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Atmospheric distribution of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyls around a steel plant Area, Northeast China

Yingming Li [a], Pu Wang [a], Lei Ding [a], Xiaomin Li [a], Thanh Wang [a], Qinghua Zhang [a,*], Hongbiao Yang [b], Guibin Jiang [a], Fusheng Wei [c]

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China
[b] Anshan Environmental Monitoring Center, Anshan 114104, China
[c] China National Environmental Monitoring Center, Beijing 100029, China

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ABSTRACT

Air monitoring of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (PCBs) was carried out in June 2008 and January 2009 to investigate the concentrations, profiles and estimating potential inhalation risks to the local residents around a steel plant area in northeast China. The air concentrations and WHO-TEQs of PCDD/Fs ranged 94–4944 fg m^{-3} (average 1352 fg m^{-3}) and 3–247 fg m^{-3} (average 81 fg m^{-3}), respectively. The WHO-TEQ concentrations of dioxin-like PCBs ranged 1–18 fg m^{-3} (average 5 fg m^{-3}), contributing to 3.6–26% of the total TEQ. Higher PCDD/F concentrations were observed in the winter, whereas higher dioxin-like PCB concentrations were found in the summer. The seasonal trend can be related to the significant correlation between the concentrations of dioxins and the reciprocal of temperature (positive for PCDD/Fs, $P < 0.01$; negative for dioxin-like PCBs, $P = 0.05$). A significant positive correlation ($P < 0.0001$) was found between the concentration of total suspended particulate (TSP) and PCDD/F concentrations, but not for PCB congeners. Although the steel plant sites showed higher dioxin levels than the residential and background areas, the PCDD/F levels in the atmosphere of the steel plant area was at a relatively low level. The results from this study provides further aid in evaluating the impact of steel plants as PCDD/Fs emission sources to the ambient air in China.

1. Introduction

The Chinese government has developed the National Implementation Plan (NIP) on persistent organic pollutants (POPs) in order to implement the Stockholm Convention that was ratified by Chinese government in 2004. The NIP project includes four categories of POPs: pesticides, stockpiles, polychlorinated biphenyls (PCBs) and unintentionally produced POPs (Zhu et al., 2008). The last inventory of POPs, which refers to polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), covers a large variety of emission sources associated with anthropogenic activities (UNEP, 2001).

Municipal solid waste incineration (MSWI) and production of iron and steel (e.g. iron ore sintering) are both considered as significant PCDD/F sources emitted to the environment (Anderson and Fisher, 2002; Quaß et al., 2004; Aries et al., 2006). Quaß et al. (2000) reported that the largest annual PCDD/Fs emission at the European scale was assessed to be released from MSWI, closely followed by emissions from iron ore sintering. In China, however, PCDD/F emissions from non-ferrous production (2.6–3389.8 g TEQ) were estimated to be much higher than that from MSWI (66.9 g TEQ if using 10% incineration ratio) due to the large quantity of iron and steel production (1.97×10^8 t y^{-1} in 2002) and the low incineration ratio of municipal waste (only 4.90% until 2003) (Zhu et al., 2008). Therefore, more attention should be paid to the PCDD/Fs emissions from steel plants and their potential impact to the ambient environment in China.

Recent studies on PCDD/Fs in China have been focused on the atmospheric PCDD/F concentrations in Chinese urban areas to evaluate the impact of PCDD/Fs to the local residents. For example, Yu et al. (2006), Li et al. (2008a,b) have reported the concentrations of PCDD/Fs in the ambient atmosphere of Guangzhou, Beijing and Shanghai city, respectively. Their results demonstrated that the levels were comparable or slightly higher than those of many other urban cities around the world. Xu et al. (2009) reported the air

* Corresponding author. Tel./fax: +86 10 62849818.
E-mail address: qhzhang@rcees.ac.cn (Q. Zhang).

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concentrations of PCDD/Fs near a MSWI in eastern China and found that the MSWI might not be the dominant dioxin source in the local area. To our knowledge, however, no research has yet to be conducted on atmospheric PCDD/Fs around steel plants in mainland China. Furthermore, studies on atmospheric dioxin-like PCBs have been rarely reported for Chinese cities.

During 2008–2009, a project was carried out to investigate the distributions of atmospheric persistent organic pollutants and their potential impact on the ambient environment around a large iron and steel plant in Anshan city, northeast China. The plant is one of the largest iron and steel plants in China, with a long production history of over 50 years and has an annual iron and steel production capacity of 32 million tons. In this work, we report the concentrations, profiles and seasonal variation of the seventeen 2,3,7,8-PCDD/Fs and the twelve dioxin-like PCBs in the ambient air around the steel plant in winter and summer. Besides the steel plant zone, sampling was also conducted at urban, residential and background areas to evaluate the impact of steel plant as a PCDD/Fs source to the ambient air and their potential risks to the local residents.

