LEVELS AND EXPOSURE RISK ASSESSMENT OF POLYCHLORINATED DIOXINS, FURANS (PCDD/Fs) AND DIOXIN-LIKE POLYCHLORINATED BIPHENYLS (DL-PCBs) IN ATMOSPHERE OF SHENZHEN, SOUTH CHINA

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Introduction

As persistent organic pollutants (POPs), Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorobiphenyls (PCBs) occurred in various environment compartments and were widely concerned by various countries in the world, because of their carcinogenicity, mutagenicity and teratogenicity.

Atmosphere is not only a sink for PCDD/Fs and PCBs but also a major medium for their transport and deposition. PCDD/Fs and PCBs in atmosphere can be migrated with environmental media air and enter human body through food chain or by inhalation, resulting in human internal exposure. Studies on ambient air in China have showed that the pollutions of PCDD/Fs and PCBs were serious in urban air of Guangzhou[1] and Hong Kong[2, 3]. But there is no report about Shenzhen, a city located close to Guangzhou and Hong Kong. Shenzhen is a famous commercial and industrial base in South China. Rapid economic growth and urban development in recent three decades have caused sharply increasing energy demands and vast annual gasoline consumption in Shenzhen, which aggravated its air pollution.

In this study, the concentrations of PCDD/Fs and dioxin-like polychlorinated biphenyls (DL-PCBs) in ambient air in Shenzhen were analyzed by referencing to international standard methods and using isotope dilution high-resolution gas chromatography/high-resolution double-focusing magnetic mass spectrometer (HRGC/HRMS). The pollution levels and distributions of total 29 monomers, including 17 PCDD/Fs and 12 dioxin-like polychlorinated biphenyls (DL-PCBs), were studied in the dry season and the rain season in 2009.

Materials and Methods

Sample Collection

Six representative sampling sites, located in four different districts, were selected to evaluate the contamination profiles of PCDD/Fs and DL-PCBs in Shenzhen in 2009. An intelligent high-volume air sampler (ECHO PUF, TECORA, Italy) was used to collect the total suspended particulate (TSP) with a quartz-fiber filter and the gaseous organic compounds with a polyurethane foam reference US EPA TO-9A. In this study, total 31 samples were collected, including 12 samples in the dry season and 19 samples in the rain season.

Sample Pretreatment and Determination

Sample pretreatment and determination were processed according to USEPA method 1613 and 1668 for PCDD/Fs and PCBs analysis. Samples were spiked with stable C^{13} isotopically labeled analogs of PCDD/Fs and DL-PCBs. Then each sample was extracted with Touene by Soxhlet extraction technique for 24h. After extraction, each extract was treated with 30% acidic silica gel, cleaned-up with acidic silica gel and alumina column. After cleanup, the extract was concentrated to near dryness. Immediately prior to injection, C^{13} isotopically labeled internal standards were added to each extract and an aliquot of the extract was injected into the gas chromatograph (60 m ×0.25 mm ×0.25μm DB-5MS). The analytes were separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer and quantitative analysis was performed.

Results and Discussion

PCDD/Fs and DL-PCBs Levels in atmosphere

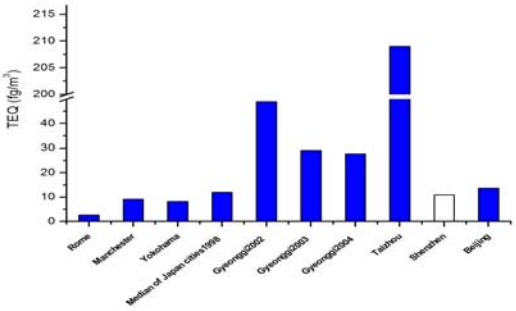
For all samples, the levels of PCDD/Fs were in the range of 103.32~11882.95 fg/m^3, with an average of 3426.84 fg/m^3 and a median of 2950.35 fg/m^3. The toxic equivalents (TEQ) were in the range of 11.45~370.12 fg I-TEQ/m^3, with an average of 157.49 fg I-TEQ/m^3 and a median of 151.24 fg I-TEQ/m^3. The concentrations of the 12 DL-PCBs were in the range of 0.83-4.28 pg/m^3, with an average of 2.55 pg/m^3 and a median of 2.69 pg/m^3. ∑TEQ-PCBs were in the rang of 1.81~19.55 fg WHO-TEQ/m^3. The average level was 10.94 fg WHO-TEQ/m^3 and the median level was 12.82 fg WHO-TEQ/m^3.

