LEVELS AND DISTRIBUTION OF PCDD/Fs AND PCBs IN SOILS FROM CHONGQING CITY IN CHINA

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs) are persistent organic pollutants (POPs) which can pose a great threat to human health and ecosystems due to carcinogenic, teratogenic, and gene mutation effects. Due to the semi-volatile property, these compounds have been shown for long-range transport in the atmosphere; and therefore, they have been detected in sediment[1], air[2] and soil[3]. The levels of PCDD/Fs and PCBs in soils were helpful to understand the present environmental quality, and whether there is any environmental risk to the area. It was reported that the concentration of PCDD/Fs in the surface soils obtained from the Taizhou e-waste recycling area of China was in the range of 218.3-3122.2 pg/g with a mean value of 659.5 pg/g dry weight (dw.)[4]. Hu et al. reported the concentrations of PCDD/Fs in nineteen soil samples from Baiyin City, North West, China varied between 20.13 and 496.26 pg/g dw with an average value of 125.59 pg/g dw, which indicated that health risk of PCDD/Fs should be paid more attention[5]. It was reported that the total concentrations of PCDD/Fs and dl-PCBs in soils from Wolong high mountain area of Sichuan Province, western China were 2.48-4.30 pg/g dw and 7.6-10.5 pg/g dw, respectively[6]. But the levels and distributions of PCDD/Fs and PCBs in western area in China was few reported. The PCDD/Fs and PCBs were urgently needed to be monitored to assess the potential risk of these compounds pose to both humans and wildlife.

Chongqing is located in the upper reaches of the Yangtze River, plays a pivotal role in the development of China national economy. Chongqing occupies an area of approximately 82 km^2 and has a population of over 29 million.

Industries in the Chongqing are mainly the manufacturing of instrumentation , chemical, pharmaceutical and other goods. PCDD/Fs and PCBs in soils from Chongqing city were investigated in this study. Absolute and relative (congener profile) concentrations and 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin and dioxin-like PCBs 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

Sample collection

331 surface soil samples (depth 0-5 cm) were collected distributed all over the Chongqing for determination of PCDD/Fs and dl-PCBs using a pre-cleaned stainless steel shovel. Sampling locations were evenly distributed across the area. The soil samples were wrapped in solvent-cleaned aluminum foil and stored at -20℃, then were

freeze dried as soon as possible for analysis. The surface soils of the 331 sampling points were mixed (N1-N37), to 37 samples. However, N16, N18, N22, N26 and N31 were lost, and 32 soil samples were analyzed.

Sample preparation and analysis

The preparation and analysis of the samples were conducted in accordance with US-EPA Method 1613B and US EPA Method 1668A for PCDD/Fs and dl-PCBs. Prior to extraction, 10 g of dried soil was homogenize and spiked with known amounts of 13C12-labeled internal standards (Wellington Laboratories, Canada). The samples were then extracted by an accelerated solvent extractor (ASE), using hexane: dichloromethane 1:1. The extracts were concentrated using a rotary evaporator (Heidolph, Germany) and the residues were purified on an acidic silica gel column (treated with 44 % sulfuric acid) and multilayer silica columns. The PCDD/Fs and dl-PCBs were fractionated on a basic alumina column and were concentrated to about 20mL by a rotary evaporator followed by a gentle stream of nitrogen. The final extracts were spiked with 13C12-labeled injection standards of PCDD/Fs and PCBs as appropriate for recovery quantification and subsequently injected into HRGC/HRMS for analysis.

Analysis of the PCDD/Fs and dl-PCBs was conducted using an HRGC/HRMS system. The HRGC (Agilent 6890, equipped with a 60.0 m×0.25 mm× 0.25 μm DB-5MS column) was operated in splitless mode, with 1 μL of sample extract injected by a CTC PAL auto-sampler. Helium was used as the carrier gas with a constant flow rate of 1.2 mL/min. The HRMS (Waters, USA) was operated under positive electron impact ionization (EI+) in selective ion monitoring (SIM) mode with an EI energy of 35 at R≥10,000.

Quality control and quality assurance

A laboratory blank was routinely performed and the values were within the acceptable limits for the different methods. The US EPA methods 1613B and 1668A were used to measure the PCDD/Fs and dl-PCBs. Recoveries of the $^{13}C_{12}$-PCDD/ Fs and $^{13}C_{12}$-dl-PCBs were found to be in the ranges of 36.5-130% and 46-126 %, respectively. The limit of detection (LOD) used for this study was defined as being three times the signal/noise (S/N) ratio. Concentrations below detection levels were calculated using 1/2 LOD. The LOD values determined for this study were in the ranges of 0.02-1.25 pg/g and 0.0025-1.7 pg/g for PCDD/Fs and dl-PCBs, respectively.

