Variations and factors that influence the formation of polychlorinated naphthalenes in cement kilns co-processing solid waste

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HIGHLIGHTS

- PCN destruction efficiencies of cement kilns were derived.
- Factors influencing PCN variation and formation were identified.
- Major pathways for PCN formation and decomposition in cement kiln were discussed.
- PCN indicators for sources involved with coal burning were proposed.

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ABSTRACT

Pilot studies of unintentionally produced pollutants should be performed before waste being co-processed in cement kilns. Polychlorinated naphthalene (PCN) formation and emission from cement kilns co-processing sorted municipal solid waste, sewage sludge, and waste acid, however, have not previously been studied. Here, PCNs were analyzed in stack gas samples and solid samples from different stages of three cement production runs. PCN destruction efficiencies were higher when waste was co-processed (93.1% and 88.7% in two tests) than when waste was not co-processed (39.1%), so co-processing waste would not increase PCN outputs. The PCN concentrations were higher in particle samples from the C1 preheater and stages at back end of kiln than in particle samples from other stages, suggesting that cyclone preheater and back end of kiln should be focused for controlling PCN emissions. Besides that, based on the variation of PCN concentrations and corresponding operating conditions in different stages, the temperature, feeding materials, and chlorine content were suggested as the main factors influencing PCN formation. The PCN homologue and congener profiles suggested chlorination and dechlorination were the main PCN formation and decomposition pathways, and congeners CN-23, CN-46, and CN-59 appear to be appropriate indicators of PCNs emitted from coal-burning sources.

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1. Introduction

Co-processing waste when producing cement is a waste management technique that offers the benefits of simultaneously destroying waste, producing cement, and recycling energy [1–3]. China has a large cement industry that accounts for about 60% of annual global cement production. Co-processing waste in cement kilns offers economic, technical, and environmental benefits that make it an attractive and promising waste treatment technique.

However, the problems such as organic chemical, carbon dioxide, and heavy metal emissions, are already associated with co-processing waste in cement kilns, and more detailed studies need to be performed before the benefits of co-processing waste in cement kilns can be considered to have been comprehensively evaluated [1,4–7].

Unintentionally produced persistent organic pollutants (POPs) are organic chemicals that can form during thermal processes. Estimations of unintentionally produced POPs formed during different thermal processes allowed emissions of unintentionally produced POPs by various industrial plants to be comprehensively recognized and effectively controlled. Polychlorinated naphthalenes (PCNs) are chemicals that have similar structures and toxicities to poly-

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Fig. 1. Diagram of a cement kiln with the sampling points marked.

chlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and have recently been added to Annexes A and C of the Stockholm Convention, indicating the obligation of reducing the unintentional release of PCNs from industrial thermal sources besides forbidding the production and use of PCNs as chemicals for signatories [8]. The unintentional production of PCNs during thermal processes has already been the main source of PCNs in ambient air. Previous studies have reported larger amounts of PCNs than PCDD/Fs were emitted during various thermal processes [9,10]. Therefore, studies of PCN emissions during different thermal processes are of significance necessary. The present study would investigate the formation of PCNs when cement is produced using co-processed waste, and improve our understanding of PCN formation and the factors that influence PCN formation during industrial processes.

The PCDD/Fs are extremely toxic, and various industries are subject to PCDD/F emission standards in many countries. Previous studies of POPs in cement kilns co-processing waste have mainly been focused on PCDD/Fs. PCDD/Fs have been found to be emitted when wastes such as fly ash, meat meal, municipal solid waste (MSW), sewage sludge, and tires are co-processed in cement kilns [1,11–13]. It has been found in previous studies that co-processing waste in cement kilns does not increase PCDD/F emissions, and the concentrations emitted in those studies were always below the European Union limit for cement kilns (0.1 ng toxic equivalents [TEQ] m⁻³) when the kilns were operated under normal conditions [1,11,14–16]. Mass balances of cement kilns have also shown that co-processing waste in cement kilns is an efficient way for destroying PCDD/Fs [11,15,17]. Co-processing different wastes in cement kilns has been found in previous studies not to markedly affect the congener profiles of the PCDD/Fs emitted, but the results of these studies provided insight into PCDD/F formation pathways and allowed specific PCDD/F sources to be identified and PCDD/F emissions to be apportioned [12,13].

