Declining polychlorinated dibenzo-*p*-dioxins and dibenzofurans levels in the sediments from Dongting Lake in China

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ARTICLE INFO

Article history:

Accepted 14 June 2007

Available online 23 May 2008

Keywords:

Dioxins
Sodium pentachlorophenol
Sediment
Dongting Lake

ABSTRACT

Dongting Lake is the second largest freshwater lake in China. Technical sodium pentachlorophenolate (Na-PCP) had been sprayed since 1960s to control the spread of snailborne schistosomiasis up to the middle of 1990s. As one of the by-products of Na-PCP, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) may enter the environment. It has been reported that the concentrations of PCDD/Fs in sediments in Dongting Lake were 130–891 pg I-TEQ g⁻¹ in 1995. High toxicity of sediment to exposed micro-organisms and fish may be risk on environment. In order to determine the present levels of the contamination, eight sediment samples from Dongting Lake were analyzed for PCDD/Fs using HRGC-HRMS. Total I-TEQ values for these samples were at a ranged of 0.7–11 pg g⁻¹, with a mean value of 4.5 pg g⁻¹. The results show that PCDD/Fs concentrations of contemporary sediment have declined since 1995. Certain PCDD/F congeners as well as OCDD, typical for Na-PCP, predominated in lake sediment indicating that the using of PCP-Na is the main source of PCDD/Fs in the lake. These variations in levels can reflect changes in PCDD/F sources to the environment over time.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a family of compounds that includes some extremely toxic congeners. PCDD/Fs are among the 12 persistent organic pollutants (POPs) of Stockholm Convention. They are highly persistent compounds and have been detected in air, water, soil, sediment, animals and foods. The contamination of PCDD/Fs in sediment was well document (Gabos et al., 2001; Prange et al., 2002). It was reported that concentrations of PCDD/Fs in the sediments were decreasing with temporal trends in some historical polluted area (Vartiainen et al., 1997; Yamashita et al., 2000). Decline in PCDD/Fs fluxes to the environment and concentrations in biota have been reported in several studies in developed countries (Päpke et al., 1994; Kjeller et al., 1996).

Dongting Lake, covering a very large surface water area of 2691 km², is located in the southern part of the People's Republic of China. It is the second largest freshwater in China and plays an important role in regulating the amount of water in the Yangtze River. Asian schistosomiasis has been endemic in the Dongting Lake region for centuries and it has a devastating effect on the public health of the local people (Li et al., 2000). Technical sodium pentachlorophenolate (Na-PCP) has been sprayed since 1960s to control the spread of snailborne schistosomiasis. As one of the by-products

of Na-PCP (Bao et al., 1995), PCDD/Fs may enter the environment and contribute to human exposure. The sediment in Dongting Lake was recognized to be highly contaminated with PCDD/Fs in 1995 (Zheng et al., 1997). Concerning the adverse effect of Na-PCP, Na-PCP has been prohibited spraying in this region since 1995. However, PCDD/Fs were chemically inert, which could remain in the environment for many years. The aim of this study was to determine the PCDD/F levels in sediment samples collected from Dongting Lake and compare them with samples collected in 1995 and 1999 in order to explore the temporal trend. Absolute and relative (congeners profile) concentrations and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxic equivalents (TEQs) were evaluated to describe possible sources and potential risk on eco-environment. Another objective was to quantify the extent, clarify the historical trend of PCDD/Fs pollution in Dongting Lake sediment and consider the interrelation between them. It is desirable that the findings may help to understand the temporal trend in level and patterns of PCDD/Fs for other history polluted regions contaminated by using Na-PCP.

2. Materials and methods

The eight samples were taken from eight different locations (shown in Fig. 1) distributed over the whole lakeland in September 2004. These locations are on the profiles of the national or the provincial key monitoring areas, which can represent environmental conditions of the lake pollution. A global positioning system

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Fig. 1. Locations of sampling sites at Dongting Lake.

(GPS) was employed to identify each location precisely. The description of the sampling sites is given in Fig. 1. Each sample was aliquot of the mixture from at least of 3 sites of the locations.