For samples collected in the dry season, the median concentration and TEQ of PCDD/Fs were 2046.34 fg/m^3, 108.16 fg I-TEQ/m^3, respectively. For the 12 DL-PCBs, the median concentration and TEQ were 2.43 pg/m^3, 10.62 fg WHO-TEQ/m^3, respectively.

For samples collected in the rain season, the median concentration and TEQ of PCDD/Fs were 3034.42 fg/m^3, 172.84 fg I-TEQ/m^3, respectively. For the 12 DL-PCBs, the median concentration and TEQ were 3.25 pg/m^3, 13.29 fg WHO-TEQ/m^3, respectively.

A clear trend was found by the comparison of the levels during two seasons. Both for PCDD/Fs and DL-PCBs, the levels in the rain season were higher than that in the dry season.

Levels of atmospheric DL-PCBs and PCDD/Fs from different countries and areas were presented in Figure 1 and Figure 2. The level of atmospheric PCDD/Fs in Shenzhen was close to the average level of Sao Paulo of Brazil, higher than Taiwan, Hong Kong and the cities in Japan and European, but lower than Korea's cities and Beijing, Guangzhou and Shanghai of China. The level of DL-PCBs was close to Manchester, lower than Gyeonggi-do of Korea and Taizhou of China.



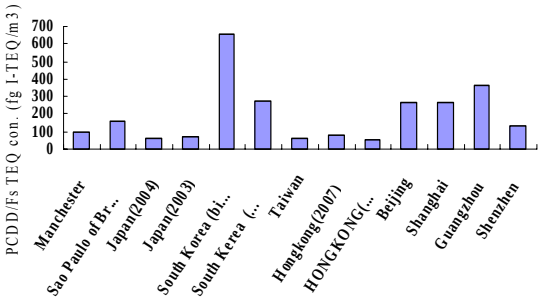


Figure1Comparison of DL-PCBs levels in atmosphere from different areas.Figure2Comparison of PCDD/Fs levels in atmosphere from different areas.

Characteristics of PCDD/Fs and DL-PCBs distribution

The distributions of PCDD/Fs monomers were presented in Figure 3 and Figure 4. In both seasons, OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, OCDF and 2,3,4,7,8-PeCDF were the main monomers. In the dry season, the percentage of induvidul monomer within the total 17 PCDD/Fs concentration was 48.21%, 15.85%, 9.70%, 7.40%, 2.74% for OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, OCDF and 2,3,4,7,8-PeCDF, respectively. In the rain season, the percentage was 23.06%, 17.24%, 14.23%, 11.45%, 5.24% for OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, OCDF and 2,3,4,7,8-PeCDF, respectively. Though OCDD was the biggest contributor to the total concentration, 2,3,4,7,8-PeCDF predominated in TEQ distribution in both seasons.

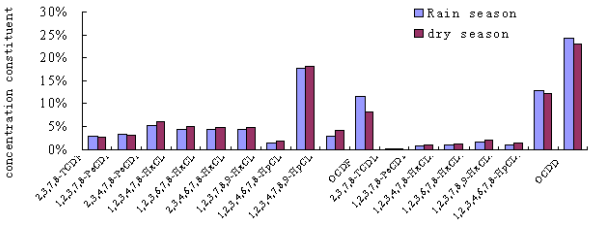


Figure 3 Relative concentrations of PCDD/Fs congeners.

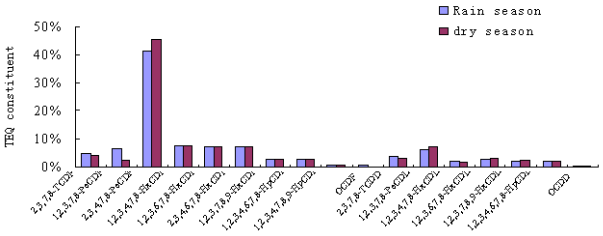


Figure 4 Relative I-TEQ values of PCDD/Fs congeners.

