs in the samples were analyzed by a direct gamma assay using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Alpha Suite α, Ortec, Shanghai, China). The standards of ^{210}Pb, ^{226}Ra and ^{137}Cs were obtained from the China Institute of Atomic Energy. ^{210}Pb was determined via its gamma emissions at 46.5 keV. and ^{226}Ra was determined by the 295 and 352 keV γ-rays emitted by its daughter isotope ^{214}Pb following 3 weeks of storage in sealed containers to allow for radioactive equilibration. ^{137}Cs was measured by its emissions at 662 keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of the self-absorption of low-energy γ-rays within the sample. Radiometric dates were calculated from ^{210}Pb and ^{137}Cs records using the procedures described in Appleby (1998) [15]. Standard errors in the dates determined by uncertainties in the measured data were calculated using the methods described in Appleby (2001) [16].

2.3. Analysis of PCDD/Fs

All reagents used in this study were of trace analysis quality and from LGC Standards GmbH (Wesel, Germany), including silica and alumina adsorbents. All ^{13}C-labeled PCDD/Fs standards were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) or Wellington Laboratories (Guelph, ON, Canada). The C^{18}- modified silica was purchased from Macherey–Nagel (Düren, Germany).

About 20 g of subsamples was used for extraction. The extraction was conducted by ASE 2000 (Dionex, Germany) using n-hexane: acetone (75:25, *v/v*) at 120 °C and 12 MPa. The extraction temperature was 120 °C at 120 bar, and then ^{13}C-labeled PCDD/Fs standards were added. The clean-up procedure encompassed alumina and carbon chromatographic columns. PCDD/F analysis was performed with a high-resolution mass spectrometer Finnigan MAT 95S (Thermo, Germany) coupled with an Agilent GC 6890 (Agilent, USA). The instrumental parameters were described in Chen et al. [17], PCDD and PCDF were identified and quantified in pg WHO-TEQ/g. The enforcing lab was operating a quality assurance system according to DIN EN ISO/IEC 17025 and was accredited for the analysis of PCDD/Fs. The method detection limits for the 17 PCDD/F congeners were in the range of 0.01 to 0.08 pg/g d.w.; these were calculated on the basis of the signal-to-noise ratio (3:1) of the mass traces quantified in each individual analysis.

2.4. Total Organic Carbon Measurement

The total organic carbon (TOC) in the sediment samples was tested by the multi N/C 2100/2100S TOC analyzer (Analytik Jena, Germany) according to the standard method. The oxidation furnace temperature is 1100 degrees, The ceramic sample boat was soaked with 2 mol/L hydrochloric acid for 20 min and then washed with the distilled water three times and dried. After that, it was put into the 900 °C mav furnace for 30 min and then put into the dryer for use. Sediment samples were directly put into the ceramic sample boat and sent into the oxidation furnace at 1100 °C.

2.5. Statistical Analysis

SPSS statistics 24.0 software was used for one-way ANOVA analysis; a *t*-Test with the least significant difference was used to identify the significant difference among different samples and locations. Principal component analysis (PCA, Canoco for Windows 4.5) was used to identify the principal component.

3. Results and Discussion

The length of the sediment cores in the upstream, midstream and downstream were 30 cm, 50 cm and 90 cm, respectively, and the mean annual water velocity was 0.73, 0.48 and 0.21 m/s, respectively. Downstream was the main sedimentation area, and the length of the sediment core was the longest. The sedimentation process showed a significant spatial difference. McAnally et al. [18] proved that the river's hydraulic regime could strongly influence the sedimentation process and led to the different lengths of the sediment depth in different areas. It was deduced that the hydrodynamics in Xiangxi River led to the difference in the sediment cores length.

The radiometry activities of ^{210}Pb, ^{226}Ra and ^{137}Cs were measured in different layers from the longest sediment core. The activities of ^{137}Cs and ^{226}Ra were low, with no regular change; the activities of ^{210}Pb showed a relative regular change (Table 1). Clear and undisturbed ^{210}Pb gradients in different layers indicated that the data were credible. The sediment accumulation rates calculated by ^{210}Pb were 1.01 cm/a, and the samples A3, A4, A5 and A6 were from the 1960s, 1970s, 1980s and 1990s, respectively.

