CONTAMINATION STATUS OF DIOXINS IN SEDIMENTS FROM XIANGXI RIVER, CHINA

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Abstract

Concentrations of dioxins in surface sediments from the Xiangxi River were determined by high resolution gas chromatography/ mass spectrometry (HRGC/HRMS). The total amount of PCDD/Fs in each sample ranged from 20.77 to 102.83pg/g dry weight (d.w.), the mean was 49.60pg/gd.w.. In surface sediments, samples from different sites showed significant difference ($p<0.05$), concentrations of both PCDD/Fs were higher in estuarythan in other sites. The apparent longitudinal gradient could be seen. All samples had the similar ingredients, proportion of PCDDs in total PCDD/DFs was higher in all samples (occupied 68.14~85.94% ∑PCDD/Fs) and OCDD was the predominant congener, PCDFs contributed to a very small extend (14.06~31.86%). Ratio of PCDDs to PCDFs was 2.14~6.11, which could be presumed that the source of dioxins in surface sediment should be the same and no combustion source might be a source of PCDD/ DFs to this region. TEQ (WHO 2005, Humans) of samples ranged from 0.23 to 0.52 pg/g d.w., the mean was 0.40 pg/g d.w. No significant difference was found in TEQ among these samples ($p>0.05$). It could be concluded that the distribution of dioxins in surface sediment showed the apparent longitudinal gradient, Dioxin had the same origin and its concentration was low with very low environmental risk potential.

Keywords: Dioxins, sediment core, Xiangxi River, Three Gorges Reservoir (TGR)

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two groups of compounds included the 22 internationally recognized POPs under the Stockholm Conventions. PCDD/Fs are halogenated aromatic by-products in a variety of industrial and thermal processes and these contaminants were found in a variety of environmental media, including air, soil, sediment and biota. The most important sources of PCDD/Fsare the organochlorine industries, incineration of mixed waste, metal smelting, refining, and chlorine bleaching of pulp (UNEP, 1999). In aquatic ecosystems, PCDD/Fs are strongly particle-associated due to their hydrophobic properties, and tend to accumulate in sediments. Like other POPs, contamination status of PCDD/Fs in sediment is very important to the environmental safety of aquatic ecosystems (Gomez-Gutierrez et al., 2007) and should be paid much more attention to its negative effects. Xiangxi River is the largest tributary of the Three Gorges Reservoir in Hubei and the closest tributary to the Three Gorges Dam. The aim of the present study is to get insight into the distribution of dioxins in Xiangxi River and assess its environmental risk.

Materials and Methods

Study area and sampling sites

The Xiangxi River is one of the main tributaries into the Yangtze，originates in the Shennongjia Forest Region, WesternHubei province, which lies in 30°57'N-31°34'N and 110°25'E-111°06'E,its distance from the Three Gorges Dam(TGD)is 38 km, with the main stream length 94 km and a watershed of 3099 km^2. It is the largest tributary of the Three Gorges Reservoir (TGR) area in Hubei, also the closest tributary to the TGD. The natural fall of Xiangxi River is 1,540 m with an average annual discharge of 66 m^3/s (Wang et al. 1997; Tang et al. 2004). After the Three-Gorges Dam was constructed and the reservoir was filled to an altitude of 135 m above sea level in 2003, a long bay of 25 km length was formed in the downstream region of the Xiangxi River. After the second water storage period ending in 2006, water level reached 156 m above sea level, after the third water storage ending in 2010, water level reached 175m above sea level and Xiangxi River disappeared over a length of about 35 km (forming a big bay with low hydrodynamic energy). Sample stations were showed in figure 1, sampling sites were located at Xiangxidukou (XX01), Jiajiadian (XX02), Xiakou (XX04), Wujiawan (WJW), Pingyikou (PYK) and Gaoyang (XX07). All sites included 4 main-channel sites (XX01, XX02,XX04 and XX07) and 2 bay sites (WJW bay and PYK bay). Six surface sediment samples were obtained in March, 2011 to screen the distribution pattern of dioxins and its environmental risk.

