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Identification of indicator congeners and evaluation of emission pattern of polychlorinated naphthalenes in industrial stack gas emissions by statistical analyses

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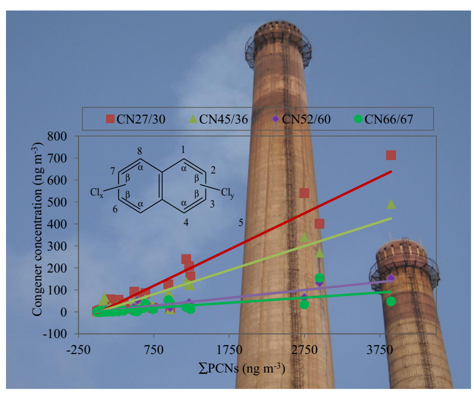
HIGHLIGHTS

- PCN data in 122 stack gas samples from 64 plants were statistically evaluated.
- CN27/30, CN52/60 and CN66/67 were suggested to be the indicator congeners of ∑PCNs.
- Equations describing relationships between indicators and ∑PCNs were established.
- Less chlorinated homologs were dominant in most of industrial stack gas emissions.
- The identification of indicator congeners are useful for predicting ∑PCN emissions.

GRAPHICAL ABSTRACT



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ABSTRACT

Identifying marker congeners of unintentionally produced polychlorinated naphthalenes (PCNs) from industrial thermal sources might be useful for predicting total PCN ($\sum_{2-8}$PCN) emissions by the determination of only indicator congeners. In this study, potential indicator congeners were identified based on the PCN data in 122 stack gas samples from over 60 plants involved in more than ten industrial thermal sources reported in our previous case studies. Linear regression analyses identified that the concentrations of CN27/30, CN52/60, and CN66/67 correlated significantly with $\sum_{2-8}$PCN ($R^2 = 0.77$, 0.80, and 0.58, respectively; $n = 122$, $p < 0.05$), which might be good candidates for indicator congeners. Equations describing relationships between indicators and $\sum_{2-8}$PCN were established. The linear regression analyses involving 122 samples showed that the relationships between the indicator congeners and $\sum_{2-8}$PCN were not significantly affected by factors such as industry types, raw materials used, or operating conditions. Hierarchical cluster analysis and similarity calculations for the 122 stack gas samples were adopted to group those samples and evaluating their similarity and difference based on the PCN homolog distributions from different industrial thermal sources. Generally, the fractions of less chlorinated homologs comprised of di-, tri-, and tetra-homologs were much higher than that of more chlorinated homologs for up to 111 stack gas samples contained in group 1 and 2, which indicating the dominance of lower chlorinated homologs in stack gas from industrial thermal sources.

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1. Introduction

Polychlorinated naphthalenes (PCNs) are structurally and toxicologically similar to that of polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs), which pose potential risk to global environment and human health. The structures (i.e., the chlorine substitution positions) of the PCN congeners and the most commonly used numbering system are shown in Fig. S1 and Table S1. Historical production has been considered as one of the major sources of PCNs, because PCNs were previously intentionally produced for a range of industrial uses. PCN production has currently ceased in many countries, so unintentional releases of PCNs from industrial thermal sources are becoming much more important than they previously were. The PCN formation mechanism during industrial thermal processes was found to be similar to that of PCDD/Fs (Imagawa and Lee, 2001; Weber et al., 2001; Oh et al., 2007). PCDD/F sources that have been identified can, therefore, also be potential sources of unintentionally produced PCNs. PCN emissions have been determined both qualitatively and quantitatively from some important PCDD/F sources, including waste incinerators, iron- and steel-making plants, and nonferrous smelting (Takasuga et al., 2004; Ba et al., 2010; Liu et al., 2010, 2012a,b; Nie et al., 2011, 2012a,b; Hu et al., 2013a).

The European Union has proposed that PCNs (from di- to octa-homologs) should be included in the annexes of the Stockholm Convention on Persistent Organic Pollutants (POPs), and PCNs have been reviewed by the POPs Review Committee. PCNs will most probably be listed as POPs in 2015 at the Conference of Parties meeting of the Stockholm Convention, signifying that there will be an increase in activities aimed at monitoring and controlling unintentionally produced PCN emissions from industrial sources around the world. Up to now, PCNs have normally not been measured in emissions from thermal sources because no regulations that require this exist. Congener-specific isotope dilution high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) is the internationally recognized optimum method for PCN analysis (Kucklick and Helm, 2006; Piazza et al., 2013). This method requires several days of complex sample pretreatment (Helm and Bidleman, 2003; Ba et al., 2010; Liu et al., 2010) and the costs involved are high. For PCDD/Fs, some studies have been conducted aimed at identifying potential indicators for PCDD/F toxic equivalent (TEQ) values. For example, monochlorobenzene was found to be an indicator for the PCDD/F TEQ emitted from a waste incinerator (Gullett et al., 2008). Tsuruga et al. suggested that the pentachlorodibenzofuran homolog is a good indicator for the PCDD/F TEQ (Tsuruga et al., 2007). However, to the best of our knowledge, no studies have yet been performed to identify possible marker congeners for total PCNs ($\sum_{2-8}$PCN) or PCN homolog production during industrial thermal processes. It is therefore significant to use regression analysis to examine the relationships between PCN congener concentrations and $\sum_{2-8}$PCN and homolog concentrations in a relatively large number of emission samples from various types of industrial plants, with the aim of identifying potential indicator congeners.