Table 1. The activities of ^{210}Pb, ^{226}Ra and ^{137}Cs in the 80 cm-long sediment core XX from the Xiangxi River.

Sample Number	Depth (cm)	^{137}Cs (Bq/kg)	^{210}Pbexe (Bq/kg)	^{226}Ra (Bq/kg)	Total ^{210}Pb (Bq/kg)
A0	10.0	1.49	236.19	84.07	280.61
A1	20.0	1.58	187.63	87.43	222.03
A2	30.0	1.73	228.41	92.35	253.04
A3	40.0	2.23	176.53	83.14	222.30
A4	50.0	4.08	142.85	64.75	160.77
A5	60.0	3.78	155.56	85.50	157.82
A6	70.0	1.26	166.74	66.28	180.61
A7	80.0	4.42	131.37	71.17	122.03
A8	90.0	2.16	102.65	61.21	117.63

The concentrations of PCDD/F are shown in Table 2. The total PCDD/F ranged from 19.28 to 70.07 pg/g d.w., with the mean being 35.06 pg/g d.w. Compared to other rivers (Table 3), the PCDD/Fs in the Xiangxi River were lower.

The mean PCDD/F concentrations in the sediment core from the upstream, midstream and downstream were 24.40 ± 10.32 pg/g d.w., 20.12 ± 23.84 pg/g d.w. and 46.91 ± 23.65 pg/g d.w., respectively. PCDD was dominant and occupied more than 80.55% of the total PCDD/Fs. OCDD and OCDF occupied 75.80% and 9.63% of the total homologues, respectively. Compared to others, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, OCDD and OCDF were higher; OCDD was the main congener (Table 2). The ratio of PCDD to PCDF was 2.26–8.08, which indicated that dioxins did not originate from local combustion but rather from the exogenous input. Similar results were obtained in other areas of the Yangtze River [19], the Xiangjiang River [20] and the Peal River. These areas have the same history suffering from schistosomiasis, which was treated by the application of sodium pentachlorophenate (Na-PCP) as a valid drug to control the spread of snail-borne schistosomiasis from the 1960s to the 1990s. PCDD/Fs, especially OCDD, were discharged into the environment, accompanied by Na-PCP as inevitable by-products, and accumulated in these areas. The samples A3, A4, A5 and A6 were deposited in the 1960s–1990s (Table 1); PCDD/Fs, especially OCDD depositing in the 1960s–1990s, were significantly higher than in other times (Table 2). It was concluded that PCDD in the Yangtze valley mainly resulted from the impurities of the exogenous Na-PCP as the important source. On the other hand, the vertical distribution of PCDD/Fs could also be seen in Table 2; samples at different depths reflected the time-scale of deposition. PCDD/Fs quantified in different depths exhibited marked differences (ANOVA, $p < 0.05$; $n = 18$), indicating significant correlations with time for the concentrations of PCDD/Fs in the core. The OCDD deposition in the samples A3, A4, A5 and A6 in the 1960s–1990s was significantly higher than that at other times (Table 2). The PCDD/F concentrations in the cores showed significant temporal heterogeneity ($p < 0.05$).

Table 2. PCDD/F concentrations (pg/g d.w.), TEQ (pg/g d.w.) and carbon contents (mg/g d.w.) in samples from the sediment cores of Xiangxi River ($n = 18$).

