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Distributions, profiles and formation mechanisms of polychlorinated naphthalenes in cement kilns co-processing municipal waste incinerator fly ash

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HIGHLIGHTS

- Major process stages of PCN formation in the cement kilns were identified.
- Lower chlorinated naphthalenes were the dominant homologs formed in cement kilns.
- Chlorination was suggested to be an important formation mechanism of PCNs.
- Mass balance indicated 50% reduction of PCNs from input to output in cement kilns.

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ABSTRACT

Co-processing municipal solid waste incinerator (MSWI) fly ash in cement kilns is challenging because the unintentional production of persistent organic pollutants (POPs) during the process is not well understood. The distributions, profiles and formation mechanisms of polychlorinated naphthalenes (PCNs) as new POPs covered under Stockholm Convention in two cement kilns co-processing MSWI fly ash were studied. The average concentrations of PCNs in stack gas samples were 710 ng m^{-3}. The PCN concentration in particle samples collected from different process stages in the cement kilns ranged from 1.1 to 84.7 ng g^{-1}. Three process sites including suspension pre-heater boiler, humidifier tower, and the kiln back-end bag filter were identified to be the major formation sites of PCNs in cement kilns co-processing MSWI fly ash. The PCN distribution patterns were similar to that of polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/Fs), which indicates the possibility for simultaneous control of PCNs and PCDD/Fs in cement kilns co-processing fly ash. Chlorination was suggested to be an important formation mechanism of PCNs, and chlorination pathways of PCN congeners are proposed based on the congener profiles. Thermodynamic calculations, including relative thermal energies (ΔE) and standard free energy of formation (ΔG), and the charge densities of the carbon atoms in PCN supported the proposed chlorination mechanisms for PCN formation. The results presented in this study might provide helpful information for developing techniques and strategies to control PCN emissions during cement kilns co-processing MSWI fly ash.

1. Introduction

Polychlorinated naphthalenes (PCNs) are persistent organic pollutants (POPs) that are toxic and have adverse effects on biota and human health (Venny et al., 2012). PCNs are ubiquitous in various environmental matrices worldwide (Kannan et al., 2000a,

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2000b; Domingo, 2004; Harner et al., 2006). The United Nations Economic Commission for Europe (UN-ECE) initiatives on POPs began in 1992 with the establishment of a Task Force on POPs under the framework of the Convention on Long-Range Transboundary Air Pollution (UN-ECE POP Protocol, 1998; Lerche et al., 2002). It has been suggested that PCNs should be classed as POPs in the UN-ECE POP Protocol (Lerche et al., 2002). Stockholm Convention on POPs is an international environmental treaty, signed in 2001 and effective from May 2004, with the aims to eliminate POPs. PCNs were recently added to Annexes A and C of the Stockholm Convention, so the intentional production of PCNs is forbidden and unintentional emissions of PCNs during various industrial processes must be controlled and regulated in the 179 signatory countries or regions (UNEP, 2015).

Major sources of PCNs to the environment are PCN technical products, polychlorinated biphenyls (PCBs) technical mixtures containing PCNs as impurities, and industrial thermal processes that release unintentionally produced PCNs (Falandysz et al., 2000; Yamashita et al., 2000; Noma et al., 2004; Falandysz et al., 2008; Liu et al., 2012; Weidemann and Lundin, 2015). Since 1980s, the technical mixtures of PCNs are no longer produced in most countries, unintentional releases from industrial thermal processes become the much more important sources of PCNs than before. The concentrations, emission profiles, and emission factors of PCNs produced during a range of industrial thermal processes, including waste incineration and metallurgical processes, have previously been presented and summarized (Falandysz, 1998; Ba et al., 2010; Liu et al., 2010, 2014a, 2015a). Waste incineration is an important source of PCNs because solid waste is often incompletely combusted (Abad et al., 1999; Sakai et al., 2006; Jansson et al., 2008; Jansson and Andersson, 2012). Fly ash produced in waste incinerators is an important source of PCNs. PCN concentrations of up to 470, 370, and 1400 ng g^{-1} have been found in fly ash from waste incinerators under start-up, steady operation, and shutdown conditions, respectively (Takasuga et al., 2004). Fly ash from waste incinerators can, therefore, contain high PCN concentrations.

