Concentrations and patterns of polychlorinated naphthalenes in urban air in Beijing, China

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HIGHLIGHTS

- Tri–octachloronaphthalenes in air in Beijing were measured from Apr 2014 to Mar 2015
- Polychlorinated naphthalene concentrations were highest in fall.
- Trichloronaphthalenes were the predominant polychlorinated naphthalenes.
- The main contributors to polychlorinated naphthalene toxicity were CN-66/67 and CN-73.
- Combustion processes were the main sources of polychlorinated naphthalene emissions.

GRAPHICAL ABSTRACT
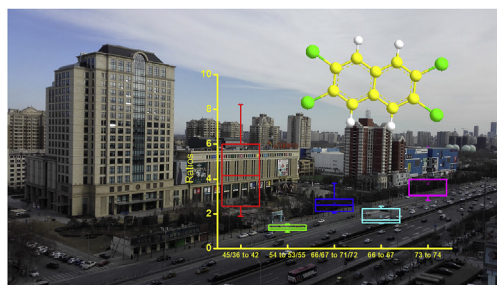
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ABSTRACT

Air samples were collected, using a high-volume air sampler, at an urban site in Beijing from April 2014 to March 2015. The polychlorinated naphthalene (PCN) concentration in the atmosphere in each season was determined. The total PCN (total target tri- to octachloronaphthalene congeners) concentrations were 1.99–19.0 pg/m^3, and the mean was 7.20 pg/m^3. The PCN concentrations were higher in fall than summer, indicating that the concentrations varied significantly over time. The trichloronaphthalene homolog was the predominant PCN homolog in all four seasons. The PCN toxic equivalent (TEQ) concentrations were 0.42–6.89 fg/m^3, and the mean was 1.74 fg/m^3. The CN-66/67 and CN-73 congeners were the predominant contributors to the TEQ concentrations. The mean seasonal TEQ concentration decreased in the order fall (3.18 fg/m^3) > winter (1.41 fg/m^3) > summer (1.11 fg/m^3) > spring (1.03 fg/m^3). The TEQ concentrations and the PCN concentrations did not follow the same seasonal trends, but the highest TEQ and PCN concentrations were both found in fall. Correlation analysis, ratio analysis, and principal component analysis were used to investigate the sources of PCNs to the Beijing atmosphere. The results suggested that combustion processes may be the main sources of PCNs to the Beijing atmosphere.

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1. Introduction

Polychlorinated naphthalenes (PCNs) are ubiquitous environmental pollutants. A PCN molecule contains between one and eight chlorine atoms, and there are 75 theoretically possible PCN congeners. The properties of PCNs are similar to the properties of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) because they all have similar structures (Bidleman et al., 2010). Being similar to PCDD/Fs, PCNs are toxic, persistent, bioaccumulative, and widely distributed throughout the environment. PCNs have recently, at the 2015 triple conference of the parties to the Stockholm convention on persistent organic pollutants, been classed as unintentionally produced persistent organic pollutants. The PCN formulations that are available are used in various industrial applications. PCNs are used in masking compounds for cable electroplating processes, engine oil additives, insulating materials, refractive index testing oils, and wood preservatives, and as dye carriers, feedstocks for producing dyes, and impregnating agents in condensers and capacitors (Bidleman et al., 2010; Lundgren et al., 2003; Zhang et al., 2015a). PCNs enter the environment after evaporating from products (in use or discarded) containing PCNs and through being released in waste, during combustion processes, during commercial processes, and through use in residential and agricultural areas (Falandysz, 1998). PCNs can also be released during some other industrial thermal processes, for example, aluminium recycling processes, secondary nonferrous metallurgical processes, coking processes, and iron foundries processes (Sinkkonen et al., 2004; Ba et al., 2010; Liu et al., 2010, 2014a). PCNs are hazardous to human and ecological health (Jerzy et al., 2014), so there is worldwide concern about and extensive research into their presence in the environment.

Beijing, the capital of China, is in northern China, has a population of 21 million people, and covers 1600 km^2. Beijing has grown and become industrialized quickly over the last three decades, and it is now one of the most densely populated and developed areas of China. Urbanization and industrialization have led to worsening air pollution in Beijing, and the city is affected by many pollution problems. PCNs are released through the combustion of coal and waste and during other industrial processes, and these processes occur throughout Beijing. PCN concentrations in the atmosphere have been investigated in a number studies around the world, including in Shanghai (Die et al., 2016), Japan (Hogarh et al., 2013), Ghana (Hogarh et al., 2012b), Toronto in Canada (Harner et al., 2006), East Asia (Hogarh et al., 2012a), and Sweden (Egeback et al., 2004), but few studies have been focused on PCN concentrations in air in Beijing. Zhu et al. (2016) determined the concentrations and distributions of PCNs in particulate matter of different sizes in the atmosphere in urban parts of Beijing to allow the risks posed to human health by PCNs in inhalable particulate matter to be assessed. They found that PCNs tended to be in the gas phase and that the less chlorinated homologs were the dominant homologs in the atmosphere. However, it is not clear how PCN concentrations in the Beijing atmosphere vary seasonally or what the main sources of PCNs to the Beijing atmosphere are.

