



Spatial distribution of polychlorinated naphthalenes in the atmosphere across North China based on gridded field observations



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ABSTRACT

Polychlorinated naphthalenes (PCNs) belong to a group of dioxin-like pollutants; however little information is available on PCNs in North China. In this study, gridded field observations by passive air sampling at 90 sites were undertaken to determine the levels, spatial distributions, and sources of PCNs in the atmosphere of North China. A median concentration of 48 pg m⁻³ (range: 10–2460 pg m⁻³) for \sum_{29} PCNs indicated heavy PCN pollution. The compositional profile indicated that nearly 90% of PCNs observed were from thermal processes rather than from commercial mixtures. Regarding the source type, a quantitative apportionment suggested that local non-point emissions contributed two-thirds of the total PCNs observed in the study, whereas a point source of electronic-waste recycling site contributed a quarter of total PCNs. The estimated toxic equivalent quantity for dioxin-like PCNs ranged from 0.97 to 687 fg TEQ m⁻³, with the electronic-waste recycling site with the highest risk.

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1. Introduction

In recent decades, persistent organic pollutants (POPs) have received significant research attention owing to their persistence in the environment, potential for global transport, bioaccumulation, and possible toxicity (Jones and de Voogt, 1999). As a result of their environmental ubiquity (Poza et al., 2006), 21 pollutants including polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) have been incorporated into the Stockholm Convention on Persistent Organic Pollutants for global regulation (Stockholm Convention on Persistent Organic Pollutants (POPs) as amended in 2009, 2009). However, the regulated POPs constitute only a small proportion of such pollutants, and there are many other unregulated organohalogenes, for instance, polychlorinated naphthalenes (PCNs) (Herbert et al., 2005; Lee et al., 2007; Rotander et al., 2012).

PCNs, comprised of 75 congeners, have a planar structure similar to PCDD/Fs, and thus have a dioxin-like toxicity (Hayward, 1998; Blankenship et al., 2000). There are two major sources of PCNs in the environment: one is from commercial mixtures

containing PCNs, and the other one is as a by-product of certain thermal processes. Commercial PCN mixtures, usually with the trade names of Halowaxes (Koppers Company, USA), Nibren waxes (Bayer, Germany), Seekay waxes (ICI, UK), Clonacire waxes (Prodelec, France), or Cerifal (Caffaro, Italy) (Noma et al., 2004), were widely used as insulators, lubricants, dielectrics, flame-retardants, and plasticizers in industrial products and household goods such as capacitors, cable coverings, and wood coatings (Bidleman et al., 2010). Similarly, PCNs were also present as impurities in technical PCB formulations. Because of their stability, PCNs are hardly degraded and can be released into the environment during their use and ultimate disposal. In addition to these intentional sources, PCNs are by-products of many thermal processes when chlorine is present, e.g., municipal solid waste incineration (MSWI) (Schneider et al., 1998; Jansson et al., 2008), metal smelting (Ba et al., 2010) and chloro-alkali process (Pan et al., 2011). Notably, although the production and consumption of commercial PCNs has ceased in many countries since 1980s (Kannan et al., 2000), the anticipated decrease in PCN levels in the environment has not occurred in some regions (Lee et al., 2005, 2007), suggesting a contribution from thermal sources.

China is the largest developing country in the world. However data on PCN production, consumption, and release into the environment in China is limited. A recent global atmospheric passive sampling (GAPS) study indicated possible heavy PCN pollution in

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China when compared with other countries (Lee et al., 2007). This could be attributed to many causes. For example, China receives more than 28 million tons of electronic-waste (e-waste) from overseas annually (Zhou and Xu, 2012) and more than 20 million tons of domestic municipal solid waste are incinerated every year (Tian et al., 2012). These processes are important sources of PCNs (Jansson et al., 2008; Li et al., 2012; Nie et al., 2012). In addition, industrial activities such as metallurgy and coking are significant sources of PCNs in China (Ba et al., 2010; Liu et al., 2010). Although this suggests the potential for high levels PCN of pollution, information on PCNs in the environment is scarce in China.

North China is one of the most developed regions in the country, being responsible for more than 25% of total gross domestic product (GDP) (China Statistical Yearbook, 2011), but little information is available on the sources, atmospheric levels, and particularly the spatial distribution of PCNs in this region. PCN pollution could have substantial health impacts on this high-population region of more than 300 million residents. The aims of this study were to measure the levels and spatial distribution of PCNs in the atmosphere across North China based on a gridded field observation campaign coupled with a passive air sampling technique, and to explore the PCN sources. On the basis of the measured concentrations, we also estimated the health risk of exposure to PCNs through inhalation. Our results provide essential information for formulating control regulations for this class of pollutant.

2. Material and methods

2.1. Sample collection

Grid-based sampling sites were assigned in North China (covering Beijing, Tianjin, Hebei Province, Shandong Province, Shanxi Province, and a small part of Henan Province) with a grid interval of approximately 70 km (Fig. 1). In mountain regions sampling sites were modified, primarily for ease of accessibility. In addition, three sites were intentionally arranged in downtown areas of Tianjin (S16) and Taiyuan (S29) and at an e-waste recycling site located in a rural area of Tianjin (S18), which were assumed to be heavily polluted regions. In total 90 sites were selected, representing various functional divisions such as megacity, town, and countryside. Geographical coordinates of each site were obtained using a global positioning system (GPS; Table S1 in the Supplementary Material). A polyurethane foam (PUF)-based passive air sampler was placed at each site, with a parallel sampler at four additional sites. Each sampler was deployed continually for 90 days (the whole

sampling period was from early June to early October in 2011). Finally, 93 of the 94 samplers were successfully reclaimed.