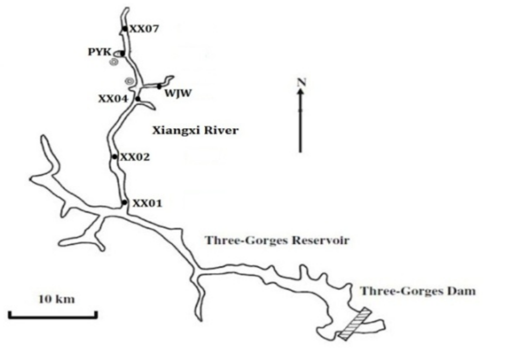


Figure 1.sketch map of Xiangxi River and the sample stations

Sample methods

Prior to sample collection, all glassware for the collection and storage of samples was thoroughly cleaned with acid (10% HNO3) and then rinsed in double-distilled (Milli-Q) water 3 times before each used. In 25th March, 2011, 6 surface sediment samples were collected with a stainless steel grab sampler. Surface samples were obtained and stored in pre-cleaned glass bottles. All visible organisms, fragments, grass leaves and roots, when present, were removed manually with the help of stainless-steel forceps.Surface sediment samples were dried in a freezing dryer at 0 °C.Dried samples were sieved to 40 mesh, stored at −20 °C until analysis.

Determination of PCDD/F

Extraction of 20 g sample was carried out using an Accelerated Solvent Extractor (ASE 200, Dionex GmbH, Idstein, Germany). The procedure was performed by using a mixture of n-hexane:acetone (75:25, v/v) at 120 °C and at a pressure of 12 MPa. Two static cycles of 10 min were applied for a complete extraction. Cleanup encompassed sandwich, alumina and carbon chromatographic columns. PCDD/F analysis were performed with a high-resolution mass spectrometer Finnigan MAT 95S (Thermo Electron GmbH, Bremen, Germany) coupled with an Agilent GC 6890 (Agilent Technogies, Palo Alto, CA, USA). The tetra to octa PCDD and PCDF were identified and quantified in pg WHO-TEQ/ g . The enforcing lab is operating a quality assurance system according to DIN EN ISO/IEC 17025 and is 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.; calculated on the basis of signal-to-noise ratio (3:1) of the mass traces quantified in each individual analysis.

Statistical evaluation

ANOVA and t-test were used to analyze the significant difference between the two stations.

Results and Discussion

Concentrations of dioxins

Seven 2,3,7,8-substituted PCDD congener and ten 2,3,7,8-substituted PCDF congener were tested in surface sediment samples from the Xiangxi River. The concentrations ofPCDD/Fs (WHO-TEQ, 2005) pg/g sample were shown in Table 1. In general it was found that all samples contained relatively low amounts of the investigated organic toxic pollutants. The same results were also obtained in the Three Gorges Dam area (Chen et al., 2013), it could be deduced that dioxins concentration in the Hubei segment of TGR was low.

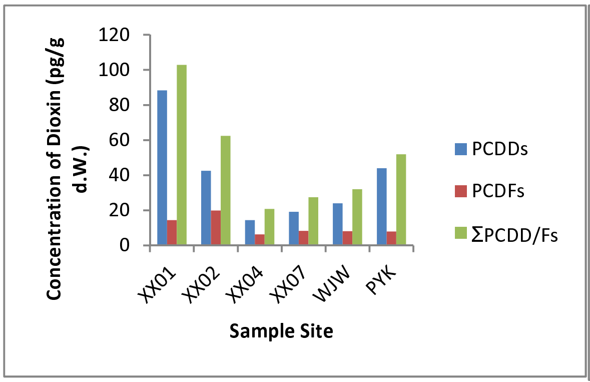
The total amount of PCDD/Fsin each sample ranged from 20.77 to 102.83 pg/g d.w., the mean was 49.60 pg/g d.w.. Figure 2 showed the dioxins concentration in different sites. In surface sediments, samples from different sites showed significant difference ($p<0.05$), concentrations of both PCDD/DFs were higher in estuary than in other sites. XX01, XX02, XX04 and XX07 located the main channel. Concentration of dioxins showed the apparent longitudinal gradient, the upper < the middle < the estuary. As to the bay, dioxins in WJW and PYK were lower than in the estuary, but higher than other sites in the main channel. It could be concluded that the main place for dioxins' deposition in Xiangxi River were the estuary, the bay was the following. due to the hydrophobic properties, PCDD/Fstend to accumulate in sediments accompanying with the depositing particle.

Under the effects of hydrodynamics, river mouth was the main place for the sedimentation. Not the uniform distribution, but the apparent longitudinal gradient of concentrations of dioxins showed the depositional characteristics of Xiangxi River didn't like the lake-type. Results of this paper could be inferred that water bodies of Xiangxi River still kept the river-type depositional characteristics of suspending particulate though it was remarkably influence by the backwater from the impoundment of TGR.

Table 1 Concentrations and TEQ of dioxins in the samples from the surface sediment of Xiangxi River (pg/g d.w.)

