Identification and preliminary evaluation of polychlorinated naphthalene emissions from hot dip galvanizing plants

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HIGHLIGHTS
- Hot dip galvanizing was found to be a source of polychlorinated naphthalenes.
- PCN emission factors in solid residues from hot dip galvanizing were derived.
- Congeners CN37/33/34, CN52/60, CN66/67, and CN73 were dominant in their respective homologs.
- Hot dip galvanizing might not be a priority for controlling PCN release.

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ABSTRACT
Hot dip galvanizing (HDG) processes are sources of polychlorinated-p-dioxins and dibenzofurans (PCDD/Fs). Close correlations have been found between the concentration of PCDD/Fs and polychlorinated naphthalenes (PCNs) that are produced and released during industrial thermal processes. We speculated, therefore, that HDG plants are potential PCN sources. In this preliminary study, PCNs were analyzed in solid residues, ash and precipitate from three HDG plants of different sizes. The total PCN concentrations (∑PCNs) in the residue samples ranged from 60.3 to 226 pg g⁻¹. The PCN emission factors for the combined ash and precipitate residues from the HDG plants ranged from 75 to 178 ng t⁻¹ for the dichlorinated and octachlorinated naphthalenes. The preliminary results suggested that the HDG industry might not currently be a significant source of PCN emissions. The trichloronaphthalenes were the dominant homologs followed by the dichloronaphthalenes and the tetrachloronaphthalenes. The PCN congeners CN37/33/34, CN52/60, CN66/67, and CN73 dominated the tetrachlorinated, pentachlorinated, hexachlorinated, and heptachlorinated naphthalene homologs, respectively. The PCNs emitted from the HDG plants had similar homolog distributions and congener profiles to the PCNs emitted from combustion plants and other metallurgical processes. The identification and preliminary evaluation of PCN emissions from HDG plants presented here will help in the prioritization of measures for controlling PCN emissions from industrial sources.

1. Introduction
Polychlorinated naphthalenes (PCNs) are ubiquitous environmental contaminants (Bidleman et al., 2010). The structures and properties of PCNs are similar to those of polychlorinated-p-dioxins and dibenzofurans (PCDD/Fs). It has been proposed that PCNs (the dichlorinated to octachlorinated homologs) should be included in Annexes A and C of the Stockholm Convention on Persistent Organic Pollutants (POPs) review committee (UNEP, 2013). It is likely that it will be decided whether the whole list (or part of the list) of PCNs will be classed as unintentionally produced POPs (which are addressed in annex C) at the next Conference of Parties in 2015. The major sources of PCNs in the environment are historic uses of technical PCN mixtures, the unintentional release of PCNs from industrial thermal sources, and PCN impurities in commercial polychlorinated biphenyl (PCB) mixtures (Falandysz, 1998; Liu et al., 2014). The production of PCNs and PCBs for use as commercial industrial chemicals has ceased; therefore, unintentional releases from industrial thermal sources are becoming more important sources of PCNs than they were previously. Identifying and quantifying the unintentional
sources of PCNs is the primary step in developing an emissions inventory and in developing policies for controlling and regulating PCN emissions.

Waste incineration (Helm and Bidleman, 2003; Hu et al., 2013) and metal smelting processes are sources of unintentionally produced PCNs. PCN emissions have been estimated, and PCN congener patterns have been evaluated for processes including iron ore sintering, the use of electric arc furnaces in steel making, and secondary nonferrous smelting (Ba et al., 2010; Liu et al., 2010; Nie et al., 2011; Liu et al., 2012a,b; Nie et al., 2012a,b).

Solid residues from industrial plants can contain high concentrations of unintentionally produced POPs. Fly ash, in particular, is an important matrix on which unintentionally produced POPs can form during industrial thermal processes. PCN concentrations in fly ash from thermal processes, including waste incineration, coking processes, and primary and secondary nonferrous smelting, have been reported (Behnisch et al., 2002; Ba et al., 2010; Nie et al., 2011; Nie et al., 2012a,b; Liu et al., 2013). However, there is still a lack of data on the identities and quantities of unintentionally produced POPs, including PCNs, released into the environment from some metal smelting processes (Liu et al., 2009, 2010).

