



Comparison of the contributions of polychlorinated dibenzo-p-dioxins and dibenzofurans and other unintentionally produced persistent organic pollutants to the total toxic equivalents in air of steel plant areas



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HIGHLIGHTS

- Level of dioxin and dioxin-like compounds in air of steel plant areas was studied.
- Relative contribution of dioxins and dioxin-like compounds was compared.
- Profiles of dioxins and dioxin-like compounds in the ambient air were stated.

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ABSTRACT

The concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and the “dioxin-like” (dl) compounds polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), polybrominated dibenzo-p-dioxins (PBDDs), and dibenzofurans (PBDFs), were determined in the air samples collected from six steel plants. The toxic equivalent (TEQ) concentrations of the PCDDs, PCDFs, dl-PCBs, dl-PCNs, PBDDs, and PBDFs in the air were 0.01–0.19 pg WHO-TEQ N m⁻³, 0.01–0.69 pg WHO-TEQ N m⁻³, 0.001–0.089 pg WHO-TEQ N m⁻³, 0.002–0.011 pg TEQ N m⁻³, 0.004–0.02 pg TEQ N m⁻³, and 0.02–0.12 pg TEQ N m⁻³, respectively. The PCNs were the most abundant compounds (by mass concentration), contributing about 87% of the total mass concentrations of the analytes that were found in the air of the steel plant areas. The PCDFs contributed about 47% of the total TEQs, following by the PBDFs (28%) and the PCDDs (18%). The dioxin-like compounds together contributed up to 40% of the total TEQs, so their contributions to the toxic effects that could be caused by exposure to the air of the steel plant areas were significant. The congener profiles in the air were similar to the congener profiles that were found in stack gas emissions, indicating that the steelmaking plants were possible sources of the PCDDs, PCDFs, and dioxin-like compounds that were found in the air of the steel plant areas.

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and “dioxin-like” (dl) compounds such as polybrominated dibenzo-p-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs) have similar physicochemical properties, toxicities, and geochemical behaviors (WHO, 1998). These compounds are persistent organic pollutants (POPs) and can be unintentionally produced (UP) during industrial thermal processes, so they are normally called UP-POPs (Liu et al., 2009, 2010).

Steelmaking processes have been widely recognized as being important sources of PCDDs, PCDFs, and PCBs (Aries et al., 2006; Grochowalski et al., 2006). In recent studies, PBDDs, PBDFs, and PCNs have also been found to be unintentionally produced and released during steelmaking processes (Anderson and Fisher, 2002; Aries et al., 2006; Wang et al., 2010; Liu et al., 2012). Emissions of PCDDs, PCDFs, and dioxin-like compounds from a steel-making plant into the surrounding environment could pose health risks to the local residents and workers at the plant. Concentrations of PCDDs, PCDFs, and dioxin-like compounds in the environment around steelmaking plants have been determined in several recent case studies. Li et al. (2010) assessed the atmospheric distributions of PCDDs, PCDFs, and PCBs around a steel plant in northeastern China and found that the concentrations in the air

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were higher around the steel plant than in control areas where no intensive industrial activities took place. Wang et al. (2008) found PCDD and PCDF concentrations of $1700 \pm 900 \text{ fg N m}^{-3}$ and tetra- to hexa-bromodibenzo-p-dioxin and tetra- to hexa-bromodibenzofuran concentrations of $46 \pm 13.3 \text{ fg N m}^{-3}$ in ambient air in areas, in which metallurgical industries were situated, and these concentrations were higher than the concentrations found in ambient air in rural and urban areas. These results clearly indicate that POP emissions during steelmaking processes contribute to POP pollution in the ambient air surrounding metallurgical plants. There is still a lack of data available on concentrations of emerging POPs (such as PBDDs, PBDFs, and PCNs) in the environment. It was found in several studies that, in specific areas, dioxin-like compounds such as PBDDs, PBDFs, and PCNs made contributions to the total toxic equivalents (TEQs) that were comparable to or even higher than the contributions made by the PCDDs and PCDFs (Kannan et al., 1998, 2001; Choi et al., 2003). However, the relative importance of PCDDs, PCDFs, and dioxin-like compounds in air of steel plant areas has not yet been determined.

In this study, air samples collected from six steel plant areas were analyzed to allow the concentrations and relative importance of the PCDDs, PCDFs, and dioxin-like compounds in the air of steel plant areas to be assessed. The analytes were PCDDs, PCDFs, PBDDs, PBDFs, dl-PCBs, and PCNs, and they were determined using an isotope dilution method using high-resolution gas chromatography coupled with high-resolution mass spectrometry. The TEQs for the compounds that were determined were compared to gain an understanding of the relative importance of the six UP-POPs in polluted air of the steel plant areas. The PCDD, PCDF, and dioxin-like compound congener profiles in the air and stack gases released from the steel plants were compared to allow the relationship between the pollutant patterns in the air and the industrial emissions to be explored.

