

SPATIAL AND SEASONAL VARIATION OF PCDD/FS AND COPLANAR PCBs IN THE AMBIENT AIR OF A STEEL CITY, NORTHEAST CHINA

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Abstract

Air monitoring of 2,3,7,8-substituted PCDD/Fs and coplanar PCBs was carried out in June 2008 and January 2009 to investigate the concentrations, profiles and seasonal variations of atmospheric dioxins in Anshan, a large steel city of Northeast China. Air samples were collected by using high volume air samplers and the glass fiber filter and polyurethane foam were used for absorbing particle-bound and gaseous chemicals, respectively. The PCDD/Fs and coplanar PCBs were analyzed by the isotope dilution HRGC/HRMS according to US EPA method 1613B and 1668A. The air concentrations of PCDD/Fs were in a low level, with the I-TEQ values in the range 0.004~0.26 pg m⁻³ (average 0.08 pg m⁻³). With regard to coplanar PCBs, TEQ concentrations varied between 0.0006~0.0186 pg m⁻³, contributing 3.6% to 26% to the total TEQ. Although the steel plant sites exhibited higher dioxin levels than the residential and background area, the impact of the steel PCDD/F emissions to the ambient air appears not in a significant level.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are well-known persistent organic pollutants (POPs) targeted by the Stockholm Convention for final elimination to protect human health and environment. Among the 210 congeners, only the 17 homologues of 2,3,7,8-substituted PCDD/Fs are especially concerned due to their high toxicities and have been assigned with toxic equivalence factors by the World Health Organization.

Atmospheric transport is important for the transfer of POPs to terrestrial and aquatic ecosystems¹. Knowledge of the atmospheric levels, profiles and trends of these toxic chemicals helps to understand their depositions, transportations and degradations in the environment. During 2008 to 2009, our research group carried out a project on investigation of atmospheric persistent organic pollutants and their potential impact to the ambient environment around Anshan city, northeast China. The city is characterized by one large iron and steel plant with an annual iron and steel production of 32 million tons and a long production history over 50 years. The main aims of this work were: to investigate the concentrations, profiles and seasonal variations between winter and summer of 17, 2,3,7,8-PCDD/Fs and 12 coplanar PCBs in the ambient air around the steel city; to evaluate the impact of steel plant as PCDD/Fs sources on the ambient air and their potential inhalation risks to the local residents.

Materials and Methods

Sample Collection

Air samples were collected by using high volume air samplers at an interval of 24 hours on June

24-27th 2008 and January 12-17th 2009 around the steel city Anshan, northeast China. Sampling sites S1 (112°59.240E, 41°08.014N), S2 (123°00.275E, 41°08.943N), S3 (122°57.907E, 41°08.370N) situate in the steel plant area, where iron and steel production is expected as the main PCDD/F sources to the ambient air. To better understand the impact of the steel production as dioxin sources to the ambient environment, the urban site S4 (122°56.068E, 41°04.974N) was selected in the vicinity of the steel plant. S5 (123°02.636E, 41°07.200N) and S6 (123°07.876E, 41°01.509N) were located at residential and background area, respectively.

Glass fiber filters (GFF) and polyurethane foam (PUF) materials were used for absorbing particle-bound and gaseous PCDD/Fs, respectively. Prior to sampling, the GFFs were baked at 450 °C to remove organic contaminants and the PUFs were extracted with acetone in an accelerated solvent extraction (ASE) apparatus, and then subjected to another ASE extraction with hexane. Detailed sampling procedure has been described previously².

Sample Analysis

Analysis of the 17, 2,3,7,8-PCDD/Fs and 12 coplanar PCBs were followed by the US EPA Method 1613B and 1668A, respectively. Briefly, 1 ng of ¹³C₁₂-labeled surrogate standards were spiked in air samples before an ASE extraction with organic solvents (hexane: dichloromethane=1:1). The extracts were concentrated by a rotary evaporator, followed by the cleanup with acid silica gel and multilayer silica columns. The final extract was spiked with 1 ng ¹³C₁₂-labeled injection standards for recovery quantification prior to the injection to a HRGC/HRMS equipped with a 60m DB-5MS column.

