Identification and characterization of the atmospheric emission of polychlorinated naphthalenes from electric arc furnaces

Guorui Liu · Minghui Zheng · Bing Du · Zhiqiang Nie ·
Bing Zhang · Jicheng Hu · Ke Xiao

Received: 14 January 2012 / Accepted: 12 June 2012 / Published online: 26 June 2012
© Springer-Verlag 2012

Abstract Electric arc furnaces (EAF) are well recognized as significant sources of dioxins. EAFs have also been speculated to be sources of polychlorinated naphthalenes (PCNs) due to the close correlation between dioxin and PCN formation. However, assessment on PCN emissions from EAFs has not been carried out. The primary aim of this preliminary study is to identify and characterize the atmospheric emission of PCNs from EAFs. In this preliminary study, stack gas samples from two typical EAFs with different scales (EAF-1, 160 t batch⁻¹; and EAF-2, 60 t batch⁻¹) were collected by automatic isokinetic sampling technique, and PCN congeners in samples were analyzed by isotope dilution high-resolution gas chromatography combined with high-resolution mass spectrometry method. Emission concentrations of PCNs were 458 and 1,099 ng m⁻³ for EAF-1 and EAF-2, respectively. The emission factors of PCNs to air were 21.6 and 30.1 ng toxic equivalent t⁻¹ for EAF-1 and EAF-2, respectively, which suggested that EAF is an important source of PCN release. With regard to the characteristics

of PCNs from EAFs, lower chlorinated homologues were dominant. The PCN congeners comprised of CN27/30, CN52/60, CN66/67, and CN73 were the most abundant congeners for tetra-, penta-, hexa-, and hepta-chlorinated homologues, respectively. EAFs were identified to be an important PCN source, and the obtained data are useful for developing a PCN inventory. The congener profiles of PCNs presented here might provide helpful information for identifying the specific sources of PCNs emitted from EAFs.

Keywords Polychlorinated naphthalenes · Electric arc furnace · Emission factor · Emission characteristic · Emission inventory · Stockholm Convention

Introduction

Polychlorinated naphthalenes (PCNs) are often termed as dioxin-like compounds given their similar properties (Weber et al. 2008; Blankenship et al. 2000). PCNs have attracted increasing attention due to their ubiquitous occurrence in environmental matrices and biota (Harner et al. 2006; Bidleman et al. 2010). Several investigations on PCN levels in some typical areas have been carried out, and some of the results show that the toxic equivalents (TEQs) of PCNs are comparable to or even higher than that of dioxins (Kannan et al. 1998, 2001). PCN TEQs in some human serum samples have also been studied (Park et al. 2010), and results show that the levels are comparable to those of dioxins. PCNs have recently been proposed for inclusion in Annexes A, B, and/or C of the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP 2011), signifying that activities for controlling and reducing PCN emission may be obligatory in the near future.

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (doi:10.1007/s11356-012-1038-2) contains supplementary material, which is available to authorized users.

G. Liu · M. Zheng (✉) · B. Du · Z. Nie · B. Zhang · J. Hu ·
K. Xiao

State Key Laboratory of Environmental Chemistry and
Ecotoxicology, Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences,
P.O. Box 2871, Beijing 100085, China
e-mail: zhengmh@rcees.ac.cn

B. Du

State Environmental Protection Key Laboratory of Dioxin
Pollution, National Research Center for Environmental Analysis
and Measurement,
Beijing 100029, China

The unintentional formation and emission of PCNs from industrial activities are speculated to be the current main sources of these pollutants, considering that their manufacture and use as industrial chemicals have been avoided in many countries since the 1970s to 1980s (Hogarh et al. 2012). Thermal-related processes are widely recognized as main sources of dioxins and dioxin-like compounds today (Grochowalski et al. 2007). Emission factors and inventories have been established for dioxins and other POPs in many countries and regions (Fiedler 2007). Intensive investigations on the dioxin emissions from industrial sectors have been conducted, and iron ore sintering, steel making using electric arc furnaces (EAFs), secondary nonferrous smelting, and waste incineration have been identified as a major contributor to dioxin emissions. Some studies have confirmed the similar formation pathways of dioxins and PCNs during some thermal-related processes (Weber et al. 2001; Imagawa and Lee 2001). Hence, these industries may also be the current major sources of PCN emission. Therefore emission factors need to be developed for the developing of emission inventories and in the frame of the Stockholm Convention—if PCN will be listed—towards a global PCN inventory. In previous studies, emissions of PCNs from secondary nonferrous smelting, waste incineration, and other thermal-related processes have been identified and estimated (Ba et al. 2010; Liu et al. 2010; Jansson et al. 2008). Although EAFs have been confirmed to be a “hot spot” for POPs emission (Odabasi et al. 2009), PCN emission from EAFs used in steel making has not yet been identified and quantified.

