Occurrence, profile and possible sources of PCNs in Hong Kong soils, and a comparison with PCBs, PCDDs and PCDFs

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Abstract Polychlorinated naphthalenes (PCNs) have been proposed for inclusion in the annexes of the Stockholm Convention by the European Union, signifying a probable increase in monitoring PCN levels at a global level. Investigations on PCN levels in the environment of Hong Kong have not been reported. In this preliminary investigation, PCN levels in surface soils samples were determined by isotope dilution HRGC/HRMS techniques, and compared with those of polychlorinated biphenyl (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). The concentrations of PCNs in the soil samples were 35–883 pg g⁻¹ (average, 201; and median, 94 pg g⁻¹), which were lower than those of PCBs PCDDs and PCDFs. This comparison suggested that PCNs are currently not priority POPs compared with dioxins and PCBs in Hong Kong soils. PCDDs were the most important contributor to the sum of toxic equivalents of PCNs, PCBs, PCDDs and PCDFs. OCDD was the most dominant dioxin congener in Hong Kong surface soils. PCB-118 was the most abundant in 12 dl-PCB congeners. PCN congeners indicating thermal related sources (CN52/60, CN66/67 and CN73) were relatively abundant in their respective homologs, which suggested PCN contamination from thermal sources. The ratio of CN73 to CN74 in soil samples suggested the contribution of PCN

contaminations in soils from both thermal-related sources and evaporative emissions of technical PCN mixtures.

Keywords Persistent organic pollutants · Polychlorinated naphthalenes (PCNs) · PCDD/Fs · Polychlorinated biphenyls · Hong Kong · Stockholm Convention

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and polychlorinated biphenyl (PCBs) belong to the 12 initial persistent organic pollutants (POPs) listed under the Stockholm Convention on POPs. Polychlorinated naphthalenes (PCNs) display similar structure and toxic properties to those of PCDDs, PCDFs and PCBs (Blankenship et al. 2000; Villeneuve et al. 2000). PCNs have been suggested as a new candidate for a POPs under the Stockholm Convention on POPs (UNEP 2011). Investigation on the occurrence and profiles of PCNs in various environmental matrices began later than that of PCDDs, PCDFs and PCBs. Recent studies associated with PCN levels and profiles in various environmental and biota samples have attracted increasing attention (Lin et al. 2013; Hu et al. 2013a; Byer et al. 2013). For some typical contamination area or human samples, the contributions of PCNs in toxic equivalents (TEQ) were comparable to or even higher than those of PCDDs, PCDFs or PCBs (Park et al. 2010; Kannan et al. 1998, 2001). Furthermore, PCNs have been detected in various environmental and biota samples from many regions, including polar areas (Bidleman et al. 2010; Piazza et al. 2013).

Besides the historical manufacturing of PCNs and PCBs as a commercial mixture, PCNs, PCBs, PCDDs, PCDFs can also be unintentionally produced from various anthropogenic sources, and are often termed unintentional POPs (uPOPs) (Liu et al. 2009, 2010, 2012b, 2013). Industrial thermal

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sources including waste combustion and metal smelting were considered important sources of uPOPs (Hu et al. 2013b; Liu et al. 2012a, b, 2014; Falandysz 1998). Unintentional atmospheric emissions from anthropogenic sources have might become much more important sources of PCNs in air than before since the moratorium on manufacture and use of PCNs and PCBs in most countries (Liu et al. 2012b, 2014; Yamashita et al. 2003).

Hong Kong is situated on the southern coast of China. Although there are no intensive industrial activities in Hong Kong, occurrences of PCBs, PCDDs and PCDFs in various matrices including the environment, biota and human samples have been reported in many reports (Choi et al. 2008; Hedley et al. 2006; Kang et al. 2011; Kueh and Lam 2008; Louie and Sin 2003; Nelson et al. 2006; Wong et al. 2013). Specific investigations on PCN levels in the environmental matrices of Hong Kong have not been reported to our knowledge. PCNs have been proposed for inclusion in the annexes of the Stockholm Convention by the European Union (UNEP), signifying that there might be an increase in activities aimed at monitoring PCN levels in environmental and human samples at a global level. It is important to investigate the contamination levels of PCNs in environmental matrices in Hong Kong covered under the Stockholm Convention, which will provide useful data for understanding the contamination status of PCNs in Hong Kong.

