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Polychlorinated naphthalenes in sewage sludge from wastewater treatment plants in China

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HIGHLIGHTS

- Occurrence of PCNs in sewage sludge from China was investigated at a national basis.
- Levels of PCNs in sludge from the east of China are higher than that from the west.
- Industrial thermal process is one of important sources of PCNs in sludge from China.

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ABSTRACT

Polychlorinated naphthalenes (PCNs) were nominated as persistent organic pollutants candidate in the Stockholm Convention in 2011. In this study, the profiles, concentrations and spatial distributions of PCNs were analyzed in 30 sewage sludge samples from wastewater treatment plants (WWTPs) in China. Concentrations of Σ_{75}PCNs in sludge samples were in the range of 1.05–10.9 ng/g dry weight (dw) with a mean value of 3.98 ng/g dw. The predominant homologues in the sludge were mono- to tetra-CNs, accounting for approximately 85% of total PCNs. The total toxic equivalent quantities (TEQs) of dioxin-like PCN congeners ranged from 0.04 to 2.28 pg/g dw with a mean value of 0.36 pg/g dw, which were lower than the maximum permissible TEQ concentrations in sludge for land application in China. Levels of PCNs and TEQs in sludge were relatively higher in samples from highly industrialized and developed cities in eastern China, implying a possible link between PCN contamination and the local economic development, but more studies are warranted to corroborate this. Industrial sources might be important contributors of PCNs to sewage sludge in China.

1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of organic contaminants which consist of 75 congeners based on a naphthalene ring substituted with one to eight chlorine atoms. In the past, they were widely used as wood preservation, electroplating masking compounds, lubricants, separators in batteries and refractive index testing oils, additives to paints and engine oils, and for cable insulation in capacitors (IPCS, 2001). Though the large production volume and usage of technical PCN formulations and PCN-contaminated PCB mixtures have ceased, unintentional formation from various sources such as waste incinerators, industrial thermal processes, fossil fuels and wood combustion still continue (IPCS, 2001; Lee et al., 2005; Wyrzykowska et al, 2009; Liu et al., 2014). As a group of persistent organic pollutant (POP) candidates proposed in the Stockholm Convention (POPRC, 2011), the contaminants (di-CNs to octa-CN) in the environment might be a serious problem due to their persistence, bioaccumulation potential, and dioxin-like toxicity.

Sewage sludge is not only a sink but also an important secondary source of semi-volatile organic pollutants. Organic contaminants (OCs) with lipophilic properties in wastewater from industrial and domestic sources can ultimately be transferred to sewage sludge during the wastewater treatment (Clarke and Smith, 2011). Residual hazard substances in the sludge may have harmful effects on soil organisms, vegetation, animals and human through secondary treatment of sewage sludge such as land filling, incineration and application on farm land (Clarke and Smith, 2011; ESWI, 2011). Several POP and POP candidates such as short chain chlorinated paraffins (SCCPs), hexachlorobutadiene (HCBD), polybrominated diphenyl ethers (PBDEs) and hexachlorobenzene (HCB) in sewage sludge from wastewater treatment plants (WWTPs) have been investigated to evaluate their spatial distributions and pattern profiles in China (Zeng et al., 2012; Sun et al., 2013; Zhang et al., 2014). Previous works have reported PCN levels in air, sediment and mussels from North China, air and surface soil from the Pearl River Delta, and yak samples from eastern Tibet–Qinghai Plateau (Lee et al., 2007; Pan et al., 2007; Pan et al., 2011; Zhao et al., 2011; Wang

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et al., 2012a, 2012b; Lin et al., 2013; Pan et al., 2013), indicating that PCN contaminants are ubiquitous in China. Limited data for PCNs in urban sludge from eight WWTPs in Beijing (Guo et al., 2008) suggested that PCNs are also present in sewage sludge in China. As one of the "emerging" OC (Clarke and Smith, 2011) and POP candidates, more investigations on PCN contamination in sludge are needed.

In this work, the status of 75 PCN congeners in sludge samples from 30 WWTPs in 24 cities in China was investigated by an isotope dilution method using high resolution gas chromatography/high resolution mass spectrometer (HRGC/HRMS) method. The objective is to investigate the general range of concentrations and examine the potential geographic distributions of PCNs in China, to identify further the possible sources of PCNs in sludge and provide relevant information for the risk assessment for the second treatment of sludge. To our knowledge, this study is the first report to investigate PCN contamination and their possible sources at a national level in China.

2. Materials and methods

2.1. Materials

Dichloromethane (DCM) and n-hexane supplied by J.T. Baker (Philipsburg, U.S.A.) were HPLC-grade. Silica gel (0.063–0.100 mm) and basic alumina (100–200 mesh) used for adsorption chromatography were purchased from Merch KGaA (Darmstadt, Germany) and Sinopharm Chemical Reagent (Shanghai, China), respectively. Native and ^{13}C isotope-labeled PCN congener standards were obtained from Cambridge Isotope Laboratories (Andover, U.S.A.). ECN-5102 (tetra-CNs to octa-CN Mixture) and ECN-5260 ($^{13}C_{10}$-CN-64) were used as surrogate standards and recovery standards, respectively.