The distributions of DL-PCBs monomers were presented in Figure 5 and Figure 6. PCB-118, PCB-77 and PCB-105 were predominant monomers. In the dry season, PCB-118 predominated (34.11%), followed by PCB-77 (19.96%) and PCB-105 (14.67%). In the rain season, PCB-118 predominated (45.59%), followed by PCB-105(17.22%) and PCB-77(14.13%). Though PCB-118 was the biggest contributor to the total concentration, PCB-126 was the dominant contributor to TEQ, accounted for about 94%, both for dry season and rain season.

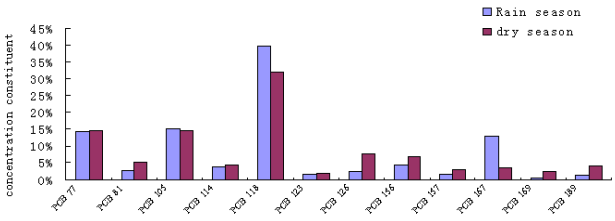


Figure 5 Relative concentrations of DL-PCBs congeners.

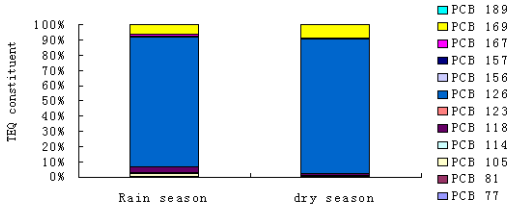


Figure 6 Relative I-TEQ values of DL-PCBs congeners.

Rough inhalation risk assessment

Diet ingestion, inhalation and dermal contact were the main pathways of direct exposure to toxic pollutants. For atmospheric pollutants, inhalation and dermal assimilation would be more important. Direct inhalation exposure to the atmospheric dioxins could be estimated as the average daily intake of I-TEQ equivalents per unit body weight with the assumption that individuals are exposed to polluted air 24 h/day and the indoor/outdoor air pollution levels are equal. Respiratory bioavailability is conservatively assumed as 100%. The daily PCDD/Fs and DL-PCBs exposure doses for adults and children were calculated by the following equation[4]:

$$Inh = V_r C_{air} f_r / BW$$

Where ***Inh*** is the inhalation exposure in pg I-TEQ/kg/day, Respiration rate V_r is 13 m^3/day for adults and 7.4 m^3/day for children, C_{air} is the average air concentration of dioxin in pg I-TEQ/m^3 or the average air concentration of DL-PCBs in pg WHO-TEQ/kg/day. The alveolar fraction retained in the lungs f_r is taken as 0.75 for both adults and children[1]. BW is the body weight (60 kg for adults and 15 kg for children).

It was found that adults and children daily exposure to PCDD/Fs was 0.023 pg I-TEQ/kg/day and 0.052 pg I-TEQ/kg/day, respectively. DL-PCBs respiratory intake for adults and children was 0.0018 pg WHO-TEQ/kg/day and 0.0040 pg WHO-TEQ/kg/day, respectively. Another study showed that the resident daily dietary intake of PCDD/Fs + DL-PCBs in Shenzhen was 1.36 pg WHO-TEQ/kg/day for adults and 5.45 pg WHO-TEQ/kg/day for children[5]. Inhalation exposure to PCDD/Fs + DL-PCBs accounted for 2.09% and 1.21% of the total intake PCDD/Fs + DL-PCBs (including inhalation, dietary intake) for adults and children, respectively.

Although Shenzhen is only a moderate-polluted city in China, higher inhalation exposure to PCDD/Fs + DL-PCBs for children than for adults indicates that children are more likely to be victims in bad air quality. More attentions should be paid to the health of children in further study.

Conclusions

Shenzhen is a moderate-polluted city for PCDD/Fs and DL-PCBs in China. A clear trend was found by the

comparison of the levels during two seasons. The levels of PCDD/Fs and DL-PCBs in the rain season were higher than that in the dry season.

OCDD was the biggest contributor to the total concentration. 2,3,4,7,8-PeCDF was the dominant contributor to TEQ in PCDD/Fs compounds. PCB-118 was the highest concentration of DL-PCBs while PCB-126 was the dominant contributor to TEQ in DL-PCB compounds.

Inhalation exposure to PCDD/Fs + DL-PCBs accounted for 2.09% and 1.21% of the total intake PCDD/Fs + DL-PCBs for adults and children, respectively. Inhalation exposure to PCDD/Fs + DL-PCBs for children was higher than that for adults. More attentions should be paid to the health of children in further study.

Acknowledgements

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