Location:					**XX**							**XK**				**PYK**	
Sample Number:	**A0**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**	**A8**	**B0**	**B1**	**B2**	**B3**	**B4**	**C0**	**C1**	**C2**
2,3,7,8-TCDD	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	0.08	n.d.	0.04	n.d.	0.06	0.21
1,2,3,7,8-PeCDD	n.d.	0.08	0.03	0.1	0.1	0.16	0.09	n.d.	n.d.	0.26	n.d.	0.08	n.d.	0.09	0.20	0.09	0.40
1,2,3,4,7,8-HxCDD	0.14	0.13	n.d.	0.09	0.11	n.d.	0.06	0.07	n.d.	0.12	n.d.	0.05	n.d.	0.06	n.d.	0.06	0.06
1,2,3,6,7,8-HxCDD	n.d.	0.15	0.06	0.12	0.1	n.d.	0.16	0.28	0.13	0.14	0.04	0.04	0.07	0.11	0.12	0.15	0.55
1,2,3,7,8,9-HxCDD	n.d.	0.12	0.08	0.16	0.13	n.d.	0.15	0.15	0.08	0.14	0.07	0.08	0.11	0.09	0.18	0.12	0.21
1,2,3,4,6,7,8-HpCDD	1.2	1.4	0.9	1.7	1.5	0.94	1.7	1.2	1	0.77	0.67	0.66	0.74	0.71	1.3	0.75	0.96
OCDD	37.9	33.8	22	58.1	43.7	26.2	56.2	33	24.9	14.3	14.6	17.6	16.5	15.5	18.5	12.0	15.0
Total PCDDs	39.28	35.68	23.07	60.27	45.67	27.31	58.47	34.69	26.11	15.73	15.38	18.59	17.42	16.6	20.30	13.27	17.39
The mean					38.95 ± 12.75							16.78 ± 1.3				16.99 ± 2.88	
2,3,7,8-TCDF	0.23	0.15	0.24	0.2	0.26	0.26	0.36	0.22	0.16	0.17	0.09	0.08	0.11	0.15	0.21	0.14	0.35
1,2,3,7,8-PeCDF	n.d.	0.18	0.12	0.19	0.17	n.d.	0.2	0.15	0.12	0.14	0.18	0.07	0.14	0.08	0.35	0.11	0.16
2,3,4,7,8-PeCDF	0.15	0.19	0.09	0.17	0.11	n.d.	0.21	0.1	0.13	0.22	0.09	0.07	0.1	0.17	0.35	0.12	0.21
1,2,3,4,7,8-HxCDF	n.d.	0.39	0.19	0.28	0.33	0.2	0.36	0.27	0.26	0.24	0.25	0.17	0.19	0.24	0.72	0.30	0.35
1,2,3,6,7,8-HxCDF	0.19	0.34	0.14	0.25	0.22	0.2	0.26	0.2	0.18	0.28	0.22	0.18	0.21	0.26	0.77	0.32	0.36
1,2,3,7,8,9-HXCDF	n.d.	0.11	0.07	0.05	0.09	n.d.	0.13	0.12	0.08	n.d.	0.07	0.04	n.d.	0.06	0.09	0.05	0.06
2,3,4,6,7,8-HxCDF	0.18	0.31	0.12	0.21	0.19	0.13	0.28	0.14	0.16	0.16	0.17	0.14	0.22	0.24	0.55	0.26	0.32
1,2,3,4,6,7,8-HpCDF	0.99	2.1	1	1.4	1.2	0.62	1.7	1.2	0.88	1.6	1.2	0.77	0.95	1.1	4.2	1.6	1.9
1,2,3,4,7,8,9-HpCDF	0.15	0.27	0.23	0.25	0.19	n.d.	0.24	0.18	0.15	0.23	0.14	0.08	0.09	0.13	0.57	0.22	0.21
OCDF	3.8	6	8	5.6	4.8	2.8	7.8	5.2	3.8	1.4	1.5	0.73	0.82	1.1	3.9	1.4	2.1
Total PCDFs	5.7	10	10.2	8.6	7.6	4.2	11.6	7.8	5.9	4.4	3.9	2.3	2.8	3.5	11.7	4.5	6.0
The mean					7.96 ± 2.27							3.38 ± 0.75				7.4 ± 3.1	
Sum	44.98	45.68	33.27	68.87	53.27	31.51	70.07	42.49	32.01	20.13	19.28	20.89	20.22	20.10	32.01	17.79	23.41
PCDD/PCDF	6.891	3.568	2.262	7.008	6.009	6.502	5.041	4.447	4.425	3.575	3.944	8.083	6.221	4.743	1.734	2.940	2.889
TEQ (WHO 2005)	0.15	0.39	0.2	0.37	0.35	0.27	0.44	0.22	0.2	0.53	0.17	0.29	0.17	0.37	0.72	0.36	0.98
TC	7.12	7.82	12.50	16.71	13.23	14.71	16.45	13.33	13.13	22.39	17.49	27.18	27.74	24.42	22.48	18.40	27.90
TOC	1.37	1.57	1.59	7.92	4.92	3.48	5.83	3.19	2.02	10.29	8.05	8.19	8.00	5.68	8.60	9.87	12.38
TIC	5.75	6.25	10.91	8.79	8.31	11.23	10.62	10.14	11.11	12.10	9.44	18.99	19.74	18.74	13.88	8.53	15.52
∑PCDD/Fs/TOC*	32.83	29.10	20.92	8.70	10.83	9.05	12.02	13.32	15.85	1.96	2.40	2.55	2.53	3.54	3.72	1.80	1.89