Close correlations have been found between PCN and PCDD/F concentrations in samples from different thermal processes [18]. Thus, the previous literature reports of PCDD/Fs released from cement kiln co-processing wastes hint that the formation and emission of PCNs from similar processes might occur. PCNs have already been found to be emitted from cement kilns with no waste co-processed [19]. However, to the best of our knowledge, no study

of PCNs in cement kilns co-processing sorted MSW, or simultaneously co-processing dried sewage sludge, wet sewage sludge and waste acid has been performed. Additionally, no study of the factors that influence the formation of PCNs when waste is co-processed in cement kilns has been carried out. Such studies would provide information that would help in the development of PCN control measures.

In this study, clinker, coal, raw meal samples, sludge, stack gas samples and particle samples from other different stages of the kiln systems in three cement production processes were collected. The samples were analyzed for PCNs by isotope dilution high-resolution gas chromatography and high-resolution mass spectrometry. The aim was to obtain detailed information on the formation of PCNs when cement was produced while co-processing different wastes, to assess variability in the PCNs formed, and to identify factors that influence PCN formation in cement kilns co-processing waste. The results of this study could improve our understanding of factors that influence PCN formation, and be useful in identifying new PCN sources and developing strategies for controlling PCN emissions from cement kilns co-processing waste.

2. Experimental

2.1. Basic information

Samples were taken during three cement production runs (Series 1, Series 2, and Series 3); information on these is given in Table 1. Series 2 was performed at a plant when sorted MSW was co-processed, and Series 1 was performed at the same plant when no waste co-processed. Non-combustible materials, such as the glass and metals, were also contained in the raw MSW. Thus, the MSW was sorted to remove those non-combustible materials and to improve the heat value before being co-processed by the cement kilns. The sorted MSW contained relatively high proportion of combustible wastes, such as plastics, wood, and papers. The proportion of combustible component was about 78% in the sorted MSW of this study. As shown in Fig. 1 insert, the sorted MSW was incinerated in the incinerator and then the flue gas was added to the bottom of the precalciner. Dried sewage sludge was mixed with raw meals, and co-processed in both Series 1 and Series 2. Series 3 was performed

Table 1

Basic information on the cement production plants.

Production Series		Samples	Raw meal (t d ⁻¹)	Clinker (t d ⁻¹)	Coal (t d ⁻¹)	Waste (t d ⁻¹)	Flow rate (Nm ³ h ⁻¹) ^a
Plant 1	Series 1	8	4879.4	3012	352.4		251,424
	Series 2	7	3385.8	2090	430.5	Sorted MSW	72
Plant 2	Series 3	8	4406.4	2754	421.9	Sewage Sludge	338
						Waste acid	10
						Wet sewage sludge	38

^a The operating time for the three series was 24 h a day.

at a plant at which dried sewage sludge, wet sewage sludge and waste acid were co-processed simultaneously. In Series 3, sewage sludge was dried in a drying system and then fed into precalciner, waste acid was fed into the kiln head, and the wet sewage sludge was fed into the bottom of the precalciner.

Each of the cement kiln systems consisted of a chimney, two bag filters (one at the kiln head and one at the back end of kiln), an air quenching cooler (later simply called the cooler), a boiler at kiln head, a coal mill, a rotary kiln, a precalciner, a five-stage cyclone preheater (C1 to C5), a suspension preheater (SP) boiler, and a humidifier tower. We divided each cement production line into three zones, the preheater zone, the kiln end zone, and the kiln head zone. The cement production process is shown in Fig. 1. The solid line represents the flow of solid materials, the dotted line represents the flow of gas, and dots indicate sampling points. Raw meals were added into the kiln between the first stage and second stage of cyclone preheaters. The raw meal used in Series 1 and Series 2 was all from the same batch and the same silo, so only one raw meal sample was analyzed for both Series 1 and Series 2.

