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.

ARTICLE INFO

Article history:

Received 20 January 2016

Received in revised form

29 March 2016

Accepted 19 April 2016

Available online 29 April 2016

Handling Editor: Caroline Gaus

Keywords:

Cement kiln

Persistent organic pollutants

Polychlorinated naphthalenes

Stockholm Convention

Municipal solid waste

Fly ash

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.

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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

Fig. 1. Schematic of a cement kiln in which municipal solid waste incinerator fly ash is co-processed (Liu et al. 2015b).

losses. After the sampling work was complete, the samples were stored in a refrigerator until they were analyzed. Sample information and the labels used are shown in Fig. 1.

2.2. Sample extraction, cleanup, and instrumental analysis

The PCN concentrations in the samples were determined by isotope dilution HRGC/HRMS. The sample extraction, cleanup, and instrumental analysis procedures have been described in detail previously (Liu et al., 2009, 2010, 2012, 2013a, 2013b). Briefly, each sample was spiked with known amounts of $^{13}\text{C}_{10}$ -labeled PCN internal standards (ECN-5102; Cambridge Isotope Laboratories). The sample was then Soxhlet extracted for about 24 h, then the extract was concentrated under decreased pressure. The extract was then passed through silica gel treated with 44% (mass fraction) sulfuric acid, a multilayer silica gel column, and a basic alumina column. The cleaned extract was then evaporated to about 20 μL at a decreased pressure and then under a gentle stream of nitrogen. $^{13}\text{C}_{10}$ -1,2,3,4,5,7-hexachloronaphthalene (ECN-5260; Cambridge Isotope Laboratories), also an injection standard, were then added to allow the internal standard recoveries to be determined.

The PCNs in the extract were determined using a HRGC/HRMS instrument, using the M^+ or $(\text{M}+2)^+$ ions or the most abundant ions in the molecular ion cluster. A DB-5ms fused-silica column (60 m long, 0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies, Santa Clara, CA, USA) was used to separate the analytes. The HRMS was operated at a resolution of around 10,000 in selected ion monitoring mode.

The chloride contents of the particulate samples were determined following the Chinese standard method for the chemical analysis of cement (GB/T 176-2008) as described in our previous study (Liu et al., 2015b).

2.3. Quality assurance and quality control

The analysis of all 75 PCN congeners at trace concentrations in

complex matrix is challenging. In this study, all of the 75 congeners were quantified. Within them 37 congeners were completely resolved. However, there are still 38 congeners were co-eluted in spite of the advance technique of HRGC/HRMS was adopted. Analyte peaks were identified by comparing their retention times with the retention times of individual analyte standards (taking the elution order of the analytes from a DB-5 column into consideration) and from the target/qualifier ion ratios. A peak was quantified if the target/qualifier ion ratio was within 15% of the theoretical value. The accuracy of the quantification by the isotope-dilution method could be achieved by calibrating the loss of the target compounds by the isotope-labeled compounds. The $^{13}\text{C}_{10}$ -labeled PCN internal standard recoveries, determined using the labeled injection standards were 35–130%. The PCN congener detection limits were 0.03–5.3 pg g^{-1} for particulate samples and 0.08–5.2 pg m^{-3} for stack gas samples. Laboratory blanks were analyzed with each batch of samples (six samples for one batch). One field blank sample was also analyzed. A few congeners, including the PCN congeners CN-1 and CN-2 were found in the blanks at concentrations higher than their limits of detection but at less than 5% of the amounts found in the samples. The concentrations of the other congeners in the blanks were lower than the limits of detection. The PCN concentrations in the samples were therefore not corrected for the concentrations in the blanks. The cost of PCN analysis by isotope-diluted HRGC/HRMS method is high. In order to save the analytical cost, triplicate analysis for one particulate sample were performed to assess the variations of PCN analysis. The relative standard deviations (RSDs) for the PCN concentrations ranged from 5% to 25% (16% for MoCN, 21% for DiCN, 23% for TrCN, 14% for TeCN, 5% for PeCN, 7% for HxCN, 9% for HpCN and 25% for OCN). These parameters met the requirements for the trace analysis of POPs in complex matrices by isotope dilution HRGC/HRMS.

