Identifying Iron Foundries as a New Source of Unintentional Polychlorinated Naphthalenes and Characterizing Their Emission Profiles

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S Supporting Information

ABSTRACT: Iron foundries have been identified as dioxin sources in previous field investigations. Similar formation mechanisms between dioxins and unintentional polychlorinated naphthalenes (PCNs) have led us to speculate that iron foundries are also potential PCN sources. In this study, PCNs in stack gas and fly ash samples representing atmospheric and residue emissions from 13 typical iron foundry plants were analyzed. The average emission factor of $\sum_{2-8}$ PCNs to residue was calculated to be $61 \mu\text{g t}^{-1}$, with a range of $10\text{--}107 \mu\text{g t}^{-1}$. The emission factors of $\sum_{2-8}$ PCNs to air in two case plants were 267 and $1472 \mu\text{g t}^{-1}$. The derived emission factors might be useful for estimating annual emissions and understanding the contribution of PCNs from iron foundries. The possible formation mechanisms of PCNs, based on the PCN profiles, are discussed. Successive reductions in the abundance of homologues were observed to occur with the increase in chlorine substituted numbers. Abundances of congeners containing more β -position chlorines in the naphthalene skeleton were much higher than those of congeners containing more α -position chlorines for penta-, hexa-, and hepta- homologues, which suggests that the β -positions are favored for chlorination. Potential chlorination pathways from tetra- to octa- homologues are proposed.

INTRODUCTION

Polychlorinated naphthalenes (PCNs), which have a similar structure (Figure 1) and toxicity to polychlorinated dibenzo-p-

Figure 1. PCN structure, with the α and β positions and carbon atom numbers indicated.⁷

dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyl (dl-PCBs), are ubiquitous persistent organic pollutants (POPs).^{1–3} Studies associated with the comparison of PCNs, PCDDs, PCDFs, and dl-PCBs in environmental matrices, biota, and human samples from some areas have suggested that PCNs might have toxic equivalents (TEQs) comparable to or even higher than PCDDs, PCDFs, and dl-PCBs.^{4–6} Moreover, the POP review committee (POPRC) has reviewed PCNs according to the screening criteria in Annex D covered under the Stockholm Convention on POPs. The POPRC concluded that di- to octachlorinated homologues of

PCNs meet the screening criteria of POPs, and has therefore listed PCNs as candidate POPs for eliminating their unintentional emissions and banning their manufacture and use in technical formulations.

The manufacture and use of technical PCN formulations has almost ceased globally, while industrial activities, including waste incineration and metal smelting, are widely considered to be the current important sources of unintentional PCNs into air.^{7,8} Metal smelting industries are considered to be much more important sources of unintentional POPs than before, and their relative importance is considered to be higher than that of waste incineration.^{9,10} Some widely recognized smelting sources of unintentional POPs, including iron ore sintering, electric arc furnaces for steel making, and secondary nonferrous smelting processes, have been investigated for PCN emissions.^{11–14} However, for some important industries with intensive activities in developing countries, there are still no available data or knowledge about emission levels and profiles of PCNs.

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Table 1. Basic Information on Iron Foundries,¹⁵ Concentrations, and Emission Factors of PCNs in Stack Gas and Fly Ash Samples

plant denotation	cupola furnace	raw material	APCS	annual capacity (10 ³ t)	ash output (t year ⁻¹)	release route	mass concn (pg g ⁻¹ or pg m ⁻³)	TEQ concn (pg TEQ g ⁻¹ or pg TEQ m ⁻³)	mass emission factor (μg t ⁻¹)	TEQ emission factor (ng TEQ t ⁻¹)
DJ	hot air cupola	iron ore lump	fabric filter	50	3750	fly ash	980	0.02	73.5	1.51
DX	hot air cupola	sinter	fabric filter	200	10000	fly ash	1122	0.05	56.1	2.34
EF	cold air cupola	scrap	fabric filter	7	108	fly ash	665	0.05	10.3	0.84
						stack gas	7339	0.49	267	17.8
ER	hot air cupola	scrap	fabric filter	30	340	fly ash	2205	0.07	25	0.81
GF	hot air cupola	iron ore lump	fabric filter	60	4000	fly ash	1379	0.01	92.7	0.98
JY	hot air cupola	scrap	cyclone	27	1000	fly ash	1649	0.03	61.1	0.95
LF	cold air cupola	scrap	wet scrubber	18	280	stack gas	104445	1.90	1472	26.8
ME	hot air cupola	iron ore lump	fabric filter	20	1020	fly ash	2108	0.04	108	1.86
MY	hot air cupola	scrap	wet scrubber	11	360	fly ash	1649	0.03	54	0.84
QZ	hot air cupola	scrap	no APCS	1	36	fly ash	1501	0.05	54	1.83
YL	cold air cupola	scrap	fabric filter	30	349	fly ash	6910	0.75	80.4	8.78
YR	hot air cupola	scrap	fabric filter	62	720	fly ash	2130	0.14	24.7	1.57
ZW	cold air cupola	scrap	fabric filter	12	150	fly ash	7664	1.04	92.7	12.6

Identifying potential sources of unintentional PCNs is the essential primary step for evaluating source priority and implementing emission controls. Thus, it is important to identify potential industrial sources, particularly from industries with intensive activities in developing countries, and to estimate and characterize their PCN emissions.