The HRMS was operated in SIM mode at R_z≥10 000. Exactly 1 μL of sample solution was injected with a CTC PAL autosampler in splitless mode. Helium served as the carrier gas with a constant flow of 1.2 ml min⁻¹. The electron emission energy was set to 35eV, and the source temperature was 270 °C. Oven temperature programs were employed as follows: start 160 °C held for 2min, 160-220 °C at 7.5 °C min⁻¹ held for 16min, 220-235 °C at 5 °C min⁻¹ held for 7min, 235-330 °C at 5 °C min⁻¹ held for 1min.

QA/QC

A breakthrough test was made by using a second half PUF in series with the first PUF and no breakthrough was found. Field and laboratory blanks were routinely analyzed and the values were below the detection limits (LOD). Sample recoveries (n=23) varied between 41% ~ 114% for PCDD/Fs and 49% ~ 147% for coplanar PCBs and all satisfied the limit of Method 1613B and 1668A, respectively. The LOD was defined as three times of signal/noise ratio and were 0.02±0.01 pg m⁻³ for Cl_{1,7}DD/Fs, 0.05±0.06 pg m⁻³ for OCDD/F, and 0.007±0.006 pg m⁻³ for 12 coplanar PCBs.

Results and Discussion

Air concentration of 2,3,7,8-PCDD/Fs and coplanar PCBs

The detailed PCDD/F concentrations and TEQ-values for the six sampling sites are showed in Figure 1 and Figure 2. In the case of values below the LOD, their concentrations were set as zero, i.e. not detected. The PCDD/Fs concentrations ranged between 0.09~4.9 pg m⁻³ (average 1.4 pg m⁻³), with the I-TEQ values in the range 0.004~0.26 pg I-TEQ m⁻³ (average 0.08 pg I-TEQ m⁻³). This result is lower than the ambient air standard of 0.6 pg TEQ m⁻³ for dioxins proposed by Japan

government. Among the six sampling sites, the steel plant site S1, S2 and S3 showed relatively higher atmospheric PCDD/Fs levels than those in residential and background sites, indicating the steel and iron production as local sources. Our group reported the PCDD/F levels in the atmosphere of Beijing with the I-TEQ values in the range 18-644 fg m^{-3} .² Yu et al³ and Li et al⁴ have reported the air concentrations of PCDD/Fs in Guangzhou and Shanghai city, respectively. By comparison, the PCDD/F levels in all the sampling sites of this study are lower than Beijing (18-644 fg m^{-3})², Guangzhou (56.7-1279.6 fg m^{-3})³ and Shanghai (2.2-20760 fg m^{-3})⁴. All these results demonstrate that the PCDD/F concentrations in the ambient air of Anshan is relatively low and impact of the steel PCDD/F emissions to the ambient air appears not in a significant level.

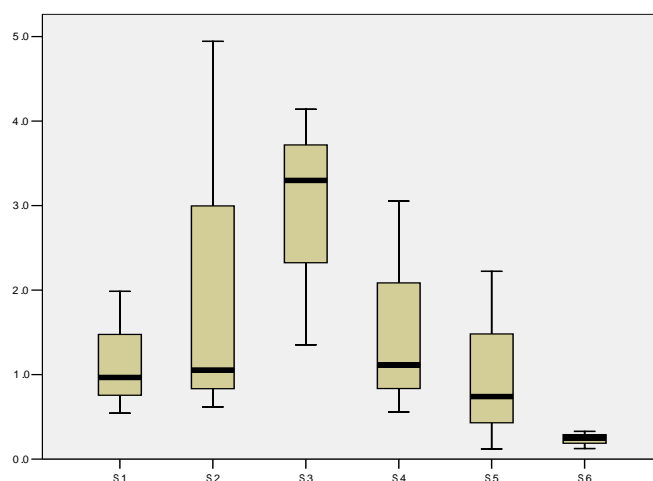


Figure 1 Concentrations of 2,3,7,8-PCDD/Fs (unit: pg m^{-3})