2.4. Calculation of thermodynamic parameters and charge densities of PCN congeners

Molecular geometries were optimized using the density functional theory method MPWB1K/6-31 + G(d,p) (Hehre et al., 1972; Kohn, 1995; Zhao and Truhlar, 2004), and vibrational frequencies were calculated to check that each geometry gave the potential energy surface minimum. MPWB1K is one of the hybrid density functionals, and has been successfully used to study the thermodynamics and kinetics for the formation and degradation of chlorinated polycyclic aromatic hydrocarbons (Zhang et al., 2014; Dang et al., 2015; Shi et al., 2015; Xu et al., 2015). Isodesmic reactions were designed to allow the relative thermal energies (ΔE), standard enthalpies of formation (ΔH), and standard free energies of formation (ΔG) of the PCN congeners used in our study to be calculated (Frisch et al., 2010; Yang et al., 2010). ΔE , ΔH , and ΔG were calculated with the following equations, and the formation energies of PCN congeners are researched:

$$\Delta E = E(c) + n E(d) - E(a) - n E(b)$$

$$\Delta H = H(c) + n H(d) - H(a) - n H(b)$$

$$\Delta G = G(c) + n G(d) - G(a) - n G(b)$$

All the theoretical calculations were carried out with the software package Gaussian 09 (Frisch et al., 2010).

The ΔE values for the chlorination processes were calculated at the MPWB1K/6-311 + G(3df,2p)/MPWB1K/6-31 + G(d,p) level with zero-point vibrational energy correction, and the values were corrected using a factor of 0.9335 to eliminate known systematic errors in the calculated frequencies. The relative energies were calculated for the isodesmic reactions. The absolute enthalpies (H) and Gibbs free energies (G) used to calculate ΔH and ΔG were obtained directly from density functional theory calculations. The charge densities of the carbon atoms in the PCN molecules were calculated using Natural Bond Orbital (version 3.1) software, using established methods (Glendening et al., 1980; Foster and Weinhold, 1980; Reed and Weinhold, 1983; Reed et al., 1985, 1988).

3. Results and discussion

3.1. Concentrations and profiles of PCNs in cement kiln stack gases

Quantifying PCN emissions in stack gases could help in the evaluation of the influences of PCNs on the environment surrounding a cement kiln. The PCN concentrations in the stack gas samples were 436–1054 ng m⁻³ (mean 710 ng m⁻³, RSD 44.4%). The standard deviations of total PCN concentrations of three stack gas samples were 44.4%. However, for several specific congeners, such as CN-59 and CN-75, the standard deviations were large. The concentrations of the PCN congeners in the stack gas samples are shown in detail in Table S2 in the Supplementary data. The PCN TEQs were also calculated using previously reported PCN toxic equivalency factors (TEFs) (Van den Berg et al., 1998; Blankenship et al., 2000; Villeneuve et al., 2000; Noma et al., 2004; Falandysz et al., 2013). The PCN TEQs were 8.15–17.83 pg TEQ m⁻³ (mean

12.33 pg TEQ m⁻³, RSD 40.3%). We found a mean PCDD/F concentration of 44.1 pg TEQ m⁻³ (range 31.5–55.6 pg TEQ m⁻³, RSD 27.4%) in stack gas samples in a previous study (Liu et al., 2015b). Therefore, the TEQ concentrations show the levels of PCN were lower than those of PCDD/Fs.

Emission patterns of unintentionally produced POPs to the atmosphere for specific industrial sources are useful when attempting to identify the specific sources of those POPs to the environment (Meijer et al., 2001; Schuhmacher et al., 2004). The PCN patterns in the stack gases in the cement kilns co-processing MSWI fly ash are shown in Fig. S1, in Supplementary data. Monochlorinated naphthalene (MoCN) was the dominant homolog, followed by di-chlorinated naphthalene (DiCN) and tri-chlorinated naphthalene (TriCN). The CN-1 and CN-2 congeners were dominant for the PCNs. For the various homologs, the following congeners were dominant: CN-11/8 for DiCN; CN-24/14 for TriCN; CN-33/34/37 and CN-27/30 for tetra-chlorinated (TeCN); CN-52/60, CN-51 and CN-54 for penta-chlorinated (PeCN); CN-66/67 for hexa-chlorinated (HxCN); and CN-73 for hepta-chlorinated (HpCN).

