

LEVELS AND PROFILES OF PCDD/Fs AND DL-PCBS IN A REGION OF CHINA WITH MULTIPLE THERMAL-RELATED INDUSTRIES

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Introduction

Some thermal-related industrial activities, such as metallurgy, coking, power generation, and cement production, are potential sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and dioxin-like polychlorinated biphenyls (dl-PCBs)^{1,2}. Once released into the environment, these pollutants are stable and highly persistent, undergo long-range atmospheric transport and can be distributed in various environmental media, such as air, soils and sediments. The rapid industrialization of China has resulted in the rapid expansion of some industries, such as metallurgy and coking. Various industrial plants have been set up in urban areas. Tangshan City, in North China, is the location of some of the most concentrated industrial activity in China, and contains clusters of industrial plants. In particular, rich mineral deposits have helped to turn the city into the biggest steel producer in China. The steel output in 2010 was about 68.3 million ton, which was about 4.9% of world production. There are also more than 20 coking enterprises, five cement mills and some thermal power plants in the area. Some of the major industries in Tangshan City, e.g., iron and steel production, coking, power generation, and cement production, have been identified as high potential sources of pollutants such as PCDD/Fs and dl-PCBs^{1,2}. Extensive investigations have focused on the pollution status of PCDD/Fs and dl-PCBs in industrial areas. However, few studies on the contamination status of these pollutants have been carried out in a region simultaneously involved in various thermal industrial activities. In the present study, the PCDD/Fs and dl-PCBs in various environmental media (air, soils and sediments) from an area with multiple thermal industries were monitored. The objective of this study is to evaluate the effects of emissions from multiple thermal industries on the environmental status of PCDD/Fs and dl-PCBs.

Materials and methods

Sample collection

Air samples were collected using high-volume air samplers continuously for 48 h following the guidelines in the Revised US EPA Reference Method TO-9A. PCDD/Fs and dl-PCBs in the particulate phase were collected using a cleaned glass-fiber filter (GFF), and polyurethane foam (PUF) was used to absorb these substances in the gas-phase. Four of the air-sampling sites were in an industrial region in which multiple thermal-related sources could potentially have an impact. The control site was in a residential area 170 km from the industrial region and had no obvious pollution sources. Two to five atmospheric samples were collected at each site for analysis. This area already has a long history of industrialization, so released pollutants may have been precipitated in

environmental sinks such as soils and sediments over a long period of time. Hence, the PCDD/F and dl-PCB levels in soils and sediments were also determined. Soil samples were collected at 11 sites in the industrial region and two sites in the residential area. Sediment samples were collected from 13 sites along the Douhe River, which is the main river running through Tangshan. All samples were collected in the period June to August 2010.

Sample preparation and analysis

The EPA Method 1613B and EPA Method 1668A modifications were used to determine the 17 2,3,7,8-PCDD/Fs and 12 dl-PCBs. Briefly, prior to extraction, all the samples were spiked with known amounts of $^{13}\text{C}_{12}$ -PCDD/Fs as internal standards and a $^{13}\text{C}_{12}$ -PCB mixture. They were accelerated solvent extracted and concentrated by a rotary evaporator, then cleaned up with acid silica-gel column and multilayer silica columns. PCDD/Fs and PCBs were fractionated using a basic alumina column. Prior to injection into a high-resolution gas chromatograph and high-resolution mass spectrometer (HRGC/HRMS), the final corresponding extracts were spiked with $^{13}\text{C}_{12}$ -labeled injection standards of PCDD/Fs and dl-PCBs for recovery quantification. The analyses of 2,3,7,8-PCDD/Fs and dl-PCBs were performed by an Agilent 6890 gas chromatograph (Agilent technologies, USA) coupled with a Waters Autospec Ultima high-resolution mass spectrometer (Waters, USA).

Results and discussion

Concentrations of PCDD/Fs and dl-PCBs

WHO-TEF values were used to calculate the toxic equivalents (TEQs) of the PCDD/Fs and dl-PCBs. For concentrations below the limit of detection (LOD), a value half of the LOD was used to calculate the total concentrations and TEQs. The mean concentrations of PCDD/Fs and dl-PCBs in ambient air, soils and sediments are shown in Table 1.

