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

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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

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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 ($112^{\circ}59.240\text{E}$, $41^{\circ}08.014\text{N}$), S2 ($123^{\circ}00.275\text{E}$, $41^{\circ}08.943\text{N}$) and S3 ($122^{\circ}57.907\text{E}$, $41^{\circ}08.370\text{N}$) 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 ($122^{\circ}56.068\text{E}$, $41^{\circ}04.974\text{N}$) was selected in the vicinity of the steel plant, $\sim 7\text{ km}$ away in the southwest of S1. Site S5 ($123^{\circ}02.636\text{E}$, $41^{\circ}07.200\text{N}$) and S6 ($123^{\circ}07.876\text{E}$, $41^{\circ}01.509\text{N}$) 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 $^{13}\text{C}_{12}$ -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 $^{13}\text{C}_{12}$ -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 $R \geq 10\,000$. 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, $160\text{--}220^{\circ}\text{C}$ at $7.5^{\circ}\text{C min}^{-1}$ held for 16 min, $220\text{--}235^{\circ}\text{C}$ at $5^{\circ}\text{C min}^{-1}$ held for 7 min, $235\text{--}330^{\circ}\text{C}$ at $5^{\circ}\text{C min}^{-1}$ 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.

below detection limits (LOD). Sample recoveries ($n = 23$) in this study varied between 41% and 114% for PCDD/Fs and 49–147% for dioxin-like PCBs, respectively, which satisfied the limit of Method 1613B and 1668A. Our lab participated in the Tenth Round of the International Intercalibration Study (Van Bavel, 2005), which also guaranteed the analytical method used in this work. The LOD was defined as three times of the signal/noise ratio and were 6–68 fg m⁻³ for Cl₁₋₇DD/Fs, 9–246 fg m⁻³ for OCDD/F, and 2–17 fg m⁻³ for the twelve dioxin-like PCBs. Detailed sample recoveries and detection limits are listed in Table S1 of the supplementary material.

3. Results and discussion

3.1. Air concentration of 2,3,7,8-PCDD/Fs and dioxin-like PCBs

All of the measured concentrations and toxicity equivalents (TEQs) are reported in Table S2–S5 of the supplementary material and summarized in Table 1. In the case of values below the LOD, their concentrations were set as zero, i.e. not detected. 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. These results are lower than the ambient air standard of 600 fg TEQ m⁻³ for dioxins proposed by Japan (Government of Japan, 2005). Of the six sampling sites, the steel plant sites S1, S2 and S3 showed relatively higher atmospheric PCDD/Fs levels (43–247 fg WHO-TEQ m⁻³) and roughly fell within the criteria category of global urban areas (100–400 fg TEQ m⁻³) reported by Lohmann and Jones (2000a), but lower than that of point sources (350–1600 fg TEQ m⁻³) (Fiedler, 1996). In comparison, the residential site S5 and background site S6 exhibited even lower PCDD/F levels and fell in the category of global rural and remote area, respectively. The PCDD/F levels in all the sampling sites were lower than other Chinese cities, including Beijing (18–644 fg I-TEQ m⁻³) (Li et al., 2008a), Guangzhou (57–1279 fg I-TEQ m⁻³) (Yu et al., 2006) and Shanghai (2.2–20 760 fg I-TEQ m⁻³) (Li et al., 2008b). We also compared the PCDD/F concentrations in this study with other urban cities around the world and found that it was comparable or slightly lower than those in Asian cities including Hong Kong (18–430 fg I-TEQ m⁻³) (Sin et al., 2002), Taiwan (56–348 fg I-TEQ m⁻³) (Chang et al., 2003), Korea (169–882 fg I-TEQ m⁻³) (Park and Kim, 2002) and Japan (83–550 fg I-TEQ m⁻³)

(Government of Japan, 2005), but consistent with those of the European countries and United States (Greece 40–119 fg I-TEQ m⁻³ (Kouimtzi et al., 2002); Manchester 26–220 fg I-TEQ m⁻³ (Lohmann et al., 2000b); London 62–180 fg I-TEQ m⁻³ (Coleman et al., 1997); Spain 10–357 fg I-TEQ m⁻³ (Abad et al., 2007); Rome 65 fg I-TEQ m⁻³ (Menichini et al., 2007); Houston 40–55 fg I-TEQ m⁻³ (Correa et al., 2004)). All these results demonstrate that the PCDD/F concentrations around the iron and steel plant in this area were not high. Therefore, the impact of the steel PCDD/F emissions to the ambient air in this region should not be at a high level.