Iron foundry is an important industry in China. There are several thousand iron foundries of different scales, employing different techniques in China. The annual production of cast iron from these plants accounted for about 30% of world production.¹⁵ Thus, the investigation of PCN emissions from Chinese iron foundries will likely be important for the preliminary estimation of total global PCN emissions. In our previous study, an intensive investigation of 14 plants of different scales and employing different techniques was carried out to estimate and characterize the emission levels and profiles of PCDD/Fs and dl-PCBs from Chinese iron foundries. Co-occurrence and similar formation mechanism between PCNs and PCDD/Fs have been reported.^{16–18} Thus, we speculate that iron foundries might also be important potential sources of PCNs. However, there are still no available data or knowledge about PCN levels, profiles, and emission factors from iron foundries to date.

In this study, stack gas and fly ash samples representing atmospheric and residue emissions collected from 13 of the plants used in our previous study¹⁵ were analyzed for PCNs by isotopic dilution high-resolution gas chromatography combined with a high-resolution mass spectrometer (HRGC/HRMS) technique. To our knowledge, this is the first intensive investigation of PCN emission concentrations, profiles, and emission factors from the iron foundry industry, which is potentially important for recognizing this new source of PCNs, for estimating and characterizing emission levels and profiles, and

for the development of an emission inventory of unintentional PCNs from industrial thermal sources.

■ EXPERIMENTAL SECTION

Information on the Investigated Iron Foundry Plants.

Iron foundries in China normally adopt cupola furnaces for metal smelting and refining. By this method, metals or alloys are melted and prepared in a furnace, and molten metal is poured into the assembled mold, either via a ladle or directly from the furnace. When the metal has cooled, the mold and core material are removed and the casting is cleaned and dressed. A cupola furnace is a tall, vertical furnace, open at the top, with hinged doors at the bottom. It is charged from the top with alternate layers of coke, limestone, and metal; the molten metal is removed from the bottom. Air is blown through the charge from openings at the bottom, and the combustion of coke heats, melts, and purifies the iron.

It is widely recognized that the scale, raw materials, process technique, and air pollution control system (APCS) are important factors influencing the formation and emission of unintentional POPs during industrial thermal processes.^{19–21} Stack gas and fly ash samples normally represent the atmospheric and residue emissions of unintentional POPs from industrial thermal sources.^{13,22} Thus, 14 typical iron foundries were chosen for our previous study; plants were selected based on their scale, raw materials used, technique, and APCS, and stack gas and fly ash samples were analyzed to estimate and characterize the levels and profiles of PCDD/Fs and dl-PCBs in our previous study.¹⁵ At present, routine monitoring of PCNs, PCDD/Fs, and dl-PCBs is normally not required for iron foundries because no regulations on these compounds exist. Thus, the sampling point set in most of the iron foundry plants in China for monitoring common pollutants such as nitrogen and sulfur oxides is not

suitable for field sampling of stack gas using automatic isokinetic sampling equipment for monitoring dioxins and dioxin-like compounds. Finally, two iron foundry plants equipped with sampling points suitable for automatic isokinetic sampling by a TCR system (TECORA, Italy) were investigated for preliminarily evaluating stack gas emissions of unintentional POPs. Solid residue is evaluated as an important medium for POP emissions. Moreover, solid residue, especially for fly ash, has been widely recognized as an important matrix for promoting formation of unintentional POPs during industrial thermal processes.^{23,24} Thus, solid residue samples were collected for the evaluation of POP contamination from those iron foundries.

The annual capacity of the iron foundry plants investigated in our previous study ranged from 1 to 200 thousand tons.¹⁵ The furnaces normally adopted in China comprising hot air cupola and cold air cupola were involved in those investigated plants. The raw materials used in the investigated plants were iron ore lump, sinter, or scrap. The adopted APCS in the investigated plants were fabric filter, cyclone, or wet scrubber systems. A large amount of air was introduced into the APCS to cool the flue gas. The output volume of stack gases ranged from about 14 000–36 500 m³ t⁻¹ for the EF and LF case plants. One plant that is not equipped with any APCS was also included in the study. Basic information on the iron foundries was reported in our previous publication¹⁵ and is provided in Table 1. In this study, the stack gas and fly ash samples from those plants were analyzed by isotopic dilution HRGC/HRMS for the purpose of obtaining the emission concentrations, profiles, and emission factors of PCNs from iron foundries.

Sample Collection, Preparation, and Chemical Analysis of PCNs. An automatic isokinetic sampling system (TECORA) was used for the collection of stack gas samples in our previous studies.^{13,15,25} The sampling train was mainly composed of a heated probe, a filter box equipped with a quartz fiber filter, and a water-cooled XAD-2 adsorbent trap. The glass fiber filter was used to collect particle-bound pollutants, and XAD-2 adsorbent resin was used for trapping the vapor-phase contaminants. A detailed description of the collection of stack gas samples has been provided in previous publications.^{13,15,25} The fly ash samples were collected from fabric filter or cyclone filters, and filter cakes were collected from wet scrubbers. For the plant that has a cupola furnace not equipped with any APCS, the fugitive ash samples were collected from around the ground surface.¹⁵