The PCN congener profiles were distinctly different from the profiles in technical PCN mixtures and the profiles of waste incineration sources. We compared the PCN congener patterns found in the stack gases analyzed in this study, in flue gases from MSWIs, and in technical PCN mixtures (Noma et al., 2004; Takasuga et al., 2004). CN-2 was the dominant MoCN congener in the stack gases analyzed in this study, but CN-1 was dominant in Halowax mixtures and CN-1 and CN-2 were found at similar concentrations in MSWI flue gases. CN-5/7 and CN-11/8 were the dominant DiCN congeners in this study, but CN-4 was dominant in MSWI flue gases and CN-5/7 were dominant in Halowax mixtures. CN-24/14 were the dominant TriCN congeners in this study and in Halowax mixtures, but CN-13/22 were dominant in MSWI flue gases. CN-27/30 and CN-33/34/37 were the dominant TetraCN congeners in this study, but CN-36/45 were dominant in MSWI flue gases, and CN-38/40 and CN-33/34/37 were dominant in Halowax mixtures. CN-51, CN-52/60, and CN-54 were the dominant PeCN congeners in this study, but CN-59 was dominant in Halowax mixtures and CN-52/60 were dominant in MSWI flue gases. CN-66/67 were the dominant HxCN congeners in this study and in MSWI flue gases, but CN-71/72 were dominant in Halowax mixtures. CN-73 was the dominant HpCN congener in this study and in MSWI flue gases, but CN-74 was dominant in Halowax mixtures. The PCN patterns in the cement kiln stack gases might be useful for apportioning the sources of unintentionally formed POPs found in the environment, including in biota.

3.2. Distributions and homolog patterns of PCNs in particulate samples from different parts of the cement kilns

Particles (e.g., fly ash) are widely considered to play important roles in the catalysis of the heterogeneous reactions that dominate the formation pathways of unintentionally produced POPs during thermal processes (Tuppurainen et al., 2003; Liu et al., 2013a; Jiang et al., 2015). PCN concentrations in particulates produced during different stages of the cement production process could be used to identify the major sites in which PCNs are formed in cement kilns co-processing MSWI fly ash and the distributions of the PCNs in the cement kilns. The PCN concentrations and homolog patterns in the particulate samples from different parts of the cement kilns are shown in Fig. 2. The concentrations of the PCN congeners are provided in Table S2. The PCN mass concentrations in the Ck-p2, Ck-p3, and Ck-p5 samples were 23.0, 23.5, and 84.7 ng g⁻¹, respectively. The PCN mass concentration in the Ck-p1 and Ck-p4 sample was 8.7 and 9.5 ng g⁻¹, respectively. The PCN mass concentrations were lower than 3.5 ng g⁻¹ in the particulate samples from all of

Fig. 2. Polychlorinated naphthalene distributions and homolog patterns in particulate samples (labeled Ck-p1 to Ck-p8) from different parts of the line 1 cement kiln (CNs = chloronaphthalenes, Mo = mono, Tr = tri, Pe = penta, Hp = hepta, O = octa).

the other parts of the kilns. The PCN concentrations were higher in the particulate samples from the suspension pre-heater boiler, humidifier tower, and bag filter at the kiln back-end (i.e., at sampling points Ck-p2, Ck-p3, and Ck-p5) than in the samples from the other parts of the kilns, which indicating that suspension pre-heater boiler, humidifier tower, and the kiln back-end bag filter might be the dominant formation sites of PCNs in the cement kiln system. The temperature is an important factor in the formation and emission of unintentionally produced POPs. The temperatures of the different parts of cement kiln 1 are shown in Fig. 1. The temperatures in the cyclone preheater outlet (C1 in Fig. 1) and the suspension pre-heater boiler (SP in Fig. 1) ranged from 233 to 396 °C. This is widely recognized as being a suitable temperature range for the formation of unintentionally produced POPs, including PCNs and PCDD/Fs. The temperatures in these parts of cement kilns could be important factors in the formation of PCNs. This information will help in the development of techniques for controlling the formation and emission of PCNs in the key parts of cement kilns co-processing of MSWI fly ash. The PCN distributions throughout the cement process line found in this study were similar to PCDD/F distributions that we previously found in cement kilns (Liu et al., 2015b). Therefore, it is indicated that it is possible to achieve the simultaneous control of those pollutants because the major formation stages of those pollutants throughout the cement process line were same.