With regard to dioxin-like PCBs, the air concentrations and WHO-TEQs ranged 415–24 622 fg m⁻³ (average 4139 fg m⁻³) and 1–18 fg m⁻³ (average 5 fg m⁻³), respectively. 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, dioxin-like PCBs showed lower TEQ values than those of 2,3,7,8-PCDD/Fs. Consequently, the relative contribution of dioxin-like PCBs to the total TEQ (TEQ_{PCDD/F} + TEQ_{PCB}) was typically low, varying from 3.6% to 26% (average 9.5%).

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 (Fig. 2). This seasonal trend is consistent with the results from other cities reported in the literature and the reasons have been discussed previously (Lee et al., 1999; Lohmann and Jones, 2000a). Generally, it can be explained by the intensification of diverse combustion activities, i.e. domestic heating during cold conditions. On the other hand, this seasonal trend can also be associated with the temperature effect. As can be observed in Fig. 3, PCDD/F concentrations showed significant correlation with the reciprocal of temperature (positive, $R = 0.73$, $P < 0.01$). Lower temperature in cold winter corresponded to higher dioxin concentrations in the air. As shown in Fig. 2, the seasonal variation of dioxin-like PCBs was also apparent, but with higher concentrations in the summer. The reason can be attributed to the significant dependence of PCBs on temperature (negative, $R = 0.57$, $P = 0.05$) (Fig. 3), resulting in elevated volatilization of PCBs during warm summer days (Halsall et al., 1995).

Table 1 also shows the TSP concentrations during the sampling campaign with the order of steel plant (373 µg m⁻³) > residential (192 µg m⁻³) > background area (145 µg m⁻³), indicating different contamination level of aerosol pollutions. A significant positive correlation ($R = 0.78$, $P < 0.0001$) was found between TSP and

Table 1
Sampling volume, TSP concentration, PCDD/F and dioxin-like (dl) PCB levels during the sampling campaign.

January 12–17th 2009	Site S1		Site S2		Site S3		Site S4		Site S5		Site S6	
	S1-1	S1-2	S2-1	S2-2	S3-1	S3-2	S4-1	S4-2	S5-1	S5-2	S6-1	S6-2
Volume (m ³)	278	290	284	270	256	269	298	322	341	286	295	233
TSP (µg m ⁻³)	352	409	344	272	616	514	313	150	468	145	67	413
ΣPCDD (fg m ⁻³)	334	504	408	1459	1548	2948	646	161	355	158	130	89
ΣPCDF (fg m ⁻³)	632	1480	643	3485	1749	1193	2408	953	1867	581	120	239
ΣPCDD/ΣPCDF	0.53	0.34	0.63	0.42	0.89	2.47	0.27	0.17	0.19	0.27	1.08	0.37
ΣPCDD/Fs (fg m ⁻³)	966	1984	1051	4944	3297	4141	3054	1114	2222	739	250	328
Σdl-PCBs (fg m ⁻³)	1002	4741	771	2734	3272	3852	1916	769	2549	859	1483	415
WHO-TEQ _{PCDD/F} (fg m ⁻³)	68	144	67	247	152	98	238	85	172	67	3	7
WHO-TEQ _{PCB} (fg m ⁻³)	4	12	4	18	9	6	11	4	7	4	1	1
June 24–27th 2008												
Volume (m ³)	S1-3	S1-4	S2-3	–	S3-3	S3-4	S4-3	S4-4	S5-3	S5-4	S6-3	S6-4
TSP (µg m ⁻³)	162	303	293	–	298	304	262	319	267	286	289	249
ΣPCDD (fg m ⁻³)	313	326	205	–	344	410	159	91	86	67	59	41
ΣPCDF (fg m ⁻³)	58	492	137	–	217	409	163	118	9	30	32	79
ΣPCDD/ΣPCDF	485	1018	479	–	1135	1058	394	323	109	64	92	104
ΣPCDD/Fs (fg m ⁻³)	0.12	0.48	0.29	–	0.19	0.39	0.41	0.37	0.08	0.47	0.35	0.76
Σdl-PCBs (fg m ⁻³)	543	1510	616	–	1352	1467	557	441	118	94	124	183
WHO-TEQ _{PCDD/F} (fg m ⁻³)	9378	5215	24 622	–	3387	4353	2704	2512	3656	3166	6610	5241
WHO-TEQ _{PCB} (fg m ⁻³)	43	81	50	–	112	119	43	31	18	8	7	6
	8	6	7	–	5	6	3	2	2	2	2	1