Sediments were collected with a grab sampler from shipboard in 2004. Samples were wrapped in aluminium foil, stored at -18°C and freeze-dried, manually ground and sieved before analysis. A blank was included in each batch samples. Prior to extraction, 10 g of dried soils were homogenized and spiked with a mixture of internal standards ($^{13}\text{C}_{12}$ PCDD/Fs congeners, Cambridge Isotope Laboratories). Then samples were mixed with anhydrous sodium sulfate which had been baked out at 660°C to remove residual impurity. The mixture were placed in pre-extracted thimbles and extracted in a Soxhlet apparatus with toluene for 24 h. The samples were rotary evaporated to less than 0.1 ml, 1 ml hexane were added. Then the extracts were cleaned by three adsorption columns. The first acid-base silica gel column was prepared by packing a glass column (15 mm i.d.) with layers of 10 g of 44% acidic silica gel and a thin layer of sodium of sulfate at the top. The column was cleaned with 50 ml hexane prior to transfer of sample extract. Samples were then eluted with 70 ml hexane and rotary evaporated to 1 ml. The second multilayer silica gel columns

(15 mm i.d.) was packed with 1 g of silica gel, 2 g of 10% AgNO_3 silica gel, 1 g of silica gel, 8 g of 44% acidic silica gel, 1 g of silica gel, 5 g of 33% basic silica gel, 1 g of silica gel and a thin layer of sodium of sulfate at the top. The column was cleaned with 70 ml hexane prior to transfer of sample extract. Samples were then eluted with 100 ml hexane and rotary evaporated to 1 ml. The third basic alumina column (10 mm i.d.) was packed with 10 g basic alumina and a thin layer of sodium of sulfate at the top. The column was cleaned with 100 ml hexane prior to transfer of sample extracts. Samples were then eluted with 100 ml 5% dichloromethane/hexane and then eluted with 50 ml 50% dichloromethane/hexane, the 50% dichloromethane/hexane were rotary evaporated to 1 ml. Then the samples were transfer to K-D concentrator and concentrated by means of a rotary evaporator to nearly 500 μl . And then the samples were concentrated by gentle nitrogen to 10 μl . The recovery internal standards ($^{13}\text{C}_{12}$ PCDD/Fs Cambridge Isotope Laboratories) were added before analysis.

Analysis of PCDD/Fs was performed on a GC (Agilent Technologies, USA) coupled with an Autospec Ultima mass spectrometer (Waters, USA) operating on a resolution of an approximately 11000. DB5-MS (J&W Scientific, USA) fused silica capillary column

Table 1
Levels of PCDD/Fs in Dongting Lake sediment in 2004 (pg g^{-1})

	S1	S2	S3	S4	S5	S6	S7	S8
2378-TCDF	4.0	2.2	<0.1	0.6	0.2	0.9	1.9	<0.1
12378-PeCDF	5.2	<0.5	<0.05	<0.04	<0.04	<0.2	0.6	<0.1
23478-PeCDF	<0.06	<0.6	<0.05	<0.04	<0.2	<0.1	0.2	<0.1
123478-HxCDF	4.2	2.2	0.4	1.5	0.3	1.7	1.1	0.8
123678-HxCDF	2.3	1.4	1.4	0.7	0.4	1.0	3.8	0.5
234678-HxCDF	2.0	1.1	0.6	0.6	0.3	0.6	1.4	<0.06
123789-HxCDF	<0.04	0.8	0.5	0.7	0.3	0.9	1.3	0.5
1234678-HpCDF	14	8.7	3.1	5.4	3.5	5.0	12	4.5
1234789-HpCDF	<0.08	0.33	<0.05	0.3	<0.06	0.9	<0.34	<0.06
OCDF	51	25.2	11	29	26	31	54	26.2
2378-TCDD	0.2	0.2	<0.06	<0.06	0.2	0.2	0.1	0.1
12378-PeCDD	0.2	<0.1	<0.2	<0.2	0.06	0.1	<0.2	0.2
123478-HxCDD	12	0.9	8.2	5.7	0.6	2.7	6.5	1.3
123678-HxCDD	2.9	1.8	1.7	0.9	0.2	0.5	1.4	0.6
123789-HxCDD	9.1	6.1	6.0	3.8	0.7	1.7	5.0	2.8
1234678-HpCDD	109	66	60	36	2.6	14	56	16.1
OCDD	5113	3280	2980	1696	100	659	2375	738
Σ 2378-PCDD/Fs	5329	3397	3073	1781	135	720	2520	792
I-TEQ	11	5.9	5.5	3.6	0.7	2.1	5.6	1.8

(60 m × 0.25 mm id., 0.25 μm film thickness) was used with helium as the carrier gas. Identification of 2,3,7,8-substituted PCDD/Fs was performed using retention times of the ^{13}C -labelled standard and isotope ratios M and M+2 or M+4. For quality control, the retention times of the analytes in a sample were quantified if it deviated by 2 s or less from the retention times of the internal standards. The limit of quantification for PCDD/Fs in a sample was defined by a signal to noise ratio greater than three times the average baseline variation and an analyte quantity in the sample greater than three times the quantity in the respective blank.