Martinez and co-workers (Martinez et al., 2008) evaluated PCDD/F emissions during the galvanizing process and studied the factors that favor PCDD/F formation. Previously, we quantified PCDD/F emissions from three hot dip galvanizing (HDG) plants in China (Lv et al., 2011). Close correlations were found between the concentrations of PCNs and PCDD/Fs produced during waste incinerations (Weber et al., 2001; Oh et al., 2007). However, it is still unknown whether PCNs are emitted from HDG processes. Therefore, we performed a preliminary evaluation of PCN emissions from those three HDG plants.

2. Materials and methods

2.1. Samples and galvanizing plants

Several methods are used for galvanizing items, including the United Engineering Center process, the Sendzimir process, and the solvent method. There are several hundred galvanizing plants in China, and the solvent method is used in approximately 40% of the galvanizing plants. The main stages in the HDG process are surface preparation, galvanizing, cooling, and inspection. The surface preparation stage includes several steps, including degreasing, rinsing, acid pickling, and fluxing. The molten zinc in the bath in which steel articles are galvanized is kept in the temperature range of approximately 430–460 °C. A demineralized water bath is used to cool the galvanized articles. The formation of unintentionally produced POPs will predominantly occur in the galvanizing and cooling stages because the temperatures of these processes are most conducive to the formation of POPs. The HDG process is shown schematically in Fig. 1. Three HDG plants of different sizes that use the solvent method were selected in our previous study, and PCDD/F and “dioxin-like” PCB emissions from these three plants were evaluated (Lv et al., 2011). In that study, diffuse ash samples from the galvanizing stage were collected, and precipitate samples were collected from the bottom of the cooling bath using a stainless steel spoon. These samples were analyzed for PCNs in this study. The stages of the HDG process from which samples were collected are indicated in Fig. 1.

Solid residues from industrial plants might contain high concentrations of unintentionally produced POPs. Fly ash, in particular, is an important matrix on which unintentionally produced POPs can form during industrial thermal processes. Most of the HDG plants in China are not suitable for the field collection of stack gas samples by automatic isokinetic sampling equipment; therefore, solid residue samples from the HDG processes were collected from the plants. In this study, ash and precipitate samples from those three HDG plants that used the solvent method were analyzed for PCNs. The samples were tightly wrapped in aluminum foil to avoid any loss of sample and to avoid becoming contaminated. Plant 1 produces steel electric pylons, and its annual capacity is 60 000 t. Plant 1 produces 60 t y⁻¹ of ash and 4 t y⁻¹ of precipitate. The ash sample from plant 1 was labeled ashP1, and the precipitate sample was labeled precipP1; the same labeling method was used for the samples from plants 2 and 3. Plant 2 produces steel and iron work pieces, and its annual capacity is 9000 t. Plant 2 produces 8 and 4 t y⁻¹ of ash and precipitate, respectively. Plant 3 produces bar steel, angle steel, and steel tube, among others, and its annual capacity is 15 000 t. Plant 3 produces 20 and 4 t y⁻¹ of ash and precipitate, respectively (Lv et al., 2011).

