



Characterization of polychlorinated dibenzo-*p*-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls, and polychlorinated naphthalenes in the environment surrounding secondary copper and aluminum metallurgical facilities in China



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ABSTRACT

Unintentionally produced persistent organic pollutants (UP-POPs) were determined in ambient air from around five secondary non-ferrous metal processing plants in China, to investigate the potential impacts of the emissions of these plants on their surrounding environments. The target compounds were polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs), and polychlorinated naphthalenes (PCNs). The PCDD/F, dl-PCB, and PCN concentrations in the ambient air downwind of the plants were 4.70–178, 8.23–7520 and 152–4190 pg/m³, respectively, and the concentrations upwind of the plants were lower. Clear correlations were found between ambient air and stack gas concentrations of the PCDD/Fs, dl-PCBs, and PCNs among the five plants, respectively. Furthermore, the UP-POPs homolog and congener patterns in the ambient air were similar to the patterns in the stack gas samples. These results indicate that UP-POPs emissions from the plants investigated have obvious impacts on the environments surrounding the plants.

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1. Introduction

Persistent organic pollutants (POPs), such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs), can be formed unintentionally during industrial thermal processes, including waste incineration (Ni et al., 2009; Hu et al., 2013b), iron ore sintering (Grochowalski et al., 2007; Liu et al., 2012a), and secondary non-ferrous metal smelting (Weber et al., 2008; Ba et al., 2009). Once emitted from a plant where industrial thermal processes are performed, these unintentionally produced POPs (UP-POPs) could potentially have great impacts on the ambient environment and human health because of their high toxicities, persistence, and abilities to bioaccumulate. Emissions of these UP-POPs from industrial thermal processes and their potential impacts

on the environments surrounding industrial plants have, therefore, attracted an increasing attention in recent years.

Intensive studies have been performed to investigate PCDD/F concentrations in environments surrounding municipal solid waste incinerators (MSWIs) (Oh et al., 2002; Shih et al., 2006; Liu et al., 2012b). Liu et al. (2012b) determined PCDD/F concentrations in a series of air and soil samples collected around a typical MSWI and found that the MSWI had potentially influenced the PCDD/F concentrations in the environment. Shih et al. (2006) found that the average PCDD/F concentration (0.0828 pg WHO-TEQ/Nm³; WHO = World Health Organization, TEQ = toxic equivalent) in air samples collected from around two MSWIs was 6.5 times higher than the concentration in air at a remote site (0.0132 pg WHO-TEQ/Nm³). Oh et al. (2002) found that characteristic PCDD/F homolog patterns in ambient air samples collected from near a MSWI were different to the patterns in background air samples but similar to the patterns in stack gases emitted from the plant. The results of these studies indicate that the MSWIs mentioned above had strong effects on the PCDD/F concentrations and homolog patterns in their

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surrounding environments. Compared with the intensive research on MSWIs described above, relatively few studies of the concentrations of UP-POPs in the environments surrounding secondary non-ferrous metal processing plants have been performed. Chen et al. (2004) found that PCDD/F concentrations in ambient air around a secondary aluminum smelter (SeAl) were higher when it was operating than when it was not operating. Colombo et al. (2011) found that PCDD/F concentrations in soil samples around a SeAl plant decreased with increasing distance from the plant, and that the most contaminated sites were less than 500 m from the plant. However, these two studies were each performed at only one plant, and intensive investigations, especially including different types and sizes of smelters, should be performed to characterize the concentrations of UP-POPs in the environments surrounding secondary non-ferrous metal processing plants.

Furthermore, previous studies have mainly been focused on PCDD/F contamination in the environments around secondary non-ferrous metal processing plants, and few investigations have been conducted on PCN contamination around such plants. Whereas PCNs have been proposed for inclusion in Annexes A, B, and/or C of the Stockholm Convention, in 2011. On the other hand, the UP-POPs concentrations in the environments surrounding secondary copper smelters (SeCu) have not been studied, to the best of our knowledge. Therefore, we determined the concentrations of UP-POPs (PCDD/Fs, dl-PCBs, and PCNs) in ambient air near five secondary non-ferrous metal processing plants. Three secondary copper smelters including TY, CX and YD plants and two secondary aluminum smelters including SC and QY plants were studied. Air samples were collected from downwind of each plant, and, at the same time, air samples were collected from upwind of each plant, to act as control samples. Additionally, the stack gas emitted from these investigated plants was also collected and analyzed during ambient air sampling period, which we have previously reported (Hu et al., 2013a). The concentrations and homolog profiles of the UP-POPs in the ambient air were compared with those found in stack gases emitted from the same plants. The results of this study will improve our understanding of characterization of UP-POPs in ambient environments surrounding secondary copper and aluminum smelters.

2. Materials and methods

2.1. Sample collection

Three SeCu and two SeAl plants, all located far from other possible pollution sources, were selected for the study, the aim of which was to assess the potential influence of UP-POPs emissions from secondary non-ferrous metal processing plants on the surrounding environments. Basic information about the five plants is given in Table 1. Ambient air samples were collected from three sampling sites near each plant. Two air samples were collected downwind of each plant (about 300 and 500 m from the stack, called A and B, respectively), and one sample was collected upwind of each plant (about 1000 m from the stack, called C), to act as a control sample. The air samples were collected using polyurethane foam (PUF) disk passive air samplers (PASs). The samplers were left at the sampling sites for about two months, between April and October 2011 (Table 1). Before use, the PUF disks (14 cm diameter and 1.35 cm thick) were cleaned by washing them with water and then Soxhlet extracting them with acetone for 12 h. When the air sampling period was complete, each sample was tightly wrapped in aluminum foil and packed in a sealed

polyethylene bag, to avoid contamination or loss of analytes. The samples were taken to the laboratory and stored at -18°C until analysis.