Results and discussion

The concentrations of 17 different 2,3,7,8-substituted PCDD/Fs and 12 dl-PCBs in the 32 soils ranged from 29.4 to 1618.2 pg/g dw and 5.7 to 126.8 pg/g dw, respectively. The total WHO-TEQ values (sum of the PCDD/Fs and dl-PCBs TEQs) in the soil samples were in the range of 0.145-1.23 WHO-TEQ pg/g dw. For all samples, the PCDD/Fs were the major contributors to the total TEQ, contributing 73.1 to 98.9 % of the total TEQ in the soils. PCDD/Fs and dl-PCBs concentrations in soil samples from Chongqing city are shown in Figure 1.The highest WHO-TEQ values was found in the soil samples N34 which is located in the Qianjiang and youyang regions of southern region of Chongqing. And the lowest WHO-TEQ concentration was found in soil N29 which is located in the Fengjie County of Chongqing. The concentrations of PCDD/Fs in the southern region of Chongqing are higher than those in the north region of Chongqing, which may be consistent with population density distribution.

PCDD/Fs and dl-PCBs congener profiles for soil samples in Chongqing city are shown in Figure 2. OCDD, 1,2,3,4,6,7,8-HpCDD, OCDF and 1,2,3,4,6,7,8-HpCDF were the predominant congeners of the 2,3,7,8-PCDD/Fs. For dl-PCBs, CB-118 was the most contributor of concentrations while CB-126 was the main toxic congener.

The TEQ values of PCDD/Fs and PCBs in Chongqing city are comparable to that of the Spanish regions[7], lower than the background concentration values reported in the United States[8] and much lower than that of Guiyu e-waste dismantling[9]. In December 2009, EPA releases its Draft Recommended Interim Preliminary Remediation Goals for Dioxin in Soil at CERCLA and RCRA Sites. The draft document recommends a cleanup goal of 72 part per trillion (ppt) for residential uses and 950 ppt for commercial or industrial uses. So the levels of PCDD/Fs and dl-PCBs measured in soils from Chongqing can classified as clean soi. This result implies that the dioxins contamination has little effect on ecological risk (human health et al) in Chongqing city.

Acknowledgements

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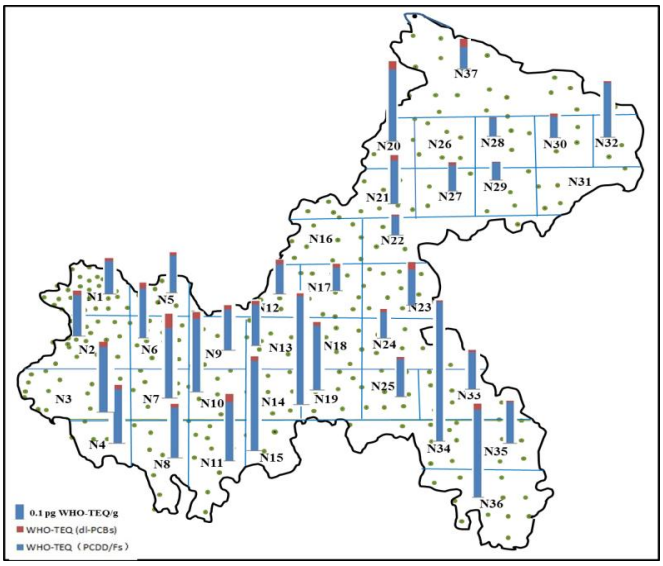

Figure 1 Levels of dioxin concentrations (pg/g) in Chongqing city

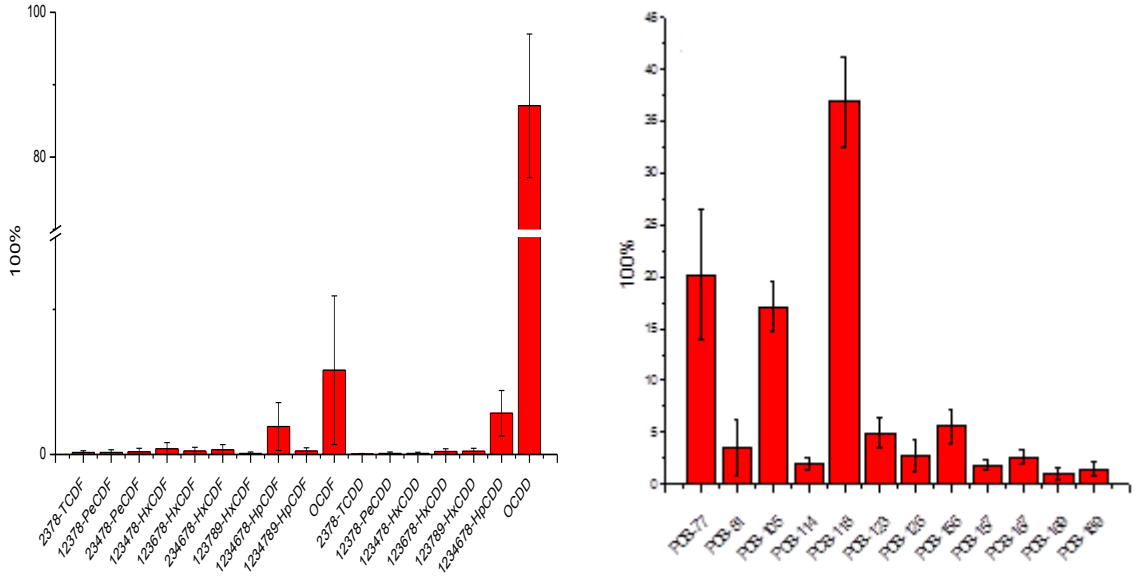

Figure 2 PCDD/Fs and dl-PCBs congener profiles for soil samples in Chongqing city

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