Estimation and Characterization of Polychlorinated Naphthalene Emission from Coking Industries

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Occurrence of polycyclic aromatic hydrocarbons (PAHs) during the coking process has been widely recognized. The formation of polychlorinated naphthalenes (PCNs) from PAHs during some thermal related processes has been confirmed in many studies. Thus, the coking process is assumed to be a potential source of PCNs. However, intensive investigations on PCN emissions during the coking process are lacking. In order to evaluate PCN emissions from the coking process, an intensive study comprising 11 typical coke plants was undertaken. PCNs were qualified and quantified by isotope dilution HRGC/HRMS techniques. The concentrations of PCNs in stack gas samples collected from the investigated coke plants were in the range of 1.6–91.8 ng Nm⁻³ (0.08–4.23 pg TEQ Nm⁻³). The emission factors of PCNs were found to be in the range of 0.77–1.24 ng TEQ per ton of coke production. The estimated annual toxic emissions of PCNs from the global coking industry vary from 430 to 692 mg TEQs. Characteristics of the PCN profiles were dominated by the lower chlorinated homologues, with mono-CN being the most abundant homologue. According to the PCN distribution and correlations of PCN homologues, it was speculated that chlorination is possibly the dominant pathway of PCN formation during the coking process.

Introduction

Polychlorinated naphthalenes (PCNs) are persistent compounds derived from the chlorination of naphthalene (Nap) and the formation of thermally related reactions (1–3). Due to their structural similarity to dioxins, PCNs exhibit toxicological properties similar to dioxins, having the ability to bind to and activate the aryl hydrocarbon receptor (4). Based on their high toxicity, persistence, bioaccumulation, and long-distance transmission, PCNs were selected as a candidate for a persistent organic pollutant (POP) by the United Nations Economic Commission for Europe (UN-ECE) POP protocol (5). In addition, studies have suggested that PCNs contribute a greater proportion of the dioxin-like activity than PCBs and PCDD/Fs in some locations (6, 7). The toxic contribution of PCNs in human serum amounts to about 26.8% of the total toxic equivalents of PCDD/Fs, PCBs, and PCNs. The PCN congener pattern in human serum indicates that

emission from combustion-related processes may be the main source of PCNs in human serum (8). Thus, in recent years, PCNs have attracted increasing attention due to their adverse effects on the global environment and human health (9, 10). Although the environmental levels of PCNs have been intensively studied (11–18), investigations on unintentional release of PCNs from potential sources are not sufficient for evaluating the entire emission of PCNs or establishing an inventory of PCN emissions.

Source identification and quantification of POPs is one of the key steps for controlling and regulating their emission and for effectively reducing further environmental exposure to POPs throughout the world (19). PCNs were widely manufactured and used as capacitor fluids, engine oil additives, electrical insulators, and flame retardants during the 1930s–1950s. Although the production and use of PCNs have been banned in most countries, PCNs still are unintentionally produced and released into the environment *via* thermal related processes (20, 21). The formation and emission of PCNs from waste incinerators (22–24), cement kilns (25), and metallurgical plants (26–28) have been confirmed. Chlorine manufacturing facilities, including chlor-alkali production, are significant sources of PCNs in the environment (6, 29–31). In addition, PCNs are also released from PCBs since they are present as impurities in technical PCB mixtures (32). Although many studies on PCN emissions have been conducted, there still are considerable uncertainties about their fluxes from potential sources into the environment.

It is well-known that toxic aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs), are formed during the coking process (33). Many researchers have demonstrated that PAHs are important precursors of dioxin-like contaminants (34–36), which are related to one another (37–41). The formation and emission of PCDD/Fs and PCBs from the coking process have been identified and quantified in previous studies (42, 43). Thus, it is likely that this process also produces PCNs.

In recent years, the production of coke has increased tremendously (43). Conversely, studies to evaluate the emission of PCNs are lacking. Furthermore, investigations of PCN emissions from coke plants in China would be of global significance. The primary aim of the present study was to evaluate the amount of PCN emissions from the coking industry. To this end, 11 typical coke plants were investigated in China. Emissions data from these plants will help us understand the degree of PCN emissions threat and provide a PCN inventory for further research.