In this study, a passive air sampler designed by Harner et al. (2004) was applied. Before sampling, PUF disks (14 cm i.d., 1 cm thickness, 0.021 g cm⁻³ density) were Soxhlet precleaned with acetone and hexane in sequence, for 22 h each. The cleaned PUF disks were dried and stored in brown glass jars until being assembled on site. After sampling, PUF disks were sealed in the same jars, shipped to the laboratory, and stored at -20 °C until analysis.

2.2. Chemicals

Two sets of PCN standards were applied in this study: one was a standard mixture with six congeners [PCN27 (1,2,3,4-CN), PCN42 (1,3,5,7-CN), PCN52 (1,2,3,5,7-CN), PCN67 (1,2,3,5,6,7-CN), PCN73 (1,2,3,4,5,6,7-CN), and PCN75 (octa-CN)] from Cambridge Isotope Laboratories (Andover, MA, USA), and the other was a commercial mixture of Halowax1014 from AccuStandard (New Haven, CT, USA). The composition of Halowax1014 was determined as described elsewhere (Noma et al., 2004). ¹³C₁₂-PCB138 and PCB65 were purchased from Cambridge Isotope Laboratories and AccuStandard, respectively. All solvents used in this study were residue grade from Fisher Scientific (Fair Lawn, NJ, USA).

2.3. Sample analysis

PUF disks were spiked with PCB65 as a recovery surrogate standard, and Soxhlet extracted with 200 mL hexane/acetone (1:1, v/v) for 22 h. After concentration, the extract was washed with 1.5 mL KOH solution (0.5 M) to remove acidic interferences. The samples were then cleaned with an alumina column chromatography (0.6 cm i.d., 6 cm length; filled with 3% water deactivated; MP Biomedicals GmbH, Eschwege, Germany). Analytes were eluted with 8 mL hexane/dichloromethane (3:2, v/v). The eluent was concentrated and further cleaned with 2 mL concentrated H₂SO₄. Finally, samples were blown down and spiked with ¹³C₁₂-PCB138 as an internal standard for gas chromatography mass spectrometry (GC-MS) analysis. Throughout the extraction and analysis procedure, samples were protected from potential photolysis by using amber containers or by wrapping the containers with aluminum foil.

PCNs were analyzed by an Agilent 7890A-5975C GC-MS with an electron-capture-negative ionization (ECNI) ion source. The GC injection port was held at 250 °C; with an injection volume of 1 μL. Target compounds were separated with a 15-m Rtx-SMS column (250 μm i.d., 0.10 μm film thickness) at a constant flow rate of 1.5 mL min⁻¹. The GC oven temperature program was as follows: held at 90 °C for 1 min; 20 °C min⁻¹–200 °C; 5 °C min⁻¹–300 °C, and held for 3.5 min. The following ions were monitored: *m/z* 264 and 266 for tetra-CNs, *m/z* 300 and 302 for penta-CNs, *m/z* 334 and 336 for hexa-CNs, *m/z* 368 and 370 for hepta-CNs, and *m/z* 402 and 404 for octa-CN.

2.4. Quality control

The following quality control criteria were applied: a) the difference in retention time of the target substance between field samples and the standard was less than

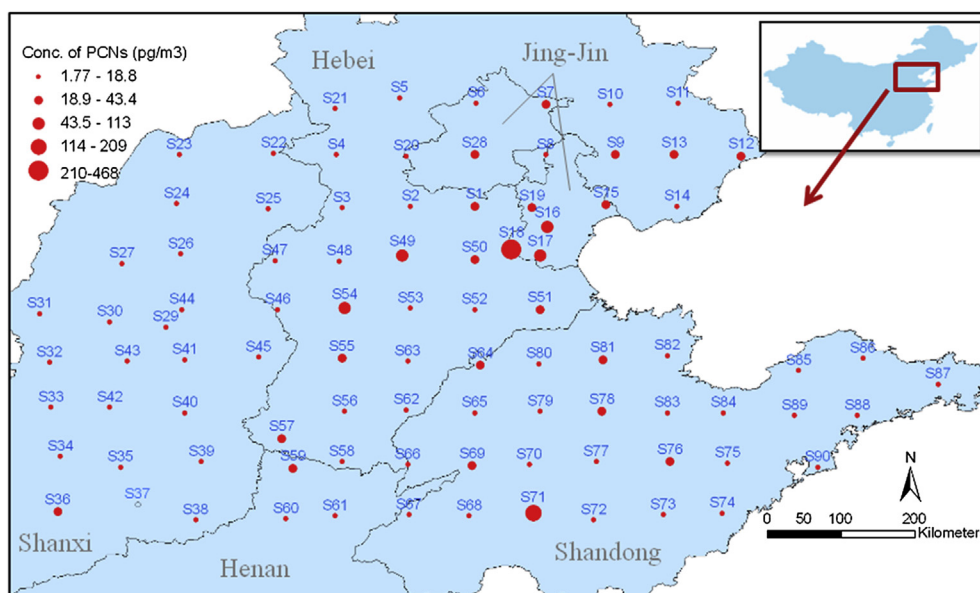


Fig. 1. Map of sampling sites and graduated PCN concentrations (\sum_6 PCNs) in North China (sample at site S37 was lost).

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