n.d.: not detectable; ΣPCDD/Fs/TOC*: the significant relationship between ΣPCDD/Fs and TOC; TCDD: Tetrachlorodibenzo-p-dioxin; PeCDD: Pentachlorodibenzo-p-dioxin; HxCDD: Hexachlorodibenzo-p-dioxin; HpCDD: Heptachlorodibenzo-p-dioxin; OCDD: Octachlorodibenzo-p-dioxin; PCDD: Polychlorinated dibenzo-p-dioxin; TCDF: Tetrachlorodibenzofuran; PeCDF: Pentachlorodibenzofuran; HxCDF: Hexachlorodibenzofuran; HpCDF: HeptacMorodibezofuran; TEQ: Toxic equivalency; TC: Total carbon; TOC: Total organic carbon; TIC: Total inorganic carbon.

Table 3. Concentrations of dioxins in different rivers (pg/g d.w.).

River Name	**Country**	**Dioxins Concentration**	**TEQ**	**References**
Estuary of Yangtze	China	62–171	0.29–0.78	[19]
Xiangjiang River	China	876–497,759	21.5	[20]
Peal River	China	472–2582	0.6–10.2	[21]
Kanzaki River	Japan	930–8200	41	[22]
Saginaw River	USA	55,200	3–3820	[23]
Detroit River	Canada	200–1600	2.30–306	[24]
Saigon River	Vietnam	250–1800	0.73−17	[25]
Elbe River	German	169,610–507,060	2290–7680	[26]
Xiangxi River	China	20.10–70.07	0.15–0.98	This study

PCDD/Fs in the midstream and upstream showed no significant difference; the two stations showed significant differences from the downstream ($p < 0.05$). The concentrations in the downstream were more than twice the concentrations in the midstream or upstream (Figure 2). PCA analysis indicated that samples could be divided into two groups (Figure 3); samples from the downstream were categorized as one group, while other samples were categorized as another group due to the different congener concentrations. The higher concentrations of OCDD, 1,2,3,4,5,7,8-HpCDD and OCDF were mainly responsible for differentiating the downstream from the others, especially OCDD and OCDF, which were primarily associated with the principal component axes, and OCDD was the main differentiating factor. When the different lengths of the sediment core from different locations were combined, all of the data differentiated downstream from other locations. Similar results [27,28] indicated that stream outlets were the main areas for PCDD/F sinks. It was deduced that hydrodynamics might be the determining factor in the spatial pattern of dioxins distribution.