Secondary steel making by the EAF technique is used in many countries worldwide and the production volumes are expected to increase considering the increasing material flows of iron. EAF secondary steel production is also extensively carried out in China. The annual output of steel produced by EAF has reached about 63.4 million tonnes in 2008. Thus, investigations on PCN emissions from Chinese EAFs may have significant implications in the evaluation of global PCN emission from EAFs. In the present preliminary investigation, stack gas samples from two typical EAFs with different scales were collected and analyzed for PCNs. The primary aims were to identify the atmospheric emission of PCNs, as well as to characterize the emission profiles of PCNs from EAFs.

Materials and methods

Information about investigated plants and sampling of stack gas

An EAF operates by a batch melting process producing batches of molten steel. The raw materials used by EAFs

mainly include steel scraps, pig iron, molten iron, and some additives. An EAF operating cycle comprises the following operations: furnace charging, melting, refining, deslagging, tapping, and furnace turnaround. The operation type is intermittent, and the duration for one batch is about 1 h. The scheme of the EAF and a detailed description of the process are provided in the “[Electronic supplementary material](#)”. In the current study, two typical EAFs (EAF-1 and EAF-2) with different scales were investigated to characterize the atmospheric emission of PCNs. The output rates were about 160 and 60 ton per batch (tonnes per batch) for EAF-1 and EAF-2, respectively. The former represents advanced and large-scale furnaces. The latter represents medium-sized furnaces. The flow rates of stack gas for EAF-1 and EAF-2 were 687,600 and 244,200 m³ h⁻¹, respectively. Bag filters were used as dust abatement for cleaning the stack gas for reduction of atmospheric emissions.

Stack gas samples for each plant were collected by an automatic isokinetic sampling technique. The sampling procedure of stack gas samples released from thermal-related processes has been described in detail in our previous studies (Ba et al. 2010; Liu et al. 2010). Briefly, the sampling system (TCR TECORA, Italy) consisted of a heated titanium probe, a filter box equipped with a quartz fiber filter and a water-cooled XAD-2 adsorbent trap, a pump, as well as a cooler. The quartz fiber filter and water-cooled XAD-2 adsorbent trap were used to collect particle-bound pollutants and vapor-phase contaminants, respectively. Three stack gas samples were collected for each furnace, and the volume of each sample was about 3 m³. The sampling time for each sample was about 3 h (covering about three sequential batches), which could well represent the general emission for the entire process.

Preparation and analysis of PCNs in stack gas samples

PCNs were analyzed by isotope dilution high-resolution gas chromatography (HRGC)/high-resolution mass spectrometry (HRMS). Detailed information on the sample extraction, cleanup, and instrumental analysis has been reported in our previous studies (Ba et al. 2010; Liu et al. 2010). The samples were spiked with a mixture of ¹³C₁₀-labeled PCN internal standards (ECN-5102, Tetra-Octa PCN Mixture comprising ¹³C₁₀-CN-27, -42, -52, -67, -73, and -75), and were then Soxhlet extracted with 250 mL of toluene for about 24 h. Subsequently, the sample extracts were concentrated and subjected to cleanups by multilayer silica gel and basic alumina columns. Finally, the extracts were concentrated to about 20 µL by a rotatory evaporation and a gentle nitrogen gas stream. Prior to injection, ¹³C₁₀-labeled PCN injection solutions (ECN-5260, ¹³C₁₀-CN-64) were added for the calculation of recoveries. PCN analysis was carried out using a HRGC system equipped with a DB-5 capillary

column (60 m×0.25 mm i.d.×0.25 µm) interfaced to a DFS HRMS (Thermo Fisher Scientific, USA). The HRMS was tuned and operated at around 10,000 resolution with an electron ionization energy of 45 eV. A selected ion monitoring mode was used for data acquisition.