Table 1. 2,3,7,8-PCDD/F and dl-PCB concentrations and TEQs in industrial area and residential area

Sample area	Industrial area			Residential area	
	Air(n=4) (fg/m ³)	Soil(n=11) (pg/g)	Sediment(n=13) (pg/g)	Air(n=1) (fg/m ³)	Soil(n=2) (pg/g)
Total 2,3,7,8- PCDDs	899 ±478	45 ±52	26 ±27	1092	92 ±94
Total 2,3,7,8- PCDFs	1419 ±651	52 ±40	14 ±14	901	28 ±17
PCDFs/PCDDs ratio	1.71 ±0.5	1.1 ±0.74	0.64 ±0.24	0.83	0.43 ±0.25
Total 2,3,7,8-PCDD/Fs	2,318 ±1092	98 ±85	40 ±39	1993	306 ±374
WHO-TEQ (PCDD/Fs)	116 ±74	3 ±2.6	1.1 ±1.1	65	2.4 ±0.45
Total dl-PCBs	3398 ±620	40 ±18	44 ±50	3567	73 ±35
WHO-TEQ (dl-PCBs)	11 ±6	0.13 ±0.05	0.07 ±0.05	6	0.26 ±0.21

Atmospheric transport is important in the transfer of dioxin to terrestrial and aquatic ecosystems³. In the present study, the 2,3,7,8-PCDD/F concentrations in the atmosphere of the industrial region ranged from 69 to 226 fg WHO-TEQ/m³, with a mean value of 116 fg WHO-TEQ/m³, and the TEQ value in the residential area was 65 fg WHO-TEQ/m³. The concentrations in the industrial area are roughly within the range for global urban/industrial

areas (100–400 fg TEQ/m³) reported by Lohmann and Jones⁴. Slightly higher atmospheric 2,3,7,8-PCDD/F TEQs were observed at sampling sites in the industrial region than at the site in the residential area, but the difference was not significant. The highest atmospheric 2,3,7,8-PCDD/F concentrations were found in the vicinity of a coking plant, revealing that the ambient air might be more affected by the coking industry. The TEQ values in the industrial area were comparable to those of an industrial area in Taiwan (150 fg I-TEQ/m³) reported by Wang et al⁵ and around a steel plant in Northeast China (3–247 fg I-TEQ/m³), but lower than those of Shanghai city (497.1 fg I-TEQ/m³) and Guangzhou city (104.6–769.3 fg I-TEQ/m³), in China. All the above results reveal that although there are large potential sources of pollution from various thermal industries in this area, the impact of PCDD/F pollution appears to be less serious than expected before this investigation. The explanation for this may be due to the raw materials used, different techniques used, or pollution-control measures during the industrial processes. Hence, the present investigation might indicate that the releases of PCDD/Fs in the regions caused by similar category of thermal-related potential sources may be varied from case to case. The concentrations of dl-PCBs in the atmosphere in the industrial region ranged from 6.7 to 19.9 fg WHO-TEQ/m³, with a mean value of 11 fg WHO-TEQ/m³; these were slightly higher than those for the residential area (6 fg WHO-TEQ/m³). However, compared with those of PCDD/Fs, the contribution of the TEQ concentrations of dl-PCBs to the total TEQs (sum of 2,3,7,8-PCDD/Fs and dl-PCBs) was very modest (average: 8%).

