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Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans in Mussels and *Gammarus* spp. from Dongting Lake in People's Republic of China

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Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are chemically stable and persistent hydrophobic organic chemicals that pervaded the environment and are thought to 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 (Bakoglu et al. 2005; Krauthacker et al. 2006; Wu et al. 2001).

Dongting Lake, covering a very large surface water area of 2691 km^2, is located in the southern part of the People's Republic of China. It is the second-largest freshwater lake 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 pentachlorophenate (Na-PCP) had been sprayed there since 1960s to control the spread of snailborne schistosomiasis. As one of the contaminants of Na-PCP (Bao et al. 1995), PCDD/Fs may enter the environment and contribute to human exposure. Concerning the adverse effect of Na-PCP, Na-PCP has been prohibited from being sprayed in this region since mid-1990s. However, PCDD/Fs are chemically inert, which could remain in the environment for many years. The sediments from Dongting Lake had been show to be heavily polluted by PCDD/Fs (Zheng et al. 1997; Zheng et al. 2003). Thus this location can serve as an ecosystem model to study transfer and impact of PCDD/Fs to organisms and humans in the field. This paper presents the levels and patterns of PCDD/Fs in benthic invertebrate animals, mussel and grammarus around Dongting Lake. Absolute and relative (congener profile) concentrations and 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (TEQs) were evaluated to describe possible sources and potential effects. The purpose of this study was to investigate the bioaccumulation of PCDD/Fs in mussel and grammarus and to provide a distribution of PCDD/Fs in mussel and grammarus contaminated by PCDD/Fs that originated in using Na-PCP.

MATERIALS AND METHODS

Mussels and grammarus samples were collected from Dongting Lake in 2004, which were analyzed within 2 months. Samples were wrapped in aluminium foil, stored at -18°C and freeze-dried and manually ground before analysis. Then each

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sample was homogenized and freeze-dried. ^{13}C-labeled surrogate standards were spiked according to the EPA method 1613B. The sample was mixed with anhydrous sodium sulfate which had been baked out at 660 °C to remove residual water and impurities. The mixture was placed in pre-extracted thimble and extracted in a Soxhlet apparatus with 50% dichloromethane in hexane for 24 h. The crude extract of the sample was concentrated by rotary evaporation to 5 ml, dried with a stream of nitrogen until constant weight. Lipid content was calculated from the residues of the extract divided by the fresh weight of sample. The lipids were also subjected to purification via manual cleanup based on the sequential use of acid-base silica, multilayer silica and basic alumina column. 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 and a thin layer of sodium of sulfate at the top. The column was cleaned with 50 ml hexane prior to transfer of sample extracts. Sample was then eluted with 70 ml hexane and rotary evaporated to 1 ml. The second multilayer silica column (15 mm i.d.) was packed with 1g of silica, 2 g of 10 % $AgNO_3$ silica, 1 g of silica, 8 g of 44% acidic silica, 1 g of silica, 5 g of 33% basic silica, 1 g of silica and a thin layer of sodium of sulfate at the top. The column was cleaned with 70 ml hexane prior to transfer of sample extracts. The sample was then eluted with 100 ml hexane and rotary evaporation to 1 ml. The third basic alumina column (10 mm i.d.) was packed with 8 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. The sample was then eluted with 100 ml 5% dichloromethane in hexane and then eluted with 50 ml 50% dichloromethane in hexane, the 50% dichloromethane in hexane was rotary evaporation to1ml. Then the sample was transfer to K-D concentrator and concentrated by means of a rotary evaporator to nearly 500 µl. Then the sample was concentrated by gentle nitrogen to 50 µl. The recovery internal standards ($^{13}C_{12}$ PCDD/Fs, Cambridge Isotope laboratories) were added before analysis.

The quantification of PCDD/F homologues was performed by HRGC/HRMS on an Agilent 6890 gas chromatography coupled with an Autospec Ultima mass spectrometer (Waters, USA) operating in the EI mode at 35 eV and the trap current was 600 µA. The details of the MS analysis and quality control are described in the EPA method 1613B. The GC was equipped with a CTC PAL autosampler.1ml sample was injected in splitless mode (splitless time, 2 min for PCDD/Fs) in a DB-5MS fused silica capillary column (60 m × 250 µm i.d. × 0.25 µm film thickness) with helium as carrier gas at a constant flow rate of 1.2 ml/min. The oven temperature programs were as follows: for PCDD/Fs: start 160°C held for 2 min, 160–220°C at 7.5°C /min held for 16 min, 220–235°C at 5°C/min held for 7 min, 235–330°C at 5°C /min held for 1 min. Quantitative determination was performed by the isotope dilution method. The acceptance criteria for data include: chlorine isotope ratio within ±15% of the theoretical ratio, peak maxima retention time within 2 s and peak response at least three times the background noise level.

RESULTS AND DISSCUSSION

The isomer distributions of 2,3,7,8-substituted PCDD/Fs in mussel and grammarus from Dongting Lake are given in Table 1. The recoveries for each sample were checked by reference to the ratios of ^{13}C labeled internal standards relative to the recovery determination standard ranging 49 to 115%, showed a satisfactory analysis procedure.