Experimental Section

Sampling. In a previous study, stack gas samples from 11 coke plants were collected by automatic isokinetic sampling system (TCR TECORA, Italy). The plants were of different scales and utilized different processing techniques, the basic information was summarized in Table 1. Three stack gas samples were collected for each plant to investigate emission of unintentionally produced POPs (UP-POPs). The coking processes and air pollution control systems of these plants are described in detail in previous publications (43). Briefly, coke is produced by carbonization of coal in coke ovens. Once in the ovens, the coal is charged and subjected to external heating in the absence of air. Coke is then removed and quenched with water or dry inert gases. The formation and emission of PCNs may occur during the charging of coal (CC) and pushing of coke (PC) through the coking process. For the CoP1 plant, the released gases from CC and PC were

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TABLE 1. Basic Information of the Investigated Coke Plants

	CoP1	CoP2	CoP3	CoP4	CoP5	CoP6	CoP7	CoP8	CoP9	CoP10	CoP11
height of ovens (m)	4.3	6	6	4.3	7.3	4.3	4.3	6	4.3	4.3	4.3
technique of charging coal	SC ^a	TC ^b	TC	TC	TC	TC	SC	TC	SC	TC	TC
coke quenching method	water	water	nitrogen	water	nitrogen	water	water	water	water	water	water
APCD ^c	BFs ^d	BFs	BFs	BFs	BFs	BFs	BFs	BFs	BFs	BFs	BFs
origin of stack gas samples	PC+CC	PC ^e	CC ^f	PC	PC	PC	PC; CC	PC	PC	CC	CC

^a Stamp charging. ^b Top charging. ^c Air pollution control device. ^d Bag filters. ^e Termed as waste gas released from pushing of coke. ^f Termed as waste gas released from charging of coal.

treated by one shared air pollution control device. Thus, the mixed gas emission from CC and PC was collected for CoP1. In the CoP4 and CoP5 plants, special techniques are used for the CC, where almost no waste gas is released when the coal is charged in the ovens. Thus, stack gas samples released from PC were collected for CoP4 and CoP5. Since not all investigated plants were suitable for field sampling of both CC and PC, stack gas samples released from CC were collected from CoP3, CoP10, and CoP11 plants to evaluate the PCN emission levels from CC. Conversely, PC-related emissions were collected from the CoP2, CoP6, and CoP8 plants. In order to estimate the emission contribution from CC and PC, the stack gas samples from CC and PC were simultaneously collected and analyzed for the CoP7 plant.

Sample Preparation and Analysis. The samples were analyzed for PCNs by isotope dilution high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) methods, cf. ref 44. Briefly, the samples were spiked with a mixture of ¹³C₁₀-labeled PCN internal standards (ECN-5102, Tetra-Octa PCN Mixture comprising ¹³C₁₀-CN-27, -42, -52, -67, -73, and -75, Cambridge Isotope Laboratories, United States), and then they were Soxhlet extracted with 250 mL of toluene for about 24 h. Subsequently the sample extracts were concentrated and subjected to a series of cleanups by adsorption chromatography, including multi-layer silica gel columns and basic alumina columns. Finally, the extracts were concentrated to about 20 μ L by rotatory evaporation and a gentle nitrogen gas stream. Prior to injection, ¹³C₁₀-labeled PCN injection solutions (ECN-5260: ¹³C₁₀-CN-64, Cambridge Isotope Laboratories, United States) were added for calculation of recoveries. Analysis of PCNs was carried out by a GC coupled with a DFS mass spectrometer (Thermo Fisher Scientific, United States). The MS was tuned and operated at around 10,000 resolution with 45 eV EI energy. A selected ion monitoring (SIM) mode was used for data acquisition. The concentrations of naphthalene also were determined for exploring their relationship to PCNs. The sample extractions were spiked with known amounts of naphthalene-D₈ and cleaned up with a silica column. The analysis of naphthalene was carried out by an Agilent 6890 gas chromatograph equipped with a HP-5MS capillary column (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m) and interfaced to an Agilent 5973N MS. The data were acquired in SIM mode, and naphthalene-D₈ was used for the isotope internal standard of naphthalene quantification.