Quality control and assurance

In the present study, the congeners were identified based on retention times compared with available individual standards and ion ratios. The elution order on the DB-5 column was also considered. Peaks were quantified if target/qualifier ion ratios were within 15 % of theoretical values. The relative standard deviations of PCN concentration and TEQ for three stack gas samples ranged from about 30 to 60 %. The recoveries of $^{13}\text{C}_{10}$ -labeled PCNs standards were between 42 and 103 %. The limits of detection (LODs) of PCNs ranged from 0.1 to 6.0 pg m⁻³. Blank experiments were carried out, and the concentrations of several congeners from monoCN and diCN in blank samples were higher than their LODs, but were far lower than 5 % of those in stack gas samples. Therefore, the PCN concentrations in stack gas samples were not corrected with the blank value.

Results and discussion

Concentrations, TEQ, and emission factor of PCNs from EAFs

The environmental burden and risk exposure associated with POPs surrounding industrial sources has attracted increasing attention. Investigations on the emission concentrations of pollutants from stationary sources may provide useful data for evaluating the influence of source emission on the surrounding environment (Schuhmacher and Domingo 2006). In this study, the emission concentrations of PCNs were 458 and 1,099 ng m⁻³ for EAF-1 and EAF-2, respectively. PCNs exhibit toxicological properties similar to dioxins, i.e., the ability to bind to and activate the aryl hydrocarbon receptor (Blankenship et al. 2000). There are currently no internationally accepted toxic equivalency factors (TEF) for PCNs. The TEF of several PCN congeners relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin have been reported (Noma et al. 2004). The toxic equivalents (TEQs) of PCNs were calculated according to the reported TEFs (Noma et al. 2004). The TEQs were 5.0 and 7.4 pg TEQ m⁻³ for EAF-1 and EAF-2, respectively, which is about two orders of magnitude lower compared to dioxin emission (160 and 560 pg I-TEQ m⁻³ for EAF-1 and EAF-2, respectively). Studies on PCN emissions have mainly focused on waste incineration, secondary metal smelting, magnesium smelting, and coking processes (Ba et al. 2010; Liu et al.

2010; Jansson et al. 2008; Nie et al. 2011). The concentrations of PCNs emitted from EAFs were generally comparable to those of reported waste incinerations and secondary metal smelting (Ba et al. 2010; Jansson et al. 2008), but were significantly higher than those of magnesium smelting and coking processes (Liu et al. 2010; Nie et al. 2011). The high emission concentrations of pollutants from stationary sources may contribute to the high-burden pollution in the surrounding environment. Thus, exposure to PCNs in environments surrounding EAFs should be a cause of concern.

Emission factor is an important parameter for estimating the pollutant emission from a given source. In our previous study, emission factors of PCNs from other metallurgical industries, such as those involved in secondary metal smelting, magnesium smelting, and coking processes, have also been reported in detail (Ba et al. 2010; Liu et al. 2010; Nie et al. 2011). The average emission factors of PCNs from secondary copper smelting, secondary aluminum smelting, secondary zinc smelting, secondary lead smelting, magnesium smelting, as well as coking processes were 428.4, 142.8, 125.7, 20.1, 412, and 1.0 ng TEQ t⁻¹, respectively.

In the present study, the emission factors of PCNs were derived to be 21.6 ng TEQ t⁻¹ (1970 µg t⁻¹) for EAF-1 and 30.1 ng TEQ t⁻¹ (4475 µg t⁻¹) for EAF-2, respectively. The emission amount of pollutants could be estimated from an emission factor by assuming a linear relation between the activity intensity and the emission resulting from this activity. Thus, these emission factors were useful for evaluating the emission of PCNs from EAFs. Combined with the emission factors of PCNs from other industries reported in previous publications, those results could be very helpful for developing a PCN inventory.

Homologue distribution and congener fingerprints of PCNs from EAFs

The concentrations of PCN homologues were normalized to the percentage of total PCNs to evaluate PCN patterns. The homologue profile of PCNs is presented in Fig. 1. PCNs were dominated by four homologues, i.e., (mono to tetra) chlorinated naphthalenes (CNs). The contributions of these homologues were comparable and together accounted for about 90 % of total PCNs. The degree of chlorination is normally used to indicate the distribution of chlorinated homologues. It is the sum of the percentages of the homologues multiplied by the numbers of substituted chlorines on the homologues. In the present study, the degrees of chlorination of PCNs were 2.0 and 2.4 for EAF-1 and EAF-2, respectively, which also indicated the dominance of lower chlorinated homologues of PCNs for EAFs. The degrees of chlorination of PCNs from other thermal-related processes, such as coking processes and municipal solid waste incineration, have also been reported (Jansson et al. 2008; Liu et

Fig. 1 Homologue profiles of PCNs emitted from EAFs

al. 2010). The chlorination degrees of PCNs for EAFs were comparable to that of other thermal-related processes,

indicating similar homologue distribution of PCNs for the thermal-related processes.