2.2. Preparation and chemical analysis

The PCNs were analyzed using an isotope dilution high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) method that has been described previously (Ba et al., 2010; Liu et al., 2013). Approximately 10 g of each sample was spiked with 1 ng of each of the 13C₃-labeled PCN internal standards (13C₀-PCNs-27, -42, -52, -67, -73, and -75; obtained as a mixture, catalog no. ECN-5102, from Cambridge Isotope Laboratories, Andover, MA, USA). Each sample was digested in 1 mol L⁻¹ HCl, rinsed with deionized water until a pH value close to 7.0 was reached, and then dried. The dried sample was Soxhlet extracted with 250 mL of toluene for 24 h. The extract was evaporated and then cleaned using a column packed with silica gel treating with 44% (by weight) sulfuric acid, a multilayer silica gel column, and a column packed with basic alumina. The volume of the final extract was 20 μL, and a 13C₀-labeled PCN-64 injection standard (catalog no. ECN-5260; Cambridge Isotope Laboratories) was added before instrumental analysis. The retention times of the PCN congener peaks were matched with those of the individual PCN congener standards, taking into account the elution order for the congeners on the DB-5 chromatographic column that was used and the ion ratios. A PCN congener peak was quantified if the ratio between the target and qualifier ion peak areas was within 15% of the theoretical value. The 13C₀-labeled PCN internal standard recoveries (calculated using the labeled injection standards as internal standards) were 53–72% for 13C₁₀-CN22, 59–76% for 13C₁₀-CN42, 49–85% for 13C₀-CN52, 83–89% for 13C₀-CN67, 52–98% for 13C₁₀-CN73, and 40–62% for 13C₁₀-CN75. The limits of detection (LODs) of the PCN homologs ranged from 0.07 to 3.1 pg μL⁻¹. A blank sample was analyzed with each batch of samples. The concentrations of the monochlorinated and trichlorinated PCN homologs in the blank samples were higher than the LODs but less than 15% of the concentrations found in the samples; therefore, blank corrections were not performed.

3. Results and discussion

The PCNs review committee screened the PCN homologs using the criteria in Annex D of the Stockholm Convention on POPs and concluded that the di- to octa-chlorinated homologs meet the screening criteria for POPs. PCNs (the di- to octa-chlorinated homologs) are, therefore, candidates for being classified as unintentionally produced POPs in Annex C of the Stockholm Convention. Steps should be taken to eliminate unintentional emissions of PCNs if they become included in Annex C. This possibility caused us to determine the concentrations and emission factors of the di- to octa-chlorinated PCN homologs in ash and precipitate produced by HDG plants. The sum of the di- to octa-chlorinated PCN homologs in fly ash from thermal processes, including waste incineration, coking processes, and primary and secondary nonferrous smelting, have been evaluated in China (Lv et al., 2011). Close correlations were found between the concentrations of PCNs and PCDD/Fs produced during waste incinerations (Weber et al., 2001; Oh et al., 2007). However, it is still unknown whether PCNs are emitted from HDG processes. Therefore, we performed a preliminary evaluation of PCN emissions from those three HDG plants. The PCNs were analyzed using an isotope dilution high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) method that has been described previously (Ba et al., 2010; Liu et al., 2013). Approximately 10 g of each sample was spiked with 1 ng of each of the 13C₃-labeled PCN internal standards (13C₀-PCNs-27, -42, -52, -67, -73, and -75; obtained as a mixture, catalog no. ECN-5102, from Cambridge Isotope Laboratories, Andover, MA, USA). Each sample was digested in 1 mol L⁻¹ HCl, rinsed with deionized water until a pH value close to 7.0 was reached, and then dried. The dried sample was Soxhlet extracted with 250 mL of toluene for 24 h. The extract was evaporated and then cleaned using a column packed with silica gel treating with 44% (by weight) sulfuric acid, a multilayer silica gel column, and a column packed with basic alumina. The volume of the final extract was 20 μL, and a 13C₀-labeled PCN-64 injection standard (catalog no. ECN-5260; Cambridge Isotope Laboratories) was added before instrumental analysis. The retention times of the PCN congener peaks were matched with those of the individual PCN congener standards, taking into account the elution order for the congeners on the DB-5 chromatographic column that was used and the ion ratios. A PCN congener peak was quantified if the ratio between the target and qualifier ion peak areas was within 15% of the theoretical value. The 13C₀-labeled PCN internal standard recoveries (calculated using the labeled injection standards as internal standards) were 53–72% for 13C₁₀-CN22, 59–76% for 13C₁₀-CN42, 49–85% for 13C₀-CN52, 83–89% for 13C₀-CN67, 52–98% for 13C₁₀-CN73, and 40–62% for 13C₁₀-CN75. The limits of detection (LODs) of the PCN homologs ranged from 0.07 to 3.1 pg μL⁻¹. A blank sample was analyzed with each batch of samples. The concentrations of the monochlorinated and trichlorinated PCN homologs in the blank samples were higher than the LODs but less than 15% of the concentrations found in the samples; therefore, blank corrections were not performed.
log ($\sum_2$-aPCNs) concentrations ranged from 60.3 to 135.2 pg g$^{-1}$ in the ash samples and from 174 to 226 pg g$^{-1}$ in the precipitate samples. PCDD/Fs were analyzed in the same residue samples from the HDG plants in our previous study (Lv et al., 2011). It has been found that PCN and PCDD/F emissions from waste incinerations correlate significantly (Imagawa and Lee, 2001; Weber et al., 2001; Oh et al., 2007). However, the correlations between PCN and PCDD/F concentrations in the samples from HDG plants that were analyzed in this preliminary investigation were not significant. Considering that only a small number of samples were collected from only three HDG plants in this preliminary investigation, an intensive investigation in which a large number of samples is taken from many more galvanizing plants might be needed to clarify the PCN formation mechanisms that occur in galvanizing processes and to determine if the emissions of PCDD/Fs and PCNs from galvanizing plants significantly correlate.