Soils and sediments are major environmental sinks for released PCDD/Fs and PCBs. In the industrial region, the 2,3,7,8-PCDD/F concentrations in 11 soil samples ranged from 0.63 to 7.71 pg WHO-TEQ/g dry weight (wt), with a mean value of 3 pg WHO-TEQ/g wt; these were slightly higher than those for the residential area (mean: 2.4 pg WHO-TEQ/g wt) and were comparable to those observed in some other industrial areas in the world (0.4–4.27 pg I-TEQ/g in Kocaeli, Turkey⁵, 0.1–1.08 pg I-TEQ/g in Spain⁶, and 4.8 pg I-TEQ/g in the Pearl River delta in China⁷). Based on the soil guideline in Sweden, which is 10 pg-TEQ/g, the soils from the industrial area seem to be safe. The 2,3,7,8-PCDD/F concentrations in the sediments from the Douhe River ranged from 0.17 to 3.55 pg WHO-TEQ/g, which are lower than those for the soil samples. Among the sampling sites, higher levels were found downstream from the sites of various industrial plants; this result suggested that these industrial activities were probably the main source of PCDD/Fs in the river, but the environmental impact levels were within a controllable range. Low TEQ concentrations of dl-PCBs were also present, with mean values of 0.13 ± 0.05 pg WHO-TEQ/g and 0.07 ± 0.05 pg WHO-TEQ/g in the soils and sediments, respectively.

Congener Profiles

The homolog profiles of PCDD/Fs and dl-PCBs in the atmosphere, soils, and sediments of the industrial area are shown in Figure 1. For PCDD/Fs, the profiles indicate that highly chlorinated congeners were dominant: 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-PCDF, and OCDF together made up 65–79% of the total 17 2,3,7,8-PCDD/Fs. The levels of PCDF congeners in the atmosphere were apparently higher than those for the PCDD groups in all air samples (ratio: 1.7 ± 0.5). These congener profiles are similar to those reported in some thermal-related industries such as sintering and coking processes^{2, 8}, revealing the strong influence of the thermal-related industries on the PCDD/F concentrations in the atmosphere. However, the PCDD/F congener patterns in the soils and sediments were obviously different from those in the atmosphere. The PCDF/PCDD

ratios decreased, with the values being 1.1 ± 0.74 and 0.64 ± 0.24 in soils and sediments, respectively, and a reduction in the percentages levels of PCDF homologs was observed with decreasing levels of chlorination. On the other hand, the contributions of OCDD to the total PCDD/Fs in soils and sediments were considerably larger than that for air, with the values being up to 41% and 49%, respectively. The different homolog patterns in various media may be explained by different atmospheric precipitation and transportation abilities among the congeners.

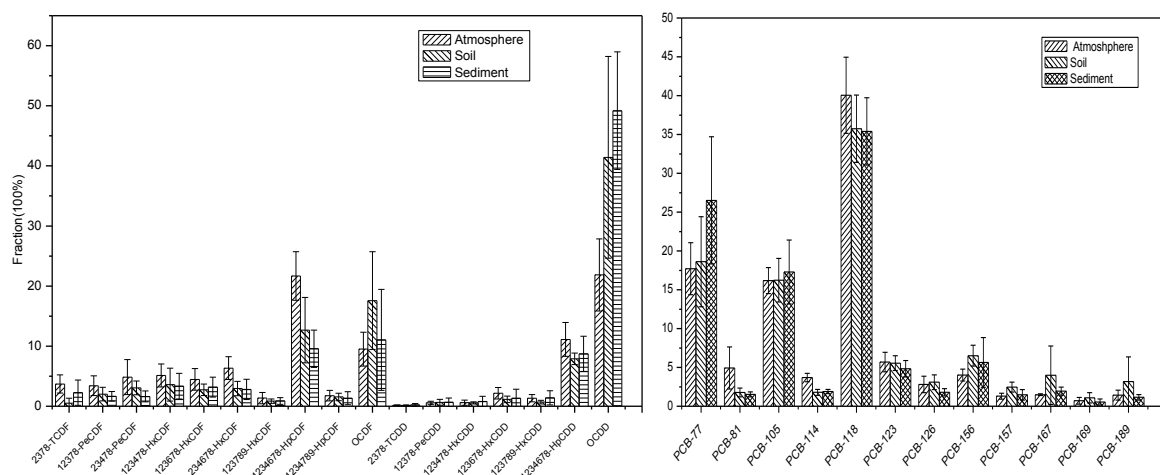


Figure 1. PCDD/F and dl-PCB congener profiles in various environmental media from the industrial region

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