

Declining dioxins Levels in the Sediments from Dongting Lake in China

Lirong Gao¹, Minghui Zheng¹, Bing Zhang¹, Wenbin Liu¹, Xingru Zhao¹

¹Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences

Introduction

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, a parasitic disease of epidemic proportions has been endemic in the Dongting Lake region for centuries and it has a devastating effect on the public health of the local people¹. Large amounts of powerful pesticide sodium pentachlorophenol (Na-PCP) salt have been sprayed over there to control schistosomiasis. Approximately 6000 tons of Na-PCP produced in China annually. Dioxins, a class of toxic, persistent compounds, are found as impurities in commercial Na-PCP products². It had been reported that PCDD/Fs in sediments^{3,4} and breast milk samples⁵ from Dongting Lake.

Concerning the adverse effect of Na-PCP, Na-PCP has been prohibited sprayed in this region since 1996. However, PCDD/Fs were chemically inert, which could remain in the environment for many years. The aim of this study was to determine PCDD/Fs in Dongting Lake in sediments collected in 2004. So we can compare them with levels and patterns of PCDD/Fs in sediments taken from between 1996 and 1999 in order to detect temporal trends.

Materials and Methods

The seven samples were taken from seven different locations⁴ distributed over the whole Lakeland in 2004. These locations are on the profiles of the national or the provinces key monitoring areas, which can represent conditions of the lake pollution. Each sample was aliquot of the mixture from at least of 3 sites of the location.

Sediments were collected with a grab sampler from shipboard. Samples were wrapped in aluminium foil, stored at -18°C and freeze-dried before analysis. A blank was included in each batch of 3 samples. Prior to extraction, 10g of dried soils were homogenized and spiked with a mixture of internal standards (¹³C₁₂ 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 water and impurity. The mixture were placed in pre-extracted thimbles and extracted in a Soxhlet apparatus with toluene for 24 h. After extraction, the crude extracts were subjected to purification via manual cleanup based on the sequential use of acid silica, multilayer silica and basic alumina adsorption columns. The first acid-base silica gel columns were prepared by packing a glass column (15mm i.d.) with 10 g of 44 % acidic silica and a thin layer of sodium of sulfate at the top. The columns were cleaned with 50 ml hexane prior to transfer of sample extracts. Samples were then eluted with 70 ml hexane and rotary evaporated to 1 ml. The second multilayer silica columns (15 mm i.d.) were packed with 1g of silica, 2 g of 10 % AgNO₃ 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 columns were cleaned with 70 ml hexane prior to transfer of sample extracts. Samples were then eluted with 100 ml hexane and rotary evaporated to 1 ml. The third basic alumina columns (10 mm i.d.) were packed with 8 g basic alumina and a thin layer of sodium of sulfate at the top. The columns were 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 1ml. 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 50 μl. The recovery internal standards (¹³C₁₂ PCBs Cambridge Isotope laboratories) were added before analysis.

Analysis of PCDD/Fs was performed on a GC (DB-5 fused silica column, 60m,0.25i.d., coupled with HRMS (MicromassAutospec-Ultima) operating on a resolution of a approximately 11000. 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. For quality control, the retention time of the analyte 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.

Results and discussion

The isomer distributions of PCDD/Fs from sediments in 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 from 69.8 to 128.6, showed a satisfactory analysis procedure. Total I-TEQ values for the samples analyzed ranged from 0.7 to 11 pg/g with a mean value of 4.5 pg/g dry weight soil.

Table 1 Levels and patterns of PCDD/Fs in sediments taken 2004 (pg/g dry weight)

