Gas and particle size distributions of polychlorinated naphthalenes in the atmosphere of Beijing, China[☆]

Qingqing Zhu, Xian Zhang, Shujun Dong, Lirong Gao, Guorui Liu, Minghui Zheng^{*}

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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ABSTRACT

Polychlorinated naphthalenes (PCNs) were listed as persistent organic pollutants in the Stockholm Convention in 2015. Despite numerous studies on PCNs, little is known about their occurrence in atmospheric particulate matter of different sizes. In this study, 49 PCN congeners were investigated for their concentrations and size-specific distributions in an urban atmosphere, and preliminary exposure assessments were conducted. Ambient air samples were collected using a high-volume cascade impactor for division into a gas fraction and four particle size fractions. Samples were collected from October 2013 to June 2014 at an urban site in Beijing, China. The concentration range for PCNs in the atmosphere (gas + particle fractions) was 6.77–25.90 pg/m³ (average 16.28 pg/m³). The particle-bound concentration range was 0.17–2.78 pg/m³ (average 1.73 pg/m³). Therefore, PCNs were mainly found in the gas phase. The concentrations of PCNs in a fraction increased as the particle size decreased ($d_{ae} > 10 \mu\text{m}$, $10 \mu\text{m} \geq d_{ae} > 2.5 \mu\text{m}$, $2.5 \mu\text{m} \geq d_{ae} > 1.0 \mu\text{m}$ and $d_{ae} \leq 1.0 \mu\text{m}$). Consequently, PCNs were ubiquitous in inhalable fine particles, and the Σ PCNs associated with PM_{1.0} and PM_{2.5} reached 68.4% and 84.3%, respectively. Tetra-CN and penta-CN (the lower chlorinated homologues) predominated in the atmosphere. The homologue profiles in different size particles were almost similar, but the particulate profiles were different from those in the gas phase. Among the individual PCNs identified, CN38/40, CN52/60 and CN75 were the dominant compounds in the atmosphere. CN66/67 and CN73 collectively accounted for most of the total dioxin-like TEQ concentrations of the PCNs. Exposure to toxic compounds, such as PCNs present in PM_{1.0} or PM_{2.5}, may affect human health. This work presents the first data on size-specific distributions of PCNs in the atmosphere.

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1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of compounds that are toxic, persistent and bioaccumulative. Their properties are similar to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) because of their similar structures (Bidleman et al., 2010). Although the production and use of PCNs have been banned in most countries, PCNs are still unintentionally produced and released into the environment via thermal-related processes (Liu et al., 2014). They have been detected in various matrices in the environment, including air, soil and sediment (Harner et al., 2006; Helm et al., 2008; Lee et al., 2007; Wang et al., 2012). Studies have suggested that PCNs are

absorbed into organisms, and they have been found in human serum (Fromme et al., 2015; Helm et al., 2008). Investigations have also shown that the contribution of PCNs to dioxin-like toxicity in some areas may overwhelm the contributions of PCDD/Fs and PCBs (Park et al., 2010). Because of their potential adverse effects on the environment and human health, PCNs have attracted increasing attention. Consequently, they have recently been listed as unintentional persistent organic pollutants at the 2015 Triple Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants.

Humans are directly exposed to PCNs in the atmosphere, and the atmosphere is a major medium for the transport and deposition of PCNs. In the atmosphere, PCNs are distributed between the gas phase and particle phase; the phase they are in greatly affects their environmental fate, including transport, transformation and removal processes (Bidleman, 1988; Harner and Bidleman, 1998). Because of their relatively high octanol-air partition coefficients,

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^{*} Corresponding author.

E-mail address: zhengmh@rcees.ac.cn (M. Zheng).

PCNs are usually present exclusively in the gas phase. Numerous epidemiological studies have illustrated that there is a strong exposure–response relationship between short-term effects of particulate air pollution (e.g., premature mortality and hospital admissions) and long-term or cumulative health effects (e.g., lung cancer, cardiovascular and respiratory diseases) (Brunekreef and Forsberg, 2005; Chen et al., 2012; Dominici et al., 2006).