Surface soils are not only sinks for POPs, but can also be secondary sources of POPs released into the environment (Liu et al. 2011). Harrad et al. (1994) noted that soils are an important reservoir for many POPs. For example, about 93 % of the environmental burden of Σ PCBs in the UK was estimated to be associated with soils (Harrad et al. 1994). Investigations on the levels and profiles of POPs in surface soil are helpful for understanding their environmental contamination and risk exposure. In this preliminary investigation, surface soil samples from Hong Kong were collected and analyzed for PCNs using isotope dilution high-resolution gas chromatography combined with high-resolution mass spectrometer (HRGC/HRMS) techniques. PCBs, PCDDs and PCDFs in those samples were also analyzed with the HRGC/HRMS techniques with the aim of comparing the toxic contribution of PCNs with those of PCBs, PCDDs and PCDFs. To our knowledge, this is the first preliminary investigation on PCN levels in surface soil samples from Hong Kong, which will be helpful for understanding baseline levels of PCNs.

Materials and methods

Surface soil sampling

Hong Kong is located at the southeast tip of the China, with a total area of slightly over 1,100 km². It is composed of Hong

Kong Island, Kowloon, the New Territories and a number of smaller islands. Hong Kong's climate is subtropical, tending towards temperate for nearly half the year. Most soils in Hong Kong are oxisols, typical of the humid tropics, characterized by strong weathering and leaching (Zhang et al. 2007). In this preliminary investigation, 14 surface soil samples (0–10 cm) were collected in 2013. Most of the samples were collected from urban parks. Each composite soil sample was comprised of six sub-samples from the sampling sites. All samples were tightly wrapped in aluminum foil and sealed in PE plastic bags. At the end of the sampling trip, the samples were immediately transferred to a refrigerator where they were stored until analysis. Sampling locations are described in Fig. 1.

Chemical analysis of PCNs, PCBs, PCDDs and PCDFs

PCNs were analyzed by isotope dilution HRGC/HRMS technique as described previously (Liu et al. 2011). The analysis of PCDD/Fs and PCBs was carried out based on the US EPA method 1613B and 1668A modifications, respectively. Briefly, the samples were spiked with known amounts of ¹³C₁₂-labeled PCDD/Fs, PCBs and PCN internal standards after grinding. The PCN internal standards (catalog no. ECN-5102) were comprised of six congeners of ¹³C₁₀-CN-27, -42, -52, -67, -73, and -75. The spiked samples were extracted by accelerated solvent extraction (ASE) with a solution mixture of *n*-hexane and dichloromethane (1:1 in volume). The concentrated extract was purified by multilayer silica gel columns. PCDD/Fs, PCBs and PCNs were fractionated by basic aluminum columns. Finally, all the fractions were reduced to about 20 µl. Prior to injection, ¹³C₁₂-labeled injection standards were added into corresponding fractions for calculation of recoveries. The ¹³C₁₀-labeled CN-64 (catalog no. ECN-5260; Cambridge Isotope Laboratories) was used as the injection standard for calculating the recoveries of PCN internal standards. The analyses of PCNs, PCBs and PCDD/Fs were performed by an HRGC/HRMS. The MS was operated at ≥10,000 resolution.

Congener peaks were identified based on retention time compared with available individual standards and ion ratios, and by considering the elution order on a DB-5 column. Peaks were quantified if target/qualifier ion ratios were within 15 % of theoretical values. The limits of detection (LODs) in the surface soil samples ranged from 0.01 to 1.2 pg g⁻¹ for PCDD/F congeners, 0.02 to 3.2 pg g⁻¹ for PCB congeners, and from 0.03 to 1.7 pg g⁻¹ for PCN congeners. The recoveries of ¹³C₁₂-PCDD/Fs and ¹³C₁₂-PCBs internal standards were 39–127 % and 43–139 %, respectively. The recoveries of ¹³C₁₀-PCN internal standards

Fig. 1 Schematic of sampling sites and TEQs of PCNs, PCBs, PCDDs and PCDFs in surface soil samples

relative to labeled injection standards in the samples ranged from about 35 to 116 %.