There are obvious differences in the PCN congener patterns that are found in intentionally produced PCNs and PCNs formed unintentionally in incineration processes (Schneider et al., 1998; Imagawa and Lee, 2001; Noma et al., 2004). The congener patterns of PCNs released from different sources have, therefore, been considered to be helpful for differentiating different PCN sources to the environment. In terms of specific industries, PCN patterns produced during metal smelting processes (including primary and secondary nonferrous smelting processes, coking processes, iron ore sintering, and electric arc furnaces) have been reported (Liu et al., 2010, 2012a,b; Nie et al., 2011, 2012a,b; Hu et al., 2013b). PCN patterns produced by waste incinerators have also been reported (Hu et al., 2013a). Statistically analyzing those patterns from various industrial case plants could be helpful in evaluating their similarities and differences (Fiedler et al., 2000; Jansson and Andersson, 2012).

Statistical analysis methods including linear regression analyses and hierarchical cluster analysis (HCA), and principal component analysis (PCA) have recently been applied intensively in studies relating to the environmental pollution (Jansson et al., 2009). For example, a statistical analysis method have been used to study mechanistic correlations between the formation of PCNs and other unintentionally produced POPs during waste incineration, and found some similar formation mechanisms among different unintentionally produced POPs (Oh et al., 2007). Jansson and Andersson (2012) recently found, employing principal component analysis (PCA), relationships between the congener distribution patterns in PCDD/Fs, polychlorinated biphenyls (PCBs),polychlorinated benzenes, polychlorinated phenols, and PCNs formed during flue gas cooling, and identified potential TEQ indicator congeners for PCDD/Fs and PCBs. Fiedler et al. (2000) applied statistical analysis to evaluate common PCDD/F patterns and found that 2,3,4,7,8-pentachlorodibenzofuran was a good indicator for PCDD/F toxic equivalent production in 109 stack gas samples from waste incineration and metal smelting. Black et al. used statistical analyses to assess 111 PCDD/F and "dioxin-like" PCB emission factors from the open burning of biomass, and suggested that this might be helpful in establishing accurate national inventories (Black et al., 2012). However, PCN patterns emitted from different industrial thermal processes have not yet been statistically evaluated based on a large emission sample size from various types of industrial plants.

We have previously reported several case studies of PCN emission concentrations, profiles, and emission factors from a number of thermally related sources, and accumulated numerous data on PCN emissions in stack gas samples (Ba et al., 2010; Liu et al., 2010, 2012a,b; Nie et al., 2011, 2012a,b; Hu et al., 2013a). In this study, we summarized and evaluated PCN emission data from 122 stack gas samples using statistical analysis methods (Ba et al., 2010; Liu et al., 2010, 2012a,b; Nie et al., 2011, 2012a,b; Hu et al., 2013a,b). The stack gas samples were from more than ten types of industrial thermal source comprised of over 60 plants, and the PCN concentration range was about four orders of magnitude. To the best of our knowledge, this is the most comprehensive statistical analysis of PCN emissions from different industrial thermal sources. The primary aim of this study was: (1) to identify potential marker congeners and assess the correlations between marker congener and $\sum_{2-8}$PCN and homolog concentrations, which could allow $\sum_{2-8}$PCN and homolog emissions to be predicted from the analysis of only the indicator congeners; and (2) to evaluate the similarities and differences in PCN congener patterns emitted from different industrial thermal sources using HCA and similarity calculations, which might enhance the further understanding associated with the homolog distribution of PCNs from industrial thermal sources.

2. Materials and methods

We have previously reported several case studies of PCN emission profiles and emission factors from a number of thermally related sources (Ba et al., 2010; Liu et al., 2010, 2012a,b; Nie et al., 2011, 2012a,b; Hu et al., 2013a). In those studies, automatic isokinetic sampling method was used for collection of stack gas samples from industrial thermal processes. Isotope dilution high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) method was used for the qualification