Estimation and Congener-Specific Characterization of Polychlorinated Naphthalene Emissions from Secondary Nonferrous Metallurgical Facilities in China

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Secondary nonferrous production is addressed as one of the potential sources of the unintentionally produced persistent organic pollutants (UP-POPs) due to the impurity of raw material. Although there are inventories of dioxin emissions from secondary nonferrous metallurgical facilities, release inventories of polychlorinated naphthalenes (PCNs) are scarce. This study selected typical secondary copper, aluminum, zinc, and lead plants to investigate the emissions of PCNs in secondary nonferrous production in China. The toxic equivalency (TEQ) emission factor for PCNs released to the environment is highest for secondary copper production, at 428.4 ng TEQ t⁻¹, followed by secondary aluminum, zinc, and lead production, at 142.8, 125.7, and 20.1 ng TEQ t⁻¹, respectively. PCNs released in secondary copper, aluminum, lead, and zinc production in China are estimated to be 0.86, 0.39, 0.009, and 0.01 g TEQ a⁻¹, respectively. Analysis of stack gas emission from secondary nonferrous production revealed that less-chlorinated PCNs are the dominant homologues, with mono- to tri-CN making the most important contributions to the concentration. However, for fly ash, the more highly chlorinated PCNs such as octa-CN are the dominant homologues.

Introduction

Polychlorinated naphthalenes (PCNs) are ubiquitous environmental pollutants that are structurally similar to polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). There are 75 possible congeners based on the naphthalene ring with one to eight chlorine atoms. It has been recognized that PCNs have dioxin-like toxicities due to their structural similarity (1, 2). PCNs have been used as ingredients in cable insulation, wood preservatives, engine oil additives, electroplate masking compounds, and dye production (3–5). The production and use of PCNs were banned in the United States and Europe in the 1980s owing to their toxicity and environmental persistence (5). However, PCNs can form as incineration byproducts, similar to PCDD/Fs and polychlorinated biphenyls (PCBs), and eventually be

released into the environment (6–8). The current interest in control measures to reduce PCN sources is not as great as the interest in measures to control PCDD/Fs and PCBs. The toxic emissions of PCNs from industrial sources should also be considered when evaluating treatment strategies for the control of unintentionally produced persistent organic pollutants (UP-POPs).

In recent years, there has been a growing demand for PCDD/F and PCB inventories, especially in the iron and steel metallurgy industries (9–12). Although some inventories of PCDD/F emissions from secondary nonferrous metallurgical facilities have been compiled (3), release inventories on PCNs are scarce. It is commonly considered that the formation mechanism of PCNs is rather similar to that of PCDD/Fs. Conditions that have been shown to promote the formation of PCDD/Fs include (i) the presence of elemental chlorine in raw materials such as polyvinyl chloride, (ii) raw materials including nonferrous metal that can catalyze UP-POP formation, and (iii) the proper temperature for the formation of UP-POPs being reached in steps of the smelting process (3, 13). Because these conditions are met in secondary nonferrous metallurgical facilities, they are generally considered to be potential sources of PCNs.

Although the smelting process in secondary nonferrous metallurgy is believed to be one of the pathways of the formation of PCNs, few data about PCN emissions by secondary nonferrous metallurgical facilities have been reported. As a part of the national UP-POP emission inventory, this study focuses on the PCN inventories for secondary copper, aluminum, zinc, and lead production in China. The combined production of these four secondary nonferrous metals was 5,295,000 t in 2007 (14). On the basis of a primary survey, 11 typical plants with end of pipe technologies were selected from secondary nonferrous metallurgical facilities in this study (see Table S1). The source-oriented method was adopted in the investigation of the emission of PCNs in secondary nonferrous production. The 2,3,7,8-tetrachlorinated dibenzo-p-dioxin toxic equivalencies (TEQs) of specific CN congeners in each sample were estimated according to relative potency factors (15). Concentrations and congener compositions of PCNs were individually analyzed by isotope dilution high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS). The total emission is calculated using the emission factors obtained from the selected plants and the total production of secondary nonferrous industries in China in 2007.