Table 1. Concentrations of PCDD/Fs in mussels and grammarus (pg/g w/w)

	M1	M2	M3	M4	M5	G1	G2	G3
Lipid content (%)	0.68	0.13	0.38	0.38	0.20	0.40	0.21	0.14
2378-TCDF	0.36	<0.05	<0.06	0.04	0.4	0.2	0.073	0.02
12378-PeCDF	0.70	<0.03	<0.06	<0.09	0.2	0.1	0.03	<0.01
23478-PeCDF	0.51	0.02	<0.06	0.04	0.5	0.1	0.04	0.01
123478-HxCDF	0.84	0.02	0.10	0.05	0.4	0.1	0.02	0.02
123678-HxCDF	0.84	0.02	0.10	0.01	0.5	0.1	0.01	0.04
234678-HxCDF	0.34	0.04	0.21	<0.06	0.6	0.1	0.02	<0.01
123789-HxCDF	0.21	0.002	0.04	<0.06	0.1	<0.04	<0.01	<0.01
1234678-HpCDF	2.8	0.1	0.525	0.328	4.8	0.5	0.02	0.017
1234789-HpCDF	0.20	<0.03	0.059	<0.06	0.5	0.1	0.004	0.006
OCDF	4.6	0.243	0.40	1.56	13.9	0.9	0.042	0.028
2378-TCDD	0.09	<0.02	<0.06	<0.1	<0.02	<0.02	<0.02	<0.04
12378-PeCDD	0.15	0.012	<0.06	<0.1	<0.03	<0.02	0.037	0.011
123478-HxCDD	0.24	0.12	0.4	0.47	0.1	0.1	0.18	0.21
123678-HxCDD	<0.1	0.03	0.03	0.05	0.1	0.1	0.04	<0.02
123789-HxCDD	0.11	0.011	<0.08	0.049	0.1	0.1	0.01	<0.02
1234678-HpCDD	1.8	0.91	1.3	0.98	0.6	1.1	0.17	0.043
OCDD	50	26	468	183	16	38	4.5	6.1
ΣPCDD/Fs	80	28	50	187	39	42	5.4	6.7
I-TEQ	0.79	0.076	0.15	0.29	0.58	0.19	0.081	0.047
WHO-TEQ	0.80	0.095	0.26	0.29	0.55	0.16	0.16	0.13

M: mussels; G: grammarus

The total concentrations of 2,3,7,8-substituted PCDD/Fs ranged from 5.3 to 42 pg/g wet weight in grammarus and 28 to 187 pg/g wet weight in mussels. TCDD toxicity equivalent (TEQ) was calculated by TCDD toxicity equivalent factor (TEF) for fish proposed by World Health Organization (WHO) in 1998 (Van den Berg et al. 1998). The summed TEQ of PCDD/Fs ranged from 0.13 to 0.16 pg/g wet weight for grammarus and 0.09 to 0.80 pg/g wet weight for mussels. The difference of dioxins levels among samples may depends on the species probably due to their fat content or habit of diet, if the difference of sampling date is ignored. Moreover, the results are comparable to those reported in literature. Hosimoto et al. (1999) reported levels of 0.91 pgWHO-TEQ/g wet weight in mussels from a rural beach contaminated by herbicides such as CNP and PCP. Gifford et al. (1996) reported levels between 0.082 and 0.1 pg I-TEQ/g fresh weight in mussels from the Lake Rotorua catchment that had been affected by PCP contamination from a sawmill. The levels of PCDD/Fs in the mussels and grammarus samples from Dongting Lake do not exceed the current European

MRL of 4 pg WHO-TEQ /g for PCDD/Fs for fish and fish products on the whole weight basis.

The ratio of levels of PCDD to PCDF is very helpful to describe the source of dioxins. The ratio was 7.5 in the technical Na-PCP. The levels of PCDD were 10 to 22 times higher as those in PCDF in grammarus samples. The levels of PCDD were also much higher than those of PCDFs in mussels except for M5. This indicates that Na-PCP was the major source of PCDD/Fs in mussels and grammarus.

Total I-TEQ values for the sediments samples collected from Dongting Lake in 2004 ranged from 0.7 to 11 pg/g weight soil (Gao et al. 2005). OCDD was the predominate congener which indicate Na-PCP was the major source of the PCDD/Fs in sediments. Total I-TEQ values were between 34 pg/g and 289 pg/g lipid weight for mussels and grammarus. OCDD was the most abundant congener in benthic animals. Bioaccumulation was found to occur among the mussels and grammarus. The contaminant groups of PCDD/Fs almost always displayed higher concentrations in mussels than in grammarus. The results show that benthic invertebrate animals are good indicators for contamination of the sediment and water. According to the living habits, mussels and grammarus taken up PCDD/Fs from the sediment and maintain the PCDD/Fs patterns of the sediment, therefore they are useful bioindicators of PCDD/Fs contamination in sediment.

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