Ultrafine and fine particles are present in the atmosphere for longer than larger particles, and are not removed efficiently by wet or dry deposition, which increases their atmospheric lifetimes (Aulinger et al., 2007; Kurokawa et al., 1998). Compared with larger particles, ultrafine and fine particles are present in higher numbers in the atmosphere, and have larger specific surface areas and more porous surfaces, which all results in higher adsorption and retention of semi-volatile pollutants such as PCNs (Valavanidis et al., 2008). It is well known that inhalable particles (such as PM_{10}) are small enough to reach deeply into the lungs, and $PM_{1.0}$ can enter the bloodstream, which may induce even higher risks than larger particles. Studies have reported that fine particles ($<0.5 \mu m$) may be the main contributor among particulate matter (PM) fractions that cause adverse health effects from air pollution, and that adverse health effects may increase as the particle size decreases (Meng et al., 2013). Therefore, information on size-specific distributions of PCNs is needed to better understand and predict their transport in the atmosphere. This information could also be used for PCN exposure assessments. To date, the particle size distributions of many contaminants have been studied extensively, including for PCDD/Fs (Chao et al., 2003; Chuang et al., 2015; Kaupp and McLachlan, 2000; Oh et al., 2002), PCBs (Chrysikou et al., 2009; Chrysikou and Samara, 2009), *n*-alkanes (Bi et al., 2005), polycyclic aromatic hydrocarbons (PAHs) (Bi et al., 2005; Duan et al., 2007; Hien et al., 2007), pesticides (Coscollà et al., 2013), heavy metals (Zereini et al., 2005), halogenated flame retardants (Cao et al., 2014; Mandalakis et al., 2009; Okonski et al., 2014), hexabromocyclododecane (HBCD) (Ni and Zeng, 2013), tetrabromobisphenol A (TBBPA) (Ni and Zeng, 2013) and some other components (ions, organic matter and mineral matter) (Sánchez-Soberón et al., 2015). Previous studies of PCNs in the atmosphere have mainly focused on the gas phase (Hogarh et al., 2012b; Li et al., 2012) and there have been few studies of particle-bound PCNs or their size distributions.

Beijing, the capital city of China, has a high population density and heavy traffic. Recently, rapid economic growth has aggravated air pollution in the city and resulted in many pollution problems, including haze events that are correlated with high concentrations of ultrafine and fine particles. Hence, knowledge of the distribution of PCNs in different particle size fractions is crucial for understanding the environmental fate of these pollutants and to perform human health risk assessments.

In this study, the gas and particle phase concentrations of PCNs were determined along with their particle size distributions in the atmosphere in Beijing. Air samples collected during different periods were fractionated into a gas phase fraction and four PM fractions to investigate the distribution of PCNs. The results were used to assess the risk that PCNs in inhalable PM pose to human health. To the best of our knowledge, this is the first report on the size-specific distributions of PCNs in the atmosphere. This study will expand on current knowledge of PCN concentrations in the air in China.

2. Materials and methods

2.1. Air sampling

Ambient air samples were collected from October 2013 to June

2014 in Beijing ($116^{\circ}12'28''$ E, $40^{\circ}00'44''$ N) using a high-volume cascade impactor (KS-303 $PM_{10}/2.5/1.0$ sampler, Kálmán System, Hungary) with size-selective inlets. The sampling site was on the rooftop of a building and approximately 12 m above ground level. There were two roads near the sampling site, with about 30,000 vehicles/day. In the surrounding area there was a university campus, research institutes and residential areas, but no industrial buildings nearby.

The gas phase and four PM fractions ($d_{ae} > 10 \mu m$, $10 \mu m \geq d_{ae} > 2.5 \mu m$, $2.5 \mu m \geq d_{ae} > 1.0 \mu m$ and $d_{ae} \leq 1.0 \mu m$) were collected simultaneously. The particles were collected onto quartz fiber filters (QFFs; Ahlstrom Munktell, Sweden), which were sized as shown in Supplementary Information (SI) Table S1. The gas phase was adsorbed onto polyurethane foam (PUF; Tisch Environmental, USA, 63 mm diameter and 76 mm length). Before sampling, the QFFs were baked at $450^{\circ}C$ to remove organic contaminants, and the PUFs were extracted by accelerated solvent extraction (Thermo Fisher Scientific, USA) with acetone. The impactor was operated at a constant flow rate of $24 m^3/h$, and each sample was collected continuously for approximately 6 d. This resulted in sampling an air volume of $\sim 3400 m^3$ per sample. Sampling details are given in SI Table S2. Before and after sampling, the QFFs were weighed using an analytical balance with a reading precision of 0.0001 g after stabilization in a constant temperature ($20 \pm 5^{\circ}C$) and humidity ($30 \pm 2\%$) chamber (Sun et al., 2006). Then they were wrapped tightly in aluminum foil, sealed in plastic bags, and kept at $-18^{\circ}C$ until required for analysis. In total, six samples were collected, each consisting of a fraction of gas phase and four QFFs with size-specific fractions of PM.