Experimental Section

In this study, a total of 33 stack gas and 22 fly ash samples were collected from 11 plants of secondary copper, aluminum, lead, and zinc recycling industries in China. For each plant, three stack gas samples and two fly ash samples were collected. The smelting process of secondary copper consists of feeding, oxidation, deoxidization, and casting in furnaces. Secondary aluminum production consists of feeding, fusion, content adjusting, treatment of aluminum liquid, and casting. The smelting process of secondary zinc production consists of feeding, melting, refining, and casting in a crucible. Finally, the smelting process of secondary lead production consists of feeding, fusion, deoxidation, content adjusting, treatment of liquid lead, and casting. Three samples of stack gas were collected during processes where PCNs might be unintentionally produced and emitted, and special attention was given to the feeding and melting steps of secondary nonfer-

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rous production because more organic components in these steps contain residual chlorine. Basic information on the smelting processes is given in Table S1 in the Supporting Information.

The stack gas samples were collected using an automatic isokinetic sampling system (TCR TECORA, Italy). The sampling point was set downstream of all air pollution control devices. Prior to collection, O₂, CO₂, and CO levels in the stack gas were measured using a GA-12 plus flue gas analyzer (Madur, Austria). Particles in the stack gas were trapped by a microfiber thimble filter (25 mm i.d., 90 mm length; Whatman International Ltd., Whatman, UK). Gases were cooled in a condensing system and then adsorbed in a trap with Amberlite XAD-2 resin (Supleco International Ltd., Varina, USA). Fly ash samples were collected from bag filters and/or quenching tower outlets during the stack gas sampling. Both the stack gas and fly ash samples were spiked with a mixture of ¹³C₁₀-labeled PCNs internal standards (¹³C₁₀-CN-27, -42, -52, -67, -73 and -75). The samples were selectively pretreated with 2 mol L⁻¹ HCl, and then subjected to Soxhlet extraction with toluene for 24 h. The extract was purified with a concentrated sulfuric acid gel column, multilayer silica gel column (from top to bottom: anhydrous sodium sulfate, 1 g of silica gel, 8 g of 44% silica gel–sulfuric acid, 1 g of silica gel, 5 g of 33% silica gel–sodium hydroxide, 1 g of silica gel, 2 g of 10% AgNO₃ silica gel, 1 g of silica gel), and basic alumina column. Before HRGC/HRMS analysis, the samples were spiked separately with ¹³C₁₀-labeled PCN recovery standards (¹³C₁₀-CN-64). All pesticide-grade solvents were purchased from Fisher Company (Thermo Fisher, USA). PCN standards, including ¹³C₁₀-labeled standards, were purchased from Cambridge Isotope Laboratories (Cambridge, USA). The parameters of the HRGC/HRMS analysis were as follows. PCNs were analyzed using a gas chromatograph coupled with a DFS mass spectrometer (Thermo Fisher Scientific, USA) with an electron impact ion source. The HRMS was operated in selected ion monitoring mode with a resolution greater than 10,000. A 1 μL quantity of sample solution was injected with an autosampler in the splitless mode. A DB-5 fused silica capillary column (60 m × 0.25 mm i.d. × 0.25 μm) was used for the separation of PCN congeners. The electron emission energy was set to 45 eV. The source temperature was 270 °C. The column temperature was initially 80 °C (for 2 min) and increased to 180 °C (for 1 min) at 20 °C/min, 280 °C at 2.5 °C/min, and 290 °C (for 5 min) at 10 °C/min. The carrier gas was helium with a flow rate of 1 mL min⁻¹.

In this study, the detection limits and quantification limits were defined as 3 and 10 times the signal-to-noise ratio, respectively. ¹³C₁₀-labeled PCN internal standards and recovery standard were used for the assurance of analytical recovery. Detailed data of the quality control are given in Tables S2–S4 in the SI.

Principal component analysis using SPSS for Windows Release 13.0 (SPSS Inc.) was applied to evaluate the distribution pattern of PCNs in this study.