2. Materials and methods

2.1. Sample collection

A total of 23 air samples were collected using high volume air samplers (GPS-1, Thermo Environmental Instruments, Inc., Franklin, MA) over a duration of 24 h on June 24–27th 2008 and January 12–17th 2009 around the Anshan Iron and Steel Corporation located in Anshan city, northeast China. Anshan is one of the most important iron and steel industrial bases in China and is known as "the capital of iron and steel". It is subject to warm continental monsoon climate. The average temperature is −7.4 °C in winter and 23.5 °C in summer. Sampling sites S1 (112°59.240E, 41°08.014N), S2 (123°00.275E, 41°08.943N) and S3 (122°57.907E, 41°08.370N) were situated in the steel plant area, where iron and steel production was expected to be the main PCDD/F source to the ambient air. To better understand the impact of steel production as dioxin sources to the ambient environment, an urban site S4 (122°56.068E, 41°04.974N) was selected in the vicinity of the steel plant, ~7 km away in the southwest of S1. Site S5 (123°02.636E, 41°07.200N) and S6 (123°07.876E, 41°01.509N) were located at a residential and background area, respectively. Details of the location of sampling sites are shown in Fig. 1.

The sampling process was conducted according to the revised US EPA method TO 9A (US EPA, 1999a). Glass fiber filters (GFF, 10.16 cm diameter) and polyurethane foam (PUF, 6.3 cm diameter, 7.6 cm length) materials were used to absorb particle-bound and gaseous chemicals, 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 (Dionex 300; pressure, 1500 psi; temperature, 100 °C; heating, 5 min; static, 8 min; flushing, 60 vol.%; purge, 120 s; 2 cycles), followed by another ASE extraction with hexane. The sampling cartridges were vacuum-dried in desiccators and stored in sealed bags. The GFFs were weighed after equilibrating for 48 h in a desiccator before and after sampling to obtain the concentrations of total suspended particulate (TSP). Detailed sampling procedure has been described previously (Li et al., 2008a).

2.2. Sample analysis

Analysis of the seventeen 2,3,7,8-PCDD/Fs and twelve dioxin-like PCBs was in accordance with the US EPA Method 1613B (US EPA, 1997) and US EPA Method 1668A (US EPA, 1999b), respectively. Briefly, 1 ng of $^{13}C_{12}$-labeled surrogate standards of PCDD/Fs and PCBs (Wellington Laboratories, Canada)) were spiked into the air samples before an ASE extraction with organic solvents (hexane: dichloromethane = 1:1). The extracts were concentrated by a rotary evaporator (Heidolph, Germany) and followed by a cleanup with acid silica gel and multilayer silica columns. The final extract was spiked with 1 ng $^{13}C_{12}$-labeled injection standards of PCDD/Fs and PCBs for recovery quantification prior to the injection into a high resolution gas chromatograph and high resolution mass spectrometer (HRGC/HRMS) equipped with a 60 m DB-5MS column.

The HRMS (Micromass Autospec Ultima, Waters, UK) was operated in electron impact ionization (EI) and selective ion monitoring (SIM) mode at $R \geqslant 10\,000$. Exactly 1 μL of sample solution was injected with a CTC PAL auto-sampler 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 35 eV, and the source temperature was 270 °C. Oven temperature program was employed as follows: start 160 °C held for 2 min, 160–220 °C at 7.5 °C min^{-1} held for 16 min, 220–235 °C at 5 °C min^{-1} held for 7 min, 235–330 °C at 5 °C min^{-1} held for 1 min.

2.3. Quality assurance/quality control (QA/QC)

A breakthrough test was performed by using a second PUF in series with the first PUF and no breakthrough was found. Field and laboratory blanks were routinely analyzed and values were

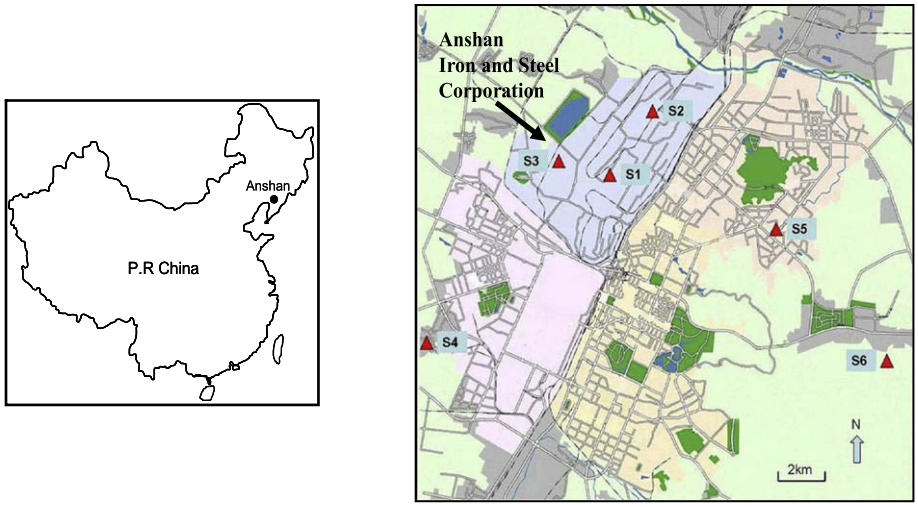

Fig. 1. Sampling location for the six monitoring sites.