Fig. 2 Congener profiles of PCNs emitted from EAFs

The congener profiles of PCNs are useful for identifying specific PCN sources from emissions of thermal-related industries, or evaporative emissions of historical uses of industrial chemicals (such as Halowaxes) (Abad et al. 1999; Meijer et al. 2001; Schneider et al. 1998). For example, the fraction of CN1 is much higher than that of CN2 for Halowax mixtures, whereas for thermal-related sources, the fraction of CN2 is comparable to that of CN1. The ratios of CN73 to CN74 ($R_{CN73/CN74}$) vary in different source samples, with values lower than one in Halowaxes (Noma et al. 2004) and higher than one in stack gases or fly ash samples collected from thermal-related sources (Abad et al. 1999; Jansson et al. 2008). The dominance of CN52/60 and CN50 has been reported for thermal-related processes (Schneider et al. 1998). Congeners comprised of CN54 and CN66/67 are the most popular and relatively abundant indicators for waste incinerations (Meijer et al. 2001).

In the current study, to clarify the congener profiles of PCNs emitted from EAFs, the concentration of each congener was expressed as a fraction of the corresponding homologue concentration. This normalization minimized the influence of the concentrations of different PCN homologues and permitted a clear comparison of congener profiles (Du et al. 2010; Gullett et al. 2006). The congener profiles of PCNs are presented in Fig. 2. The fractions of CN1 were comparable to that of CN2 in monoCN. In diCN and triCN, CN3 and CN13 were the dominant congeners, respectively. In tetraCN, the fractions of CN37/33/34, CN45/36, and CN27/30 were much higher than that of other congeners. The highest fractions of CN52/60 in pentaCN and CN66/67 in hexaCN homologues were observed for EAFs. The ratios of CN73 to CN74 were also higher than one for EAFs. Generally, the congener profiles of PCNs emitted from EAFs were similar to those of other thermal-related processes, but obviously different from those of technical PCN mixtures. These congener profiles may provide more detailed PCN fingerprint information for identifying the sources of PCNs emitted from EAFs.

Conclusions

A preliminary investigation aimed at identifying and characterizing the atmospheric emission of PCNs from EAFs was carried out. Electric arc furnaces were identified to be an important PCN source. The emission factors were derived based on the obtained data, which provide useful data for developing a PCN inventory. However, much more intensive investigations were still needed for the development of robust emission factors of PCNs from global EAFs. With regard to the characteristics of PCNs, lower chlorinated homologues were dominant. The congener profiles of PCNs emitted from EAFs were similar to those of other

thermal-related processes, but were obviously different from those of technical PCN mixtures. These congener profiles may aid in identifying the specific sources of PCNs.

Acknowledgments Financial support for the present work was obtained from the National 973 Program (no. 2009CB421606) and the National Natural Science Foundation of China (nos. 21107123 and 21037003).

References

- Abad E, Caixach J, Rivera J (1999) Dioxin like compounds from municipal waste incinerator emissions: assessment of the presence of polychlorinated naphthalenes. *Chemosphere* 38:109–120
- Ba T, Zheng MH, Zhang B, Liu WB, Su GJ, Liu GR, Xiao K (2010) Estimation and congener-specific characterization of polychlorinated naphthalene emissions from secondary nonferrous metallurgical facilities in China. *Environ Sci Technol* 44:2441–2446
- Bidleman TF, Helm PA, Braune BM, Gabrielsen GW (2010) Polychlorinated naphthalenes in polar environments—a review. *Sci Total Environ* 408:2919–2935
- Blankenship AL, Kannan K, Villalobos SA, Villeneuve DL, Falandysz J, Imagawa T, Jakobsson E, Giesy JP (2000) Relative potencies of individual polychlorinated naphthalenes and halowax mixtures to induce Ah receptor-mediated responses. *Environ Sci Technol* 34:3153–3158
- Du B, Zheng MH, Tian HH, Liu AM, Huang YR, Li LL, Ba T, Li N, Ren Y, Li YW, Dong SP, Su GJ (2010) Occurrence and characteristics of polybrominated dibenzo-p-dioxins and dibenzofurans in stack gas emissions from industrial thermal processes. *Chemosphere* 80:1227–1233
- Fiedler H (2007) National PCDD/PCDF release inventories under the Stockholm convention on persistent organic pollutants. *Chemosphere* 67:S96–S108
- Grochowalski A, Lassen C, Holtzer M, Sadowski M, Hudyma T (2007) Determination of PCDDs, PCDFs, PCBs and HCB emissions from the metallurgical sector in Poland. *Environ Sci Pollut Res* 14:326–332
- Gullett BK, Touati A, Huwe J, Hakk H (2006) PCDD and PCDF emissions from simulated sugarcane field burning. *Environ Sci Technol* 40:6228–6234
- Harner T, Shoeib M, Gouin T, Blanchard P (2006) Polychlorinated naphthalenes in Great Lakes air: assessing spatial trends and combustion inputs using PUF disk passive air samplers. *Environ Sci Technol* 40:5333–5339
- Hogarh JN, Seike N, Kobara Y, Masunaga S (2012) Atmospheric polychlorinated naphthalenes in Ghana. *Environ Sci Technol* 46(5):2600–2606
- Imagawa T, Lee CW (2001) Correlation of polychlorinated naphthalenes with polychlorinated dibenzofurans formed from waste incineration. *Chemosphere* 44:1511–1520
- Jansson S, Fick J, Marklund S (2008) Formation and chlorination of polychlorinated naphthalenes (PCNs) in the post-combustion zone during MSW combustion. *Chemosphere* 72:1138–1144
- Kannan K, Imagawa T, Blankenship AL, Giesy JP (1998) 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* 32:2507–2514
- Kannan K, Kober JL, Kang YS, Masunaga S, Nakanishi J, Ostaszewski A, Giesy JP (2001) 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* 20:1878–1889

