

POLYCHLORINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS IN SEDIMENTS FROM THE PEARL RIVER OF CHINA

Gao LR, Tian HZ, Liu LD, L C, Liu WB

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are a family of compounds that includes some extremely toxic and potent congeners. PCDD/Fs are among the 12 POPs (persistent organic pollutants) of Stockholm Convention. They are highly persistent compounds and have been detected in air, water, soil, sediments, animals, and food [1]. Sediments are important environmental media acting as sinks for hydrophobic organic contaminants. PCDD/Fs associated with sediments may be exposed to human beings via food chain. Quantifying the concentration levels of these chemicals in sediments can provide important information for ecological and environmental risk assessment.

The Pearl River is the third largest river in China after the Yangtze River and the Yellow River. The Pearl River Delta (PRD) is located along the southern coastline of China, and plays a pivotal role in the development of China national economy. The PRD occupies an area of approximately 41 000 km² and has a population of over 41 million. Industries in the PRD are mainly the manufacturing of electronic products, garments, textile products, plastic toys and other goods. PCDD/Fs in sediments from Pearl River were investigated in this study. Absolute and relative (congener profile) concentrations and 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin toxic equivalents (TEQs) were evaluated to describe possible sources and potential for effects of human health. The information of this study will be used for strategic planning of future industrial development and urbanization of this region.

Materials and methods

The nineteen samples were taken from nineteen locations which can represent environmental conditions of the river pollution (shown in Fig.1). A global positioning system (GPS) was employed to identify each location precisely. The description of the sampling sites is also 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. 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 sediments 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 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 were prepared by packing a glass column (15mm i.d.) with layers of 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 hexanes 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 10 g basic alumina and a thin layer of sodium of sulfate at the top. The columns were cleaned with 100 ml hexanes prior to transfer of sample extracts. Samples were then eluted with 100 ml 5 % dichloromethane/ hexanes and then eluted with 50 ml 50% dichloromethane/ hexanes, the 50% dichloromethane/ hexanes 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 10 µl. The recovery internal standards (¹³C₁₂ PCDD/Fs Cambridge Isotope

laboratories) were added before analysis.

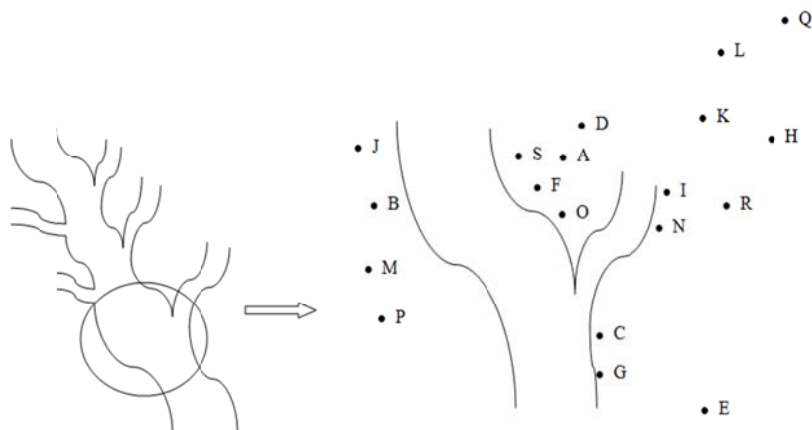


Figure.1 Locations of sampling sites at Pearl River of China

Analysis of PCDD/Fs was performed on a GC (DB-5 fused silica column, 60 m, 0.25i.d.) coupled with an Autospec Ultima mass spectrometer (Waters Micromass, Manchester, UK) 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 or M+4. 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. The MDLs varied for the different congeners and mostly ranged between 0.3–1.5 pg per sample. 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 55 to 128%, showed a satisfactory analysis procedure.

Results and discussion

The isomer distributions of 2,3,7,8-substituted PCDD/Fs from sediments collected in 2009 from Pearl River 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 52 to 128 percent, showed a satisfactory analysis procedure. The total 2,3,7,8-substituted PCDD/Fs were at a range of 64 to 9365 $\mu\text{g g}^{-1}$. The highest sum PCDD/Fs concentrations were measured at location I and the minimum concentration of 64 $\mu\text{g g}^{-1}$ was determined at location O. Different sources of PCDD/Fs are characterized by different congener and homologue patterns. Bao et al. [2] reported that OCDD contributes 76% 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 and 1,2,3,4,6,7,8-HpCDD. This indicates that Na-PCP was the major source of the PCDD/Fs in Pearl River.

