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-CN, 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.

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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-CN 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 Merck 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 ($^{13}\text{C}_{10}$ -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 $-20\text{ }^{\circ}\text{C}$ 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 $^{13}\text{C}_{10}$ -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 $100\text{ }^{\circ}\text{C}$ 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 $^{13}\text{C}_{10}$ -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 $270\text{ }^{\circ}\text{C}$, respectively. A DB-5 fused silica capillary column (60 m $\times$ 0.25 mm inner diameter $\times$ 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 $\pm 15\%$ 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 $^{13}\text{C}_{10}$ -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 ($\Sigma_{75}\text{PCNs}$) 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 $\Sigma_{75}\text{PCNs}$ in this work are comparable to $\Sigma_9\text{PCNs}$ 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 $\Sigma_{75}\text{PCNs}$ in eight sludge samples from WWTPs located in Beijing were in the range of 1.48–28.2 ng/g dw

Fig. 1. Concentrations and distributions of PCNs and TEQs in sludge samples from WWTPs located in (1) Heilongjiang; (2–5) Beijing; (6) Hebei; (7–12) Shandong; (13–14) Hubei; (15–17) Shaanxi; (18–19) Anhui; (20–21) Henan; (22) Guangdong; (23) Gansu; (24) Sichuan; (25) Qinghai; (26–28) Zhejiang; (29) Shanghai; and (30) Xinjiang.

with a mean value of 7.79 ng/g dw whereas the present work showed lower levels of PCNs (1.87–2.78 ng/g dw with a mean value of 2.49 ng/g dw) in sludge samples from the same city.

Relative potency factors (RPFs) summarized by Noma et al. (2004) were used to calculate TEQs of dioxin-like PCN congeners in the sludge (Table S4). The TEQs were in the range of 0.04–2.28 pg/g dw with a mean value of 0.36 pg/g dw, which were lower than the maximum permissible TEQ concentrations for polychlorinated dibenzo-p-dioxins and dibenzofurans in sludge for land application in China (100 pg TEQ/g) (MEP, 2002) and Canada (4 pg TEQ/g) (CCME, 2007). The level of TEQ (0.06–0.17 pg/g dw with a mean value of 0.13 pg/g dw) in the sludge in Beijing in this work was also much lower than that (0.11–2.45 pg/g dw with a mean value of 0.72 pg/g dw) in the sludge from the same city collected four years ago (Guo et al., 2008).

3.2. Spatial distributions of the total PCNs and TEQs

As shown in Fig. 1, concentrations of PCNs in sludge from the east side of Jingguang Railway were somewhat higher than those from the west

side although the difference was not significant ($p = 0.25$; Mann–Whitney U -test). Levels of TEQs of dioxin-like congeners in the sludge were significantly higher in samples from the eastern part ($p = 0.03$; Mann–Whitney U -test). As the predominant contributor to TEQs among the dioxin-like PCN congeners, the relative abundance of CN-73 to TEQs in sludge samples from the east side was about 1.5 times that of sludge samples from the west side (Fig. 2A). The concentrations of CN-73 were significantly different in the sludge from the two parts (mean; frequency of detection: 124 pg/g dw; 100% and 37.5 pg/g dw; 72% for the samples from the east side and west side, respectively). Cities located at the east side of Jingguang Railway have higher development and life index (NBS, 2012), are more economically developed and have a denser population than those at the west side. The contributors of local industries to the national industry production are also higher in eastern China, and processing industries such as metallurgy and building material production are mainly concentrated in this part (NBS, 2001). Secondary smelting processes, coking industries and cement production have been identified as important industrial thermal sources of PCNs, and CN-73 have been found to be relatively abundant

Table 1
Comparison of concentrations of PCNs in sewage sludge in this work with those in other reports.

	Number of samples	Sampling time	Number of congeners	Σ_n PCNs concentrations (ng/g)		Reference
				range	Mean	
Sweden	2	1988	9	3.17–5.81	4.49	Nylund et al. (1992)
U.K.	1	1968	52	240–250	–	Meijer et al. (2001)
U.K.	14	–	35	50–190	83	Stevens et al. (2003)
China	8	2007	75	1.48–28.2	7.69	Guo et al. (2008)
Spain	28	–	4	$20-1.78 \times 10^3$	124	Roig et al. (2012)
China	30	2010–2011	75	1.05–10.9	3.98	This work

Fig. 2. Contributions of dioxin-like congeners to the TEQs (A) and the homologues to the total PCNs (B). Eastern China included Shandong, Anhui, Shanghai, and Zhejiang, and western China included other provinces in Fig. 1.

in their emissions (Liu et al., 2014). Spatial distribution trends indicated a possible link between PCN contamination in the sludge and the local economic development. In previous investigations, higher levels of PCNs in air, surface soil, and riverine sediment in China (Pan et al., 2011; Wang et al., 2012a, 2012b) were also found in industrialized areas than those in less developed areas.