Results and Discussion

Concentration of PCNs Released from the Secondary Nonferrous Metallurgical Facilities. The concentrations of PCNs in stack gas and fly ash of secondary nonferrous metallurgical facilities are given in Table 1. Concentrations varied considerably among different metallurgies and also among different plants for a given metal. Among the four types of metallurgy, the highest concentration of PCNs in stack gas samples came from the secondary zinc plant (8021 ng Nm⁻³). Investigations of unintentionally released PCNs have been very limited. Existing studies mainly focused on the emission of PCNs from waste incineration. For example, Abad et al. (7) assessed the release of PCNs from five

TABLE 1. Concentrations and TEQs of PCNs in Stack Gas and Fly Ash Released from the Secondary Nonferrous Metallurgical Facilities

	stack gas		fly ash	
	ng Nm ⁻³	ng TEQ Nm ⁻³	ng TEQ g ⁻¹	ng g ⁻¹
Al 1	98.9	0.03	4.41	6.9
Al 2	185	0.007	52	91.6
Al 3	333	0.01	3.78	16.8
Al 4	2245	0.05	852	6000
Cu 1	712	0.05	622	1097
Cu 2	56.2	0.002	125	267
Cu 3	41.3	0.0008	1349	2726
Cu 4	1107	0.3	3211	20830
Cu 5	79	0.006	0.15	9.5
Zn	8021	0.28	54	2670
Pb	887	0.01	0.29	2.3

municipal solid waste incinerators and found that the levels of total PCNs (mono- to octachlorinated) varied from 1.08 to 21.36 ng Nm⁻³. The concentrations of PCNs emitted during secondary metal smelting were higher than those of municipal waste incineration.

The patterns of PCNs in stack gas and fly ash of secondary nonferrous metallurgical facilities are shown in Figure 1. The stack gas congener patterns of aluminum plant 1 and copper plant 4 have relatively even distributions. However, for each of the remaining plants investigated, the stack gas congener patterns are dominated by the lower chlorinated homologues, particularly mono- to tetra-CN.

The PCN homologues in fly ash of secondary nonferrous metallurgical facilities distributed evenly for secondary aluminum and copper plants 1 through 3. However, PCN congener profiles in the fly ash for the remaining facilities were dominated by octa-CN.

A relatively consistent difference between the homologue distributions in solid phase and gas phase was observed. In stack gas, the lower chlorination PCNs are the dominant homologues, with mono- to tri-CN making the most important contributions to the concentration. However, for fly ash, the higher chlorination PCNs, like octa-CN, are the dominant homologues. This result is similar to the pattern of PCBs in stack gas released from the secondary nonferrous metallurgical facilities, which are dominated by mono- to di-CBs. The pattern of PCNs released from the secondary nonferrous metallurgical facilities differs from that of PCDD/Fs. The PCDD/F pattern is dominated by higher chlorination homologues for secondary copper, aluminum, and lead plants. Secondary zinc is the exception however, as its profile is dominated by tetra-CD/Fs (16, 17).

The primary aims of principal component analysis are to evaluate the distribution pattern and determine possible groupings with similar emissions characteristics among the plants in this study. The homologues from mono-CN to octa-CN were selected as variables for principal component analysis. On the basis of extraction sums of squared loadings, two components were selected, which together accounted for 97.7% of the squared loading.

As shown in Figure 2, the first principal component (PC1) has higher loading for homologue mono- to hexa-CN than PC2, while PC2 has higher loading for homologue hepta- to octa-CN than PC1. Thus PC1 and PC2 are aggregative indicators of the homologues mono- to hexa-CN and hepta- to octa-CN, respectively.

The principal component scores for each plant are displayed in Figure 3. The plants were divided into three groups on the basis of component scores: (1) secondary zinc plants, (2) secondary copper plant 4, and (3) all other plants. Secondary zinc has the highest PC1 score and lower

FIGURE 1. PCN homologue profiles in stack gas (a) and fly ash (b) of secondary nonferrous metallurgical facilities.