The aim of the study presented here was to determine the PCN concentrations in air samples collected in Beijing between April 2014 and March 2015 to allow seasonal variations in PCN concentrations in Beijing to be assessed and to allow potential sources of PCNs to the Beijing atmosphere to be identified.

2. Materials and methods

2.1. Sampling

The sampling site was on the roof of a building at 39° 59′ N and 116° 25′ E. The roof was 40 m above ground level. There were almost no industrial areas around the sampling site, but the site was near a main street affected by heavy traffic in a residential area. A sample was collected once each month between April 2014 and March 2015. The samples were collected using a high-volume air sampler (HV-700F; Sibata Scientific Technology, Soka, Japan). The flow rate was 700 L/min, and each sample was collected for about 24 h. The vapor phase was collected using a polyurethane foam plug (0.016 g/cm^3, 90–100 mm diameter; Sibata Scientific Technology), and the particulate phase was collected using a quartz-fiber filter (203 mm × 254 mm; Pall, Port Washington, NY, USA). Before being used to collect a sample, each quartz-fiber filter was heated to 500 °C for 6 h to remove organic contaminants. The filter was then conditioned overnight in a desiccator at a constant humidity. Before being used to collect a sample, each polyurethane foam plug was extracted with a 1:1 mixture of methylene chloride and acetone in an accelerated solvent extraction system (ASE 300; Dionex, Sunnyvale, CA, USA). The extraction was performed at 1500 psi and 100 °C, with 5 min heating and two cycles. Each used quartz-fiber filter or polyurethane foam plug was wrapped in aluminized paper and stored at −20 °C until it was extracted. The sampling details are shown in Table S1 in the Supplementary Material.

2.2. Sample pretreatment

All of the samples were subjected to the same extraction, cleanup, and quantification procedures. An internal standard solution (ECN-5102, containing 10.0 ng each of $^{13}C_{10}$-labeled CN-27, CN-42, CN-52, CN-67, CN-73, and CN-75), supplied by Cambridge Isotope Laboratories (Andover, MA, USA), was added to each sample before the sample was extracted. The internal standards were used to monitor the effectiveness of the extraction and cleanup procedures. Each sample was then extracted with a 1:1 mixture of methylene chloride and hexane using an ASE 300 accelerated solvent extraction system (Dionex). The extraction was performed at 1500 psi and 100 °C, with 5 min heating, a 60 s nitrogen purge, and three cycles. The extract was concentrated to about 2 mL using a rotary evaporator (R-100; Büchi Labortechnik, Flawil, Switzerland). The extract was then cleaned (to remove material that would potentially interfere with the instrumental analysis) by passing it through a multilayer silica gel column (Presep 291-41653, containing 13% H_2SO_4; Wako Pure Chemical Industries, Osaka, Japan), which was eluted with 150 mL of *n*-hexane. The extract was then concentrated to approximately 200 μL using a rotary evaporator and then under a gentle stream of nitrogen. An injection standard (ECN-5260, containing 20.0 ng of $^{13}C_{10}$-labeled CN-64; Cambridge Isotope Laboratories) was then added to the sample. The injection standard was used to allow the internal standards to be quantified.

2.3. PCN analysis

The PCNs in each extract were analyzed using a gas chromatograph coupled to a triple quadrupole mass spectrometer (7890-7000B GC-QqQ MS/MS; Agilent Technologies, Santa Clara, CA, USA). The mass spectrometer was used in multiple reaction monitoring mode. The carrier gas was helium, and it was used at a constant flow rate of 1.0 mL/min. Splitless injection mode was used. The injection volume was 1.0 μL. A J&W DB-5MS column (60 m long, 0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies) was used to separate the PCN congeners. The temperature program started at 80 °C, which was held for 2 min, increased at 20 °C/min to 180 °C, which was held for 1 min, then increased at 2 °C/min to 255 °C, then increased at 5 °C/min to 280 °C, which was held for 9.5 min. The injector and quadrupole temperatures were 280 °C