Location:	**XX01**	**XX02**	**XX04**	**XX07**	**WJW**	**PYK**
Sample Number:	c1110003	c1110004	c1110005	c1110006	c1110007	c1110008
Sample Time	25.03.2011	25.03.2011	25.03.2011	25.03.2011	25.03.2011	25.03.2011
2,3,7,8-TCDD	0.06	0.06	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8-PeCDD	0.11	0.09	n.d.	0.19	n.d.	n.d.
1,2,3,4,7,8-HxCDD	0.14	0.09	n.d.	0.10	n.d.	n.d.
1,2,3,6,7,8-HxCDD	0.22	0.16	0.14	0.21	0.11	0.13
1,2,3,7,8,9-HxCDD	0.20	0.14	0.09	0.20	0.13	0.15
1,2,3,4,6,7,8-HpCDD	2.6	1.4	0.70	1.1	1.2	1.4
OCDD	85.0	40.6	13.5	17.4	22.6	42.3
Total PCDDs	88.37	42.55	14.45	19.17	23.98	43.99
2,3,7,8-TCDF	0.33	0.33	0.11	0.15	0.16	0.15
1,2,3,7,8-PeCDF	0.19	0.29	0.12	0.21	0.23	0.23
2,3,4,7,8-PeCDF	0.23	0.18	0.16	0.23	0.16	0.19
1,2,3,4,7,8-HxCDF	0.39	0.45	0.41	0.43	0.50	0.42
1,2,3,6,7,8-HxCDF	0.33	0.35	0.30	0.52	0.55	0.51
1,2,3,7,8,9-HXCDF	0.10	0.25	0.10	0.06	0.12	0.06
2,3,4,6,7,8-HxCDF	0.24	0.34	0.29	0.44	0.46	0.49
1,2,3,4,6,7,8-HpCDF	1.9	2.5	2.0	3.0	2.9	2.6
1,2,3,4,7,8,9-HpCDF	0.34	0.44	0.33	0.33	0.35	0.25
OCDF	10.4	14.7	2.5	3.0	2.6	3.1
Total PCDFs	14.5	19.9	6.3	8.3	8.1	8.0
∑PCDD/DFs	102.83	62.44	20.77	27.50	32.07	51.97
PCDDs/PCDFs	6.110	2.139	2.285	2.302	2.966	5.509
TEQ (WHO 1998)	0.55	0.52	0.26	0.57	0.34	0.34
TEQ (WHO 2005)	0.52	0.49	0.23	0.52	0.31	0.31

All samples had the similar ingredients (Table 1), Figure 3 showed the proportion of PCDDs in total PCDD/Fs was higher in all samples (occupied 68.14~85.94% ∑PCDD/Fs) and OCDD was the predominant congener, PCDFs contributed to a very small extend (14.06~31.86%). Ratio of PCDDs to PCDFs was 2.14~6.11, the mean was 3.55, which could be presumed that the source of dioxins in surface sediment should be the same and no combustion source might be a source of PCDD/Fs to this region. The similar results could be seen in other documents (Lei, et al., 2013; Sun et al., 2005; Bao, et al., 1995), the similar ingredients of dioxins in sediment from TGR meant the origination of dioxins might be the same



Figurre2 Dioxins concentration in surface sediment from different sites

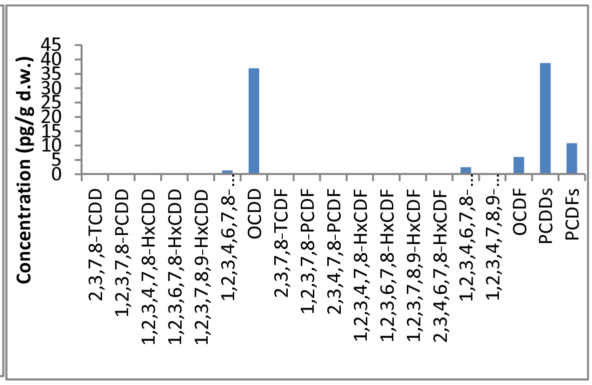


Figure 3 The mean concentration of each compound in the surface sediment from Xiangxi River

Risk Assessment

TEQ (WHO 2005, Humans) of samples ranged from 0.23 to 0.52 pg/g d.w., the mean was 0.40 pg/g d.w. (Figure 4). No significant difference was found in TEQ among these samples ($p>0.05$). Compared to otherwater bodies (Masaaki et al., 2003; Birch et al., 2007; Simo et al., 2008; Gao et al.,2008; Patrick et al.,2013), the value of TEQ in Xiangxi River is very low and thus the environmental risk is low.

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