2.2. Sample extraction and analysis

The tetra- to octachloro-CNns were analyzed by an established isotope dilution high-resolution gas chromatography/high-resolution mass spectrometry method (Jiang et al., 2015; Liu et al., 2010). The samples were spiked with 1 ng $^{13}C_{10}$ -labeled PCN internal standards (CN27, 42, 52, 67, 73 and 75), and then extracted by accelerated solvent extraction with dichloromethane and hexane (1:1, v:v). The sample extracts were concentrated and cleaned up using a series of chromatography columns, including a multilayer silica gel column, a basic alumina column and an activated carbon column. The activated carbon column was used to separate PCNs from interfering components. Finally, the extracts were concentrated to approximately 20 μL by rotary evaporation and under a gentle stream of nitrogen gas. Before injection, $^{13}C_{10}$ -labeled PCN recovery standards (CN64) were added to each of the concentrated extracts.

The target PCNs were analyzed by a gas chromatograph (GC) coupled with a DFS mass spectrometer (Thermo Fisher Scientific, Hudson, NH, USA) using an electron impact (EI) source. A DB-5 MS capillary column ($60 m \times 0.25 mm \times 0.25 \mu m$, Agilent Technologies, Santa Clara, CA, USA) was used to separate the PCN congeners. The electron energy was set to 45 eV. The source temperature was $270^{\circ}C$. The high-resolution mass spectrometer was operated in selected ion monitoring mode with a resolution greater than 10,000. The GC oven program was as follows: held at $80^{\circ}C$ for 2 min, increased at a rate of $20^{\circ}C/min$ to $180^{\circ}C$ (held 1 min), increased at a rate of $2.5^{\circ}C/min$ to $280^{\circ}C$, and increased at a rate of $10^{\circ}C/min$ to $290^{\circ}C$ (held 5 min). The injector and interface temperatures were set to $260^{\circ}C$ and $290^{\circ}C$, respectively. The carrier gas was helium at a flow rate of 1 mL/min. The sample size was 1 μL and samples were injected in split-less mode. Peaks corresponding to the individual PCN congeners were identified based on their retention times relative to those of internal standards and by their ion ratios.

2.3. Quality assurance/quality control

The recoveries of PCN internal standards ranged from 37 to 117%. The limits of detection (LOD) were calculated using a signal-to-noise ratio of 3:1. The LOD of PCNs ranged from 0.081 to 3.12 fg/m³. In our study, less than 5% of the data was below LOD (as shown in SI Table S3–S8). The common substitution of “0, 1/2 LOD, LOD/√2 and LOD” were used to calculate the undetected values, which verified substitution of 1/2 LOD has little difference with other values (as shown in SI Table S9–S10). So concentrations of PCNs below the LOD were assigned values equal to half the LOD.

As a quality control measure, field blanks and laboratory blanks were analyzed. The field blanks taken at the sampling site consisted of QFFs and PUFs. They were spiked with the same amount of internal standard as the samples. No difference was found between the concentrations in the field and laboratory blanks and the concentrations were all below LOD.