2.2. Sample collection

The criteria for sample collection include the geographical distribution, local economic development, treatment processes of WWTPs, etc. The Jingguang Railway, a major arterial railway that connects Beijing in the north with Guangzhou in the south, is usually considered as the geographical boundary of developing regions (western part) and developed regions (eastern part) in China, and we used this to divide our collection sites into two regions in order to investigate potential differences in spatial distributions and congener profiles of PCNs in sewage sludge. Most of the sampling WWTPs are located in the provincial capitals or in cities with high industrial activities. Detailed information of each WWTP from which samples were collected and the total organic carbon (TOC) of the samples are given in Table S1 in the Supporting information. In all, thirty sewage sludge samples were collected from WWTPs in different regions in China (Fig. 1) from October 2010 to May 2011. Fresh sludge samples were directly collected from the dewatering process, packed in aluminum foil, sealed in polypropylene bags, and immediately sent to the laboratory. After freeze-drying and homogenization, the sludge samples were kept at −20 °C until analysis.

2.3. Sample analysis

The pretreatment and analysis of PCNs were carried out using the isotope dilution-HRGC/HRMS method from Guo et al. (2008) and Hu et al. (2013) with some modifications. In brief, approximately 0.5 g dry weight (dw) of sewage sludge was combined with 10 g anhydrous sodium sulfate and spiked with 1 ng $^{13}C_{10}$-labeled PCN surrogate standards. An accelerated solvent extractor (ASE 350, Dionex, Canada) was used to extract the samples with mixture solvent of DCM/n-hexane (1:1, v/v) (flush volume 60%) at 100 °C under 1500 psi in two static extraction cycles (10 min). Then three cleanup columns were used step by step. Before loaded onto the columns, the extract was concentrated to about 2 mL by rotary evaporation. An acid silica gel column (from bottom to top, 8 g of silica/H_2SO_4 44% (w/w) gel, 4 g of silica/H_2SO_4 22% (w/w) gel, and anhydrous sodium sulfate) was used first and eluted with 100 mL n-hexane. The second column was a multilayer silica gel column (from bottom to top, 1 g of active silica gel, 2 g of silica/$AgNO_3$ 10% (w/w) gel, 1 g of active silica gel, 3 g of silica/NaOH (1 mol/L) 33% (w/w) gel, 1 g of active silica gel, 8 g of silica/H_2SO_4 44% (w/w) gel, 1 g of activated silica gel, and anhydrous sodium sulfate), eluting with 120 mL 5% DCM in n-hexane. The third column was filled with 8 g basic alumina and 2 cm anhydrous sodium sulfate, eluting with 120 mL 5% DCM in n-hexane. Finally, the extract was concentrated to approximately 20 μL by rotary evaporation and a gentle nitrogen gas stream. Prior to injection into the HRGC/HRMS, 1 ng of $^{13}C_{10}$-labeled PCN recovery standard was added to the extract.

A Trace GC coupled to a DFS mass spectrometer (Thermo Fisher Scientific, USA) with an electron impact ion source was used for the instrumental analysis. Selected ion monitoring mode was used with resolutions around 10,000. The electron energy and source temperature were set at 45 eV and 270 °C, respectively. A DB-5 fused silica capillary column (60 m × 0.25 mm inner diameter × 0.25 μm, Agilent) was chosen to separate the PCN congeners. Detailed parameters were the same as those described elsewhere (Guo et al., 2008).

2.4. Quality assurance and quality control

Strict criteria for identification and quantification of the analytes were adopted based on the previous research (Hu et al., 2013). Briefly, the retention time of analyte peaks with a signal-to-noise ratio (S/N) of >3:1 should match that of the corresponding standard compounds. The isotopic ratios between the quantitative and confirmation ions should be within ±15% of the theoretical values. The limit of detection (LOD) for individual congener defined as the value corresponding to the peak with S/N of 3 is shown in Table S2.

For each batch of eleven samples, a procedural blank (solvent obtained from extraction of anhydrous sodium sulfate and surrogate standards) was processed. Only trace amounts of mono-CNs and di-CNs were detected in blanks and all the results in this study were blank corrected. The mean recoveries for surrogate standards of $^{13}C_{10}$-labeled CN-27, 42, 52, 67, 73, and 75 were 93.7%, 90.5%, 72.0%, 55.5%, 82.1%, and 67.1%, respectively (Table S3). Concentrations of PCNs in the samples reported were recovery corrected.

2.5. Statistical methods

Statistical analysis was performed using SPSS V18.0. Concentrations lower than LODs were substituted values at one-half of the LODs. Principal component analysis (PCA) was executed using the varimax rotation method with Kaiser normalization. Correlation analysis was determined with Spearman correlation coefficient (R). Concentrations of PCNs and toxic equivalent quantities (TEQs) of dioxin-like PCN congeners for different districts were compared using non-parametric Mann–Whitney test. Probabilities of 0.05 or lower were considered as statistically significant.

3. Results and discussion

3.1. Levels of the total PCNs and TEQs

Concentrations of total PCNs (Σ_{75}PCNs) in sludge samples were in the range of 1.05–10.9 ng/g dw with a mean value of 3.98 ng/g dw (Fig. 1). Comparison between levels of PCNs in this study and those in other countries is shown in Table 1. The Σ_{75}PCNs in this work are comparable to Σ_9PCNs in sewage sludge from Sweden in the early 1990s (Nylund et al., 1992), while they are much lower than those of U.K. (Meijer et al., 2001; Stevens et al., 2003) and Spain (Roig et al., 2012), indicating generally low levels of PCNs in the collected sludge in China. Previous work (Guo et al., 2008) reported that Σ_{75}PCNs in eight sludge samples from WWTPs located in Beijing were in the range of 1.48–28.2 ng/g dw