Emission factors are helpful parameters for estimating contaminant emissions from whole industries using limited data from field investigations (Liu et al., 2009, 2013). An emission factor can be considered to be the emission rate of a given contaminant relative to the intensity of a specific activity in an industrial source. The PCN emission factors were calculated using Eq. (1) (Liu et al., 2009, 2013).

$$\text{Emission factor (ng t}^{-1}) = \frac{\text{concentration (pg g}^{-1}) \times \text{amount of fly ash per tonne of products (kg t}^{-1})}{\text{PCN}}$$

Using the results of this preliminary field investigation, the PCN ($\sum_2$-aPCNs) emission factors for the HDG industry per ton of product were found to be 60–126 ng t$^{-1}$ in ash and 15–58 ng t$^{-1}$ in precipitate. The PCN ($\sum_2$-aPCNs) emission factors for the combined ash and precipitate residues were 75–178 ng t$^{-1}$ (per ton of product).

The PCN concentrations that have been found in ash samples from different industrial thermal processes are summarized in Table 1. The PCN concentrations in the residue samples from the HDG plants were relatively low. They were comparable to the PCN concentrations in ash from primary magnesium production and coking processes and in slag from waste incinerators but were clearly lower than PCN concentrations in fly ash from waste incinerators and from other metal smelting processes. This result suggests that the HDG industry might not currently be seen as a priority for implementing measures to control unintentional emissions of PCNs.

The PCN homolog distributions (A) and congener concentration profiles (B) found in the samples are shown in Fig. 2. The homolog patterns were dominated by the trichlorinated homologs followed by the di- and tetra-chlorinated homologs. The contributions of the homologs to the total PCN concentrations decreased with increasing levels of chlorination from the tri- to the octa-chlorinated homologs. The PCN homolog distribution in the HDG samples was clearly different from the distributions that have been found in some technical PCN formulations, such as Halowaxes (Noma et al., 2004). For example, the dichlorinated PCN homolog was found to be dominant in the HW1000 product, but the mono- and di-chlorinated homologs were found to be dominant in the HW1031 product. The octachlorinated homolog was found to be dominant in the HW1051 product. The tetrachlorinated homolog was found to be dominant in the HW1013 and HW1099 products, and the pentachlorinated homolog was found to be dominant in the HW1014 product. Bidleman et al. reviewed reports of the occurrence of PCNs in polar environments and found that the trichlorinated homolog was strongly dominant over the more chlorinated homologs in some biota, such as krill, silverfish, and seals (Bidleman et al., 2010).

