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PCDD/FS IN SURFACE SEDIMENTS FROM DONGTING LAKE, CHINA

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Introduction

Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans(PCDD/Fs) have caused extensive concern due to their adverse effects on the environment and human health. The release of PCDD/Fs from the production and use of Sodium pentachlorophenate (Na-PCP) has been identified as one of the most important sources. Dongting Lake is the second largest fresh water lake of China, which is also an area with most widely distributed oncomelaniahupensis and has the most severe schistosomiasis epidemic situation in China. Na-PCP has been sprayed as molluscicide in Dongting Lake from 1960s to 1990s, it was estimated that over 9.8 ×106 kg of Na-PCP had been devoted into the lake; PCDD/Fs were also carried into the lake with using of Na-PCP.

Previous research on PCDD/Fs in Dongting Lake was mainly focus on their contamination status of central lake regions. However, historical trend and hydrodynamic effects on the distribution of PCDD/Fs have not been reported. The aims of this study were 1) to investigate current contamination status, distribution, and historical trend of PCDD/Fs in Dongting Lake; 2) to assess the environment risk of PCDD/Fs to the aquatic biota; and 3) to analyze the effect of hydrodynamic on PCDD/Fs distribution in Dongting Lake.

Materials and Methods

Surface sediment samples (about 10 cm depth) were collected in September 2013 from 14 sites in Dongting Lake: Xiang estuary (Zhangshugang), Zi estuary (Wanjiazui), Yuan estuary (Potou), west Dongting Lake region (Nanzui, Jiangjiazui, Xiaohezui), East Dongting Lake region (Lujiao, Bianshan, Dongdongtinghu, Daxiaoxihu), South Dongting Lake region (Wanzihu, Hengling, Yugongmiao), and outlet (Dongtinghuchukou). The sampling locations was shown in Fig.1, the samples were placed into precleaned dedicated sampling containers, labeled with a unique code and proper sampling date. All samples were transported to the analytical laboratory as soon as possible and stored in the dark at -20°C until analysis.

Standard solutions in nonane (EPA-1613 CS1 to CS5, EPA-1613 LCS, and EPA-1613 ISS) were purchased from Wellington Labs (USA). All solvents used (hexane, dichloromethane) were of pesticide grade (J.T.Baker, USA), n-nonane were purchased from Sigma (USA). Silica gel (100-200 mesh) was purchased from Merck (Germany).

Concentrations of 17 2,3,7,8-substituted PCDD/F congeners were determined according to the US EPA method 1613. All samples were identified and quantified by injecting an aliquot into HRGC-HRMS (Autospec-Premier, equipped with a DB-5MS capillary column, Agilent Technologies, USA; 60 m; i.d. 0.25 mm; film thickness 0.25 μm) with a selective ion monitoring (SIM) mode. The mass spectrometer was operated in the electron impact (EI) ionization mode; electron energy was set at 35 eV. Samples (1 μL) were injected splitless, at an injector temperature of 280°C. The temperatures of ion source and the transfer line were kept at 280°C. The carrier gas was helium at a constant flow rate of 1.0 mL/min. The column oven temperature was programmed from 150°C (initial time, 2 min) to 230°C at a rate of 20°C/min, and held for 18 min, then from 230°C to 235°C at a rate of 5°C/min, held for 10 min, then from 235°C to 320°C at a rate of 4°C/min, held for 5 min.

Quality assurance/quality control (QA/QC) measures included analysis of method blanks, duplicate samples, matrix spikes, and laboratory control samples. All laboratory QA/QC procedures had results within acceptable limits as specified in EPA1613, no target compounds were detected in the whole analysis process. The recoveries of the 13C-labelled internal standards ranged from 50 % to 105 %. LOD for all analyses was defined as three times the signal/noise ratio, LOD ranged from 0.1 to 1.4 pg/g dw for PCDD/Fs.