2.2. Sampling and analytical methods

Solid samples were collected from the cement production plants, and were homogenized before analysis. Stack gas samples were collected using an automatic isokinetic sampling system (TCR TECORA, Italy). The stack gas sampling method has been described in detail previously [20,21]. An isotope dilution high-resolution gas chromatography and high-resolution mass spectrometry method described previously was used to determine the PCN concentrations in the samples [20,22,23]. Each stack gas or solid sample was spiked with a ¹³C₁₀-labeled PCN internal standard mixture (ECN-5102, containing the ¹³C₁₀-labeled tetra- to octa-chlorinated naphthalenes CN-27, CN-42, CN-52, CN-67, CN-73, and CN-75; Cambridge Isotope Laboratories, Andover, MA, USA). Each solid sample was acidified by adding 1 mol L⁻¹ HCl, then washed with distilled water until the washings were close to pH = 7. The solid samples were then freeze-dried. Each freeze-dried sample or stack gas sample was Soxhlet extracted with toluene (250 mL) for 20 h. Each extract was cleaned by passing it through a multilayer silica gel column and an activated carbon column. The cleaned extract was then concentrated to about 20 µL using a rotary evaporator and then under a gentle stream of nitrogen. A ¹³C₁₀-labeled PCN recovery standard (ECN-5260, ¹³C₁₀-labeled CN-64; Cambridge Isotope Laboratories) was added before injection.

Each extract was analyzed for 75 PCN congeners using a gas chromatograph coupled to a high resolution mass spectrometer (DFS; Thermo Fisher Scientific, Waltham, MA, USA). The gas chromatograph was equipped with a J&W DB-5 MS fused silica column (60 m long, 0.25 mm i.d., 0.25 µm film thickness; Agilent Technologies, Santa Clara, CA, USA). The mass spectrometer was operated at a resolution of 10,000 in positive electron impact ionization mode, with an electron energy of 45 eV. The carrier gas was helium, and the flow rate was 1 mL min⁻¹. The inlet, source, and auxiliary temperatures were 260, 250, and 290 °C, respectively. The oven temperature program started at 80 °C, which was held for

2 min, then increased at 20 °C min⁻¹ to 180 °C, held for 1 min, then increased at 2.5 °C min⁻¹ to 280 °C, then increased at 10 °C min⁻¹ to 290 °C, held for 5 min. Blank samples were analyzed with each batch. The recovery ranges of ¹³C₁₀-labeled CN-27, -42, -52, -67, -73, -75 in the samples were 44–83%, 44–81%, 60–94%, 42–94%, 39–87%, 39%–117% respectively. The detection limits for the chemicals in solid samples were in the range of 0.01–0.48 pg g⁻¹, while for the stack gas samples, the detection limits were 0.53–1.92 pg m⁻³.

3. Results and discussion

3.1. Concentrations of PCNs in input and output samples

In this study, the important process – from raw meal to clinker was studied. Coal, raw meal, and sewage sludge were the original solid materials added to the kilns, so they were defined as input samples. Clay, limestone, and dried sewage sludge were homogenized to form raw meals used in Series 1 and Series 2. Raw meal (containing clay, limestone, and other materials) and dried sewage sludge were added separately in Series 3, so they were analyzed separately. The clinkers and stack gases produced were defined as output samples.

The PCN mass concentrations and TEQs in the clinkers, coals, raw meals, and dried sewage sludge are shown in Table 2. The PCN mass concentrations in clinker (20.8 ng g⁻¹) and raw meal sample (21.5 ng g⁻¹) from Series 1 were similar. For Series 2, the PCN mass concentration was 21.5 ng g⁻¹ in raw meal sample but only 1.7 ng g⁻¹ in clinker. This indicated that PCNs in raw meal were effectively degraded when sorted MSW was co-processed. The PCN mass concentrations in raw meal and in sewage sludge of Series 3 were 1.7 and 2.5 ng g⁻¹, respectively, but in clinker it was only 0.3 ng g⁻¹. The total PCN TEQ for a sample was defined as the sum of the mass concentration of PCN congener multiplied by the relative potency factor of that congener, as described by Noma et al. [24,25]. As shown in Table 2, the PCN TEQs were also lower in clinkers than in the corresponding raw meals. The PCN TEQs in clinkers of Series 1, Series 2, and Series 3 were 240.0, 32.1, and 21.7 pg TEQ kg⁻¹, respectively. The PCN TEQs in raw meal samples of Series 1, Series 2, and Series 3 were 583.4, 583.4, and 62.5 pg TEQ kg⁻¹, respectively. The PCN concentrations in stack gas samples of Series 1, Series 2, and Series 3 were 379.1, 277.1, and 88.3 ng Nm⁻³, respectively, and the PCN TEQs were 10.4, 8.8, and 0.3 pg TEQ Nm⁻³, respectively. The concentrations of PCNs without any waste co-processed in cement kiln system were reported to be 111.1 ng Nm⁻³ (tetra- to octa- homologues), which was lower than that of Series 1 and Series 2, but higher than that of Series 3 investigated in this study [19].