PCNs were analyzed by isotope dilution HRGC/HRMS, which has been described previously.^{13,26} Briefly, the samples were spiked with known amounts of ¹³C₁₀-labeled PCN internal standards (catalog ECN-5102, containing ¹³C₁₀-1234-tetraCN, ¹³C₁₀-1357-tetraCN, ¹³C₁₀-12357-pentaCN, ¹³C₁₀-123567-hexaCN, ¹³C₁₀-1234567-heptaCN, and ¹³C₁₀-12345678-octaCN). For fly ash samples, samples were digested with 1 mol L⁻¹ hydrochloric acid, rinsed with deionized water, and dried completely before Soxhlet extraction. Those samples were then Soxhlet extracted for approximately 24 h. The extracts were concentrated, then subjected to column cleanups, including silica gel treated with 44% (by weight) sulfuric acid, multilayer silica gel columns, and basic alumina columns. The final extracts were reduced to about 20 μL and a ¹³C₁₀-123457-hexaCN injection standard (catalog ECN-5260; Cambridge Isotope Laboratories, Cambridge, MA, USA) was added prior to instrumental analysis. Peaks of congeners were identified based on retention time compared with available individual standards and ion ratios, and considering the elution order on the DB-5 column. Peaks were quantified if target/qualifier ion ratios were within 15% of

theoretical values. The recoveries of ¹³C₁₀-PCN internal standards relative to labeled injection standards in the samples were evaluated in this study. The recoveries of internal standards were 56–108% for ¹³C₁₀-1234-tetraCN, 51–112% for ¹³C₁₀-1357-tetraCN, 49–85% for ¹³C₁₀-12357-pentaCN, 69–121% for ¹³C₁₀-123567-hexaCN, 52–88% for ¹³C₁₀-1234567-heptaCN, and 35–62% for ¹³C₁₀-12345678-octaCN.

RESULTS AND DISCUSSION

Concentrations and TEQs of PCNs in Fly Ash and Stack Gas Samples. PCNs have been proposed to be included in the list of POPs covered under the Stockholm Convention. The POP review committee evaluated the properties of PCNs and concluded that the homologues from di- to octachlorinated naphthalenes meet the four main characteristics of POPs. Thus, the total PCNs ($\sum_{2-8}$ PCNs) were termed the sum of di- to octa-homologues in this study. As shown in Table 1, the concentration of $\sum_{2-8}$ PCNs in fly ash samples ranged from 665 to 7664 pg g⁻¹, with an average value ($\pm$ standard deviation) of 2497 $\pm$ 2297 pg g⁻¹. The median and geometric values of $\sum_{2-8}$ PCNs in fly ash samples were 1649 and 1896 pg g⁻¹, respectively. The concentrations of $\sum_{2-8}$ PCNs in the stack gas samples were converted to dry standard conditions (273 K and 101.3 kPa). The average concentrations of $\sum_{2-8}$ PCNs in stack gas samples were 7339 pg m⁻³ for the EF plant and 104 445 pg m⁻³ for the LF plant.

PCNs could induce aryl hydrocarbon receptor-mediated responses and thus display toxic mechanisms similar to those of dioxins.^{27,28} Toxic equivalent factors (TEFs) of several PCN congeners relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) have been studied.^{27–31} Noma et al. summarized the TEF of PCN congeners in 2004,³² and Falandysz et al. (2013) recently evaluated and updated the relative potency factors of PCN congeners relative to 2,3,7,8-TCDD.³³ In this study, the TEFs of several PCN congeners summarized by Noma et al.³² were used for the calculation of $\sum_{2-8}$ PCN TEQs for facilitating the comparison with other industrial sources reported in previous publications.^{11–13,25,34} The $\sum_{2-8}$ PCN TEQs in fly ash samples ranged from 0.01–1.04 pg TEQ g⁻¹, with an average value ($\pm$ standard deviation) of 0.19 $\pm$ 0.34 pg TEQ g⁻¹. The median and geometric values of $\sum_{2-8}$ PCN TEQs in fly ash samples were 0.05 and 0.07 pg TEQ g⁻¹, respectively. The average TEQs of $\sum_{2-8}$ PCNs in stack gas samples were 0.49 pg TEQ m⁻³ for the EF plant and 1.90 pg TEQ m⁻³ for the LF plant.

To our knowledge, this study is the first intensive investigation of the concentrations of PCNs in fly ash and stack gas samples from iron foundries, and no other published data on PCN levels from iron foundries are available for comparison. In our previous studies, we have investigated and reported PCN levels from metal smelting processes, including primary copper (5.8–253 ng m⁻³ in stack gas, 18.4–164 ng g⁻¹ in fly ash) and magnesium (2.5–93.4 ng m⁻³ in stack gas, 0.18–0.49 ng g⁻¹ in fly ash) smelting, secondary copper (41.3–1107 ng m⁻³ in stack gas, 9.5–20840 ng g⁻¹ in fly ash), aluminum (98.9–2245 ng m⁻³ in stack gas, 6.9–6000 ng g⁻¹ in fly ash), zinc (8021 ng m⁻³ in stack gas, 2670 ng g⁻¹ in fly ash), and lead (887 ng m⁻³ in stack gas, 2.3 ng g⁻¹ in fly ash) smelting, iron ore sintering (3–983 ng m⁻³ in stack gas), and electric arc furnace for steel-making processes (458–1099 ng m⁻³ in stack gas).^{11–14,35} The levels of PCNs in fly ash samples from iron foundries were far lower than those of secondary copper, aluminum, and zinc smelting processes, and were higher than those of primary magnesium smelting processes. In our previous investigation, we analyzed PCDD/

Fs in those samples.¹⁵ Although the mass concentrations of PCNs (7339–104 445 pg m⁻³ in stack gas, 665–7664 pg g⁻¹ in fly ash) were higher than those of PCDD/Fs (712–2619 pg m⁻³ in stack gas, 8.13–983 pg g⁻¹ in fly ash), the PCN TEQs (0.49–1.90 pg TEQ m⁻³ in stack gas, 0.01–1.04 pg TEQ g⁻¹ in fly ash) were far lower than those of PCDD/Fs (56.5–232 pg TEQ m⁻³ in stack gas, 1.83–57.6 pg TEQ g⁻¹ in fly ash) as a result of the much lower TEF of PCN congeners compared with those of PCDD/F congeners. The correlations between PCNs and PCDD/Fs produced from iron foundry processes were examined in this study (Supporting Information (SI) Figure S1). There were no significant correlations between PCNs and PCDDs observed for iron foundry processes. The correlation coefficients (R) between PCNs and PCDFs were about 0.7. The much closer correlation observed between PCNs and PCDFs than that observed between PCNs and PCDDs for iron foundry processes is in agreement with correlations reported for waste incineration processes.¹⁷