3. Results and discussion

3.1. PM mass concentrations and size distributions

Mass concentrations of total suspended particles (TSP) at the sampling site ranged from 119 to 362 µg/m³ (mean 234 µg/m³) (SI Fig. S1). The average concentrations of PM₁₀ and PM_{2.5} were 209 and 180 µg/m³, respectively. The average PM_{2.5} concentration in this study was 5.14 times higher than the new annual standard of 35 µg/m³ set by China's National Ambient Air Quality Standards (Chang, 2012). Many studies have identified PM pollution in the atmosphere (Table 1). The mass concentrations of PM determined in this study were almost at the same level as those measured in earlier studies in Beijing, China (Zhao et al., 2005), Guangzhou, China (Duan et al., 2007), and some Indian cities (Sharma and Maloo, 2005). However, the PM mass concentrations in this study were much higher than those reported in Shanghai, China (Ma et al., 2013), the Czech Republic (Okonski et al., 2014), Nagoya, Japan (Kadowaki and Naitoh, 2005), Western Europe and North America (Sharma and Maloo, 2005) and Illmitz, Austria (Barmpadimos et al., 2012).

More of the PM was present in the smaller size fractions than the larger size fractions (Fig. 1). The PM fraction with particle diameters ≤1.0 µm was the most abundant fraction and contributed nearly 63.5% of the total PM mass. The finding that the majority of PM was in the fine particle range is in agreement with an earlier study where outdoor aerosols contained mostly fine particles ($d_{ae} \leq 2.5$ µm, especially $d_{ae} \leq 1.0$ µm) (Vette et al., 2001).

Fig. 1. Size distribution of particulate matter.

3.2. Concentrations of PCNs in the atmosphere

In this study, tetra- to octachloro-CNs were analyzed. The ΣPCNs is the sum of the concentrations of the 49 individual PCN congeners that were detected in the air samples. Atmospheric concentrations (gas + particle fractions) of ΣPCNs in the urban atmosphere ranged from 6.77 to 25.90 pg/m³ (Fig. 2) and the range of particle-bound concentrations was 0.17–2.78 pg/m³. The total concentration of PCNs in sample F (sample details are provided in SI Table S2) was lower than that in any of the other samples collected and it is possible that this sample was affected by rain that fell during

Fig. 2. Concentrations of PCNs in the particle phase and gas phase.

Table 1
Particulate matter mass concentrations in different regions (unit µg/m³).

Region	Sampling period	Particle range	Concentration (µg/m ³)	References
Beijing, China	2005	PM ₁₀	179.8	(Zhao et al., 2005)
Guangzhou, China	2003–2004	PM ₁₀	80–397	(Duan et al., 2007)
Kanpur, India	2002–2003	PM ₁₀	45–589	(Sharma and Maloo, 2005)
		PM _{2.5}	25–200	
Czech Republic	2009–2010	PM ₁₀	5.08–90.5 (rural site) 16.1–78.0 (urban site)	(Okonski et al., 2014)
Shanghai, China	2011–2012	PM ₁₀	150	(Ma et al., 2013)
		PM _{2.5}	90.5	
NAAQS	–	PM _{2.5}	35	(Chang, 2012)
the U.S. annual health standard	–	PM _{2.5}	12	(Ma et al., 2013)
Nagoya, Japan	2000–2001	TSP	55–160	(Kadowaki and Naitoh, 2005)
Western Europe and North America	–	PM ₁₀	10–55	(Sharma and Maloo, 2005)
Illmitz, Austria	2001–2010	PM ₁₀	25	(Barmpadimos et al., 2012)
		PM _{2.5}	20	
Beijing, China	2013–2014	PM ₁₀	209	This study
		PM _{2.5}	180	This study

sampling. Therefore, wet deposition may help to remove contaminants from the atmosphere. Principal components analysis (PCA) (SI Fig. S2) identified notable PCN combustion markers such as CN-52/60, -50, -51, -54, -49 and -66/67 (Falandysz, 1998; Hogarh et al., 2012a; Lee et al., 2007; Liu et al., 2015; Noma et al., 2006). This suggested that combustion emerged certain contribution to the measured PCN concentrations. Some earlier studies have reported PCN concentrations in the atmosphere (Hogarh et al., 2012a,b). Because the concentrations of PCNs vary with the type of air samples (e.g., gas phase, particle phase, or both) and the numbers of identified compounds, it is difficult to directly compare the concentrations of PCNs measured in different studies. A rough comparison suggested that PCN concentrations in Beijing during this study were comparable to, or slightly lower than, concentrations measured during other studies, as shown in Table 2. PCN concentrations in the gas phase ranged from 6.60 to 24.63 pg/m³ and were on average 8.41 times higher than those in the particle phase (0.17–2.78 pg/m³). Because they are semi-volatile organic compounds, most PCNs have relatively high volatilities and can easily evaporate from various matrices. Volatilization is an important migration pathway for PCNs to the atmosphere, and especially for transferring from the particle phase to the gas phase. The high volatilities of PCNs certainly contribute to their high abundances in the gas phase. The high contribution of gas phase PCNs to the total PCNs (almost 88.5%) in the atmosphere agrees with the results reported by Odabasi et al. (2012) (33–94%) and Gregoris et al. (2014) (95.7%).