PC2 score, indicating that the pattern is dominated by the lower chlorination homologues. In contrast, the secondary copper plant 4 has the highest PC2 score and lower PC1 score, indicating that the pattern is dominated by higher chlorination homologues. The third group of plants can be divided into three subgroups on the basis of similar properties: (1) secondary aluminum plant 4, secondary copper plant 1, and the secondary lead plant, which are all similar to the secondary zinc plant in that they have higher PC1 scores than PC2 scores, (2) secondary aluminum plant 1, which is similar to secondary copper plant 4, and (3) all other plants, which have similar PC1 and PC2 scores, indicating no significant difference between contributions of higher and lower chlorination homologues for these plants.

TEQ of PCNs in Stack Gas and Fly Ash from the Secondary Nonferrous Metallurgical Facilities. Table 1 shows the TEQ of PCN levels in stack gas and fly ash samples collected from the secondary nonferrous plants. The TEQ of stack gas and fly ash released from secondary copper plant 4 is higher than that of any other secondary nonferrous production plant.

The TEQ patterns of PCN congeners in stack gas and fly ash are shown in Figure 4. The stack gas congener abundance patterns are quite different among plants from the different secondary nonferrous metallurgical facilities. The most abundant congeners in stack gas from the secondary aluminum, copper, lead, and zinc plants are CN-73 (30.6%), CN-73 (44.6%), CN-2 (39%) and CN-66/67 (59.1%) respectively. In contrast, the TEQ patterns of PCN congeners in fly ash samples are quite similar; CN-66/67 and CN-73 are the main contributors for all four types of metallurgy.

Estimation of PCN Emission Factors and Total Release from Secondary Nonferrous Metallurgical Facilities in China. The following three equations were used to calculate the emission factors and total release of PCNs.

$$\begin{aligned} &\text{Emission factor of stack gas in concentration (ng/ton)} \\ &= \text{Concentration of PCNs (ng/m}^3\text{)} \times \\ &\quad \frac{\text{Dry stack gas flow rate (m}^3\text{)}}{\text{Metal production (ton)}} \end{aligned} \quad (1)$$

Emission factor of stack gas in TEQ (ng TEQ/ton)

= TEQ of PCNs (ng TEQ/m³) ×

$\frac{\text{Dry stack gas flow rate (m}^3\text{)}}{\text{Metal production (ton)}}$

(2)

Total Emission amount (g TEQ/year)

= Emission factor (ng TEQ/ton) ×

activity level of reference year (ton/year)

(3)

The emission factors of the stack gas concentration and TEQ for secondary nonferrous metallurgical facilities in China were calculated using eqs 1 and 2, respectively. The data are presented in Table 2. The results vary among different types of metallurgy and also among different plants for a given metal.

The PCN emission factors of the stack gas concentration of aluminum plants 1–4 are 575, 835, 1306, and 13,610 $\mu\text{g t}^{-1}$, respectively. The differences may be due to the differences in raw materials. The raw material of aluminum plant 1 is mainly waste aluminum profile with small amounts of organic impurities. The raw materials of the other three plants are waste aluminum profile and crushed vehicle material with a higher content of organic impurities to different degree. When the technological processes for aluminum plants are similar, the high content of organic impurities in raw materials corresponds to a high PCN emission factor for stack gas. The raw material also affects the congener patterns. As shown in Figure 1, the pattern of aluminum plant 1 has an even distribution, while the patterns of aluminum plants 2–4 are dominated by lower chlorination congeners like 1-MoCN,

FIGURE 2. Loading plot of PC1 and PC2 for PCN principal component matrix.

FIGURE 3. Score plot of PCA for the secondary nonferrous metallurgical facilities.

FIGURE 4. TEQ congener patterns of PCNs in stack gas (a) and fly ash (b) from the secondary nonferrous metallurgical facilities.