2.2. Sample analysis

We have previously reported the details of the methods used to analyze the samples for UP-POPs (Guo et al., 2008; Hu et al., 2013a). Briefly, the samples were spiked with known amounts of $^{13}\text{C}_{12}$ -labeled PCDD/Fs, $^{13}\text{C}_{12}$ -labeled PCBs, and $^{13}\text{C}_{10}$ -labeled PCNs, for use as internal standards (Table S1), then they were Soxhlet extracted with toluene for approximately 24 h. Each sample extract was concentrated and then subjected to a series of adsorption chromatography clean-up procedures, which were an acidified silica gel column, a multilayer silica gel column (filled, from top to bottom, with anhydrous sodium sulfate, 1 g activated silica gel, 8 g silica gel containing 44% (w/w) of H_2SO_4 , 1 g activated silica gel, 5 g silica gel containing 33% (w/w) of 1 M NaOH, 1 g activated silica gel, 2 g of silica gel containing 10% (w/w) of AgNO_3 , and 1 g activated silica gel), and a basic alumina column. Finally, each extract was concentrated to approximately 20 μL by rotary evaporation and under a gentle stream of nitrogen. $^{13}\text{C}_{12}$ -labeled PCDD/F, $^{13}\text{C}_{12}$ -labeled PCB, and $^{13}\text{C}_{10}$ -labeled PCN standards (Table S1) were added to the extracts, to enable the recoveries of the internal standards to be estimated, before instrumental analysis. The PCDD/F and PCB analyses were performed using an Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) coupled with an Autospec Ultima high-resolution mass spectrometer (Waters, Milford, MA, USA). A DB-5ms capillary column (60 m long, 0.25 mm id, 0.25 μm film thickness; Agilent Technologies) was used to separate the analytes. The mass spectrometer was equipped with a positive electron impact (EI+) source, selected ion monitoring mode was used, and the resolving power was 10,000. The electron energy was 35 eV and the source temperature was 250°C . The PCNs were analyzed using a Trace GC Ultra gas chromatograph coupled with a DFS mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The DFS mass spectrometer was fitted with an electron impact ion source and it was operated in selected ion monitoring mode, with a resolution of $>10,000$. A DB-5ms capillary column (60 m long, 0.25 mm id, 0.25 μm film thickness; Agilent Technologies) was used to separate the PCN congeners. The electron emission energy was 45 eV and the source temperature was 270°C .

2.3. Quality assurance and quality control

The recoveries of the PCDD/F, PCB, and PCN internal standards in the ambient air samples were in the ranges of 42–118%, 42–119%, and 45–115%, respectively (Table S1). The following quality control criteria were used when identifying a target compound: (a) the chromatographic retention time matched that of the corresponding standard compound; (b) the signal-to-noise ratio was greater than 3:1; and (c) the isotopic ratio between the quantitation and confirmation ions was within $\pm 15\%$ of the theoretical value. One method blank was included in each batch of samples, and the blanks were spiked with the same amounts of internal standard as were the samples. No target compounds were detected in any of the blank samples.

3. Results and discussion

3.1. Atmospheric UP-POPs concentrations in the ambient air from around the plants

The UP-POPs concentrations in the ambient air around the five plants were estimated from the concentrations found in the PUF samplers by applying a typical sampling rate of $3.5\text{ m}^3/\text{day}$ (Mari et al., 2008; Hogarth et al., 2012b; Zhang et al., 2013). The TEQ concentrations for the PCDD/Fs and dl-PCBs were calculated using the WHO 2005 toxic equivalence factors (TEFs) (Van den Berg et al., 2006). The PCDD/F and dl-PCB concentrations in the ambient air samples from near the secondary copper and aluminum smelters were $4.70\text{--}178\text{ pg}/\text{m}^3$ (mean $41.8 \pm 60.2\text{ pg}/\text{m}^3$) and $8.23\text{--}7520\text{ pg}/\text{m}^3$ (mean $1560 \pm 2600\text{ pg}/\text{m}^3$), respectively, and the WHO-TEQ concentrations were $0.37\text{--}15.5\text{ pg}/\text{m}^3$ (mean $4.45 \pm 5.76\text{ pg}/\text{m}^3$)

Table 1
Sampling dates and basic information on the SeCu and SeAl plants investigated.

	Plant	Date of PAS deployment	Date of PAS harvest	Capacity/year (1000 t)	Fuel	Air pollution control system	Stack height (m)
SeCu	TY	23-Aug-2011	25-Oct-2011	100	Heavy oil	–	20
	CX	27-Apr-2011	28-Jun-2011	10	Heavy oil	Bag filters	15
	YD	25-Aug-2011	28-Oct-2011	200	Heavy oil	Bag filters	30
SeAl	SC	21-Apr-2011	22-Jun-2011	26	Natural gas	Cyclone + bag filters	10
	QY	25-Apr-2011	24-Jun-2011	180	Natural gas	Electrostatic precipitators	25

PAS = passive air sampler.

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