3. Results and discussion

3.1. PCDD/Fs in sediments collected in 2004

The isomer distributions of 2,3,7,8-substituted PCDD/Fs in sediments collected in 2004 from Dongting Lake are given in Table 1. Recovery for each sample was checked by reference to the ratios of ^{13}C labeled internal standards relative to the recovery determination standard ranging from 80% to 128%, showed a satisfactory analysis procedure.

The total 2,3,7,8-substituted PCDD/Fs in samples were in a range of 135–5329 pg g⁻¹ with a mean value of 2218 pg g⁻¹. The highest sum of PCDD/Fs concentration was measured at location S1 and the minimum concentration of 135 pg g⁻¹ was determined at location S5.

Different sources of PCDD/Fs are characterized by different congener and homologue patterns. Bao et al. (1995) reported that OCDD contributes 76% (as shown in Table 2) to the sum 2,3,7,8-substituted PCDD/Fs in Chinese technical Na-PCP. The PCDD/Fs congener profiles in all samples in this study are dominated by OCDD which contributed 74–97% to the $\sum 2,3,7,8\text{-PCDD/F}$ concentration in the samples. This indicates that Na-PCP was the major source of the PCDD/Fs in Dongting Lake. The observation is similar to that of Mai Po Marshes (Müller et al., 2002) which contaminated by PCP. OCDD contributed 94–97% to the $\sum 2,3,7,8\text{-PCDD/Fs}$ concentration in Mai Po Marshes.

To normalize concentrations and the toxicity of the different PCDD and PCDF congeners, international toxicity equivalent factors (I-TEFs) were used to calculate the international toxicity equivalent (I-TEQ) for the samples (For the concentrations below MDL values, concentrations were set as 0). I-TEQ for the samples analyzed was in a range of 0.7–11 pg g⁻¹, with a mean value of 4.5 pg g⁻¹ dry weight sediment. The contribution of each contaminant to the total toxicity of environmental sample depended on the relative order of potency along with the contamination level in the environment. The highest I-TEQ was found at location S1 there was also the maximum $\sum 2,3,7,8\text{-PCDD/Fs}$ concentration determined. The lowest I-TEQ of 0.7 pg g⁻¹ was determined at S5 there was also the minimum concentration of $\sum 2,3,7,8\text{-PCDD/Fs}$ detected.

Table 2
2 Concentrations of PCDD/Fs in Chinese technical Na-PCP (ng g⁻¹)

Congeners	Congeners	Congeners	Congeners
2,3,7,8-TCDF	3.1	2,3,7,8-TCDD	4
1,2,3,7,8-PeCDF	40.9	1,2,3,7,8-PeCDD	2.1
2,3,4,7,8-PeCDF	2.4		
1,2,3,4,7,8-HxCDF	76.1	1,2,3,4,7,8-HxCDD	244
1,2,3,6,7,8-HxCDF	9.4	1,2,3,6,7,8-HxCDD	13.8
2,3,4,6,7,8-HxCDF	0.9		
1,2,3,7,8,9-HxCDF	0.3	1,2,3,7,8,9-HxCDD	2.1
1,2,3,4,6,7,8-HpCDF	135	1,2,3,4,6,7,8-HpCDD	1702
1,2,3,4,7,8,9-HpCDF	18.3		
OCDF	1647	OCDD	12,514

In this study the concentrations of the sum of PCDDs were higher than those of the sum of PCDFs, with the ratio $R_{(\text{I-TEQ PCDDs/I-TEQ PCDFs})} > 1$ for all the samples. The values ranged between 2.5 and 16 (with a mean value 5.8), while in Chinese technical Na-PCP, the value was 4.0. So the results in this experiment were consistent with Na-PCP. Hepta-CDD and OCDD were the major PCDD congeners in technical Na-PCP and the sediments. The contribution of octa- and hepta-CDDs in sum PCDD/Fs in technical Na-PCP was 87%. The contribution of octa- and hepta-CDDs in sum PCDD/Fs in the eight sediment samples ranged from 76% to 99%, with a mean value of 94%.