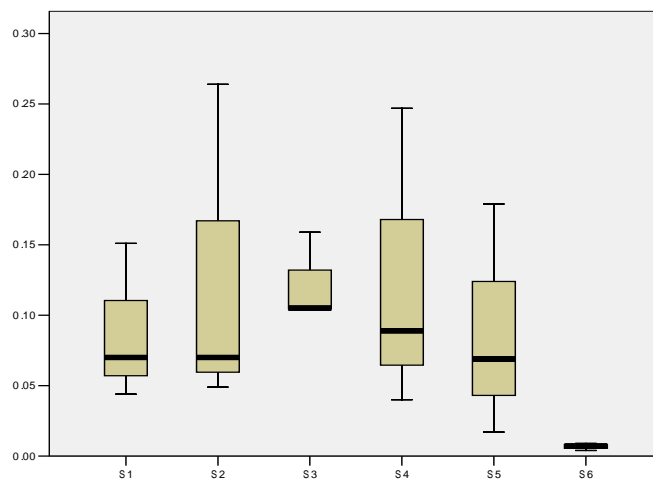


Figure 2 I-TEQs of 2,3,7,8-PCDD/Fs (unit: pg m^{-3})

By comparing the summer and winter results, an apparent seasonal trend was found with higher PCDD/F concentrations in the winter and lower levels in the summer period. This seasonal variation is consistent with the results from other cities reported in the literature and the reasons have been discussed many times previously. Generally, the seasonal trend can be explained by the intensification of diverse combustion activities (e.g. domestic heating) and the worse dispersion of PCDD/Fs in the ambient air during winter.

With regard to coplanar PCBs, WHO-TEQ concentrations varied between 0.0006~0.0186 pg

m^{-3} , with an average of 0.0054 pg m^{-3} . The steel plant site S1, S2, S3 exhibited slightly higher TEQ values than the residential site S5 and the background site S6. For all the measurements, coplanar PCBs showed lower TEQ values than those of 2,3,7,8-PCDD/Fs. Consequently, the relative contribution of coplanar PCBs to the total TEQ ($\text{TEQ}_{\text{PCDD/F}} + \text{TEQ}_{\text{PCB}}$) was typically low, varying from 3.6% to 26% (average 9.5%).

Congener Profiles

Generally, the PCDD/F congeners were quite similar for the six monitoring sites. It was characterized by increasing concentrations with increasing levels of chlorination. Among the seven PCDD congeners, only 1,2,3,4,6,7,8-PeCDD and OCDD were detected, while the most toxic 2,3,7,8-TCDD was not found for all the measurements. Most PCDF congeners were detected in the air samples except 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-PeCDF. The PCDF concentrations were found higher than PCDD groups, with average concentrations of 0.46 pg m^{-3} and 0.90 pg m^{-3} , indicating contamination from combustion sources. The most abundant congener was OCDF and 1,2,3,4,6,7,8-HpCDF, which was responsible for average contributions of $20 \pm 6.9\%$ and $17 \pm 6.8\%$, respectively. The 12 coplanar PCBs were mostly detected in all air samples, with the abundant congener of PCB-118, PCB-77 and PCB-105.

With respect to TEQ congener profiles, the TEQ value of PCDFs was found higher than that of PCDDs. Congener 2,3,4,7,8-PCDF was the single dominant contributor to the $\text{TEQ}_{\text{PCDD/Fs}}$, with an average contribution of 53%. The other main contributors were 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF and 2,3,4,6,7,8-HxCDF, accounting for 10%, 8%, and 8% to the $\text{TEQ}_{\text{PCDD/Fs}}$, respectively. Among 12 coplanar PCBs, only PCB-126 contributed dominantly to the TEQ_{PCBs} (average contribution 91%) due to its relatively higher TEF values in comparison with the other coplanar PCB congeners.

Acknowledgements

We would like to thank the Environmental Monitoring Center in China for financial supports and the Anshan Environmental Monitoring Center for their incorporation and help in sample deployment.

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