Results and Discussion

Spatial distribution and historical trend of PCDD/Fs in Dongting Lake
The concentration of PCDD/Fs ranged from 153 to 7144 pg/g dw, PCDD/Fs WHO2005-TEQ ranged from 0.08 to 9.67 pgTEQ/g dw. The highest concentrations of PCDD/Fs and total TEQs in sediments were found at sampling sites Yugongmiao and Hengling, respectively. PCDD/Fs concentrations in sediments decreased in the following order: lake district > outlet > estuaries, and it followed the order in the lake district: south lake district (778-7144 pg/g dw) > east lake district (156-1964pg/g dw) > west lake district (153-646 pg/g dw). Total organic matter (TOM) content ranged from 1.31% to 4.63% in sediments, which showed significant differences among these samples, median particle diameter of sediments ranged from 14.1 to 135 μm. There are no significant correlations between TOM, particle diameter and concentrations of PCDD/Fs ($P > 0.05$).

PCDD/Fs in sediments from eight sampling sites (Nanzui, Maocaojie, Xiaohezui, Wanzihu, Hengling, Yugongmiao, Bianshan, and Dongdongtinghu) in Dongting Lake were reported by other studies (Zheng et al., 1997; Gao et al., 2004). PCDD/Fs concentrations in the sediment samples in 1995 were about one or two orders of magnitude higher than those reported in 2004, the possible cause is that Na-PCP was banned in 1996, which lead to the decreased input of PCDD/Fs, besides, catastrophic floods in 1998 may flush surface sediments of Dongting Lake into the Yangtze River. PCDD/Fs levels in this study were comparable to those observed in 2004; similar profiles are also found between the two studies.

Domestic and international comparison of PCDD/Fs concentrations in sediment
PCDD/Fs levels (153 to 7144 pg/g dw) observed in this study were generally higher than those reported in the sediments from Jiaozhou Bay (2.8-26.3pg/g dw, Pan et al., 2012) ,Yellow Estuary and Yangtze Estuary (2.33-253 pg/g dw, Hui et al., 2009), Taihu Lake (120.1-1315.1 pg/g dw, Zhang et al., 2005), Spanish Northern Atlantic Coast (0.15-3.99 pg/g dw, Gómez et al., 2011), Northern Alberta, Canada (1.82-4.98 pg/g dw, Gabosa et al., 2001), Muroran Port, Japan (69-410 pg/g dw, Anezaki et al., 2014), River Nile, Egypt (240-775 pg/g dw, El-Kady et al., 2007); whereas which is lower than the Xiangjiang River, China (876-497,7592.8pg/g dw, Chen et al., 2012), Haihe River, China (11.6-1,180,924 pg/g dw, Li et al., 2013), Lower Passaic River and Newark Bay, New Jersey (452-31,700 pg/g dw, Wenning et al., 1993), TokyoBay, Japan (424-34,930 pg/g dw, Kannan et al., 2000).

Potential risk to aquatic biota
The sediment quality guidelines of the Canadian Council of Ministers of the Environment (CCME 1999) present a threshold effect level (TEL, 0.85 ng WHO-TEQ/kg dw) and a probable effect level (PEL, 21.5 ng WHO-TEQ/ kg dw). The detected concentrations in Dongting Lake (0.08-9.67 ngWHO-TEQ/kg dw) were much lower than the PEL, which shows toxic biological effects on aquatic biota are slight due to PCDD/Fs contamination in these sediments.

Hydrodynamic effects on the distribution of PCDD/Fs in Dongting Lake
Flow velocity is quite different in the whole Dongting Lake region, flow velocity ranged from 0.00007 to 0.43 m/s, maximum and minimum velocity were found at Dongtinghuchukou and Daxiaoxihu, respectively. Water in Dongting Lake flows through Nanzui, Wanzihu, Hengling, Yugongmiao, Bianshan, and Dongdongtinghu. PCDD/Fs concentration increased in the sampling sites with lower velocity, such as Hengling, Yugongmiao, Dongdongtinghu, compared to the PCDD/Fs concentration in 2004, PCDD/Fs concentration in the study decreased in the sampling sites with higher velocity, such as Nanzui, Xiaohezui, and Wanzihu. The slow flow rate of water permits sufficient time for PCDD/Fs to reach equilibrium between suspended particles and water, and deposit onto sediments. Significant relationship between flow rate and PCDD/Fs concentration in sediments can be observed. PCDD/Fs concentrations were relatively higher in the sampling sites Dongdongtinghu and Dongtinghuchukou, which indicates that PCDD/Fs in these sediments of Dongtinghu may be flushed into the Yangtze River with water flow.

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