OCDD contributes more to PCDD/Fs in sediments than those in technical Na-PCP. Although there was no reasonable explanation, some researchers also reported that OCDD contributes 56–91% to the sum of PCDD/Fs in the sediments of Nanpawu River and Bohai Bay in China contaminated by using PCP-Na (Hu et al., 2005).

3.2. Declining PCDD/F levels in sediments with temporal trends

During the 1990s, the sediment in Dongting Lake was recognized to be highly contaminated with PCDD/Fs (Zheng et al., 1997). Total I-TEQ values of PCDD/Fs ranged from 130 to 891 pg g⁻¹ with a mean value of 274 pg g⁻¹ in the sediment samples collected in 1995. Total I-TEQ values in the samples collected in 2004 were much lower than those measure in the samples collected in 1995, with a decrease of 61 times in mean values (Zheng et al., 2000). The I-TEQ of PCDD/Fs values in the sediments collected in 1999 were in a range of 9–49 pg g⁻¹ with a mean value of 29 pg g⁻¹ dry weight sediment. Therefore, the PCDD/F levels determined in the contemporary sediment study were substantially lower than the mean value reported for the sediments in 1995 (as shown in Fig. 2).

Three factors that affected declining PCDD/F levels in Dongting Lake: (1) ceasing utilizing PCP-Na in Dongting Lake stop releasing PCDD/Fs to the local environment. Na-PCP was prohibited using since 1995 except that some stock Na-PCP was still used in specific sites until 1998. (2) Dilution effect of flood. Dongting Lake receives the flow and sediment from the 4 outlet of Yangtze River, Xiang, Ziyuan and Lishui Rivers. There were three serious floods in 1996, 1998 and 2002. Most PCDD/Fs entering the aquatic environment are associated with particle matter brought by flood. The floods might dilute the PCDD/Fs concentrations in the sediment. The dilution effect of the flood in one sampling site differs from that in another sampling site. So the highest level was observed at different locations in different years. (3) Biodegradation effect. Some literatures (Adriaens and Grbic-Galic, 1994; Beurskens et al., 1995) had reported anaerobic biodegradation for some PCDD and PCDF congeners in sediments. The declining dioxins levels in this study were mainly due to the dilution effect of the flood.

Fig. 2. Declining PCDD/Fs levels in sediments collected in the year 1995, 1999 and 2004.

It should be noted that the concentration of 1,2,3,7,8-PeCDF were 20 times higher than that of 1,2,3,7,8-PeCDD in commercial Na-PCP. However, the levels of 1,2,3,7,8-PeCDF were much lower than those of 1,2,3,7,8-PeCDD in sediment samples of almost all sites collected in 1995 and 1999. In the sediment samples collected in 2004, 1,2,3,7,8-PeCDD and 1,2,3,7,8-PeCDF were all below the detection limit except S1.

In August, 2003 US EPA region 5 bought forward ecological screening level for sediment. About 11 pg g^{-1} of PCDD/Fs level was suggested for sediment in Resource Conservation and Recovery Act plan (US EPA, 2003). Although the concentrations of PCDD/Fs have declined a lot since 1995, the PCDDs in all the samples exceeded the EPA sediment quality criterion. Holobec et al. (1993) presented a simple classification for PCDD/F concentrations in sediment samples, where $<200 \text{ pg g}^{-1}$ d.w. present background area, $200\text{--}1000 \text{ pg g}^{-1}$ slightly polluted area, $1000\text{--}2000 \text{ pg g}^{-1}$ polluted area, $2000\text{--}10,000 \text{ pg g}^{-1}$ heavily polluted area and $10,000\text{--}100,000 \text{ pg g}^{-1}$ very heavily polluted area. Most of the sediments in this study of 2004 were classified as slightly polluted area or polluted area and most of sediments collected in 1995 were sort as heavily polluted area.

Acknowledgments

This study was supported by National Basic Research Program of China (2003CB415006) and National Natural Science Foundation of China (20621703, 40332023).

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