| | S1 | S2 | S3 | S4 | S5 | S6 | S7 |
|---------------|-------|------|-------|-------|-------|------|-------|
| 2378-TCDF | 4.0 | 2.2 | <0.1 | 0.6 | 0.2 | 0.9 | 1.9 |
| 12378-PeCDF | 5.2 | <0.5 | <0.05 | <0.04 | <0.04 | <0.2 | 0.6 |
| 23478-PeCDF | <0.06 | <0.6 | <0.05 | <0.04 | <0.2 | <0.1 | 0.2 |
| 123478-HxCDF | 4.2 | 2.2 | 0.4 | 1.5 | 0.3 | 1.7 | 1.1 |
| 123678-HxCDF | 2.3 | 1.4 | 1.4 | 0.7 | 0.4 | 1.0 | 3.8 |
| 234678-HxCDF | 2.0 | 1.1 | 0.6 | 0.6 | 0.3 | 0.6 | 1.4 |
| 123789-HxCDF | <0.04 | 0.8 | 0.5 | 0.7 | 0.3 | 0.9 | 1.3 |
| 1234678-HpCDF | 14 | 8.7 | 3.1 | 5.4 | 3.5 | 5.0 | 12 |
| 1234789-HpCDF | <0.08 | 0.33 | <0.05 | 0.3 | <0.06 | 0.9 | <0.34 |
| OCDF | 51 | 25.2 | 11 | 29 | 26 | 31 | 54 |
| 2378-TCDD | 0.2 | 0.2 | <0.06 | <0.06 | 0.2 | 0.2 | 0.1 |
| 12378-PeCDD | 0.2 | <0.1 | <0.2 | <0.2 | 0.06 | 0.1 | <0.2 |
| 123478-HxCDD | 12 | 0.9 | 8.2 | 5.7 | 0.6 | 2.7 | 6.5 |
| 123678-HxCDD | 2.9 | 1.8 | 1.7 | 0.9 | 0.2 | 0.5 | 1.4 |
| 123789-HxCDD | 9.1 | 6.1 | 6.0 | 3.8 | 0.7 | 1.7 | 5.0 |
| 1234678-HpCDD | 109 | 66 | 60 | 36 | 2.6 | 14 | 56 |
| OCDD | 5113 | 3280 | 2980 | 1696 | 100 | 659 | 2375 |
| 13468-PeCDF | <0.7 | 0.5 | 0.6 | 0.3 | <0.2 | 1.6 | 0.9 |
| TEQ | 11 | 5.9 | 5.5 | 3.6 | 0.7 | 2.1 | 5.6 |

Octachlorodibenzo-p-dioxin (OCDD) and octachlorodibenzofurans (OCDF) were the most predominant congeners. The concentrations of the sum PCDDs were higher than those of the sum PCDFs for all the samples, which matched reasonably well those observed by Rappe et al⁶. So the results in this experiment were good consistent with which of Na-PCP, we can conclude that chemical pesticide Na-PCP is a major source of environmental dioxins exposure in Dongting Lake.

It can be seen from Figure.2 that the levels of PCDD/Fs declined dramatically since 1996. Total I-TEQ values ranged from 130.2 to 890 with a mean value of 273.6 pg/g in the sediment samples collected in 1996. In sediments taken from 1999, total I-TEQ values ranged from 9.3 to 50 with a mean value of 21pg/g dry weight soil. So total I-TEQ values in the samples collected 2004 were much lower than those measured in the samples collected in 1996 and 1999.

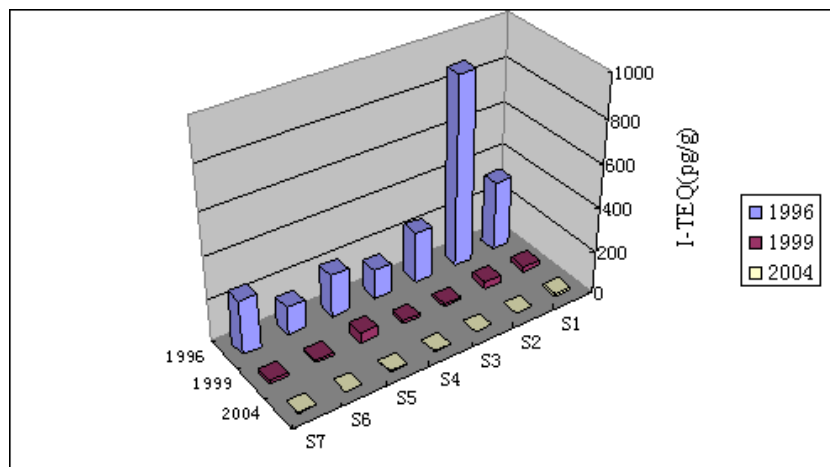


Figure 2 Declines in total I-TEQ of PCDD/Fs in sediments 1996, 1999 and 2004

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