Raw materials, scale, and technique employed might be important factors influencing emissions of unintentional POPs during industrial thermal processes. The possible influences of raw materials, furnace types, and plant scales on PCN concentrations in fly ash samples were preliminarily discussed in this study. There were no significant correlations observed between plant scale and emission concentrations in fly ash samples for iron foundries in this study. The emission concentrations of PCNs were evaluated according to the classification of the furnace types and raw materials. The average concentration of PCNs in fly ash was 5080 pg g⁻¹ (geomean value 3278 pg g⁻¹; median 6910 pg g⁻¹; range 665–7664 pg g⁻¹) for plants using cold air cupola furnaces with scrap as raw materials; this was higher than the average concentration of plants using hot air cupola furnaces with scrap as raw materials, which had an average value of 1827 pg g⁻¹ (geomean value 1805 pg g⁻¹; median 1649 pg g⁻¹; range 1501–2205 pg g⁻¹). For plants with iron ore lump as raw materials using hot air cupola furnaces, the average concentration of PCNs in fly ash was 1489 pg g⁻¹ (geomean value 1418 pg g⁻¹; median 1379 pg g⁻¹; range 980–2108 pg g⁻¹). Thus, the preliminary comparison results show that the PCN concentrations in fly ash samples from iron foundries using scrap as raw materials were slightly higher than those of iron foundries using iron ore lump as raw materials when both types of plants used hot air cupola furnaces. The concentrations of PCNs in fly ash samples from the plants using sinter as raw materials were lower than the average values in fly ash samples of plants using scrap or iron ore lump as raw materials when all plants used hot air cupola furnaces. The possible occurrence of organic impurities in scrap might be an important factor contributing to the higher concentrations of PCNs in fly ash from plants using scrap as raw materials. However, further simulation studies are needed to clarify the underlying factors influencing PCN emission levels.

Homologue Distribution and Congener Profiles of PCNs in Stack Gas and Fly Ash Samples. Homologue distribution and congener profiles of PCNs might provide useful information for understanding the formation mechanism of PCNs. In this study, the homologue concentrations were normalized to the $\sum_{2-8}$ PCN, and the PCN homologue distributions in the fly ash and stack gas samples from iron foundries are shown in Figure 2. As shown in Figure 2, the homologue patterns were dominated by the trichlorinated homologues, followed by the di- and tetrachlorinated homologues. Generally, successive reductions of homologues (through

Figure 2. Homologue profiles of PCNs in stack gas and fly ash samples.

tri- to octa- homologues) were observed to occur with the increase in chlorine substituted numbers, which indicates that chlorination might be an important pathway for PCN formation. The homologue distributions of PCNs between fly ash and stack gas emissions were very similar, indicating possible similar formation mechanisms of PCNs in both fly ash and stack gas phases.

The concentrations of PCN congeners were expressed as the fractions of their corresponding homologue concentrations to obtain a clear comparison of congener abundances in respective homologues. The PCN patterns in stack gas from EF and LF foundry plants are compared in SI Figure S2. Although the difference in concentrations between EF and LF plants was large, the PCN patterns in stack gas from the two plants were generally similar (SI Figure S2). Hierarchical cluster analysis (HCA) has been widely used to compare congener patterns between dioxins and dioxin-like compounds.^{11,17} In this study, HCA was adopted to cluster the fly ash samples based on the PCN congener profiles. Three clusters of fly ash samples were obtained (SI Figure S3). The average PCN profiles of each cluster are presented in SI Figure S4. The fractions of 14/16-DiCN and 145-TiCN in cluster 1 were higher than those in clusters 2 and 3. For the tetra-homologue, the fractions of 1368/1256-, 1234-, and 1267-TeCN in cluster 3 were higher than those in clusters 1 and 2, while the fractions of 2367/1248-, 1258/1268-, and 1458-TeCN, in cluster 3 were lower than those in clusters 1 and 2. The congener fractions of 12356- and 12367-PeCN in cluster 3 were higher than those in clusters 1 and 2. The fractions of 12358/12368- and 12345-PeCN in cluster 3 were lower than those in clusters 1 and 2, while for hexa- and hepta- homologues, the congener profiles were similar among the three clusters.

The average congener profiles are shown in Figure 3. As shown in the figure, the lower chlorinated homologues displayed relatively even isomer distribution patterns. The formation of several 18- and 128-congeners indicate that the chlorination of α -positions of the naphthalene ring were thermodynamically unfavorable;³⁶ these congeners were also found in very low abundances in samples from waste incineration under normal combustion conditions.³⁷ In this study, the abundances of 18- and 128-congeners in iron foundry processes were very low. For the tetraCN homologue, congeners comprising 1257/1246/1247-, 1467-, 1368/1256-, 1234-, and 1267-chlorinated congeners were dominant over other congeners in both fly ash and stack gas emissions. Those congeners are substituted by two β - and two α -position chlorines with the exception of the 1267-congener with three β - and one α -position chlorines. With the successive chlorination of PCNs, the abundances of congeners

Figure 3. Profiles of PCN congeners relative to their corresponding homologues.