The identification and complete separation of PCN congeners was difficult and remains uncertain (13, 45). In this study, peaks were identified based on retention time compared to available individual standards and ion ratios and considering the elution order on the DB-5 column (29, 46). Peaks were quantified if target/qualifier ion ratios were within 15% of theoretical values. The recoveries of ¹³C₁₀-PCN internal standards relative to labeled injection standards in the samples ranged from 35 to 125%. Blank experiments were carried out to evaluate any possible contamination. Concentrations of MoCNs and DiCNs in blanks were higher than their LODs but were far lower than those in the samples.

The PCN concentrations in samples were not corrected with blank values in this study.

Statistical Analysis. In this study, discrepancies on PCN patterns among the coke plants were observed. In order to evaluate the distribution pattern as well as possible groupings of similar emission characteristics among them multivariate statistical analysis, principal component analysis (PCA), and hierarchical cluster analysis (HCA) were applied. The concentrations of PCN homologues were normalized to total PCN concentrations to minimize the influence of total concentration and permit a comparison of compositional similarities among samples. PCA and HCA were performed using SPSS 13.0 for Windows. A rotation method using varimax with Kaiser Normalization was adopted in the PCA. The HCA was conducted with a cluster method of "nearest neighbor" linking with Euclidean distances.

Results and Discussion

Concentration of PCNs from Coke Plants. Understanding the emission levels of PCNs to the atmosphere is important for regulation and source reduction purposes. The average concentrations and TEQs of PCNs emission for each coking process are presented in Table 2. Results indicate that the concentrations of total PCNs from coke plants ranged from 1.6 to 91.8 ng Nm⁻³. The RSDs of PCN concentrations and TEQs for three samples collected from each coke plant ranged from 10% to 58%. There was increasing evidence that PCNs present similar toxicity to dioxins (47, 48). The relative potency factors (RPFs) of individual PCN congeners to 2378-TeCDD have been estimated and used for toxic evaluations of PCNs (1, 44, 49). The concentrations of dioxin-like PCNs (dl-PCNs), for which toxic equivalent factors have been suggested, ranged from 0.7 to 90.0 ng Nm⁻³. The TEQs of dl-PCNs were in the range of 0.08–4.23 pg TEQ Nm⁻³ for the investigated coke plants. For plant CoP7, the concentration and TEQ of PCNs in the samples from charging of coal were higher than those from pushing of coke. Although the concentrations of dl-PCNs were higher than 2378-PCDD/Fs, the TEQs of PCNs were lower than that of PCDD/Fs due to the relative low RPFs of dl-PCNs compared with that of PCDD/Fs (43). The TEQs of dl-PCNs were comparable with TEQs of dl-PCBs in spite of the higher concentrations of dl-PCNs than that of dl-PCBs (43).

Profiles of PCN Emission from Coking Processes. Based on the components extracted from the PCA, PC1 and PC2 together accounted for 84% of the total variance. The loading plot of the PCA, based on the percentages of PCN homologues, is presented in Figure S1. The score plot results of the PCA indicate three groups (Groups 1, 2, 3) for the homologue patterns in stack gas samples from investigated coke plants (shown in Figure 1). Group 1 (CoP3, CoP5, CoP7(CC), CoP8, CoP10, CoP11) was mostly related to the stack gas sample emissions from CC. Group 2 comprised the stack gas sample emissions from the PC (CoP2, CoP4, CoP6, CoP7(PC), CoP9). Group 3 (CoP1) was assigned to the CoP1 plant where mixed stack gases from charging of coal and pushing of coke were collected. The PCA results showed that there were some differences in the distributions of PCN emissions between

TABLE 2. Average Concentration of Nap and PCNs and the Degree of Chlorination

denotation	total PCNs (ng Nm ⁻³)	DI-PCNs (ng Nm ⁻³)	DI-PCNs TEQs (pg TEQ Nm ⁻³)	Nap (μg Nm ⁻³)	PCN/Nap ratio (×10 ⁻⁵)	degree of chlorination ^a
CoP1	28.2	18.2	4.23	299	9.4	2.2
CoP2	24.0	6.9	1.15	213	11	3.2
CoP3	16.7	15.1	0.40	105	16	1.3
CoP4	3.7	1.4	0.19	33	11	2.8
CoP5	11.7	9.0	0.30	101	12	1.7
CoP6	3.0	1.4	0.14	38	7.9	2.6
CoP7(PC)	6.2	1.4	0.32	54	12	3.3
CoP7(CC)	48.4	43.2	2.14	412	12	1.4
CoP8	22.9	20.9	0.36	76	30	1.2
CoP9	1.6	0.7	0.08	28	5.6	2.6
CoP10	91.8	90.0	1.89	57	160	1.1
CoP11	22.7	21.2	0.45	660	3.4	1.2

^a Calculated as $\Sigma[(\text{homologue sum}/\Sigma\text{PCNs}) \times \text{no. of Cl}]$.