Due to different proportions of the dioxin-like PCN congeners with high RPF values such as CN-73, CN-66/67 and CN-69, spatial distributions of concentrations of PCNs are not always consistent with that of TEQs. For instance, although Σ_{75} PCNs in the sludge from Xinjiang (No. 30) was relative high (10.4 ng/g dw), its TEQ was at the lower level (0.35 pg/g dw). The total PCNs in the sludge from Laixi (No. 9) in Shandong was relatively low (3.36 ng/g dw) but had a higher TEQ (0.92 pg/g dw).

3.3. Homologue profiles

As shown in Fig. 2B, the homologue profiles of PCNs in sludge samples from the east side and west side of China divided by Jingguang Railway were similar. There was also no significant difference of PCN homologue profiles among the sludge samples from WWTPs using different treatment processes (Fig. S1). Fig. S2 shows more details about the homologue profiles of PCNs for each sludge sample. The lower chlorinated congeners (mono- to tetra-CNs) are generally dominating in the sludge, altogether accounting for 50.7–95.8% of total PCNs. Di-CNs in most samples (21/30) were the most predominant contributor to total

PCN concentrations, followed by tri-CNs, tetra-CNs and mono-CNs. This may be due to three aspects: (1) lower chlorinated PCN homologues (mono-CNs to tetra-CNs) were the dominant homologues in typical technical PCN formulations, and are also released from main sources of PCNs such as waste incinerator and industrial thermal processes (Helm and Bidleman, 2003; Noma et al., 2004; Ryu et al., 2013; Liu et al., 2014). (2) Water solubility decreases with the increase of degree of chlorination (IPCS, 2001). Lower chlorinated PCNs with relatively higher water solubility are more prone to enter the urban wastewater system. (3) Mono-CNs are less sorbed to sewage sludge (24%) than di- to tetra-CNs (50–90%) (calculated by EPI Suite Version 4.1). Furthermore, mono-CNs could be more easily degraded compared to di-CNs, tri-CNs and tetra-CNs (IPCS, 2001). Highly chlorinated homologues (penta-CNs to octa-CN) were also detected although their contributions were relatively low in the samples with the exception of a few samples such as No. 18 and No. 22 (Fig. S2).

3.4. Possible sources

The results of the Spearman correlation analysis are shown in Table S5. There was no obvious influence of the serving population of WWTPs on concentrations of different homologues and the total PCNs with the exception of octa-CN. Furthermore, no significant linear relationship was found between TOCs of samples and concentrations of total PCNs or PCN homologues. A previous work by Guo et al. (2008) demonstrated that wastewater inputs affect the levels of PCNs in sewage sludge and indicated that point sources (industrial effluent discharges) could be important contributors of PCNs to the sludge in Beijing. In this study, concentrations of PCNs showed a positive correlation to the treatment volume of industry effluent (Table S5, $R = 0.432$, $p = 0.05$). Principal component analysis (PCA) was carried out to further investigate the possible influence of wastewater sources to the level and composition of PCNs in the sludge. Three major principal components (PCs) with eigenvalues greater than 1 were extracted, which accounted for 78.6% of the variability in the original data. In the loading plot (Fig. S3A and S3B), component 1 which contributed to 40.0% of the total variance was strongly associated with mono-CNs ($R = 0.870$), di-CNs ($R = 0.793$) and tri-CNs ($R = 0.801$). Component 2 accounted for 24.8% of the total variance and was predominated by hexa-CNs ($R = 0.874$) and octa-CN ($R = 0.892$) and the third component showed a strong linear relationship with tetra-CNs ($R = 0.853$) and penta-CNs ($R = 0.759$). The results shown in Fig. S3C and S3D suggested that concentrations of PCN homologues in sewage sludge from the treatment of waste water inputs with only domestic sources were slightly lower than those with industrial inputs although the differences were not significant.

According to the model prediction by EPI Suite Version 4.1, about 80–93% of tri-CNs to octa-CN could be sorbed to sewage sludge. Congener profiles of PCNs in sewage sludge can give an important indication on their possible sources, assuming that no significant change of PCN composition (tetra-CNs to hexa-CNs) has occurred in the sludge (Järnberg et al., 1999). Significant positive linear correlations ($p < 0.05$) among most PCN homologues in sewage sludge listed in Table S5, suggested that they might share similar sources from the wastewater system.