Fig. 2. Seasonal trend of PCDD/Fs and dioxin-like PCBs at the six monitoring sites.

PCDD/F concentrations, but not for PCB congeners ($P = 0.32$). This result indicates the close relation between the PCDD/F and aerosols, as described in other studies (Chang et al., 2003). It is also consistent with the gas-particle partitioning in the ambient air, i.e. PCDD/Fs are dominantly distributed in the particles, whereas PCBs mainly exist in the gaseous phase (Lohmann et al., 2000b).

3.2. Congener profiles

The congener profiles in the six sampling sites were expressed in two ways; the relative contribution of individual congener to the total concentration of congeners (concentration profiles) and to the total TEQs (TEQ profiles).

The concentration profiles of PCDD/Fs are illustrated in Fig. 4. Generally, PCDD/F congeners were quite similar for the six monitoring sites. It was characterized by increasing concentrations with increasing levels of chlorination if concentrations of each homologue were summed together, similar to the world average profiles from Europe, the United States, Japan and Australia (Lohmann and Jones, 2000a). OCDF and 1,2,3,4,6,7,8-HpCDF dominated PCDD/F concentration profiles, which was responsible for relative contributions of $20 \pm 6.9\%$ and $17 \pm 6.8\%$, respectively. Among the seven PCDD congeners, only 1,2,3,4,6,7,8-HpCDD and OCDD were detected, while the most toxic 2,3,7,8-TCDD was not found in any samples. 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-HpCDF. The PCDF concentrations were found at higher levels than PCDD groups for each measurement, with average concentrations of 456 and 896 fg m^{-3} , respectively.

With respect to TEQ congener profiles, the TEQ value of PCDFs was found higher than that of PCDDs (Fig. 5). Congener 2,3,4,7,8-

Fig. 3. Temperature dependence of PCDD/Fs and dioxin-like PCBs.

PeCDF was the single dominant contributor to the $\text{TEQ}_{\text{PCDD/Fs}}$, accounting for an average contribution of 53% to the toxic equivalents of PCDD/Fs. This result is also consistent with the world average ambient air (Lohmann and Jones, 2000a). 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 average contributions of 10%, 8%, and 8% to the $\text{TEQ}_{\text{PCDD/Fs}}$, respectively.

With regard to PCBs, the 12 dioxin-like congeners were detected in all air samples, with higher contribution of congeners PCB-118, PCB-105 and PCB-77, accounting for 30.6–51.9%, 14.0–25.1%, 7.3–45.9% to the total concentration of PCBs. With regard to the TEQ of dioxin-like PCBs, only PCB-126 contributed dominantly to the TEQ_{PCBs} (average contribution 91%) due to its relatively higher toxicity equivalent factor (TEF) values in comparison with the other dioxin-like PCB congeners.