The PCN destruction efficiency (DE) was introduced to normalize the efficiencies at which PCNs were degraded in the three runs. The PCN DE by mass or TEQ was calculated using Eq. (1), in which W_i is the amount of total ($\sum$) PCNs (by mass or TEQ) fed into the kiln through coal, raw meal, and dried sewage sludge, and W_0 is the amount of $\sum$ PCNs output from the kiln in stack gas and clinker. The PCN DE results are shown in Table S1.

$$DE = \frac{(W_i - W_0)}{W_i} \times 100\% \quad (1)$$

Table 2

Mass concentrations and toxic equivalents (TEQs) of the polychlorinated naphthalenes (PCNs) in the solid samples collected during the cement production processes.

	Series1			Series2			Series3		
	Label	$\sum$ PCNs (ng g ⁻¹)	TEQ (pg TEQ kg ⁻¹)	Label	$\sum$ PCNs (ng g ⁻¹)	TEQ (pg TEQ kg ⁻¹)	Label	$\sum$ PCNs (ng g ⁻¹)	TEQ (pg TEQ kg ⁻¹)
Bag Filter 1	B1	15.0	191	C1	0.50	30.8	D1	0.50	22.4
Boiler at kiln head	B2	8.10	135	C2	1.90	30.4			
C1 Preheater	B3	18.1	148	C3	4.20	113	D3	8.60	430
SP boiler + Humidifier tower	B4	8.30	92.2	C4	16.5	339	D4	42.7	768
Bag Filter 2	B5	29.3	646	C5	19.0	541	D5	38.0	512
Raw Meal	B6	21.5	583				D6	1.70	62.5
Coal	B7	4.00	58.7	C7	0.70	35.0	D7	4.80	101
Clinker	B8	20.8	240	C8	1.70	32.1	D8	0.30	21.7
Sludge							D9	2.50	290

As is shown in Table S1, the amount of $\sum$ PCNs was decreased by 41.6, 68.2, and 9.4 g d⁻¹ and by 2.1, 1.9, and 0.4 mg TEQ d⁻¹ in Series 1, Series 2, and Series 3, respectively. The PCN DEs by mass and TEQ were higher for Series 2 (93.1% and 94.2%, respectively) and Series 3 (88.7% and 85.3%, respectively) than for Series 1 (39.1% and 72.6%, respectively). The tentative explanation about the low PCN destruction efficiency in Series 1 than Series 2 and 3 was provided as follows. First of all, as listed in Table 1, the amount of coals added in Series 1 was lower than in Series 2 and Series 3. The higher contents of coals as fuels in Series 2 and 3 might make the combustion more complete in Series 2 and 3 than Series 1, and this would be one of important reasons of lower destruction efficiency of Series 1 than Series 2 and 3. Secondly, the raw meal added in Series 1 was of larger amount than in Series 2 and Series 3, which might contribute to the much higher load of thermal treatment in Series 1 than Series 2 and 3. The lower destruction efficiency in Series 1 than Series 2 and 3 might be explained by the combining effect of the lower amount of coals as fuel and the larger amount of raw meals together. The wastes that were added (sorted MSW in Series 2 and wastes except for dried sewage sludge in Series 3), which were likely to contain PCNs, were not included in the DE calculations. The actual DEs for Series 2 and Series 3 could therefore be higher than the DEs that were calculated using Eq. (1). The results described above indicated that producing cement while co-processing waste did not cause PCNs to be produced but rather to effectively help decrease the PCN mass outputs.

3.2. Variations and the factors influencing PCN concentrations in particle samples

Particle samples were collected from different stages of the cement production processes, and the PCN concentrations found in the samples are shown in Table 2. The PCN mass concentrations in the particle samples were 0.5–42.7 ng g⁻¹. In terms of the general conditions of the three series, the PCN mass concentrations were higher in samples from C1 preheater and samples from back end zone (including bag filter at the back end of kiln, and SP boiler and humidifier tower) than in samples from other stages, indicating that PCNs were more likely to form in the cyclone preheater and the back end of kiln than elsewhere. This agreed with the results of a previous study, in which it was found that the main sites at which PCDD/Fs were formed in a cement kiln co-processing fly ash from MSW incinerators were the cyclone preheater, the SP boiler, the humidifier tower, and the bag filter at the back end of kiln [11].