Results and discussion

Concentrations of PCNs, PCBs, PCDDs and PCDFs

The concentrations of the contaminants in the surface soil samples were 35–883 pg g⁻¹ (average, 201; median, 94 pg g⁻¹) for Σ_{4-8} PCNs, 151–99,100 pg g⁻¹ (average, 9,990; median, 469 pg g⁻¹) for Σ_{4-8} PCBs, 162–3,450 pg g⁻¹ for 2,3,7,8-substituted PCDDs (average, 1110; median, 701 pg g⁻¹), and 3–213 pg g⁻¹ for 2,3,7,8-substituted PCDFs (average, 28; median, 9). The concentrations of dioxin-like PCBs and indicator PCBs in the surface soil samples were 8–5,390 pg g⁻¹ (average, 567; median, 39 pg g⁻¹),

and 56–61,700 pg g⁻¹ (average, 5,950; median, 278 pg g⁻¹), respectively. The concentrations of PCNs in the surface soil samples were obviously higher than those of 2,3,7,8-substituted PCDFs. The concentrations of PCNs in soil samples were obviously lower than those of 2,3,7,8-substituted PCDDs and PCBs.

Previous studies associated with the occurrences and profiles of PCBs, PCDDs and PCDFs in Hong Kong have focused on marine sediment, the atmosphere, biota and human breast milk (Choi et al. 2008; Hedley et al. 2006; Kang et al. 2011; Kueh and Lam 2008; Louie and Sin 2003; Nelson et al. 2006; Wong et al. 2013). There is still little available information on PCBs, PCDDs and PCDFs in the soils of Hong Kong. Zhang et al. (2007) determined the concentrations of PCBs in the soils of Hong Kong using a GC equipped with a ⁶³Ni electron capture detector- μ ECD. The concentrations of seven indicator PCB congeners (Σ_7 PCBs) were 70–9,870 pg g⁻¹. The average was 2,450 pg g⁻¹, which was lower than the value

of 5,947 pg g⁻¹ reported in this study. The median value reported by Zhang et al. (2007) was 530 pg g⁻¹, which was higher than the median value of 278 pg g⁻¹ in this study.

Some publications have reported PCN levels in soil samples from many regions (Schuhmacher et al. 2004; Kannan et al. 1998; Krauss and Wilcke 2003; Meijer et al. 2001; Odabasi et al. 2010; Wang et al. 2012; Wyrzykowska et al. 2007). Table 1 summarizes the concentration of PCNs in soil samples from different areas. The PCN levels in Hong Kong soil samples were comparable to those of other urban soils, but were lower than those of industrial contamination sites. The comparison of PCN levels in Hong Kong soils with those of other regions, as well as the comparison with levels of dioxins and PCBs in Hong Kong soils, indicated a relatively low contamination status for PCNs in Hong Kong soil samples.

TEQs of PCNs and its comparison with PCBs, PCDDs and PCDFs

PCNs display similar toxic mechanisms to dioxins, inducing aryl hydrocarbon receptor (AhR) mediated responses, and are often referred to as dioxin-like compounds (Blankenship et al. 2000; Villeneuve et al. 2000). Although there are currently no internationally authorized toxic equivalency factor (TEF) schemes for PCN congeners, many studies have been performed to evaluate the TEF for individual PCN congeners relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) (Hanberg et al. 1990; Villeneuve et al. 2000; Blankenship et al. 2000; Behnisch et al. 2003; Kannan et al. 2000). Some TEFs for individual PCN congeners have been proposed and used to evaluate the toxicities of PCNs. The TEFs of several PCN congeners relative to 2,3,7,8-TCDD

have been summarized and reported by Noma et al. (2004). These estimated TEFs ranged from 1.8×10^{-8} to 3.0×10^{-3} , and the TEFs of CN66/67, CN64/68, CN69, CN63, CN70, and CN73 were over 1.0×10^{-3} . Falandysz et al. (2013) recently evaluated and updated the relative potency factors of PCN congeners relative to 2,3,7,8-TCDD. In this study, the toxic equivalent (TEQ) of PCNs were calculated according to the TEFs of PCN congeners relative to 2,3,7,8-TCDD obtained by in vitro assays.

The TEQs of PCBs, PCDDs and PCDFs were calculated using the TEF of congeners suggested by the World Health Organization (Van den Berg et al. 1998). The TEQs of the investigated contaminants in the soil samples were 0.18–5.52 pg TEQ g⁻¹ (average, 1.5; median, 0.93 pg TEQ g⁻¹) for PCDDs, 0.14–2.89 pg TEQ g⁻¹ (average, 0.73; median, 0.40 pg TEQ g⁻¹) for PCDFs, 0.023–4.42 pg TEQ g⁻¹ for PCBs (average, 0.48; medium, 0.11 pg TEQ g⁻¹), and 0.0004–0.25 pg TEQ g⁻¹ for PCNs (average, 0.02; medium, 0.003 pg TEQ g⁻¹). The TEQs of PCBs, PCDDs and PCDFs in Hong Kong soil samples in this study were comparable to other urban soils (Cai et al. 2008; Wang et al. 2008). The TEQs of PCNs, PCBs, PCDDs and PCDFs, and their distribution and comparison in soil samples are shown in Fig. 1. The TEQs of PCDDs were highest for most of the samples, followed by PCDFs. The TEQs of PCNs were the lowest. The TEQs of PCBs were lower than those of PCDFs, but higher than those of PCNs.