2. Materials and methods

2.1. Collection of air samples

Samples were collected at six typical steel plants in northern China. Each steel plant had one sintering workshop and one converter steelmaking workshop. Basic information on the sintering and converter steelmaking processes in the six steel plants is provided in Table S1 in the Supporting Information. An air sample was collected downwind of the stack emitting gases produced during the iron ore sintering process at each of the steel plants (i.e., six samples in total), and the samples were labeled XH-1, HX-1, XJ-1, RC-1, TG-1, and SG-1. An air sample was also collected downwind of the stack emitting gases produced during the converter steelmaking process at five of the steel plants (i.e., five samples in total), and the samples were labeled XH-2, XJ-2, RC-2, TG-2, and SG-2. Each air sample was collected using a high-volume air sampler (Echo Hi-Vol; Tecora, Paris, France). The particulate matter was collected on a clean glass-fiber filter, and the target POPs in the gas phase were collected on a polyurethane foam plug. Each air sample was collected continuously for approximately 7 h at a flow rate of $0.22 \text{ m}^3 \text{ min}^{-1}$. The samples were transported to the laboratory and stored at $-18 \text{ }^\circ\text{C}$ until they were analyzed.

2.2. Analysis of the target POPs in the air samples

Each air sample was spiked with ^{13}C -labeled internal standards (Catalog Nos. EPA-1613 LCS, EPA-1668B LCS, ECN-5102, and EDF-5408; Wellington Laboratories, Guelph, Canada) and then extracted with a 1:1 mixture of hexane and dichloromethane in an accelerated solvent extraction system (ASE300; Dionex, Sunnyvale, CA, USA). The extract was cleaned by passing it through a multilayer silica gel

column (from top to bottom: 2 cm anhydrous sodium sulfate, 1 g of activated silica-gel, 10 g of 44% (w/w) silica-gel-sulfuric acid, 1 g of activated silica-gel and 4 g of 33% (w/w) silica-gel-NaOH, 1 g activated silica gel) and an activated carbon (1.5 g) column. The activated carbon column was eluted with 80 mL dichloromethane/hexane (5/95, v/v), to elute the PCBs and PCNs, and then 250 mL toluene, to elute the PCDDs, PCDFs, PBDDs, and PBDFs. Each extract fraction was then concentrated to a volume of about 20 μL . ^{13}C -labeled injection standards (Catalog Nos. EPA-1613 IS, EPA-1668B IS, ECN-5260, and EDF-5409; Wellington Laboratories, Guelph, Canada) were added to each extract fraction and then homogenized by vortex before it was injected into the gas chromatograph to allow the recoveries of the internal standards to be determined.

The extracts were analyzed for PCDDs, PCDFs, and dioxin-like compounds using a gas chromatograph coupled to a DFS mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The data were acquired using the mass spectrometer in selected ion monitoring mode. A DB-5MS fused silica column (60 m long, 0.25 mm i.d., 0.25 μm film thickness) was used to separate the PCDD, PCDF, PCB, and PCN congeners. The instrumental analytical methods that were used to analyze the chlorinated compounds have been described in detail previously (Liu et al., 2012; Nie et al., 2012).

The following details are for the PBDD and PBDF analyses only. A DB-5MS fused silica column (15 m long, 0.25 mm i.d., 0.10 μm film thickness) was used to separate the PBDD and PBDF congeners. The gas chromatograph injection port was at $300 \text{ }^\circ\text{C}$ and it was operated in pulsed splitless mode with a pulse pressure of 220 kPa. The gas chromatograph oven temperature program started at $120 \text{ }^\circ\text{C}$ (held for 1 min), then increased at $12 \text{ }^\circ\text{C min}^{-1}$ to $220 \text{ }^\circ\text{C}$, then increased at $4.0 \text{ }^\circ\text{C min}^{-1}$ to $260 \text{ }^\circ\text{C}$, and finally increased at $3 \text{ }^\circ\text{C min}^{-1}$ to $320 \text{ }^\circ\text{C}$ (held for 7 min). The carrier gas was helium. The glass transfer line was kept at $280 \text{ }^\circ\text{C}$, and a positive electron impact ionization (EI+) source was used in the mass spectrometer with an electron energy of 45 eV. The mass spectrometer was tuned to and operated at a resolution of around 10000, and it was operated in selected ion monitoring mode to analyze the PBDDs and PBDFs.

2.3. Quality control and quality assurance

The recoveries of the ^{13}C -labeled tetra- to hepta-bromodibenzo-p-dioxin and tetra- to hepta-bromodibenzofuran internal standards ranged from 45% to 109% and the recoveries of the ^{13}C -labeled OBDF and OBDD internal standards ranged from 17% to 45% (see in Fig. S1). The recoveries of the ^{13}C -labeled PCDD and PCDF internal standards were 42–112%, and the recoveries of the PCB and PCN internal standards were 40–108% and 37–115%, respectively. A blank sample was included in each batch of samples analyzed. The detection limit was defined as the concentration required to give a signal-to-noise ratio (using the peak to peak definition) greater than three. Each concentration below the limit of detection for that congener was replaced with a value of half the limit of detection when calculating the total concentrations.

3. Results and discussion

3.1. Concentrations and TEQs of PCDDs, PCDFs, and dioxin-like compounds in the air

The toxic equivalence factors authorized by the World Health Organization (WHO) in 2005 were used to calculate the toxic equivalents (TEQs) of the PCDDs, PCDFs, and dl-PCBs. The total PCN TEQ was defined as the sum of the product of the concentration and potency factor (relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin) of each of the PCN congeners (Noma et al., 2004;

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