A number of factors affect PCN formation during industrial thermal processes. It has previously been found that the technique used, residence time, and raw material composition influence the formation of organic compounds during thermal processes [16,26]. The gases and solid materials flow in opposite directions in cement kiln system, meaning that the performance in terms of PCN formation will be affected by many factors.

Temperature is one of important factors influencing the formation and destruction of POPs. In general, POPs can be completely destroyed at temperatures >800 °C but can form easily between 200 and 450 °C [27,28]. The temperature has been found to affect PCN formation, and the PCN concentration has been found always to reach a maximum at 200–300 °C [29–31]. The mean temperatures of the stages in Series 1, Series 2, and Series 3 are shown in Fig. S1. The rotary kilns were at >1200 °C. This caused the PCNs to completely decompose at this stage. The temperature decreased from about 800 °C to 400 °C in the cyclone preheater zone, where the formation rate would have been lower than the decomposition rate. This was verified by the PCN concentrations in samples from C1 preheater in Series 1 and Series 2 (18.1 and 4.2 ng g⁻¹, respectively) being lower than the PCN concentration in the raw meals (21.5 ng g⁻¹) and in samples from bag filter at back end of kiln (29.3 and 19.0 ng g⁻¹, respectively), which were re-introduced into the kiln. The kiln end zones were at 150–400 °C, which includes the most suitable temperature range for PCN formation. This would have been why higher PCN concentrations were found in the samples from the bag filter at back end of kiln than in the samples from C1 preheater. The PCN concentrations in samples from back end of kiln may also have been high because PCNs volatilize at 259–365 °C, so some of the PCNs in the gaseous phase would have become adsorbed to particles at temperatures <259 °C of back end of kiln [32,33].

The kiln head zones were at similar temperature range to the kiln end zones, but the PCN concentrations were significantly higher in the kiln end zone samples than in samples from kiln head. One reason for this could be the effect of the feeding materials under the flowing gas. Feeding materials make important contributions to PCN concentration and formation during thermal processes [34]. PCNs present in feeding materials could be important sources of PCNs emitted during thermal processes. Moreover, PCN formation pathways from precursors such as naphthalene, aromatic hydrocarbons, and chlorophenols, which were most likely to exist in feeding materials, have been proposed [30,35–37]. The feeding materials of the cement kilns included fuel, raw meal, and waste. Raw meal and re-introduced bag filter dust were fed into each kiln between first and second stage of cyclone preheater. 65% of the coals were fed into the precalciner, and 35% were fed into the rotary kiln. The flowing gases would draw raw meal dust and the re-introduced fly ash into the kiln end zone and clinker dust into the kiln head zone. Therefore, PCNs and precursors in the raw meal and re-introduced bag filter dust would affect the PCN concentrations in the samples from C1 preheater and back end of kiln, and PCNs in the clinkers would affect the PCN concentration in samples from kiln head. As a result, lower PCN concentration in the clinkers than in raw meals resulted in lower PCN concentration in samples from kiln head zone than in samples from back end of kiln.

Another important factor was the chlorine content of the feeding materials. It has been found in a number of studies that the chlorine content affects POPs concentrations and that chlorination

Fig. 2. Polychlorinated naphthalene homolog patterns in the solid input and output samples collected from the cement kilns. CN: chloronaphthalene, Mo: mono, Ti: tri, Te: tetra, Pe: penta, Hx: hexa, Hp: hepta, O: octa.