- Liu GR, Zheng MH, Lv P, Liu WB, Wang CZ, Zhang B, Xiao K (2010) Estimation and characterization of polychlorinated naphthalene emission from coking industries. *Environ Sci Technol* 44:8156–8161
- Meijer SN, Harner T, Helm PA, Halsall CJ, Johnston AE, Jones KC (2001) Polychlorinated naphthalenes in UK soils: time trends, markers of source, and equilibrium status. *Environ Sci Technol* 35:4205–4213
- Nie ZQ, Zheng MH, Liu WB, Zhang B, Liu GR, Su GJ, Lv P, Xiao K (2011) Estimation and characterization of PCDD/Fs, dl-PCBs, PCNs, HxCBz and PeCBz emissions from magnesium metallurgy facilities in China. *Chemosphere* 85:1707–1712
- Noma Y, Yamamoto T, Sakai SI (2004) Congener-specific composition of polychlorinated naphthalenes, coplanar PCBs, dibenzo-p-dioxins, and dibenzofurans in the halowax series. *Environ Sci Technol* 38:1675–1680
- Odabasi M, Bayram A, Elbir T, Seyfioglu R, Dumanoglu Y, Bozlaker A, Demircioglu H, Altioek H, Yarkin S, Cetin B (2009) Electric arc furnaces for steel-making: hot spots for persistent organic pollutants. *Environ Sci Technol* 43:5205–5211
- Park H, Kang JH, Baek SY, Chang YS (2010) Relative importance of polychlorinated naphthalenes compared to dioxins, and polychlorinated biphenyls in human serum from Korea: contribution to TEQs and potential sources. *Environ Pollut* 158:1420–1427
- Schneider M, Stieglitz L, Will R, Zwick G (1998) Formation of polychlorinated naphthalenes on fly ash. *Chemosphere* 37:2055–2070
- Schuhmacher M, Domingo JL (2006) Long-term study of environmental levels of dioxins and furans in the vicinity of a municipal solid waste incinerator. *Environ Int* 32:397–404
- UNEP (2011) UNEP/POPS/POPRC.7/2. <http://chm.pops.int/Convention/POPsReviewCommittee/POPRCMeetings/POPRC7/POPRC7Documents/tabid/2267/language/en-US/Default.aspx>. Accessed 2 Jan 2012
- Weber R, Iino F, Imagawa T, Takeuchi M, Sakurai T, Sadakata M (2001) Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: mechanistic aspects and correlation to fluidized bed incinerators. *Chemosphere* 44:1429–1438
- Weber R, Gaus C, Tysklind M, Johnston P, Forter M, Hollert H, Heinisch E, Holoubek I, Lloyd-Smith M, Masunaga S, Moccarelli P, Santillo D, Seike N, Symons R, Torres JPM, Verta M, Varbelow G, Vijgen J, Watson A, Costner P, Woelz J, Wycisk P, Zennegg M (2008) Dioxin- and POP-contaminated sites-contemporary and future relevance and challenges. *Environ Sci Pollut Res* 15:363–393