The homolog pattern of a class of organic compounds with similar molecular structures normally reflects the underlying formation mechanism for that class of compounds (Weber and Hagenmaier, 1999; Weber and Sakurai, 2001). The PCNs were dominated by the MoCNs, followed by the DiCNs and TriCNs. The less chlorinated homologs were dominant in the particulate samples collected from most parts of the kilns. The PCN homolog patterns in the different particulate samples were similar, with the contribution to the total concentration decreasing as the chlorination level increased.

It has previously been found that memory effects can promote the formation and emission of POPs during industrial thermal processes (Weber et al., 2002; Cunliffe and Williams, 2009). PCN

concentrations in different parts of the line 2 cement kiln, which had not previously been used to co-combust MSWI fly ash, were determined so that any effects of the long-term thermal treatment of MSWI fly ash on the formation of PCNs in the line 1 cement kiln could be identified. The line 1 and line 2 kilns were both dry-process rotary kilns, and were very similar in operational conditions. The same batch of MSWI fly ash produced by a single waste incinerator was used in the line 1 and line 2 kilns. The PCN concentrations in the samples from the different parts of the line 1 and line 2 kilns are shown in Fig. S2 (Supplementary data). The PCN mass concentrations and TEQs were higher in the line 1 kiln samples than in the line 2 kiln samples. The differences between the concentrations in the samples from the line 1 and line 2 kilns were higher for the samples from sites Ck-p2, Ck-p3, and Ck-p5 than for the samples from the other sampling sites. This further showed that PCNs were predominantly formed at sampling sites Ck-p2, Ck-p3, and Ck-p5 in the kilns. Periodically cleaning solid residues from these areas could therefore decrease the amounts of POPs that will be unintentionally formed.

3.3. Mass balance calculation of PCNs from input to output

A mass balance would help understand PCN inputs, outputs, and net emissions from a cement kiln co-processing MSWI fly ash (Liu et al., 2015b). We calculated mass balances based on the PCN concentrations in the feedstocks, stack gases, and clinker, and using the parameters for the cement production activities. The raw meal and coal powder feed rates were 176.9 t h⁻¹ and 15.6 t h⁻¹, respectively. The clinker output rate was about 120.3 t h⁻¹. The mean stack gas flow rate was 23 3599 m³ h⁻¹ (Liu et al., 2015b). The PCN concentrations were 603 pg g⁻¹ in the raw meal and 324 pg g⁻¹ in the coal powder. The hot air produced in the cyclone preheater outlet was cooled to about 200 °C and then introduced to the coal mill to dry the coal powder. The cyclone preheater outlet in each kiln was found to be an important site for the formation of PCNs. Introducing air from the cyclone preheater outlet to the coal mill could, therefore, increase the PCN contents of the coal powder used as fuel. We found similar results for PCDD/Fs in a previous

study (Liu et al., 2015b). The PCN concentrations in the MSWI fly ash added to the cement kilns were $279,793 \text{ pg g}^{-1}$. Particulates collected by the air pollution control devices at the kiln head and back end are normally recycled by adding them to the raw materials, so no PCNs would have been released in the particulates collected by the air pollution control devices (Liu et al., 2015b). The PCN mass balances are shown in Table S4 (Supplementary data). The net amounts of PCNs emitted by the cement kilns were -196 mg h^{-1} . The PCN outputs were about 50% lower than the inputs.

3.4. Congener profiles of the PCNs in particulate samples from different parts of the kilns

The congener profiles of unintentionally produced POPs could be used to identify the POP formation mechanisms (Iino et al., 2001). The concentrations of $\sum_{1-8}$ PCNs in the original MSWI fly ash were 280 ng g^{-1} . The PCN congener profiles in the MSWI fly ash and particulate samples from cement kilns are presented in Fig. 3. The PCN congener profiles in the MSWI fly ash were generally similar to that of the particulate samples from the cement kilns. However, for several congeners, such as CN-11/8, CN-9 and CN-18, the fractions were obviously different in MSWI fly ash from that in particulate samples from the cement kilns. Further simulation studies on lab scale might be needed for clarifying the underlying reason.