The differences in congener patterns between technical PCN-containing mixtures and that released from incineration and other industrial thermal processes could be helpful for identifying specific PCN sources. Normally, the relative abundance of some combustion-related PCN congeners (CN-17/25/26, CN-36/45, CN-39, CN-35, CN-52/60, CN-50, CN-51, CN-54, and CN-66/67) to the total PCNs (tri- to octa-CN) ($\Sigma\text{PCN}_{\text{combustion}}/\Sigma\text{PCNs}$) in Halowaxes and Aroclors should be in the range of 0–11%, while this ratio in fly ashes from high temperature sources (municipal waste incinerator, cement kiln, iron sintering, and medical waste incinerators) was estimated to be higher than 49% (Helm and Bidleman, 2003; Noma et al., 2004). In the present work, the fractions of $\Sigma\text{PCN}_{\text{combustion}}/\Sigma\text{PCNs}$ for most of the samples (26/30)

Fig. 3. Ratios of the combustion-related PCN congeners (CN-17/25/26, 36/45, 39, 35, 50, 52/60, 51, 54, and 66/67) to total PCNs (tri- to octa-CN) in sludge samples (sample number indicated in parentheses).

were in the range of 12–35% (Fig. 3). Since no commercial PCN technical products were produced in China (Guo et al., 2008) and there are currently no known usage of commercial PCN-containing products due to the halt of production and industrial use of PCN and PCB formulations (Liu et al., 2014), it is considered that re-emission from historic usage of PCN-containing products and high temperature sources might both influence the concentrations and patterns of PCNs in these samples.

The fractions of $\Sigma\text{PCN}_{\text{combustion}}/\Sigma\text{PCNs}$ for the samples from Puyang (No. 21) and Yuyao (No. 28) (33% and 35%) were quite high, suggesting that high temperature processes could be dominant sources of PCNs to these WWTPs. This may due to the fact that Puyang situates several petrochemical industries and there are secondary metallurgical industries such as aluminum, copper and nickel recycling in Yuyao. Unintentional formation of PCNs from these industrial thermal processes have been demonstrated previously (Schuhmacher et al., 2004; Sinkkonen et al., 2004; Ba et al., 2010; Nie et al., 2012). PCNs released from thermal process may enter WWTPs through direct discharge or/and atmospheric deposition followed by runoff (Guo et al., 2008).

The composition of PCN congeners in individual sludge sample Nos. 18, 22, 27 and 30 are shown in Fig. S4. The fractions of $\Sigma\text{PCN}_{\text{combustion}}/\Sigma\text{PCNs}$ in these four samples were lower than 11% (Fig. 3), indicating that re-emission of technical CN/CB formulations might be the main sources. PCNs from household combustion such as coal and wood combustion (Wyrzykowska et al., 2009), PCNs as byproducts from chlor-alkali plants (Järnberg et al., 1997; Kannan et al., 1998) and PCNs existing as impurities in other industrial products (Pan et al., 2011) might also be possible contributors for the low ratios, although these sources are currently difficult to identify due to insufficient information.

3.5. Comparison to other halogenated compounds in the sludge

Besides PCNs in the present work, HCB, HCB, PBDEs, and SCCPs in the sludge samples collected during the same period were also analyzed in our previous investigations (Zeng et al., 2012; Sun et al., 2013; Zhang et al., 2014). Fig. S5 shows distributions and levels of these four chemicals in the sludge. Higher levels of HCB were found in the sludge from coastal cities in the east side of China, where concentrations of PCNs were also relatively higher (Fig. 1). SCCPs showed opposite spatial distribution comparing to that of PCNs and HCB. No significant geographic trends were found for HCB and PBDEs. Level of PCNs contamination in the sludge was comparable with that of HCB (3.13 ng/g dw),

lower than those of HCB and PBDEs (20.7 and 20.6 ng/g dw), and significantly lower than that of SCCPs (1.07×10^4 ng/g dw). The reasons for these different spatial trends and concentrations are not very clear. PCNs might be more influenced by the economic development since it is a group of unintentional produced POPs from various industries using thermal processes, fuel and waste combustion, and the distributions of the other compounds seemed to be more related to the release from relevant commercial products and usage.

4. Conclusion

PCN contamination in sewage sludge in China was found at the low levels in a global perspective. However, secondary disposal and application of sewage sludge need to be investigated as they might be important secondary sources of PCNs. Even though the re-emission from historic usage of PCN-contained technical mixtures might still occur, the release of PCNs from unintentional sources such as industrial thermal processes should also be a concern as PCNs might share similar sources with dioxins in China.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.05.052>.

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