3.3. Inhalation risk assessment

Human dioxin exposure pathways include food ingestion, inhalation and dermal contact. Food ingestion is considered the dominant uptake route and accounts for about 95% of the total daily intakes (TDI) of dioxins (Government of Japan, 2005). Inhalation is responsible for the direct exposure to dioxins and this exposure pathway would be more important for atmospheric pollutants. Moreover, atmospheric POPs tend to partition into soil and vegetation and can bioaccumulate in the food chain, resulting in a number of indirect sources for human exposure (Nouwen et al., 2001).

Fig. 4. Concentration profile of individual PCDD/Fs.

Fig. 5. Relative contribution of individual congener to the total TEQ of PCDD/Fs.

Yu et al. (2006) and Li et al. (2008b) assessed the inhalation risk of atmospheric PCDD/Fs to the residents of Guangzhou and Shanghai, but did not include dioxin-like PCBs. In this study, we calculated the inhalation exposure of PCDD/Fs and dioxin-like PCBs to the local residents around the steel plant by using the following equation (Nouwen et al., 2001):

$$\text{Inh}_{\text{ad/ch}} = V_{\text{r,ad/ch}} C_{\text{air}} f_{\text{r}} t_{\text{f,ad/ch}} / W_{\text{ad/ch}} \quad (1)$$

Where $\text{Inh}_{\text{ad/ch}}$ is inhalation exposure for adults/children in $\text{fg TEQ kg}^{-1} \text{d}^{-1}$; $V_{\text{r,ad/ch}}$ is ventilation rate ($20 \text{ m}^3 \text{d}^{-1}$ for adults, $7.6 \text{ m}^3 \text{d}^{-1}$ for children); C_{air} is the air concentration expressed in fg TEQ m^{-3} ; f_{r} is the alveolar fraction retained in lung (0.75 for adults/children); $t_{\text{f,ad/ch}}$ is the time fraction that adults/children spend at the impact site, which is conservatively assumed as 1; body weight $W_{\text{ad/ch}}$ is set at 70 kg for adults and 15 kg for children.

The PCDD/Fs inhalation of the steel plant workers ($24 \text{ fg TEQ kg}^{-1} \text{d}^{-1}$) was found higher than the urban ($22 \text{ fg TEQ kg}^{-1} \text{d}^{-1}$), residential ($15 \text{ fg TEQ kg}^{-1} \text{d}^{-1}$) and background adult residents ($2 \text{ fg TEQ kg}^{-1} \text{d}^{-1}$), as summarized in Table 2. If the PCB inhalation was taken into account, the average total inhalation was $19 \text{ fg TEQ kg}^{-1} \text{d}^{-1}$ for adults, $34 \text{ fg TEQ kg}^{-1} \text{d}^{-1}$ for children, respectively. This result is lower than those in Guangzhou (Yu

Table 2

Dioxin inhalation assessment for the local residents.

		PCDD/Fs inhalation ($\text{fg TEQ kg}^{-1} \text{d}^{-1}$)	PCBs inhalation ($\text{fg TEQ kg}^{-1} \text{d}^{-1}$)	Total inhalation ($\text{fg TEQ kg}^{-1} \text{d}^{-1}$)
S1	Adult	18	1.6	20
	Children	32	2.9	35
S2	Adult	26	2.1	28
	Children	46	3.7	50
S3	Adult	26	1.4	27
	Children	46	2.5	49
S4	Adult	21	1.1	22
	Children	38	1.9	40
S5	Adult	14	0.9	15
	Children	25	1.5	27
S6	Adult	1.3	0.2	1.5
	Children	2.3	0.4	2.7
Average	Adult	18	1.2	19
	Children	32	2.2	34

et al., 2006) and Shanghai (Li et al., 2008b). The contribution of PCB to the total inhalation was small compared to PCDD/Fs, varying from 4.9% to 13.3%. It should be noted that children were at

higher risk of exposure to dioxins compared to the adults according to the inhalation assessment of this study.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.01.061.

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