BIOACCUMULATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN DIFFERENT SPECIES OF FISH：A CASE STUDY IN DONGTING LAKE, CHINA

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Abstract

Dongting Lake is the second largest freshwater lake in China. Technical sodium pentachlorophenate (Na-PCP) had been sprayed in this lake since 1960s to control the spread of snailborne schistosomiasis up to the middle of 1990s. However, as one of the by-products of Na-PCP, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) may enter into the environment. In order to determine the present levels of the contamination, several species of fish samples from Dongting Lake were analyzed by HRGC-HRMS for PCDD/Fs. The results show that the total WHO-TEQ values for these fish samples in the range 0.10-3.65 pg/g wet weight (ww), are lower than the European Union regulation limit, 4.0 pg WHO-TEQ/ g ww and the differences of PCDD/Fs concentrations and patterns in the fish are not partly due to their feeding habits and fat percentage. Intriguingly, it is found that the Biota-sediment accumulation factors (BSAF) values tended to decrease with the increase of the chlorines numbers of PCDD/F isomers.

Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are chemically stable and persistent hydrophobic organic pollutants that pervaded the environment and could be biomagnified via food chain. Many studies have revealed that these compounds are found in a variety of environmental media including air, water, soil, sediment, animals and human[1-3]. Due to their inherent chemical and physical properties, bioaccumulation of these compounds in aquatic biota is of increasing concern.

Dongting Lake is the second largest freshwater lake in China. Technical sodium pentachlorophenate (Na-PCP) had been sprayed in this lake since 1960s to control the spread of snailborne schistosomiasis up to the middle of 1990s. However, as one of the by-products of Na-PCP, PCDD/Fs may enter into the environment. Thus, this location can serve as a good ecosystem to study the transfer and impact of PCDD/Fs to organisms in the field.

The levels and patterns of PCDD/Fs in sediments from Dongting Lake collected in 1995, 1999 and 2004 had been reported [4-6]. Herein, in order to investigate bioaccumulated PCDD/Fs in fish samples, several species of fish grouped according to their feeding habits as granivores (Chinese bream), omnivores (Crucian and carp) and piscivores (Yellow cartfish, pomfret and catfish) taken from Dongting Lake were analyzed. Absolute and relative (congener profile) concentrations of PCDD/Fs and TEQs were evaluated. The purpose of this study was to provide a distribution of PCDD/Fs in fish contaminated by Na-PCP and to investigate the bioaccumulation of PCDD/Fs in different species of fish.

Materials and Methods

Fish including Chinese bream (*Megalabrama terminalis*), common carp (*Parabramis pekinensis*), crucian carp (*Carassius auratus*), catfish (*Parasilurus asotus*), pomfret *(Parastromateus niger)*, yellow catfish (*Pseudobagrus fulvidraco*) mandarin (*Siniperca chuatsi*).were collected from Dongting Lake. The weights of the fishes ranged from 0.2 kg to 2 kg. All of the samples were kept frozen at −20°C until analysis.

The fish muscle with skin was homogenized and then was freeze-dried. ^{13}C-labeled surrogate standards were spiked according to the EPA method 1613B. Soxhlet extraction was carried out by about 20 g fish for 24 h. The solvents were 50% dichloromethane in hexane for muscle. The lipid content was determined by gravity. The sample cleanup and analysis can be seen everywhere [7, 8].

Results and Discussion

Detectable concentrations of PCDD/Fs were found in all the fish samples. The recoveries for each sample were checked by reference to the ratios of ^{13}C labeled internal standards. The recovery determination standard ranging from 51 to 126% indicated that sample preparation (extraction and cleanup) worked properly. Due to variation in percent lipid concentration among tissues, the concentration data are presented on a wet weight basis. Mean concentrations of 2,3,7,8-substitued PCDD/Fs and total PCDD/Fs are listed in table 1. The greatest concentrations for the sum of PCDD/Fs, 238 pg/g wt, were found in Chinese bream, and the smallest concentrations for the sum of PCDD/Fs, 10.11 pg/g wt, were found in catfish. The concentrations of PCDD/Fs were in the range 1,204-24,117 pg/g lipid weight (lw) in the fish collected in Dongting Lake. The fat percentage of Chinese bream was significantly higher than other species of fish. Concentrations of PCDD/Fs in Chinese bream were higher than in other fish, partly due to their higher fat content. It was expected that differences in fat percentage would solely explain concentrations differences in fresh weight basis. However, the concentrations on a fat basis were not equal. The differences of PCDD/Fs concentrations and patterns in the fish are not partly due to their feeding habits and fat percentage. The concentrations of the sum PCDD/Fs were 742-4,168 pg/g lw in fish from Ya-er Lake[3] and 7.22-1,315 pg/g wt from Taihu Lake[9]. So the concentrations of the sum PCDD/Fs in fish from Dongting Lake are in the same magnitude with those from other Chinese lakes.