The contributions of PCNs, PCBs, PCDDs and PCDFs to their sum TEQs were calculated in this study. The most important contributor to the sum TEQ was PCDDs, accounting for an average value of 59 % of the total TEQs, followed by PCDFs with an average of 29 %. The average contribution

Table 1 Concentrations of PCNs in soil samples from Hong Kong compared with levels found in other areas

Location	Samples	Sampling year	Concentration (pg g ⁻¹)		Homolog	Analytical method	Reference
			Range	Average			
Tarragona, Catalonia, Spain	Industrial site soil	2002	70–121	95	4–8	HRGC/HRMS	(Schuhmacher et al. 2004)
Tarragona, Catalonia, Spain	Urban soil	2002	180		4–8	HRGC/HRMS	(Schuhmacher et al. 2004)
Tarragona, Catalonia, Spain	Unpolluted site	2002	32		4–8	HRGC/HRMS	(Schuhmacher et al. 2004)
Brunswick, GA	Industrial site	1996		17,900,000	3–8	GC/MS	(Kannan et al. 1998)
Bayreuth, Bavaria, Germany	Urban soils		<100–15,400		2–8	GC/MS	(Krauss and Wilcke 2003)
Bayreuth, Bavaria, Germany	Industrial site soil		670–15,000		2–8	GC/MS	(Krauss and Wilcke 2003)
Bayreuth, Bavaria, Germany	Rural soils		<100–820		2–8	GC/MS	(Krauss and Wilcke 2003)
London, UK	Agricultural soil	1986		320	3–7	GC/MS	(Meijer et al. 2001)
Hatay and Iskenderun, Turkey	Industrial site soil	2008		280,000	3–8	GC/MS	(Odabasi et al. 2010)
Poland	Agricultural soil	2002		350–1,100	3–8	HRGC/HRMS	(Wyrzykowska et al. 2007)
Pearl River Delta, China	Surface soil	2009		59.9	4–6	GC-ECNI-MS	(Wang et al. 2012)
Shanxi province, China	Surface soil	2009	45–414	172	1–8	HRGC/HRMS	(Liu et al. 2011)
Hong Kong	Surface soil	2013	34–883	201	4–8	HRGC/HRMS	This work

of PCBs to the sum TEQ was 11 %. The average fraction of PCN TEQ in the sum TEQ of PCNs, PCBs, PCDDs and PCDFs was only around 1 %. This indicated very low TEQ contributions from PCNs in Hong Kong surface soils compared with those of PCBs, PCDDs and PCDFs.

Congener profiles of PCNs, PCBs, PCDDs and PCDFs, and possible sources of PCNs

The congener profiles of PCDDs and PCDFs are presented in Fig. 2. OCDD was the most dominant congener in PCDDs, followed by 1,2,3,4,6,7,8-HpCDD. OCDF and 1,2,3,4,6,7,8-HpCDF were the dominant congeners in PCDFs. The congener profiles of dl-PCBs and indicator PCBs are presented in Fig. 3. PCB-118 was the dominant congener out of 12 dl-PCB congeners, followed by PCB-105 and PCB-156. The concentration of PCB-126 among the 12 dl-PCB congeners was relatively low. However, the contributions of PCB-126 to the TEQs of dl-PCBs were significant owing to its higher TEF compared with the other dl-PCB congeners. The four PCB congener fractions PCB-28, PCB-138, PCB-153 and PCB-180 were obviously larger than those of PCB-52 and PCB-101.

The concentration of each PCN congener was expressed as a fraction of the corresponding homolog concentration. This normalization permitted a clear comparison of congener profiles in corresponding homologs (Liu et al. 2012a). The profiles of PCN congeners relative to tetraCN, pentaCN, hexa- and hepta-CN homologs are shown in Fig. 4. In Fig. 4a, it can be seen that congeners of CN33/34/37, CN45/36 and CN38/40 were much more abundant than others in tetraCN. For congeners in pentaCN, CN52/60, CN51 and CN59 were dominant. For the hexaCN homolog, CN66/67, CN69 and

CN71/72 dominated over other congeners. The fractions of CN73 were comparable to those of CN74.