The effect of temperature on the gas/particle partitioning of PCNs was also evaluated (SI Fig. S3). The correlation analyses of temperature with the concentrations of Σ PCNs were conducted using the SPSS Statistics 20 software. The Pearson rank correlation coefficients are listed in SI Table S11. Table S11 shows that the concentrations of Σ PCNs in the gas fraction had little correlation with the temperature. The ratio of Σ PCNs in the gas fraction to Σ PCNs in total fractions (gas + particle fractions) showed a small positive correlation (0.643) with temperature. This suggested that the relationship between temperature and the gas/particle partitioning of PCNs in urban air was not significant.

3.3. Size-specific distributions of PCNs in PM fractions

Four airborne PM fractions with different diameters were collected. The total concentrations of the PCNs in the different fractions are presented in Fig. 3. The mean and median concentrations of Σ PCNs in the TSP were 1.73 and 1.85 pg/m³, respectively, with a range of 0.169–2.78 pg/m³. The mean and median concentrations of Σ PCNs in PM₁₀ were 1.65 and 1.77 pg/m³, respectively, with a range of 0.157–2.65 pg/m³. For PM_{2.5}, the mean and median

Fig. 3. Distribution of PCNs in different particulate matter fractions.

concentrations of Σ PCNs were 1.52 and 1.55 pg/m³, respectively, with a range of 0.12–2.51 pg/m³. For PM₁₀, the mean and median concentrations of Σ PCNs were 1.30 and 1.34 pg/m³, respectively, with a range of 0.0676–2.27 pg/m³. The concentration of PCNs in PM_{2.5} was comparable to that in TSP. This highlighted that fine particles were the main contributors (70.7–95.9%) to the TSP. For the toxic equivalency (TEQ) of PCNs in PM, PM_{2.5} was also the main contributor, accounting for 77.3–98.5% of the TSP, as shown in Fig. 4a and 4b.

The distribution patterns of organic pollutants in airborne particles (Ni and Zeng, 2013; Okonski et al., 2014) or dust (Cao et al., 2014; Wang et al., 2013a,b) have raised concern recently. However, to date, there has been no research on the size-specific distributions of PCNs in PM fractions in the atmosphere. Earlier studies have reported the particle size distributions of other pollutants, including PCDD/Fs, PCBs, organochlorine pesticides, PAHs and brominated flame retardants. The distributions of these chemicals generally varied with particle size, and they also depended on the type of chemical. For example, HBCD and TBBPA tended to be present in the fraction of 0.4–2.2 μm rather than the fraction of 2.5–8.9 μm in office air (Ni and Zeng, 2013). The size-specific distributions of polybrominated diphenyl ether featured a distinct enrichment in smaller particles, with >46% of polybrominated diphenyl ether associated with particles <0.57 μm in diameter in urban air (Mandalakis et al., 2009). PAHs were mainly associated with the smallest particle sizes (<0.4 μm) among nine fractions of atmospheric PM collected at a roadside (Hien et al., 2007). Similarly, PCBs predominantly tended to be present in the smallest

Table 2
PCN concentrations in different regions (unit pg/m³).