Fig. 3. Mass concentration of the polychlorinated naphthalene homologues in the solid samples collected at each stage of the cement production process at each plant. CN: chloronaphthalene, Mo: mono, Ti: tri, Te: tetra, Pe: penta, Hx: hexa, Hp: hepta, O: octa.

is an important POPs formation pathway [30,38]. The chlorination of naphthalene and less-chlorinated PCNs could be catalyzed by

metal chlorides, such as CuCl_2 and FeCl_3 [29,30,38]. The presence of metals in cement kilns has already been identified as a problem

Fig. 4. Polychlorinated naphthalene congener profiles relative to the corresponding homologue group concentrations in each of the three groups determined using hierarchical cluster analysis.

that needs solving [4]. The average proportion of plastics in the sorted MSW was around 25% in this study. In many previous publications, plastics (such as PVC) have been identified to be important chlorine source for MSW, and would affect the formation of POPs during industrial thermal processes [39,40]. Waste acid (average content of HCl was 5.5%) was added to the rotary kiln in Series 3, and also acted as a chlorine source to promote PCN formation in Series 3. Therefore, the correlation analysis of $\sum$ PCN concentrations and chlorine contents were performed. Correlations between the $\sum$ PCN concentrations and chlorine contents in Series 1, Series 2, and Series 3, shown in Fig. S2, were significant, the correla-

tion coefficients (R^2) being 0.59, 0.92, and 0.94, respectively. This showed that chlorine played an important role in PCN formation.

3.3. Homologues of PCNs in the solid samples

The PCN homologue distributions in the clinkers, coals, sludge, and raw meals, expressed as fractions of the total PCN mass concentrations, are shown in Fig. 2. The profiles were all dominated by the less-chlorinated homologues, the monochloronaphthalenes (MoCNs), dichloronaphthalenes (DiCNs), and trichloronaphthalenes (TriCNs) contributing >65% of the total

PCN concentrations. The homologue patterns changed significantly from raw meals to clinkers. The MoCN and TiCN contributions decreased, the DiCN and tetrachloronaphthalene (TeCN) contributions increased in Series 1 and Series 2. The MoCN and DiCN contributions increased and the TiCN, TeCN, and pentachloronaphthalene (PeCN) contributions decreased in Series 3. This could be evidence for the roles of kiln system in changing PCN homologue distributions. The DE for each homologue is shown in Table S2. The DEs were higher for the less-chlorinated naphthalenes than for the more-chlorinated naphthalenes, indicating that the less-chlorinated naphthalenes were more effectively decomposed than were the more-chlorinated naphthalenes.

The PCN homologue mass concentrations in particle samples from different stages are shown in Fig. 3. The less-chlorinated homologues (MoCNs–TiCNs) were dominant and the concentration decreased as the chlorination level increased. This was similar with the studies in which naphthalene was chlorinated to give PCNs [30,31]. As shown in Table S3, the concentration of each PCN homologue correlated well with the concentrations of the adjacent homologues. These results were similar to the results of studies on MSW combustion processes, in which the most likely main PCN formation and destruction mechanisms were found to be chlorination and dechlorination [31,41]. Thus, chlorination and dechlorination were proposed as the main formation and decomposition pathways for PCNs within kiln system.

The concentrations of the different PCN homologues at different stages of Series 1 followed similar trends. In Series 2 and Series 3, the concentrations of the different PCN homologues followed similar trends before the SP boiler and humidifier tower, but the MoCN concentrations followed the opposite trend to the more-chlorinated homologues after that. Outside factors (such as temperature and the feeding materials), which would simultaneously affect the less-chlorinated and more-chlorinated homologue concentrations, could cause the variations in the PCN homologue concentrations at stages of Series 1 and stages before the SP boiler in Series 2 and Series 3. The difference between the MoCN and more-chlorinated homologue trends in SP boiler, humidifier tower and bag filter at back end of kiln in Series 2 and Series 3 indicated that chlorination and dechlorination played major roles in PCN formation and degradation in the SP boiler and humidifier tower and in bag filter at back end of kiln in Series 2 and Series 3. This was consistent with the operating conditions that more chlorines were introduced through the wastes co-processed in Series 2 and Series 3.

3.4. Congener profiles of PCNs in the solid samples

The PCN congener profiles were investigated to allow the factors involved in PCN formation to be assessed further. Three groups (Group 1, Group 2, and Group 3) were defined from a dendrogram (shown in Fig. S3) produced from the hierarchical cluster analysis of the relative contributions of the PCN congeners in the solid samples. The samples from bag filter at kiln head and boiler at kiln head in Series 1 and the clinkers from Series 1 and Series 2 were in Group 2. The C1 preheater, coal, raw meal, and sludge samples from Series 3 were in Group 3. The other solid samples were in Group 1. The samples from C1 preheater and the raw meals were always in the same group, indicating that the PCN concentration in C1 preheater was affected by the raw meal, which was consistent with the conclusions drawn earlier. The samples of C1 preheater were not always in the same group as the samples from bag filter at back end of kiln, and clinkers were not in the same group as the input materials, suggesting that the kiln system would affect the PCN congener profiles.