The concentration of each congener was expressed as a fraction of the corresponding homolog concentration to minimize the influences of the concentrations of different PCN homologs and to allow the PCN congener profiles to be compared. The PCN congener profiles in the particulate samples from different parts of the kilns are shown in Fig. 3. The fractions of CN-1 were similar to that of CN-2 in particulate samples from different parts of the kilns, indicating that CN-1 and CN-2 were formed to the similar extent. The values for the DiCNs CN-5/7 were lower for the samples from the five kiln-back-end parts than for the samples from the kiln head boiler, the clinker area, and the kiln head bag filter. The CN-11/8 values were higher for the samples from the five kiln-back-end parts than for the samples from the kiln head boiler, clinker area, and kiln head bag filter. This pattern suggested that CN-11/8 were the major congeners formed at the back end of the kilns and that CN-5/7 formation was not favored there. The TriCN congener values were all relatively similar. It appeared that the formation of CN-13, CN-16, CN-17, CN-19, and CN-21 was favored at the back end of the kilns but that the formation of CN-23 and CN-24/14 was favored less than the formation of the other TriCN congeners.

The dominant TetraCNs were CN-27/30, CN-29, CN-33/34/37, CN-39, CN-44/47, and CN-45/36. Differences between the congener patterns in samples from different parts of the kilns suggested that CN-29, CN-33/34/37, and CN-39 were likely to form at the back ends of the cement kilns. CN-52/60 was the dominant PeCN, followed by CN-50, CN-51, and CN-54. Differences between the congener profiles in samples from different parts of the kilns suggested that CN-50, CN-51, and CN-54 were much more likely than the other PeCNs to form at the back ends of the kilns. The HxCNs were strongly dominated by CN-66/67. Differences between the congener patterns in samples from different parts of the kilns indicated that CN-66/67 formation was favored more than the formation of other HxCN congeners at the back ends of the kilns. CN-73 contributed more than 90% of the HpCNs, which was much more than CN-74 contributed. No obvious differences were found in the HpCN patterns in samples from different parts of the kilns.

The chloride contents of the particle samples from the back ends of the kilns ($52.6\text{--}92.1 \text{ pmol g}^{-1}$) were much higher than the chloride contents of the samples from the heads of the kilns

($5.5\text{--}24.8 \text{ pmol g}^{-1}$). It has been suggested, from theoretical calculations and experimental studies, that chlorination occurs much more easily at the β positions than at the α positions of a PCN molecule (Luijk et al., 1994; Zhai and Wang, 2005; Jansson et al., 2008). The main difference between the PCN congener patterns found in samples from the head and back ends of the kilns was that PCNs with β -position chlorines contributed much higher proportions of the PCNs in the back end samples than in the kiln head samples. We therefore speculated that the higher chloride contents of the back end samples than in the kiln head samples contributed to the different PCN congener patterns that were found in the head and back end samples. The different PCN congener patterns in the head and back end samples suggested that chlorination reactions at the β positions of PCNs occurred more frequently at the back ends of the kilns than at the kiln heads. Chlorination reactions would have occurred less readily at the kiln heads than at the back ends because the chloride contents were much lower at the kiln heads than at the back ends.

3.5. Potential PCN formation mechanisms in cement kilns

In 2015, PCNs were added, as new POPs, to Annex C of the Stockholm Convention. It then became obligatory for the signatory countries or regions to control and regulate unintentional emissions of PCNs. An understanding of PCN formation mechanisms could be useful when attempting to decrease unintentional emissions of PCNs. We identified the dominant PCNs in the back end samples, which were from the suspension pre-heater boiler, humidifier tower, back end bag filter, as mentioned above. The kiln heads were not considered to be major PCN formation sites. The congeners found at higher proportions in the back end samples than in the head end samples were considered to be the main compounds that were formed in the cement kilns. The PCN homolog and congener patterns presented in Fig. 3 were inspected, and we found that a chlorination mechanism was probably responsible for PCNs forming in cement kilns co-processing MSWI fly ash. The mechanism is presented in Fig. 4. The thick black arrows are the proposed major chlorination reaction pathways, whereas the thin blue arrows are minor chlorination pathways. Thermodynamic parameters were calculated to verify these proposed chlorination pathways, and the results are presented in Table S5 (Supplementary data).