Congener profiles of PCNs could provide helpful information for speculating on their possible sources including emissions from thermal-related industries, or evaporative emissions of historical uses of industrial chemicals (such as Halowaxes). For example, Hanari et al. detail reported the profile of PCN congeners in Halowaxes 1001 and 1014 (Hanari et al. 2013). For tetraCN homolog, CN38 and CN46 were the most dominant congeners, and CN59 was the most abundant congener in pentaCN homolog. Several markers have also been suggested for identifying the sources of PCNs (Wyrzykowska et al. 2009; Orlikowska et al. 2009; Helm and Bidleman 2003). Wyrzykowska et al. (2009) and Orlikowska et al. (2009) reported the homolog and congener profiles of PCNs from household combustions and identifying the possible sources of PCNs in environmental and biota samples by principal component analysis (Orlikowska et al. 2009; Wyrzykowska et al. 2009). Helm et al. evaluated the contribution of combustion related sources to the air contamination of PCN in Toronto, Canada, by using CN52/60, CN54, CN66/67 as the combustion markers (Helm and Bidleman 2003). Furthermore, the dominance of CN52/60 and CN50 has been reported for thermal-related processes (Schneider et al. 1998). Congeners composed of CN54 and CN66/67 are the most popular and relatively abundant indicators for waste incinerations (Meijer et al. 2001). In this study, CN52/60 and CN66/67, indicating combustion or other thermal-related sources, were dominant in the soil samples. This indicated the contribution of PCNs from combustion or other thermal related sources. The congeners of CN38 and CN59 indicating the possible release from Halowaxes were also relatively abundant in tetra- and penta-homologs in soils samples, which indicating the possible occurrence of PCNs

Fig. 2 Congener profiles of PCDDs (a) and PCDFs (b) in surface soil samples

Fig. 3 Congener profiles of dl-PCBs (a) and indicator PCBs (b) in surface soil samples

from evaporative emissions of technical PCN formulations. The ratios of CN73 to CN74 ($R_{CN73/CN74}$) vary in different source samples, with values far lower than one (0.2–0.4) in Halowaxes (Noma et al. 2004) and markedly higher than one (2–25, with average of 5.7) in stack gases or fly ash samples collected from thermal-related sources (Liu et al. 2014). In the soil samples, fractions of CN73 were comparable to those of CN74. This phenomenon might signify the mixed effect of two types of sources: thermal-related sources, and evaporative emissions of technical PCN mixtures (such as Halowaxes).

The contamination levels of PCNs relative to those of PCBs ($\sum PCN/\sum PCB$) have been used to speculate on the sources of PCNs in the atmosphere (Harner et al. 2000). It was suggested that a ratio of $\sum PCNs/\sum PCBs$ from 0.2 to 0.25 denotes the background levels of PCNs in the air, and a ratio >0.25 indicates “non-diffuse” or “point sources”. In this study, the $\sum PCNs/\sum PCBs$ ratios in soil samples were also determined, and the ratios of $\sum PCNs/\sum PCBs$ were below 0.20 for most of those samples with an average of 0.23. The PCN contamination in Hong Kong surface soils was regarded as background levels of PCN without intensive “point sources”. Long range input of PCNs from thermal-related sources and

evaporative emissions of technical PCN mixtures appear to be the sources of PCNs in Hong Kong soils.

Conclusions

PCN levels in surface soils samples from Hong Kong were determined by isotope dilution HRGC/HRMS techniques, and were compared with those of dioxins and PCBs in this preliminary study. The concentrations and TEQs of PCNs in the soil samples were far lower than those of dioxins and PCBs, which indicates that PCNs should not be the current priority POPs compared with dioxins and PCBs in Hong Kong surface soils. PCDDs were the most important contributor to the sum of TEQs of PCNs, PCBs, PCDDs and PCDFs. OCDD and PCB-118 were the most dominant congeners in seventeen 2,3,7,8-substituted PCDD/F and 12 dl-PCB congeners, respectively. According to the congener profiles of PCNs, it was speculated that the contribution of PCN contaminations in Hong Kong soils come from long range input including

Fig. 4 Profile of PCN congeners relative to corresponding tetraCN (a), pentaCN (b), hexa- and hepta-CN (c) homologs

both thermal-related sources and evaporative emissions of technical PCNs mixtures (such as Halowaxes).

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