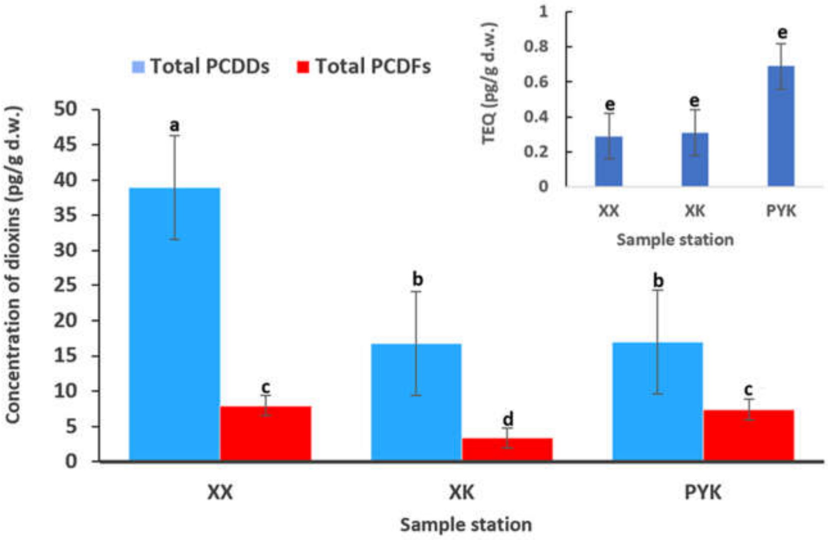

Figure 2. The concentrations of PCDD, PCDF and TEQ (WHO, 2005) in different areas of the Xiangxi River. TEQ was at the top-right corner; the dioxin concentration in the downstream area was higher, but the TEQ in the upstream was higher. Different letters indicated significant differences between sample stations.

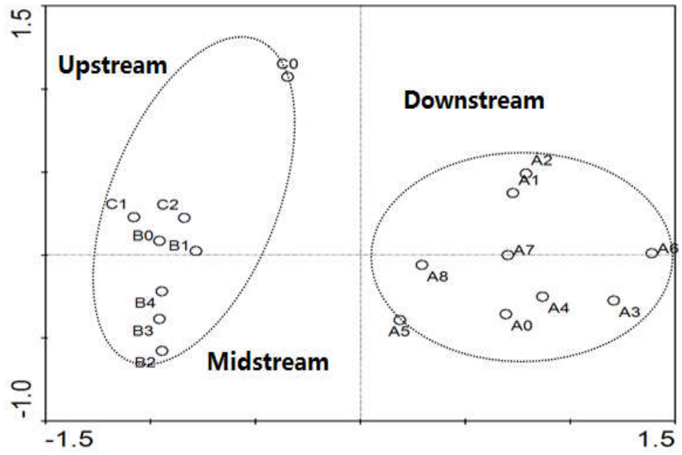

Figure 3. PCA analysis of the different samples from different depths in the sediment cores from the Xiangxi River. Samples A0~A8 were from the downstream, and samples B0~B4 and samples C0~C2 were from the midstream and upstream, respectively, which indicated a significant difference between the two groups at $p < 0.05$.

TOC, TIC, TC and the carbon-based concentrations of PCDD/F (Table 2) indicated significant spatio-temporal heterogeneity in organic carbon distribution (ANOVA, $p < 0.05$). The relationship between TOC and PCDD/F and the correlation between TOC and the PCDD/F/TOC value were significant ($p < 0.01$). Nie et al. [29] also found that the distribution of organic matter in the sediments decisively affected the partitioning of dioxins. Dioxins were usually partitioned predominantly in the organic matter of the sediment, while TOC played an important role in the distribution of dioxins.

The average TEQ was 0.36 pg/g d.w., ranging from 0.15 to 0.98 pg/g d.w. The vertical TEQ in different layers showed no significant difference (Table 2). The mean TEQ from upstream to downstream (Figure 3) indicated an obvious difference. The TEQ levels in the Xiangxi River were lower, and the pollution risk was low according to the Canadian Sediment Quality Guidelines, with its threshold value of 0.85 pg/g d.w.

4. Conclusions

The PCDD/F content in the sediment from the Xiangxi River was low, with a low environmental pollution risk. The PCDD/F distribution showed a heterogeneous spatio-temporal pattern; hydrodynamics and TOC played determining roles. PCDD/Fs indicated that the origins and the exogenous input of by-products of Na-PCP were the main sources.

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