with more β -position chlorines were much higher than those of congeners with more α -position chlorines, suggesting that β -positions are more favored for chlorination than α -positions in PCN formation during iron-casting processes. For example, abundances of congeners composed of 12357/12467-, 12346-, 12356-, and 12367- (with three β -position chlorines) were much higher than abundances of congeners composed of 12457-, 12468-, 12456-, 12478-, and 12458- (with three α -position chlorines). Similar trends in congener abundance have also been observed for hexa- and hepta-homologues. Congeners of 123467/123567- with up to four β -position substituted chlorines were the most dominant in hexaCN. The abundance of congener 1234567- with four β -position chlorines was also much higher than the 1234568-congener with four α -position chlorines. The

relative abundances of the congeners in penta-, hexa-, and hepta-homologues unintentionally produced during iron-casting processes were also in good agreement with the stability estimate obtained by density functional theory.³⁶

Generally, the successive reductions in homologue fractions that occur with the increase in chlorine numbers were observed to begin from trichlorinated homologues and continue through octa-chlorinated homologues. Obviously favored chlorination at the β -position was observed to begin from tetra-chlorinated homologues. Based on the homologue distributions and congener profiles in stack gas and fly ash phases, we speculate that successive chlorination might be a dominant formation pathway of higher chlorinated homologues (from penta- to octa-homologues) during iron foundry processes. The possible chlorination pathways we propose for major congeners from tetra- to octa-homologues during iron foundry processes are shown in Figure 4. The congener profiles of PCNs between fly ash and stack gas emissions were generally similar for most congeners in tetra- to hepta-homologues, as shown in Figure 3. This phenomenon indicates that similar formation mechanisms might occur for higher chlorinated homologues in both fly ash and stack gas phases. The formation pathways of lower chlorinated homologues (from di- to tetra-) might be much more complex. Several studies by Kim et al. have indicated that mono- and dichlorophenols were important precursors for the formation of di-, tri-, and tetra-chlorinated naphthalenes.^{38–40} Formation of PCNs through specific polycyclic aromatic hydrocarbons (PAHs) isomers have also been confirmed by Weber et al.¹⁶ and Iino et al.⁴¹ Results of these studies indicate that, in addition to chlorination pathways, the formation of di- to tetra-homologues from some precursors, such as chlorophenols or specific PAHs, might also be important pathways during iron foundry processes.^{16,38–40} Although the PCN profiles were similar for most congeners between stack gas and fly ash samples, there were substantial differences observed between several congeners, especially for lower chlorinated congeners, including 145-, 124/146-, 127-triCN, and others. This might also indicate the occurrence of other formation pathways of PCNs besides chlorination during iron foundry processes.

Emission Factors and Preliminary Estimations of PCNs from Iron Foundries. The emission factor of contaminants is typically used for estimating total annual emissions and for establishing inventory based on limited data.^{25,26,42} The emission factor can be considered the emission rate of PCNs relative to the intensity of iron foundry activities. The emission factor of PCNs in residue and stack gas for the investigated iron foundries was derived using the following equations:^{25,26,42}

Emission factor by fly ash

$$= \text{concentration} \times \text{amount of fly ash per ton of products} \quad (\text{eq 1})$$

Emission factor by stack gas

$$= (\text{concentration} \times \text{flow rate of stack gas}) \div \text{output rate} \quad (\text{eq 2})$$

The mass emission factors of $\sum_{2-8}$ PCNs in fly ash from the investigated iron foundry plants ranged from 10–107 $\mu\text{g t}^{-1}$, with an average value ($\pm$ standard deviation) of $61 \pm 30 \mu\text{g t}^{-1}$. The median and geometric mean values of emission factors of $\sum_{2-8}$ PCNs in fly ash samples were 59 and 51 $\mu\text{g t}^{-1}$, respectively. The average emission factors of $\sum_{2-8}$ PCNs in stack gas samples were 267 $\mu\text{g t}^{-1}$ for the EF plant and 1472 $\mu\text{g t}^{-1}$ for the LF plant. The TEQ

Figure 4. Proposed possible chlorination pathways for major congeners through tetra- to octa- homologues during iron foundry processes. The data shown in parentheses are the percentages of congeners relative to their respective homologues. The superscript indicates the unresolved congeners on DB-5 column and the corresponding data in the parentheses indicate the percentages of the coeluted congeners

emission factors of PCNs in fly ash from the investigated iron foundry plants were also derived and the values ranged from 0.81–12.6 ng TEQ t⁻¹ with an average value (±standard deviation) of 2.91 ± 3.75 ng TEQ t⁻¹. The median and geometric values of emission factors of $\sum_{2-8}$ PCN TEQs in fly ash samples were 1.54 and 1.79 ng TEQ t⁻¹, respectively. The average TEQ emission factors of $\sum_{2-8}$ PCNs in stack gas samples were 17.8 ng TEQ t⁻¹ for the EF plant and 26.8 ng TEQ t⁻¹ for the LF plant. The PCN emission factor from stack gas was higher than that from fly ash for the EF plant, while for PCDD/Fs, in some industrial thermal plants equipped with advanced APCS, the emission factors in stack gas were lower than those in fly ash. We speculate that the following factors may contribute to the converse trends observed between PCNs and PCDD/Fs. First, the different physicochemical properties of PCNs and PCDD/Fs, such as higher vapor pressure of PCNs than PCDD/Fs, might lead to a greater distribution of PCNs in the gas phase compared with PCDD/Fs. For example, the fraction of PCNs occurring in

the gas phase of air samples was higher than that of PCNs in the particle phase,^{43,44} while for PCDD/Fs, most were distributed in the particle phase.⁴⁵ Second, the absorption and removal efficiency of PCNs only through bag filters is potentially low; this observation has been made in waste incinerators.⁴⁶ It has also been observed that the absorption of activated carbon could decrease PCN emissions from waste incinerations.⁴⁶ For the EF iron foundry plant, no absorbent was used to control atmospheric emissions in this study, and the low absorbent and removal ability of only bag filters might lead to higher PCN emissions in stack gas than in fly ash.