FIGURE 1. The score plot of the PCA based on the relative contributions of PCN homologues.

FIGURE 2. The representative homologue profiles of PCNs in three groups.

CC and PC. Three main clusters were created according to the dendrogram results in HCA (Figure S2). The cluster analysis results were almost the same as those obtained with the PCA.

The representative PCN homologue patterns are shown in Figure 2. PCN profiles in all groups were dominated by the lower chlorinated homologues, which were similar to other thermal related sources (20, 21). The fractions of MoCN in Group 1 clearly were higher than those of Group 2, which

indicated that higher fractions of MoCN were formed from CC than those from PC. Samples in Group 3 were the mixed stack gas emissions from both PC and CC. The fractions of MoCN in Group 3 were higher than those of Group 2 and lower than those of Group 1. The degrees of chlorination of PCNs ranged from 1.1 to 3.3 (presented in Table 2), which were comparable with those from MSW combustion (21). The results demonstrate that the average degree of chlorination from PC (2.9, Group 2) was clearly higher than that from CC (1.4, Group 1). Much higher concentration of naphthalene from charging of coal compared to that of pushing of coke might account for the lower degree of chlorination produced during charging of coal.

Different PCN profiles for different catalogued sources may provide helpful information to identify the specific sources of PCNs in the environment (6, 13, 20, 44, 50, 51). Batch production of technical PCN mixtures (such as Halowax series) and unintentional release of PCNs from thermal processes or chlorine-based chemical manufacturing are major sources of PCNs in the environment. Many studies have compared the PCN congener profiles for thermally related processes and technical PCN mixtures (such as Halowax Series) (1, 24, 46). Several congeners, including CN45/36, CN54, CN66/67, and CN73, are relatively abundant for thermally related processes compared with their far lower contents in Halowax mixtures (10, 13). Thus, these congeners have been recognized widely as thermally related congeners. For MoCN and DiCN homologues, the ratios of CN1 to CN2 and CN5/7 to CN6/12 were distinctly different for fly ash samples from MSW incineration and Halowax samples (46). In this study, the ratios of several characteristic congeners were also determined and shown in Figure 3. Obvious different profiles were observed for the several characteristic congeners between the coking process and technical PCN mixtures (46), which may help identify the PCN sources from the coking industry.

With regard to the toxic pattern of PCNs from coke plants, the toxic contributions of PCN congeners, for which RPFs have been suggested, are shown in Figure S3. For plants in Groups 2 and 3, the most dominant toxic congeners were CN66/67 and CN73 due to their relatively high RPFs compared with other PCN congeners. Moreover, CN66/67 and CN73, CN1 and CN2 also were dominant toxic contributors due to their high concentrations for plants in Group 1.

Jansson et al. (21) showed that injection of naphthalene into the postcombustion zone could increase the formation of MoCN. However, the effect of adding naphthalene to more highly chlorinated naphthalene was not observed. It is well-known that formation and emission of naphthalene normally occurs during the coking process. Furthermore, MoCN was the most abundant PCN homologue for the coking process.

FIGURE 3. Ratios of several characteristic PCN congeners.

TABLE 3. Pearson Correlations of Nap and PCN Homologues

	Nap	MoCN	DiCN	TrCN	TeCN	PeCN	HxCN	HpCN	OCN
Nap	1								
MoCN	0.14	1							
DiCN	0.31	0.20	1						
TrCN	0.18	-0.21	0.77 ^a	1					
TeCN	0.18	-0.20	0.42	0.87 ^a	1				
PeCN	0.34	0.01	0.44	0.71 ^a	0.82 ^a	1			
HxCN	0.32	0.04	0.82 ^a	0.63 ^b	0.29	0.56	1		
HpCN	0.24	0.12	0.94 ^a	0.79 ^a	0.44	0.54	0.93 ^a	1	
OCN	0.08	0.19	0.76 ^a	0.88 ^a	0.78 ^a	0.57	0.46	0.73 ^a	1

^a Correlation is significant at the 0.01 level (2-tailed).