Region	Year	Sampling method	Type of air samples	Identified PCN numbers	Concentration (pg/m ³)	References
The north–south Atlantic transect Izmir, Turkey	2001	AAS ^a	gas + particle phase	13	0.3–86	(Jaward et al., 2004)
	2004–2005	PAS ^b	gas phase	32	5.2–162 (summer) 3.7–229 (winter)	(Odabasi et al., 2012)
Japan	2008	PAS	gas phase	63	9.5 ± 1.5	(Hogarh et al., 2012a)
China					61 ± 6	
Korea					16 ± 2.4	
The Pearl River Basin, China	2010	PAS	gas phase	36	6.4–832	(Wang et al., 2012)
Ghana	2010	PAS	gas phase	63	27–95	(Hogarh et al., 2012b)
Venice	2009	AAS	gas + particle phase	6	89	(Gregoris et al., 2014)
	2012				0.29	
Beijing, China	2013–2014	AAS	gas + particle phase	49	6.77–25.90	This study

^a AAS = active air sampler.

^b PAS = passive air sampler.

Fig. 4. Concentrations of PCNs (a) and TEQ concentrations of PCNs (b) in different particle size fractions. Concentrations of dioxin-like PCNs (c) and TEQ concentrations of dioxin-like PCNs (d) in the atmosphere (gas + particle fractions).

fraction ($d_{ae} < 0.95 \mu\text{m}$) among five fractions collected from traffic-impacted outdoor air (Chrysikou et al., 2009).

In agreement with these studies, our study found large differences in the distributions of Σ PCNs among the PM fractions. The PCN concentrations in each PM fraction increased as the particle size decreased ($d_{ae} > 10 \mu\text{m}$, $10 \mu\text{m} \geq d_{ae} > 2.5 \mu\text{m}$, $2.5 \mu\text{m} \geq d_{ae} > 1.0 \mu\text{m}$ and $d_{ae} \leq 1.0 \mu\text{m}$), and the Σ PCNs associated with particles $\leq 2.5 \mu\text{m}$ in diameter was high (range 70.7–95.9%, mean 84.3%). These results showed that fine particles contained higher concentrations of PCNs. This suggests that Σ PCNs may tend to adsorb onto finer PM. For the partitioning of organic pollutants between particles of different sizes, the absorption capacity of the particles is proportional to the organic content and surface area, which means that fine particles have higher mass transfer rates than larger particles (Li and Davis, 1996; Liu et al., 2013). Therefore, the enrichment of PCNs on fine particles ($\text{PM}_{1.0}$ or $\text{PM}_{2.5}$) could be attributed to their larger surface areas compared with larger particles.

3.4. Homologue composition and fractionation

SI Fig. S4 summarizes the profiles of the PCNs (gas + particle fractions) obtained in this study. From Fig. S4 it is evident that tetra-CNs and penta-CNs, which are lower chlorinated homologues, predominated. In this study, these two homologues accounted for approximately 86.5% of total PCNs. By comparison, lower chlorinated homologues (tri-CNs and tetra-CNs) accounted for approximately 80% of total PCNs in East Asian countries (Hogarh et al., 2012a) and approximately 90% in Ghana (Hogarh et al., 2012b). The large contribution of lower chlorinated homologues in the atmosphere in Beijing could be attributed to the high saturation vapor pressures of PCNs, which was similar to PCBs because of their similar properties (Li et al., 2010).

The PCN profiles in the different size particles were almost similar (SI Fig. S5), but as the particle size decreased, the contribution of higher chlorinated homologues increased. For example, in the $\leq 1.0 \mu\text{m}$ fraction, the contributions were in the order: octa-CN > hepta-CNs > hexa-CNs > tetra-CNs > penta-CNs. By comparison, in the $> 10 \mu\text{m}$ fraction, the contributions were in the order: tetra-CNs > octa-CN > hepta-CNs > penta-CNs > hexa-CNs. Finer particles could adsorb more of the less volatile pollutants than larger particles. This further verified that the fine particles are more enriched with PCNs than larger particles. In addition, the homologue profiles were clearly different in the particle and gas phases (SI Fig. S5). In the particle phase, octa-CN was the main contributor, while tetra-CNs predominated in the gas phase and contributed approximately 79.2% of the total PCNs. The homologue profiles in the gas and particle phases were reversed.