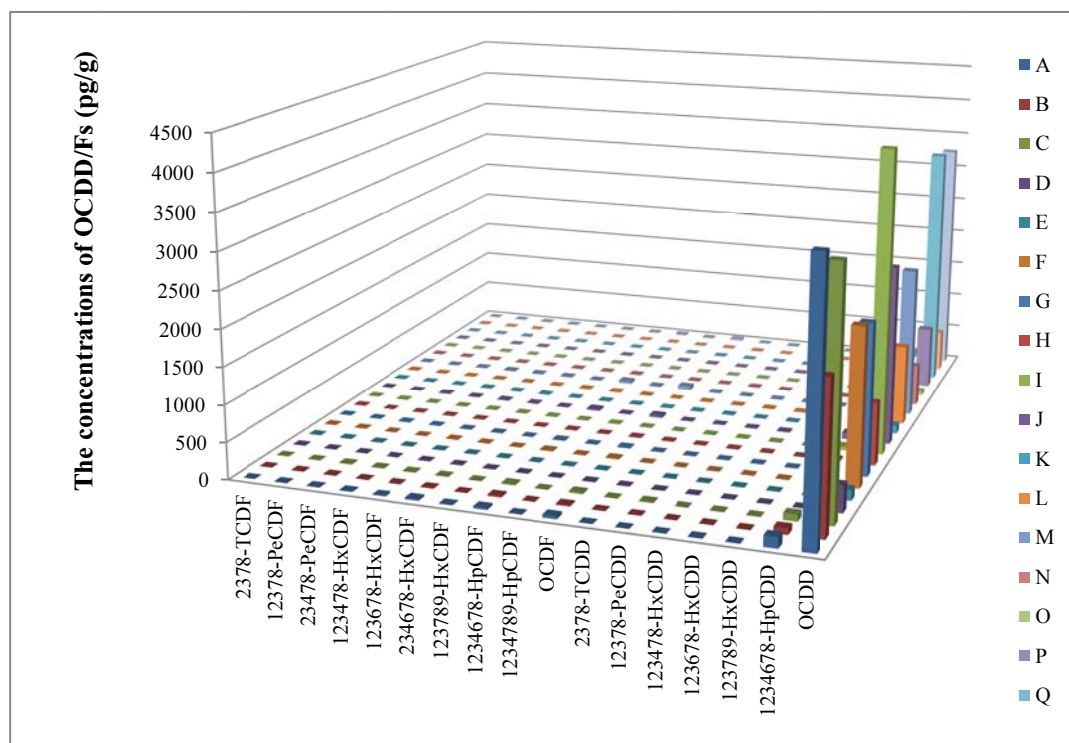


Fig.2 The concentrations of PCDD/Fs in sediments collected from Pearl River of China

To normalize concentrations and the toxicity of the different PCDD and PCDF congeners, World Health Organization (WHO) toxicity equivalent factors (WHO-TEFs) [3] were used to calculate the WHO toxicity equivalent for the samples. The WHO-TEQ for the samples analyzed were at a range of 0.14 to 9.82 pg g^{-1} . The highest WHO-TEQ concentration was found at location C. The lowest WHO-TEQ determined at E there was not the minimum concentration of 2378-PCDD/Fs detected.

Holoubec and co-workers [4] has presented a simple characterization 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, $2000\text{-}10000 \text{ pg/g}$ heavily polluted area and $10000\text{-}100000 \text{ pg g}^{-1}$ very heavily polluted area. Rose and co-workers [5] mitigated the categorization by one step, where $<200 \text{ pg g}^{-1}$ d.w. present remote area, $200\text{-}1000 \text{ pg g}^{-1}$ background area and so on. Location E, K and O in this study were classified as remote area. Location D, H, L, N and R in this study were classified as background area and other locations were classified as slightly polluted area.

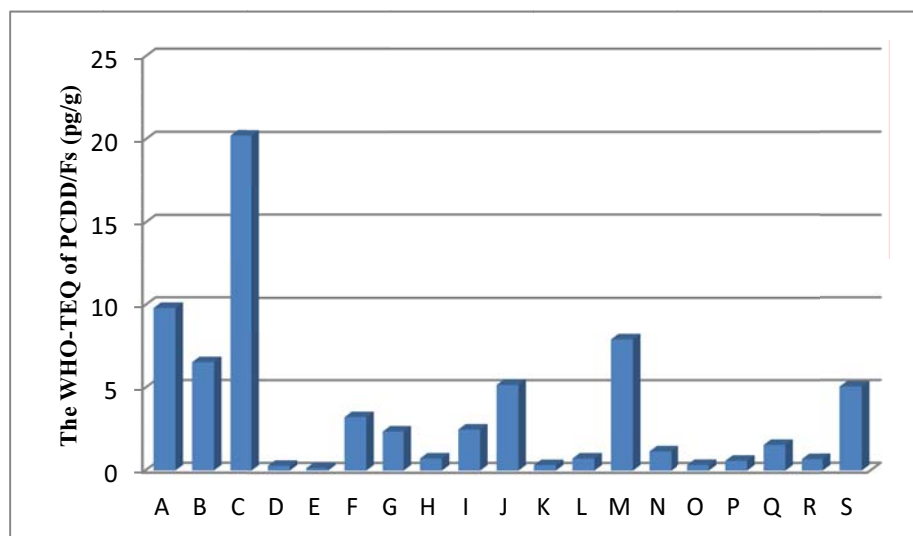


Fig.2 The WHO-TEQ of PCDD/Fs in sediments collected from Pearl River of China

Acknowledgements

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