The annual production from iron foundry plants with cupola furnaces in China was about 44.6 million tons in 2008.¹⁵ Average emission factors of PCNs by fly ash and stack gas emissions were adopted for preliminarily estimating the annual emissions of PCNs from iron foundry industries in this study. The annual total emissions of $\sum_{2-8}$ PCNs from Chinese iron foundry plants with cupola furnaces were preliminarily estimated to be about 2.7 kg

(0.13 g in TEQ) by fly ash and 39 kg (1 g in TEQ) by stack gas, which were far lower than the estimated annual emissions of PCDD/Fs from Chinese iron foundry plants with cupola furnaces (16.3 g TEQ by residue and 121 g TEQ by stack gas).¹⁵ The preliminary estimation indicated that PCN atmospheric emissions from iron foundries (995 mg TEQ) were lower than those of iron ore sintering industries (1390 mg TEQ), but higher than those of secondary nonferrous smelting industries (860, 390, 10, and 9 mg TEQ for secondary copper, aluminum, zinc, and lead smelting, respectively), primary magnesium smelting industries (16 mg TEQ), and coking industries (430–692 mg TEQ),⁷ indicating that emissions from iron foundries in China are relatively high. These derived emission factors and preliminary estimates of annual emissions of PCNs might be useful for understanding the contribution of iron foundries to PCN contamination. However, there might be uncertainties in estimating the emission factors and annual emissions of PCNs because of relatively small sample numbers, especially for stack gas emissions. Much more intensive investigations are needed to establish a comprehensive PCN emission inventory.

Emission factors of PCNs were also evaluated according to the furnace types and raw materials used. The average mass emission factors of PCNs were $44 \mu\text{g t}^{-1}$ (geomean value $41 \mu\text{g t}^{-1}$; median $54 \mu\text{g t}^{-1}$; range $25\text{--}61 \mu\text{g t}^{-1}$) for hot air cupola furnaces with scrap as raw materials, and $61 \mu\text{g t}^{-1}$ (geomean value $42 \mu\text{g t}^{-1}$; median $80 \mu\text{g t}^{-1}$; range $10\text{--}93 \mu\text{g t}^{-1}$) for cold air cupola furnaces with scrap as raw materials. This indicates that mass emission factors of PCNs in fly ash samples from cold air cupola furnaces were higher than those from hot air cupola furnaces; this finding is in agreement with the observed PCN concentrations in fly ash samples. The average mass emission factors of PCNs in fly ash were $91 \mu\text{g t}^{-1}$ (geomean value $90 \mu\text{g t}^{-1}$; median $93 \mu\text{g t}^{-1}$; range $74\text{--}107 \mu\text{g t}^{-1}$) for plants with iron ore lump as raw material using hot air cupola furnaces. The mass emission factors of PCNs in fly ash samples from iron foundries using iron ore lump as raw materials were higher than those of foundries using scrap as raw materials, which was in opposition to the findings on the influence of raw materials on PCN concentrations in fly ash samples. This phenomenon might be attributed to the larger amount of fly ash produced from plants using iron ore lump as raw materials than those that use scrap as raw materials.

