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Short Communication

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 ($\sum_{2-8}$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.

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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) by the 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

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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 60000 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 15000 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 $^{13}C_{10}$-labeled PCN internal standards ($^{13}C_{10}$-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 treated 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 $^{13}C_{10}$-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 $^{13}C_{10}$-labeled PCN internal standard recoveries (calculated using the labeled injection standards as internal standards) were 53–72% for $^{13}C_{10}$-CN27, 59–76% for $^{13}C_{10}$-CN42, 49–85% for $^{13}C_{10}$-CN52, 83–89% for $^{13}C_{10}$-CN67, 52–98% for $^{13}C_{10}$-CN73, and 40–62% for $^{13}C_{10}$-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 mono- and tri-chlorinated 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 POPs 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 classed 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 homo-

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