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Gas and particle size distributions of polychlorinated naphthalenes in the atmosphere of Beijing, 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/m^3 (average 16.28 pg/m^3). The particle-bound concentration range was 0.17–2.78 pg/m^3 (average 1.73 pg/m^3). Therefore, PCNs were mainly found in the gas phase. The concentrations of PCNs in a fraction increased as the particle size decreased ($d_{ae} > 10$ μm, $10\ \mu m \geq d_{ae} > 2.5$ μm, $2.5\ \mu m \geq d_{ae} > 1.0$ μm and $d_{ae} \leq 1.0$ μm). Consequently, PCNs were ubiquitous in inhalable fine particles, and the ΣPCNs associated with $PM_{1.0}$ and $PM_{2.5}$ reached 68.4% and 84.3%, respectively. Tetra-CNs and penta-CNs (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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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 μm) 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°12′28″ E, 40°00′44″ N) using a high-volume cascade impactor (KS-303 PM10/2.5/1.0 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 ($d_{ae} > 10$ μm, $10\ \mu m \geq d_{ae} > 2.5\ \mu m$, $2.5\ \mu m \geq d_{ae} > 1.0\ \mu m$ 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 °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 ~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 ± 5 °C) and humidity (30 ± 2%) chamber (Sun et al., 2006). Then they were wrapped tightly in aluminum foil, sealed in plastic bags, and kept at −18 °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-CNs 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 × 0.25 mm × 0.25 μm, 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 °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 °C for 2 min, increased at a rate of 20 °C/min to 180 °C (held 1 min), increased at a rate of 2.5 °C/min to 280 °C, and increased at a rate of 10 °C/min to 290 °C (held 5 min). The injector and interface temperatures were set to 260 °C and 290 °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.

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