^b Correlation is significant at the 0.05 level (2-tailed).

Thus, it was speculated that chlorination of naphthalene also may be an important pathway of MoCN formation during the coking process. Pearson's correlations that indicate interrelationships could be used to understand the mechanistic relationships among possible relevant chemicals (38). In this study, Pearson's correlations between naphthalene and PCN homologues were determined and are presented in Table 3. The results show that HpCN and OCN had good positive relationships with most of the homologues, which is in agreement with Oh et al. (38). However, the Pearson's coefficients for Nap and MoCN homologues were low compared with those for the MSW incineration (38). It is well-known that the concentrations of Nap emissions from the coking process were high. However, the contents of chlorine in coal used for coke production were very low compared with those of municipal solid waste (52, 53). The chlorine contents may be low for the chlorination of Nap during the coking process, which may be responsible for the different Pearson's correlations between the coking process and the MSW incineration for Nap and MoCN (38). From Table 3, the correlation between DiCN and TrCN was better than that between DiCN and TeCN (or PeCN). The Pearson's coefficients between TrCN and TeCN (or PeCN) also were higher than that between TrCN and HxCN. The correlation between TeCN and PeCN was more significant than that between TeCN and other higher chlorinated CNs. The correlation coefficients between HxCN and HpCN were greater than those between HxCN and OCN. In general, adjacent PCN homologues were closely related to each other. These results also indicate that chlorination is likely to be an important PCN formation pathway, similar to previous studies for dioxin-like compounds (21, 22, 37, 38, 54–56).

TABLE 4. Emission Factors of PCNs for the Investigated Coke Plants

denotation	Σ PCNs ($\mu\text{g ton}^{-1}$)	Σ dl-PCNs ($\mu\text{g ton}^{-1}$)	Σ TEQ-PCNs (ng TEQ ton^{-1})
CoP1	5.1	3.3	0.77
CoP2	7.3	2.1	0.35
CoP3	7.2	6.5	0.17
CoP4	1.8	0.73	0.10
CoP5	11.4	8.8	0.29
CoP6	3.4	1.5	0.16
CoP7(PC)	4.4	1.1	0.24
CoP7(CC)	19.9	17.8	0.88
CoP8	16.2	14.8	0.25
CoP9	2.1	0.94	0.11
CoP10	125.1	122.6	2.58
CoP11	22.3	20.8	0.44
CC (mean)	43.6	41.9	1.02
PC (mean)	6.7	4.3	0.22
PC+CC (mean)	50.3	46.2	1.24

Estimation of PCN Emissions from the Coking Industry.

Emission factors are important parameters for estimating the total emission of a given pollutant from a given source. In this study, the emission factors of PCNs from the coking process were derived based on the obtained data and are listed in Table 4. Stack gases collected from CoP3, CoP7(CC), CoP10, and CoP11 plants were classified as CC. The average emission factors from CC were calculated to be 1.02 ng TEQ ton^{-1} . From the data for the CoP2, CoP4, CoP5, CoP6, CoP7(PC), CoP8, and CoP9 plants, the average emission factors from PC were 0.22 ng TEQ ton^{-1} . The average emission factor for the sums of CC and PC was 1.24 ng TEQ ton^{-1} . As for the CoP1 plant, the emission factor for the mixed gas emission from both CC and PC was 0.77 ng TEQ ton^{-1} . Thus, the derived emission factors of PCNs for the sums of CC and PC ranged from 0.77 to 1.24 ng TEQ ton^{-1} .

For the emission factors of PCNs, the toxic contributions of PCNs were far lower than those of PCDD/Fs for each ton of coke production but were comparable to those of dl-PCBs (43). Based on the 558 million tons of coke produced in 2007, the estimated annual emission amounts of PCNs from the global coking industry ranged from 430 to 692 mg TEQ, which was comparable to that of dl-PCBs (43).

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Supporting Information Available

The RPFs of PCN congeners, loading plot of the PCA, hierarchical dendrogram of the HCA, and the TEQ contribution of individual congeners. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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