■ ASSOCIATED CONTENT

■ Supporting Information

Table S1 and Figures S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Falandysz, J. Polychlorinated naphthalenes: An environmental update. *Environ. Pollut.* **1998**, *101*, 77–90.
- (2) Falandysz, J. Chloronaphthalenes as food-chain contaminants: A review. *Food Addit. Contam.* **2003**, *20*, 995–1014.
- (3) Falandysz, J.; Strandberg, B.; Strandberg, L.; Bergqvist, P. A.; Rappe, C. Concentrations and biomagnification of polychlorinated naphthalenes in black cormorants *Phalacrocorax carbo sinensis* from the Gulf of Gdansk, Baltic Sea. *Sci. Total Environ.* **1997**, *204*, 97–106.
- (4) Park, H.; Kang, J. H.; Baek, S. Y.; Chang, Y. S. Relative importance of polychlorinated naphthalenes compared to dioxins, and polychlorinated biphenyls in human serum from Korea: Contribution to TEQs and potential sources. *Environ. Pollut.* **2010**, *158*, 1420–1427.
- (5) Kannan, K.; Imagawa, T.; Blankenship, A. L.; Giesy, J. P. Isomer-specific analysis and toxic evaluation of polychlorinated naphthalenes in soil, sediment, and biota collected near the site of a former chlor-alkali plant. *Environ. Sci. Technol.* **1998**, *32*, 2507–2514.
- (6) Kannan, K.; Kober, J. L.; Kang, Y. S.; Masunaga, S.; Nakanishi, J.; Ostaszewski, A.; Giesy, J. P. Polychlorinated naphthalenes, biphenyls, dibenzo-p-dioxins, and dibenzofurans as well as polycyclic aromatic hydrocarbons and alkylphenols in sediment from the Detroit and Rouge Rivers, Michigan, USA. *Environ. Toxicol. Chem.* **2001**, *20*, 1878–1889.
- (7) Liu, G. R.; Cai, Z. W.; Zheng, M. H. Sources of unintentionally produced polychlorinated naphthalenes. *Chemosphere* **2014**, *94*, 1–12.
- (8) Falandysz, J.; Nose, K.; Ishikawa, Y.; Lukaszewicz, E.; Yamashita, N.; Noma, Y. HRGC/HRMS analysis of chloronaphthalenes in several batches of Halowax 1000, 1001, 1013, 1014 and 1099. *J. Environ. Sci. Health A* **2006**, *41*, 2237–2255.
- (9) Aries, E.; Anderson, D. R.; Fisher, R.; Fray, T. A. T.; Hemfrey, D. PCDD/F and “dioxin-like” PCB emissions from iron ore sintering plants in the UK. *Chemosphere* **2006**, *65*, 1470–1480.
- (10) Anderson, D. R.; Fisher, R. Sources of dioxins in the United Kingdom: The steel industry and other sources. *Chemosphere* **2002**, *46*, 371–381.
- (11) Liu, G. R.; Zheng, M. H.; Du, B.; Nie, Z. Q.; Zhang, B.; Liu, W. B.; Li, C.; Hu, J. C. Atmospheric emission of polychlorinated naphthalenes from iron ore sintering processes. *Chemosphere* **2012**, *89*, 467–472.
- (12) Liu, G. R.; Zheng, M. H.; Du, B.; Nie, Z. Q.; Zhang, B.; Hu, J. C.; Xiao, K. Identification and characterization of the atmospheric emission of polychlorinated naphthalenes from electric arc furnaces. *Environ. Sci. Pollut. Res.* **2012**, *19*, 3645–3650.
- (13) Ba, T.; Zheng, M. H.; Zhang, B.; Liu, W. B.; Su, G. J.; Liu, G. R.; Xiao, K. Estimation and congener-specific characterization of polychlorinated naphthalene emissions from secondary nonferrous metallurgical facilities in China. *Environ. Sci. Technol.* **2010**, *44*, 2441–2446.
- (14) Nie, Z. Q.; Liu, G. R.; Liu, W. B.; Zhang, B.; Zheng, M. H. Characterization and quantification of unintentional POP emissions from primary and secondary copper metallurgical processes in China. *Atmos. Environ.* **2012**, *57*, 109–115.
- (15) Lv, P.; Zheng, M. H.; Liu, G. R.; Liu, W. B.; Xiao, K. Estimation and characterization of PCDD/Fs and dioxin-like PCBs from Chinese iron foundries. *Chemosphere* **2011**, *82*, 759–763.
- (16) Weber, R.; Iino, F.; Imagawa, T.; Takeuchi, M.; Sakurai, T.; Sadakata, M. Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: Mechanistic aspects and correlation to fluidized bed incinerators. *Chemosphere* **2001**, *44*, 1429–1438.
- (17) Oh, J. E.; Gullett, B.; Ryan, S.; Touati, A. Mechanistic relationships among PCDDs/Fs, PCNs, PAHs, CIPhs, and CIBzs in municipal waste incineration. *Environ. Sci. Technol.* **2007**, *41*, 4705–4710.
- (18) Imagawa, T.; Lee, C. W. Correlation of polychlorinated naphthalenes with polychlorinated dibenzofurans formed from waste incineration. *Chemosphere* **2001**, *44*, 1511–1520.
- (19) Tuppurainen, K.; Asikainen, A.; Ruokojärvi, P.; Ruuskanen, J. Perspectives on the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during municipal solid waste (MSW) incineration and other combustion processes. *Acc. Chem. Res.* **2003**, *36*, 652–658.

