



# Concentrations and patterns of polychlorinated naphthalenes in surface sediment samples from Wuxi, Suzhou, and Nantong, in East China



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## HIGHLIGHTS

- High polychlorinated naphthalene (PCN) concentrations were found in sediment samples.
- The predominant PCNs were hexa- to octachlorinated.
- The main contributors to PCN toxicity were hexa- and heptachlorinated.
- Of the “dioxin-like” PCNs, CN-66/67 and CN-73 had the highest toxic equivalents.
- Chemical and manufacturing plants are the dominant PCN sources in the study areas.

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## ABSTRACT

The concentrations and patterns of polychlorinated naphthalenes (PCNs) were determined in surface sediment samples from Wuxi, Suzhou, and Nantong, in the Yangtze River Delta (East China), which has become urbanized rapidly. The total PCN (tri- to octachlorinated naphthalenes) concentrations in the samples from Wuxi, Suzhou, and Nantong were 0.89–40, 2.8–4600, and 0.60–34 ng/g dry weight, respectively. Unexpectedly high PCN concentrations were found in four of the sediment samples. The PCN concentrations were much higher in the samples from the Beijing–Hangzhou Grand Canal than in the samples from the Yangtze River. The toxic equivalent (TEQ) concentrations (determined from the concentrations of the “dioxin-like” PCNs) ranged from  $1.45 \times 10^{-7}$  to 2.16 ng TEQ/g, and the congeners CN-66/67 and CN-73 were the predominant contributors to the TEQs. Independent samples *t*-tests were performed, and no significant differences were found between the PCN concentrations in the samples from the metropolitan area and the development zone when the four development-zone samples that contained very high PCN concentrations were excluded. The PCN profiles were dominated by the hexa- to octachlorinated naphthalene homologs. The CN-66/67 to CN-71/72 and CN-66 to CN-67 concentration ratios were used to identify specific PCN sources. Emissions from chemical and other industrial plants were found to have strongly influenced the PCN concentrations in sediment in the study area.

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## 1. Introduction

Polychlorinated naphthalenes (PCNs) are persistent and ubiquitous environmental pollutants. There are 75 PCN congeners, with between one and eight chlorine substituents at different positions on the naphthalene rings (Liu et al., 2013, 2014). The PCN formulations that are available are used in various industrial applications. PCNs are used in cable electroplating masking compounds, engine oil additives, insulation 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). PCNs can be released into the environment through the improper use and disposal of material containing PCNs, and they can also be released by municipal solid waste incinerators and during some other industrial thermal processes (Abad et al., 1999; Liu et al., 2015), for example, iron ore sintering processes and converter steelmaking processes (Liu et al., 2012b; Li et al., 2014). The production and use of technical PCN formulations has decreased since the early 1980s, but products containing PCNs are still in use (Pan et al., 2011). It is not currently possible to assess PCN pollution in the Chinese environment because no comprehensive investigation into PCN pollution across

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China has been performed and because there have been very few studies of PCNs in the Chinese environment (Wang et al., 2012). According to currently available information, PCNs have not been intentionally produced in China. However, it has been estimated that between 52 and 7300 kg of PCNs were discharged as byproducts of the polychlorinated biphenyl (PCB) production process in China (Guo, 2008). The total amounts of PCNs used in China have not been reported (Guo et al., 2009). PCNs are known to be 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.

Wuxi, Suzhou, and Nantong are cities in southeastern Jiangsu Province, China. These cities are all in the Yangtze River Delta area, which has a subtropical monsoon climate. The Yangtze River and the Beijing–Hangzhou Grand Canal (BHGC) flow through the Yangtze River Delta area. Suzhou is one of the most economically developed cities in China and is the most important economic center in the Yangtze River Delta economic area. More importantly, Suzhou is the dominant industrial center in the southern part of Jiangsu Province. Wuxi is the traffic hub of the Taihu Basin, and about 226 km of Yangtze River riverbanks are in Nantong. Wuxi and Nantong also have developed economies and large populations. There are many industrial parks in the Wuxi, Suzhou, and Nantong area, and the main industries are the chemical, electronic, machinery production, pharmaceutical, and textile industries (Zhang et al., 2011).

Sediment is one of the most important environmental sinks for PCNs, and determining PCN concentrations in sediment samples will allow a PCN inventory to be built for use in further research (Liu et al., 2013). In this study we investigated the concentrations and distributions of PCNs in sediment in waterways in Wuxi, Suzhou, and Nantong, and aimed to explore the factors that have influenced the occurrence and distributions of PCNs in the waterways in these areas.