The thermodynamic results showed that the proposed formation pathways were favorable. For example, for the DiCNs, ΔE and ΔG were higher for CN-4 and CN-5 than for CN-7, CN-8, and CN-11. For the TriCNs, ΔE and ΔG were higher for CN-23 than for the other dominant congeners. For the TetraCNs, ΔE and ΔG were higher for CN-46 than for the other congeners. As is shown in Fig. 4, CN-4, CN-5, CN-23, and CN-46 would have been formed through minor pathways. For the PeCNs, HxCNs, and HpCNs, ΔE and ΔG were higher for CN-59, CN-63, and CN-74, respectively. These congeners would also have been formed through minor pathways, as shown in Fig. 4. The thermodynamic calculation results therefore theoretically supported our proposed PCN formation pathways.

The chlorination of a PCN is widely thought to occur via the electrophilic substitution of hydrogen with chlorine. The charge density of the PCN molecule is very important to such an electrophilic substitution reaction. The charge densities of the PCNs (shown in Table S6 in the Supplementary data) were therefore calculated to improve our understanding of the chlorination processes. The charge density results generally agreed with our proposed chlorination pathways. For example, the chlorination of CN-16 at the 3β , 4α , 7β , or 8α position would give CN-29, CN-33, CN-39, or CN-40, respectively. The charge density was much lower for the carbon atom at 8α (-0.205) than for the carbon atoms at 3β

Fig. 3. Congener profiles of PCNs in particulate samples from different parts of the line 1 cement kiln (the congener concentration is shown relative to its total homolog concentration, as a wt%). (CN = chloronaphthalene, Mo = mono, Di = di, Tr = tri, Te = tetra, Pe = penta, Hx = hexa, Hp = hepta).

(-0.242), 4α (-0.206), and 7β (-0.246), so the chlorination of CN-16 to give CN-29, CN-33, and CN-39 could occur more readily than the chlorination of CN-16 to give CN-40. The charge densities at the

4α , 7β , and 8α positions of CN-51 were found to be -0.213 , -0.237 , and -0.233 , respectively. We therefore speculated that CN-51 would be more readily chlorinated at the 7β and 8α positions

Fig. 4. Proposed formation mechanisms for polychlorinated naphthalenes in cement kilns co-processing municipal solid waste incinerator fly ash (CN = chloronaphthalene).

than at the 4 α position, which would mean that more CN-67 and CN-68 than CN-63 would be produced. This agreed with the proposed pathways for the transformation of CN-51 to give CN-63, CN-67, and CN-68, shown in Fig. 4. Chlorination of CN-68 at the 4 α and 7 β positions would give CN-74 and CN-73, respectively. The charge density was higher at the 7 β position than the 4 α position of CN-68,

which could be an important underlying reason for CN-73 being more dominant than CN-74, as can be seen in the congener profiles for our samples and in the proposed formation mechanisms.

Generally, there are three kinds of mechanisms for PCN formation: (i) chlorination mechanism, (ii) formation by the degradation of polycyclic aromatic hydrocarbons and successive chlorination

(iii) formation by chlorinated phenols as precursor (Weber et al., 2001; Kim and Mulholland, 2005; Liu et al., 2014b). Chlorination was one of the formation mechanisms and we considered the chlorination mechanism because we have observed the decreasing trends in fractions from less chlorinated homologs to more chlorinated homologs in the cement kiln process. Further simulation studies in lab scale will be needed to give a comprehensive mechanism for PCN formation.

4. Conclusions

In this study, a field pilot study on two cement kilns co-processing MSWI fly ash were performed to characterize the distributions and congener profiles of PCNs in cement kiln systems. Suspension pre-heater boiler, humidifier tower, and the kiln back-end bag filter were identified to be the dominant formation sites of PCNs in the cement kiln systems. Lower chlorinated homologs were much more dominant over higher chlorinated homologs of PCNs. Chlorination was suggested to be one of important formation mechanisms for PCNs, and chlorination pathways of PCN congeners are proposed based on the congener profiles. The mass balance calculations of PCNs indicated a 50% of PCN reduction from the input to the output by the cement kilns.

Acknowledgments

We gratefully acknowledge support from the National 973 program (2015CB453100), National Natural Science Foundation of China (91543108), Strategic Priority Research Program of the CAS (XDB14020102) and Youth Innovation Promotion Association CAS (2016038).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.04.069>.

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