The concentration profiles of the PCN congeners in the samples are presented in Fig. 2B. The congeners CN37/33/34, CN52/60, CN66/67, and CN73 dominated the tetra-, penta-, hexa-, and hepta-chlorinated naphthalene homologs, respectively. Helm et al. found that CN52/60 and CN66/67 were major congeners in fly ash samples from municipal solid waste incinerators and an iron sintering plant (Helm and Bidleman, 2003; Helm et al., 2004). Liu et al. summarized the PCN profiles in emissions from municipal solid waste incinerators, medical waste incinerators, secondary non-ferrous smelting processes, electric arc furnaces for steel making, and iron ore sintering processes, along with others (Liu et al., 2014). They found that CN66/67 and CN73 were much more abundant than the other hexa- and hepta-chlorinated congeners in emissions from these thermal related sources, respectively (Liu et al., 2014). Therefore, the congeners CN52/60, CN66/67, and CN73 are considered to be the main indicators of PCN emissions from combustion and metallurgical plants (Liu et al., 2014). The CN73 concentrations were far higher than the CN74 concentrations in the samples analyzed from the HDG plants, whereas CN73 to CN74 concentration ratios in the range 0.13–0.4 have been found in technical PCN mixtures, including seven Halowax formulations (Noma et al., 2004). The PCN congener profiles emitted from the HDG processes were similar, to some extent, to the profiles emitted from combustion and metallurgical sources but different from the profiles in technical PCN mixtures. These congener profiles may provide information that is helpful in differentiating between industrial thermal emissions of PCNs and releases from technical PCN mixtures.
Polychlorinated naphthalene (PCN) concentrations in residues from typical industrial processes.

| Industrial source               | Sample                  | PCN Concentration (ng/g) | Homologs                        | Reference                      |
|--------------------------------|-------------------------|--------------------------|---------------------------------|--------------------------------|
|                                |                         | Range                    | Average | Median | Log$_{10}$ |                          |                                |
| Municipal waste incineration    | Fly ash                | 370–1400                 | 747     | 470    | NR         | Behnisch et al. (2002)  |
|                                | Fly ash in FF$^a$      | 120–1200                 | 530     | 270    | NR         | Behnisch et al. (2002)  |
|                                | Fly ash in EP$^b$      | 33                       | NR      | NR     | NR         | Behnisch et al. (2002)  |
|                                | Slag                   | 0.38–1.2                 | 0.79    | 0.79   | NR         | Behnisch et al. (2002)  |
|                                | Bottom ash             | 4.0–4.5                  | 4.3     | 4.3    | NR         | Behnisch et al. (2002)  |
| Secondary aluminum smelting    | Fly ash                | 6.9–6000                 | 1529    | 54.2   | Mono-octa-chlorinated | Ba et al. (2010) |
| Secondary copper smelting       | Fly ash                | 9.5–20830                | 4886    | 1907   | Mono-octa-chlorinated | Ba et al. (2010) |
|                                | Fly ash                | 39.6–2813                | 1426    | 1426   | Mono-octa-chlorinated | Nie et al. (2012a) |
| Secondary zinc smelting         | Fly ash                | 2670                     |         |        |            |                                |
| Secondary lead smelting         | Fly ash                | 2.3                      |         |        |            |                                |
| Coking processes               | Fly ash                | 0.055–0.682              | 0.256   | 0.223  | Mono-octa-chlorinated | Liu et al. (2013) |
| Primary copper smelting         | Fly ash                | 18.4–164                 | 67      | 19     | Mono-octa-chlorinated | Nie et al. (2012a) |
| Hot dip galvanizing            | Ash                    | 0.096–0.225              | 0.162   | 0.165  | Mono-octa-chlorinated | This work          |
|                                | Precipitate            | 0.228–0.269              | 0.249   | 0.251  | di-octa-chlorinated | This work          |
|                                |                        | 0.174–0.226              | 0.176   | 0.174  | di-octa-chlorinated | This work          |

$^a$ FF: Fiber filter.  
$^b$ EP: Electrostatic precipitator.  
$^c$ NR: Not reported.

We identified and quantified PCNs in solid residue samples from HDG processes. The HDG process samples had similar PCN homolog distributions and congener profiles to those that have been found in samples from combustion and metallurgical processes. The HDG process PCN homolog distributions and congener profiles were significantly different from those that have been found in technical PCN mixtures. The results suggest that controlling PCN emissions from the HDG industry might not currently be of a high priority. These results will be helpful in terms of identifying new sources of PCNs and developing an emission inventory for PCNs.

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