Fly ash produced in waste incinerators is classed as a hazardous material because it contains toxic inorganic and organic pollutants (McKay, 2002; Weidemann and Lundin, 2015). Fly ash should therefore be treated before being disposed of. The amount of municipal solid waste incinerator (MSWI) fly ash produced in China increased from between 431,000 and 718,000 t in 2007 to between 1,390,000 and 2,317,000 t in 2013 (Liu et al., 2015b). It is therefore challenging to dispose of the fly ash produced in waste incinerators in China. Cement kilns can be used to destroy solid waste because they operate at high temperatures (normally around 1200 °C). The amounts and distributions of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs and PCDFs, together called PCDD/Fs) emitted by cement kilns co-processing contaminated soil or refuse-derived fuel have been studied (Conesa et al., 2011; Yang et al., 2012). We previously studied PCDD/F formation in cement kilns co-processing MSWI fly ash (Liu et al., 2015b). However, the distributions within kiln systems, homolog and congener profiles, and formation mechanisms of dioxin-like compounds, such as PCNs, in cement kilns co-processing MSWI fly ash have not been clarified. It is important for further investigations to be performed so that emissions of dioxin-like compounds during the destruction of MSWI fly ash in cement kilns can be controlled.

We performed a pilot study in the field using two cement kilns co-processing MSWI fly ash. The aim was to characterize the PCN distributions and homolog and congener profiles in cement kiln systems. Stack gas and particulate samples from different stages of the cement production process were analyzed by isotope dilution high resolution gas chromatography combined with high resolution mass spectrometry (HRGC/HRMS). The PCN distribution patterns were determined, and the main stages in which PCNs were unintentionally formed in the cement kiln systems were identified. This information will help in the development of techniques to decrease PCN emissions. Possible PCN formation mechanisms in cement kilns were identified from the PCN congener profiles that were found, and thermodynamic parameters and charge densities for the PCNs formed were calculated. This information will help in the development of techniques to prevent PCNs being formed and emitted from cement kilns.

2. Materials and methods

2.1. Cement kilns and sample collection

Samples were collected from a cement plant with two cement kilns. The two cement kilns that were used in this pilot study were both advanced dry-process rotary kilns. More than 95% of the cement produced in China is made using this technique, so the kilns that were studied were representative of the main current cement-making techniques. The scheme of the cement kilns are presented in Fig. 1, and were described in detail in a previous publication (Liu et al., 2015b). The daily clinker outputs of cement lines 1 and 2 were about 2000 and 2500 t, respectively. The line 1 cement kiln had been continuously used to co-process MSWI fly ash for about 300 days, at a typical rate of 20 t d^{-1} (about 1% of the amount of cement clinker produced). Memory effects from the long-term treatment of MSWI fly ash on PCN formation and distributions were attempted to be identified by also studying the line 2 cement kiln, in which MSWI fly ash had not previously been used. The MSWI fly ash was washed three times with water before being co-combusted in the kilns to decrease the chloride, sodium, and potassium contents. High chloride, sodium, and potassium contents in the feedstock could cause the cement kiln equipment to deteriorate and negatively affect the cement quality. Washing with water decreased the chloride content of the ash from 9–26% to <1% and the sodium and potassium contents from ~8% to <3% (Liu et al., 2015b).

Stack gas samples were collected using an automatic isokinetic sampling method that has been described in detail in previous publications (Ba et al., 2010; Liu et al., 2010; Lv et al., 2011). The gas samples from the stack were collected using an automatic isokinetic sampling system. The sampling point was set downstream of air pollution control devices. Briefly, the sampling train consisted of a heated probe, a filter box equipped with a silica glass microfiber thimble (25 mm i.d., 90 mm length; Whatman International Ltd., Whatman, UK), a water-cooled Amberlite XAD-2 adsorbent trap (Supleco International Ltd., Varina, USA), an Isotack Basic (TCR Tecora, Italy) pump and an Isofrost cooler (TCR Tecora, Italy). There is no suitable field sampling platform and sampling hole with proper size for other locations of the cement kiln lines. Thus, collections of gas samples from other sampling locations using the automatic isokinetic sampling equipment were not performed.

Particulate samples were collected from various process sites in the kilns to allow the major PCN formation sites to be identified and to determine the PCN distributions. Samples of the particulates produced at each sampling point were collected after the cement kilns had been operating continuously and stably for more than 48 h. Stable operation of the kilns for 48 h allowed sufficient particulate to be produced at each sampling point for samples to be taken. Each particulate sample was therefore a good representative of the particulate produced in each part of the cement-making process. The particulate samples from clinker and raw mill were collected by using stainless steel spoon. The particulate samples from C1 outlet and other sites were captured by the quartz microfiber thimble connected to a gas pump. Each sample was wrapped tightly in aluminum foil to minimize contamination and