- (20) Gullett, B.; Grandesso, E.; Touati, A.; Tabor, D. Effect of moisture, charge size, and chlorine concentration on PCDD/F emissions from simulated open burning of forest biomass. *Environ. Sci. Technol.* **2011**, *45*, 3887–3894.
- (21) Chi, K. H.; Chang, S. H.; Chang, M. B. Reduction of dioxin-like compound emissions from a Waelz plant with adsorbent injection and a dual baghouse filter system. *Environ. Sci. Technol.* **2008**, *42*, 2111–2117.
- (22) Fiedler, H. National PCDD/PCDF release inventories under the Stockholm convention on persistent organic pollutants. *Chemosphere* **2007**, *67*, S96–S108.
- (23) Cieplik, M. K.; De Jong, V.; Bozovic, J.; Liljelind, P.; Marklund, S.; Louw, R. Formation of dioxins from combustion micropollutants over MSWI fly ash. *Environ. Sci. Technol.* **2006**, *40*, 1263–1269.
- (24) Cains, P. W.; McCausland, L. J.; Fernandes, A. R.; Dyke, P. Polychlorinated dibenzo-p-dioxins and dibenzofurans formation in incineration: Effects of fly ash and carbon source. *Environ. Sci. Technol.* **1997**, *31*, 776–785.
- (25) Liu, G. R.; Zheng, M. H.; Lv, P.; Liu, W. B.; Wang, C. Z.; Zhang, B.; Xiao, K. Estimation and characterization of polychlorinated naphthalene emission from coking industries. *Environ. Sci. Technol.* **2010**, *44*, 8156–8161.
- (26) Liu, G. R.; Liu, W. B.; Cai, Z. W.; Zheng, M. H. Concentrations, profiles, and emission factors of unintentionally produced persistent organic pollutants in fly ash from coking processes. *J. Hazard. Mater.* **2013**, *261*, 421–426.
- (27) Blankenship, A. L.; Kannan, K.; Villalobos, S. A.; Villeneuve, D. L.; Falandysz, J.; Imagawa, T.; Jakobsson, E.; Giesy, J. P. Relative potencies of individual polychlorinated naphthalenes and halowax mixtures to induce Ah receptor-mediated responses. *Environ. Sci. Technol.* **2000**, *34*, 3153–3158.
- (28) Villeneuve, D. L.; Kannan, K.; Khim, J. S.; Falandysz, J.; Nikiforov, V. A.; Blankenship, A. L.; Giesy, J. P. Relative potencies of individual polychlorinated naphthalenes to induce dioxin-like responses in fish and mammalian in vitro bioassays. *Arch. Environ. Contam. Toxicol.* **2000**, *39*, 273–281.
- (29) Hanberg, A.; Waern, F.; Asplund, L.; Haglund, E.; Safe, S. Swedish Dioxin Survey - Determination of 2,3,7,8-TCDD toxic equivalent factors for some polychlorinated-biphenyls and naphthalenes using biological tests. *Chemosphere* **1990**, *20*, 1161–1164.
- (30) Behnisch, P. A.; Hosoe, K.; Sakai, S. Brominated dioxin-like compounds: In vitro assessment in comparison to classical dioxin-like compounds and other polyaromatic compounds. *Environ. Int.* **2003**, *29*, 861–877.
- (31) Kannan, K.; Yamashita, N.; Imagawa, T.; Decoen, W.; Khim, J. S.; Day, R. M.; Summer, C. L.; Giesy, J. P. Polychlorinated naphthalenes and polychlorinated biphenyls in fishes from Michigan waters including the Great Lakes. *Environ. Sci. Technol.* **2000**, *34*, 566–572.
- (32) Noma, Y.; Yamamoto, T.; Sakai, S. I. Congener-specific composition of polychlorinated naphthalenes, coplanar PCBs, dibenzo-p-dioxins, and dibenzofurans in the halowax series. *Environ. Sci. Technol.* **2004**, *38*, 1675–1680.
- (33) Falandysz, J.; Fernandes, A.; Gregoraszczuk, E.; Rose, M. Aryl hydrocarbon receptor mediated (dioxin-like) relative potency factors for chloronaphthalenes. *Organohalogen Compd.* **2013**, *75*, 336–338.
- (34) Nie, Z. Q.; Zheng, M. H.; Liu, G. R.; Liu, W. B.; Lv, P.; Zhang, B.; Su, G. J.; Gao, L. R.; Xiao, K. A preliminary investigation of unintentional POP emissions from thermal wire reclamation at industrial scrap metal recycling parks in China. *J. Hazard. Mater.* **2012**, *215*, 259–265.
- (35) Nie, Z. Q.; Zheng, M. H.; Liu, W. B.; Zhang, B.; Liu, G. R.; Su, G. J.; Lv, P.; Xiao, K. Estimation and characterization of PCDD/Fs, dl-PCBs, PCNs, HxCBz and PeCBz emissions from magnesium metallurgy facilities in China. *Chemosphere* **2011**, *85*, 1707–1712.
- (36) Zhai, Z. C.; Wang, Z. Y. Computational study on the relative stability and formation distribution of 76 polychlorinated naphthalene by density functional theory. *J. Mol. Struct.: THEOCHEM* **2005**, *724*, 221–227.
- (37) Jansson, S.; Fick, J.; Marklund, S. Formation and chlorination of polychlorinated naphthalenes (PCNs) in the post-combustion zone during MSW combustion. *Chemosphere* **2008**, *72*, 1138–1144.
- (38) Kim, D. H.; Mulholland, J. A. Temperature-dependent formation of polychlorinated naphthalenes and dihydrofurans from chlorophenols. *Environ. Sci. Technol.* **2005**, *39*, 5831–5836.
- (39) Kim, D. H.; Mulholland, J. A.; Ryu, J. Y. Formation of polychlorinated naphthalenes from chlorophenols. *Proc. Combust. Inst.* **2005**, *30*, 1245–1253.
- (40) Kim, D. H.; Mulholland, J. A.; Ryu, J. Y. Chlorinated naphthalene formation from the oxidation of dichlorophenols. *Chemosphere* **2007**, *67*, S135–S143.
- (41) Iino, F.; Imagawa, T.; Takeuchi, M.; Sadakata, M. De novo synthesis mechanism of polychlorinated dibenzofurans from polycyclic aromatic hydrocarbons and the characteristic isomers of polychlorinated naphthalenes. *Environ. Sci. Technol.* **1999**, *33*, 1038–1043.
- (42) Liu, G. R.; Zheng, M. H.; Liu, W. B.; Wang, C. Z.; Zhang, B.; Gao, L. R.; Su, G. J.; Xiao, K.; Lv, P. Atmospheric emission of PCDD/Fs, PCBs, hexachlorobenzene, and pentachlorobenzene from the coking industry. *Environ. Sci. Technol.* **2009**, *43*, 9196–9201.
- (43) Gregoris, E.; Argiriadis, E.; Vecchiato, M.; Zambon, S.; De Pieri, S.; Donato, A.; Contini, D.; Piazza, R.; Barbante, C.; Gambaro, A. Gas-particle distributions, sources and health effects of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) in Venice aerosols. *Sci. Total Environ.* **2014**, *476*, 393–405.
- (44) Odabasi, M.; Bayram, A.; Elbir, T.; Dumanoglu, Y.; Kara, M.; Altio, H.; Cetin, B. Investigation of seasonal variations and sources of atmospheric polychlorinated naphthalenes (PCNs) in an urban area. *Atmos. Pollut. Res.* **2012**, *3*, 477–484.
- (45) Li, Y. M.; Jiang, G. B.; Wang, Y. W.; Cai, Z. W.; Zhang, Q. H. Concentrations, profiles and gas-particle partitioning of polychlorinated dibenzo-p-dioxins and dibenzofurans in the ambient air of Beijing, China. *Atmos. Environ.* **2008**, *42*, 2037–2047.
- (46) Sakai, S.; Yamamoto, T.; Noma, Y.; Giraud, R. Formation and control of toxic polychlorinated compounds during incineration of wastes containing polychlorinated naphthalenes. *Environ. Sci. Technol.* **2006**, *40*, 2247–2253.