The PCN congener profiles found in the solid samples are shown in Fig. 4. The Group 1 and Group 3 congener profiles were sim-

ilar. CN-1 and CN-2 were more or less equally abundant. CN-5/7 contributed more than the other DiCNs, followed by CN-11/8 and CN-3. The TiCNs were dominated by CN-24/14, and CN-37/33/34 contributed more than the other TeCNs. The largest contributor to the PeCNs was CN-52/60, followed by CN-50, CN-51, and CN-54. The hexachloronaphthalenes (HxCNs) were dominated by CN-66/67, and, of the heptachloronaphthalenes (HpCNs), CN-73 was dominant over CN-74. Similar congener profiles have been found for other thermal processes [31]. There were also clear differences between the Group 1 and Group 3 congener profiles, the less-chlorinated congeners being dominant in Group 1 and the more-chlorinated congeners being dominant in Group 3. This meant that the feeding materials in Series 3 accounted for the domination of the more-chlorinated PCN congeners and that the less-chlorinated congeners were dominant in other samples of Series 3. These results indicated that cement production processes can change PCN congener profiles and that dechlorination could be a pathway through which PCN masses become lower in clinker than in raw meal.

The PCN congener profiles for Group 2 were different from the congener profiles for Group 1 and Group 3. In Group 2, CN-1 was more abundant than CN-2, and CN-5/7 was clearly the dominant DiCN. CN-24/14 and CN-23 made similar contributions to the TiCNs, and the other congeners made smaller contributions. CN-46 was the dominant TeCN congener. The PeCNs were dominated by CN-59, followed by CN-53. CN-71/72 dominated the HxCNs; CN-73 made a smaller contribution than CN-74 to the HpCNs. Congeners such as CN-23, CN-46, and CN-59 have relatively high Gibbs free energies compared with other congeners with the same numbers of chlorine atoms, and therefore generally been found at lower concentrations than other congeners [42]. However, high CN-23, CN-46, and CN-59 concentrations have been found in samples collected during thermal processes and in samples from the natural environment [42–44]. CN-23, CN-46, and CN-59 made larger contributions to the PCN patterns in the kiln head zone samples from Series 1 than to the patterns in the other Series 1 samples. These congeners also made larger contributions to the PCN patterns in the kiln head zone ash samples and clinkers (which could be affected by coal because of the material and gas flows) from Series 2 and Series 3 than to the patterns in the kiln end zone samples from Series 2 and Series 3. Coal contained larger proportions of these congeners than did the other feeding materials and samples from back end of kiln (data not shown). We therefore concluded that the coal contained some precursors that could cause CN-23, CN-46, and CN-59 to form. The results of previous studies of PCN congener patterns in samples from thermal processes in which coal was used were compared to attempt to verify our conclusion. Relatively high proportions of CN-23, CN-46, and CN-59 have been found in samples taken during coal charging in the coking process and in PCNs emitted when coal and hardwood were burned [45,46]. From the results of our study and previous studies, we suggest that CN-23, CN-46, and CN-59 could be appropriate indicators of PCN sources with burning of coal involved.

4. Conclusion

The PCNs in stack gas samples and solid samples collected during cement kiln co-processing solid waste were analyzed and quantified. Based on the calculation of PCN reduction efficiencies of the three production runs, using waste as a supplementary fuel would not increase PCN emissions but rather to effectively help decrease the PCN mass outputs. Kiln end zone and preheater zone were the major zones for the formation of PCNs, and the formation of PCNs within kiln system was affected by temperature, feeding materials and chlorine content. The analysis of PCN homologues

and congener profiles suggested that chlorination and dechlorination were the major pathways for the formation and decomposition of PCNs during cement production co-processing waste, and CN23, CN46 and CN59 could be indicators of PCN sources with burning of coal involved. Further studies associated with the formations and variations of other dioxin-like compounds in cement kilns co-processing waste are still needed with the aim of simultaneously controlling the emissions of multiple organic pollutants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.05.003>.

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