Toxic equivalents (TEQs) were calculated by multiplying congener concentrations by a congener-specific fish toxic factor (TEFs) as recommended by the World Health Organization[10]. Concentrations of TEQ were in the range 0.10-3.65 pg/g ww and 7.00-135.7 pg/g lw in fish. 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDFs, 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,4,7,8-HxCDD were the dominant congeners to the WHO-TEQ. The concentrations of PCDD/Fs in fish from Dongting Lake were lower than the European Union regulation limit, 4.0 pg WHO-TEQ/ g ww [11].

Table1. Mean concentrations of PCDD/Fs in fish

	Chinese bream (n=3)	Crucian Carp (n=3)	carp (n=3)	Yellow cartfish (n=4)	pomfret (n=3)	mandarin (n=2)	catfish (n=2)
Lipid content (%)	19.8	2.69	3.0	2.9	10.1	0.36	0.6
2378-TCDF	2.91	1.29	0.46	0.46	0.02	0.02	0.01
12378-PeCDF	1.05	1.42	0.04	0.60	0.05	0.04	0.01
23478-PeCDF	1.81	1.32	0.20	0.85	0.15	0.06	0.03
123478-HxCDF	1.39	2.99	0.10	2.85	0.03	0.04	<0.009
123678-HxCDF	0.04	1.05	0.05	1.62	0.02	0.03	0.01
234678-HxCDF	0.25	0.79	0.07	0.20	<0.029	0.02	<0.015
123789-HxCDF	0.04	0.91	0.01	0.03	<0.057	<0.078	<0.015
1234678-HpCDF	0.26	2.01	0.11	2.65	0.02	0.07	0.02
1234789-HpCDF	0.05	0.8	0.01	0.04	<0.044	0.03	<0.014
OCDF	0.30	2.32	0.11	0.16	0.03	0.04	0.05
2378-TCDD	0.08	0.74	0.02	0.14	0.07	0.02	<0.015
12378-PeCDD	0.50	0.12	0.03	0.48	0.05	0.03	0.05
123478-HxCDD	2.15	2.65	0.14	1.33	0.03	0.20	0.25
123678-HxCDD	0.03	1.27	0.04	0.66	<0.062	0.01	0.05
123789-HxCDD	0.61	0.37	0.02	0.58	0.11	0.02	0.01
1234678-HpCDD	1.67	2.74	0.23	0.74	0.50	0.15	0.08
OCDD	4.73	6.16	1.76	2.77	1.52	1.40	2.07
Totals Tetra-Furans	6.92	11.44	4.07	17.35	23.52	1.44	2.07
Totals Tetra-Dioxins	2.23	6.41	2.27	12.76	18.08	0.67	0.02
Totals Penta-Furans	22.79	24.16	22.93	34.59	48.55	74.32	0.46
Totals Penta-Dioxins	25.41	25.23	1.85	11.70	48.14	0.67	0.05
Totals Hexa-Furans	8.66	16.31	6.39	16.78	4.92	0.06	0.62
Totals Hexa-Dioxins	36.65	46.04	6.18	12.04	75.16	0.69	0.84
Totals Hepta-Furans	42.90	23.19	3.44	5.52	1.15	0.07	0.60
Totals Hepta-Dioxins	87.85	25.99	26.48	8.46	4.47	7.46	3.33
Σ2,3,7,8-PCDD/Fs	17.87	28.95	3.4	16.16	2.6	2.18	2.64
ΣPCDD/Fs(ww)	238	187	75.5	122	225	86.8	10.1
ΣPCDD/Fs(lw)	1204	6961	2516	4211	2233	24117	1685
WHO-TEQ[a] (ww)	1.92	3.65	0.21	1.70	0.20	0.11	0.10
WHO-TEQ[a] (lw)	9.70	135	7.00	58.6	1.98	30.6	16.7

[a]In the calculations of TEQs, concentrations below LODs were considered as zero

It has been reported that the concentrations of PCDD/Fs were in the range 0.7-11 pg I-TEQ /g dw and OCDD was the predominant congener to the sum of PCDD/Fs and TEQ in the sediment taken from Dongting Lake [6]. In comparison, OCDD contribute less to the sum of PCDD/Fs in fish. In general, sediments are thought to be a major reservoir for PCDD/Fs in the aquatic environment. However, the low bioaccumulation potential for fish is probably not an important direct source of PCDD/Fs due to the lesser impact of sediments on fish, which live higher in the water column. The BSAF values tended to decrease as the number of chlorines increased on both groups of PCDD and PCDF isomers. This declining trend appears to be consistent with the BSAF for aquatic biota from previous reports [12, 13]. PCDD/Fs are very insoluble in water and the solubility decreases with the increase of the chlorine substitution. For example, the water solubility of OCDD is about two or three orders of magnitude lower than that of 2,3,7,8-TeCDD[14]. The relatively low BSAF values observed for the more highly chlorinated congeners in this study are generally understood in terms of a low bioavailability of these congeners due to their low solubility in comparison to lower-chlorinated congeners. Perhaps it can be assumed that the reflection of reduced diffusion across biological membranes also plays a role. The results show that the differences of PCDD/Fs concentrations and patterns in the fish were not partly due to their feeding habits and fat percentage. Dioxins in fish maybe depend on their fat contents, the extent to which fish migrate, the times they spawn, their ages, feeding habits, species, tissue and organs as well as the contamination of water.

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

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