TABLE 2. Emission Factors of PCNs in Concentration and TEQ for the Secondary Nonferrous Metallurgical Facilities

	emission factors	
	$\mu\text{g t}^{-1}$	ng TEQ t^{-1}
Al 1	575	182
Al 2	835	33.8
Al 3	1,306	39.8
Al 4	13,610	316
Cu 1	624	44.4
Cu 2	246	8.2
Cu 3	141	2.8
Cu 4	7,014	1989
Cu 5	1,237	96.9
Zn	3,431	126
Pb	1,336	20.1

2-MoCN, 1,2-DiCN, 1,4,6/1,2,4-TiCN, and 1,2,5,7/1,2,4,6/1,2,4,7-TeCN.

The PCN emission factors of stack gas concentration of copper plants 1–5 are 624, 246, 141, 7014, and 1237 $\mu\text{g t}^{-1}$, respectively. The raw material of copper plants 1–3 has a

higher content of copper scrap than copper plants 4–5 and the raw material of copper plants 4–5 contains many impurities of oil and enameled wire. The difference in raw material leads to a lower concentration of PCN emission from copper plants 1–3 than from copper plants 4–5. The air pollution control technology of copper plant 5 is more advanced than the technology of the other copper plants. Copper plant 5 has a tilting furnace for smelting and after-combustion chamber for the purification of exhaust gas. Although the raw material composition of copper plant 5 is complex, the concentration of PCNs in emissions is relatively low. As shown in Figure 1, the pattern of copper plant 4 is dominated by 1,2,3,4,5,6,8-HpCN and octa-CN, and the congener patterns of copper plants 1–3 are dominated by lower chlorination homologues mono-CN, di-CN, and tri-CN. It seems that the high emission factor of the PCN concentration at copper plants corresponds to the dominance of a higher chlorination homologue, which is opposite from the case for aluminum plants.

The mean TEQ emission factors for PCNs are presented in Table 3. The mean emission factor is highest for secondary copper production at 428.4 ng TEQ t^{-1} . For secondary

TABLE 3. Average Emission Factors and Total PCN Release from the Secondary Nonferrous Metallurgical Facilities

	emission factor (ng TEQ t ⁻¹)	production level (thousand t a ⁻¹)	total emissions (g TEQ a ⁻¹)
Al	142.8	2,750	0.39
Cu	428.4	2,000	0.86
Pb	20.1	450	0.009
Zn	125.7	96	0.01
total		5,296	1.27

aluminum, lead, and zinc production, the mean emission factors are 142.8, 20.1, and 125.7 ng TEQ t⁻¹, respectively.

The total emission amounts of PCNs released to air can be determined using mean emission factors and the total production level of secondary nonferrous industries in China in 2007, according to eq 3. The data are summarized in Table 3. Secondary copper production has the highest emission amount at 0.86 g TEQ a⁻¹. The PCNs released from secondary aluminum, lead, and zinc production are 0.39, 0.009, and 0.01 g TEQ a⁻¹, respectively. These values are much lower than emission amounts of PCDD/Fs for 4 types of metallurgy facilities, but slightly higher than emission of dioxin-like PCBs released from Cu and Al facilities in former studies (16, 17). However, there might be uncertainties in evaluating the PCN emission from secondary zinc and lead production on the basis of the results for one investigated plant. Much intensive investigation on PCN emissions from secondary zinc and lead production is needed.

In a secondary nonferrous plant, fly ash is recycled to recover residual metal, and the final emission in fly ash per ton of product is therefore very small. As a result, although the TEQs are higher for fly ash than for stack gas, the emission factors of fly ash are somewhat less than those of stack gas and were not calculated in this study. The values in Table 3 can thereby be considered as total emission amounts of PCNs released to the environment. The total emissions estimated from emission factors developed in this study are based on data from large- and medium-sized companies that use necessary pollution control equipment. Smaller secondary nonferrous plants in China are usually equipped with simple and crude devices for pollution control and thus could not fulfill the requirements of isokinetic sampling. It is speculated that the emission factors for smaller plants are higher than those summarized in this study. Therefore, the reported values may be considered as the minimum PCN emissions released from secondary nonferrous metallurgical facilities in China in 2007.

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Note Added after ASAP Publication

This paper published ASAP March 4, 2010 noting incorrect units in the fly ash sample column of Table 1; the corrected version published ASAP March 10, 2010.

Supporting Information Available

Additional data tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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