With regard to the toxicity, 17 PCN congeners with known toxic equivalency factors (TEFs) were used to assess the overall PCN TEQ in this study (Fig. 4d). The TEQs of PCNs were estimated as $\sum_{n=1}^{17} C_n \times \text{TEF}_n$, where C_n and TEF_n are the PCN concentrations and TEF of the n th congener, respectively. The TEFs are listed in SI Table S12. Because PCNs act through a similar mechanism to dioxins, the TEFs of PCNs were determined by comparing their toxicity to that of the most toxic dioxin 2,3,7,8-TCDD, which is assigned a TEF of 1 (Hogarh et al., 2012b). Here, the dominant toxic congeners were CN66/67 and CN73, which showed relatively high TEFs compared with the other PCN congeners. Moreover, CN38/40, CN52/60 and CN75 were the dominant PCN congeners in all samples, accounting for 39.4–44.5% of the total concentration of dioxin-like PCNs (dl-PCNs).

3.5. Preliminary assessment of exposure to PCNs via inhalation

Environmental exposure to PCNs for humans was calculated for

Table 3

Evaluation of the inhalation risk from PCNs in Beijing, China.

Sample number	TEQ of inhalable fractions (fg TEQ/m ³)	PCN inhalation (fg TEQ/kg/d)	
		Adult	Children
A	4.05	0.87	1.54
B	4.20	0.90	1.60
C	5.11	1.09	1.94
D	5.43	1.16	2.06
E	5.77	1.24	2.19
F	1.67	0.36	0.64
Arithmetic mean	4.37	0.94	1.66

the main exposure pathways of dietary ingestion, dermal absorption and inhalation. For atmospheric pollutants, inhalation and dermal absorption are more important than dietary ingestion. Daily inhalation exposure doses of PCNs for adults and children were calculated with reference to calculation for dioxins (SI Eq. (1)) (Nouwen et al., 2001).

PCN concentrations in the inhalable particles (PM₁₀) fraction and gas fraction were used to calculate the daily PCNs inhalation exposure. The results are summarized in Table 3. The results showed that residents in the sample collection area were at risk of exposure to PCNs, with an average inhalation of 0.94 fg TEQ/kg/d for adults and 1.66 fg TEQ/kg/d for children. Compared with previous studies, these results were similar to those in Ghana (Hogarh et al., 2012b) and much lower than areas near municipal solid waste incinerators in Spain (Vilavert et al., 2014). Furthermore, children are at a much higher risk of PCN exposure than adults, and that they are the main victims of poor air quality.

The World Health Organization (WHO) specifies a tolerable daily intake (TDI) for dioxins of 1–4 pg TEQ/kg/d (Van Leeuwen et al., 2000). For an adult weighing 60 kg, the maximum WHO-TDI for dioxins is estimated as 240 pg TEQ/d (4 pg TEQ/kg/d × 60 kg). We estimated that daily exposure to the highest dioxin-like toxicity from PCNs in urban air might account for approximately 0.03% of the maximum WHO-TDI for dioxin toxicity. Based on our results for inhalation, we can infer that the TDIs for residents in Beijing are low. Although the contribution of dioxin-like toxicity from PCNs in the air was low, there are other routes of exposure, such as through food and water, and other dioxin-like compounds in these media should be monitored to evaluate the total dioxin-related burden in Beijing.

4. Conclusion

In this study, the concentrations and size-specific distributions of 49 PCN congeners were investigated in Beijing and used to conduct a preliminary exposure assessment. The atmospheric ΣPCNs concentrations (gas + particle) varied from 6.77 to 25.90 pg/m³, and were comparable to, or slightly lower than, those reported in other regions. Overall, PCNs mainly tended to be in the gas phase, which was consistent with earlier studies.

To the best of our knowledge, this is the first study to investigate the distribution of PCNs in different particle size fractions in the atmosphere. The PM mass concentrations and PCN concentrations were highest in the ≤1.0 μm fraction. ΣPCNs associated with PM_{1.0} and PM_{2.5} reached 68.4% and 84.3%, respectively. The lower chlorinated homologues, tetra-CN and penta-CN, predominated in the atmosphere. The homologue profiles in different size particles were similar, but different to that in the gas phase. Also, the particle size distributions of PCNs affected their potential impact on human health. Further research is necessary to assess whether long-term inhalation exposure to PCNs associated with PM_{1.0} or PM_{2.5} in

urban areas poses a significant threat to human health.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.01.065>.

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