## 2. Material and methods

### 2.1. Sampling

The sampling campaign was conducted during the wet season. A total of 25 surface sediment samples were collected between 29 June and 12 July 2009. A sample was collected, using a grab sampler, from each of nine sites in Wuxi, nine sites in Suzhou, and seven sites in Nantong (see Fig. 1). The study area and sampling sites have been described in detail elsewhere (Zhang et al., 2011, 2014b). Each sample was air-dried, ground, passed through a sieve with a 149  $\mu\text{m}$  mesh, homogenized, and stored in a brown jar at 4 °C until analysis.

### 2.2. Sample pretreatment

A 10 g aliquot of a sediment sample was mixed with 10 g of diatomaceous earth and 5 g of activated copper powder (to remove elemental sulfur). Aliquots of two internal standard solutions, ECN-5102 (containing 10 ng each of  $^{13}\text{C}_{10}$ -labeled chloronaphthalenes (CNs-) 27, 42, 52, 67, 73, and 75) and DLM-2005-S (containing 10 ng of hepta-deuterated CN-2), both supplied by Cambridge Isotope Laboratories (Andover, MA, USA), were added to the mixture, then the mixture was extracted using an accelerated solvent extraction system (ASE 300; Dionex, Sunnyvale, CA, USA). The extract was concentrated to about 2 mL using a rotary evaporator (Büchi Labortechnik, Flawil, Switzerland) and then purified by passing it through a multilayer silica gel column (Presep 291-41653, containing 13%  $\text{H}_2\text{SO}_4$ ; Wako Pure Chemical Industries, Osaka, Japan) eluted with 150 mL of *n*-hexane to

remove potential interferences during instrumental analysis. Finally, the extract was concentrated to approximately 200  $\mu\text{L}$  using a rotary evaporator and then under a gentle stream of nitrogen, then an injection standard (ECN-5260, containing 20 ng of  $^{13}\text{C}_{10}$ -labeled CN-64; Cambridge Isotope Laboratories) was added. The total organic carbon (TOC) content of each dry sediment sample was determined using a TOC analyzer (TOC-V CSH; Shimadzu, Kyoto, Japan).

### 2.3. PCN analysis

The PCNs were identified and quantified using a gas chromatograph coupled with a triple quadrupole mass spectrometer (7890-7000B GC-QqQ MS/MS; Agilent Technologies, Santa Clara, CA, USA). A J&W DB-5MS column (60 m long, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness; Agilent Technologies) was used to separate the PCN congeners. The carrier gas was helium, and it was used at a constant flow rate of 1.0 mL/min (maintained by an electronic pressure controller). Splitless injection mode was used, and the injection volume was 1.0  $\mu\text{L}$ . The oven temperature started at 80 °C, which was held for 2 min, then increased at 20 °C/min to 180 °C, which was held for 1 min, 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 transfer line temperature was maintained at 280 °C. The optimum triple quadrupole mass spectrometer operating parameters were an ion source temperature of 230 °C, a quadrupole temperature of 150 °C, and an electron energy of 70 eV. The quenching gas (helium) and collision gas (nitrogen) flow rates were 2.25 mL/min and 1.5 mL/min, respectively. The PCNs were determined in multiple reaction monitoring mode. We used a Rt- $\beta$ DExcst chromatography column (30 m long, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness; RESTEK, Bellefonte, PA, USA) to separate CN-66 from CN-67. The specific column and multiple reaction monitoring mode parameters used have been described elsewhere (Zhang et al., 2014a).

### 2.4. Data analysis

The instrument was controlled and the data analyzed using MassHunter Workstation version B.05.00 software (Agilent Technologies). Principal component analysis was performed using SPSS Statistics 20 for Windows software (IBM, Armonk, NY, USA).

### 2.5. Quality control

The procedures described above were monitored carefully by analyzing procedural blank samples. We used  $^{13}\text{C}_{10}$ -labeled CN-42 as an internal standard for the quantitative analyses of the tri-CN and tetra-CN, and used each of the other  $^{13}\text{C}_{10}$ -labeled PCN internal standards to quantify the PCNs with the same number of chlorine substituents. Every sample was spiked with known amounts of ECN-5102 before being extracted, and this allowed the repeatability and accuracy of the analytical method to be assessed. The mean recoveries of the  $^{13}\text{C}_{10}$ -labeled tri- to octa-CN in the real sediment samples ranged from 29.5% to 125%. None of the PCN analytes were detected in the blank samples, demonstrating that no contamination occurred during the sample processing procedures.

The mono-CN and di-CN were not included in this study because they could not be determined adequately because of the presence of chromatographic interferences and because their recoveries were low. The limits of detection and limits of quantification were 0.48–12 and 1.62–40 pg/g, respectively.

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