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Atmospheric polychlorinated naphthalenes (PCNs) in India and Pakistan

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HIGHLIGHTS

- Atmospheric PCNs in India and Pakistan were determined by passive air sampling.
- PCN levels were relatively lower than the reported values in other Asian countries.
- Tri- and Tetra-CNs were the predominant congeners in the both countries.
- Major sources were re-emission of Halowax and industrial thermal.
- The potential health impact was comparable to non-urban sites in the world.

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ABSTRACT

Polychlorinated naphthalenes (PCNs) are now under review by the Stockholm Convention as candidates for persistent organic pollutants (POPs) due to their persistence, toxicity, bioaccumulation, and long-range atmospheric transport. Data on PCN levels are sparse in South Asia. Atmospheric PCNs in India and Pakistan were monitored during the winter by polyurethane foam disk passive air samplers (PUF-PAS). The average concentrations were 29 pg/m^3 and 7.7 pg/m^3 in the Indian and Pakistani samples, respectively. Those concentration levels were relatively lower than the previously reported values in other Asian countries, but still considerably higher than in other sites in the world. Tri-CNs and tetra-CNs were the dominant homologues in the air, especially in India. Spatially, the PCNs were ubiquitous in the target areas, and local distribution was generally impacted by the proximity to potential sources. Major sources of PCNs in this study were the re-emission of Halowax and industrial thermal processes. Biomass burning influenced some sites in Pakistan. However, the enrichment of tri-CNs in Indian cities cannot be ascribed to either the signature of a specific source or the preferential volatilization and/or photodegradation in tropical areas. Despite this unclear issue in South Asia, the present study indicates that the potential health impact was generally comparable to that in non-urban sites worldwide.

1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of widespread atmospheric contaminants that have been detected in both populated and remote areas, such as Chicago (Harner and Bidleman, 1997) and the Arctic (Lee et al., 2007). As compounds similar to dioxin, PCNs are toxic, persistent and bio-accumulative enough to meet the persistent organic pollutants (POPs) criteria and thus, were targeted as candidates of POPs by the UN-ECE in 1998 (Lerche et al., 2002). Therefore, extensive scientific studies have been conducted to investigate their properties, sources, and environmental behaviors (Domingo, 2004; Bidleman et al., 2010).

The usage and emission information of PCNs are limited in South Asia. A global monitoring program was launched by Lee et al. (2007), but South Asia was not included. Based on atmospheric emission, South Asia presumably harbors some potential sources. The historical application of a technical mixture in extensive industrial activities, combustion processes such as incineration and metal refining, coal and wood burning and PCB-associated (polychlorinated biphenyls) application can release PCNs into the atmosphere (Harner and Bidleman, 1997; Lee et al., 2007; Hogarh et al., 2012). In South

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Asia, the industrial sector contributes approximately 26.4% and 25.4% to the overall GDP in India and Pakistan, respectively (http://en.wikipedia.org/wiki/Economy_of_India and http://en.wikipedia.org/wiki/Economy_of_Pakistan). Coal consumption, which is considered a source of PCNs (Orlikowska et al., 2009; Wyrzykowska et al., 2009), in India ranked third in the world. The PCB pollution in some hotspots was in the highest range (Zhang et al., 2008). The PCNs might be introduced into the environment by those processes and even transported to remote areas by high temperatures and South Asia monsoon outbreaks.

Passive Air Sampling (PAS) has been widely applied to determine the spatial and temporal variations of atmospheric PCNs on the global or regional scale (Harner et al., 2006; Lee et al., 2007; Baek et al., 2008; Hogarh et al., 2012; Wang et al., 2012). Some urban areas in India and Pakistan with potential PCN sources were selected as targets to monitor the PCNs in the air by PAS because previous studies showed that urbanized and industrialized areas were prone to pollution (Harner and Bidleman, 1997; Lee et al., 2007). With many questions concerning PCNs in South Asia, the present study is the first that aimed to outline the concentration levels, the composition profiles and the potential sources of PCNs in this region.

2. Materials and methods

2.1. Passive air sampling

The air samples were taken at urban, suburban and rural sites from a previous sampling campaign by polyurethane foam (PUF) disks (14.0 cm diameter; 1.30 cm thick; 0.0170 g cm^{-3} density). The Indian sampling campaign was conducted in three urban areas (Kolkata, Mumbai and Chennai) during the winter of 2006, while the PUF samples from Punjab Province, Pakistan, were collected during the winter of 2011 (Fig. 1 and S1). Details of the Indian sampling campaign were previously described (Chakraborty et al., 2010). The Pakistani sampling campaign was conducted in the industrial/urban and agricultural/rural areas of Punjab Province (Syed et al., 2013). A brief introduction to the sampling sites can be found in the supporting information. The PUF disks were Soxhlet-extracted with methanol for 48 h followed by acetone for 24 h and dichloromethane (DCM) for 24 h. The extracted PUF disks were wrapped with clean aluminum foil, sealed in Teflon bags and transported to the sampling sites before the sampling campaign. The PUF disks were used according to the standard procedures (Zhang et al., 2008). After the 28-day Indian sampling period and the 56-day Pakistani sampling period, the PUF disks were wrapped, sealed and transported to the lab, where they were kept at −18 °C before further analyses.

2.2. Sample extraction and analysis

The exposed PUF disks were spiked with ^{13}C-trans-Chlordane as a surrogate and were Soxhlet-extracted with DCM for 24 h. Activated copper granules were added to remove the sulfur. The extracts were concentrated and solvent-exchanged into hexane through a rotary evaporator. Afterwards, the extract was first cleaned by a multi-layer column containing anhydrous Na_2SO_4, neutral silica gel (3% deactivated) and neutral alumina (3% deactivated) from top to bottom and then by a column containing 50% (w/w) sulfuric acid–silica gel, florisil (2% deactivated) and neutral alumina. The eluent solvent was concentrated to approximately 25 μl, and ^{13}C-PCB141 was added as the internal standard prior to the instrumental analysis.

2.3. Instrumental analysis

The targeted PCNs were analyzed using Agilent 7890A gas chromatography electron capture negative-ion mass spectrometry (GC-ECNI-MS) in selected ion monitoring (SIM) mode. A DB-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was selected to separate each compound. The initial oven temperature was set at 80 °C for 0.5 min, 15 °C/min to 160 °C, 3 °C/min to 240 °C, and 6 °C/min to 270 °C, which was held for 10 min. The temperatures of the MSD source and quadrupoles were all 150 °C. The relative contributions of each congener of Halowax 1014 were previously reported (Helm and Bidleman, 2003). The technical PCN mixture Halowax 1014 containing known amounts of PCN congeners (tri-CNs: CN-19, -24, -14, -15, -16, -17/25, -23; tetra-CNs: CN-42, -33/34/37, -47, -36/45, -28/43, -27/30, -39, -32, -35, -38/40, -46; penta-CNs: CN-52/60, -58, -61, -50, -51, -54, -57, -62, -53, -59, -49, -56; hexa-CNs: CN-66/67, -64/68, -69, -71/72, -63, -65; hepta-CNs: CN-73, -74; octa-CN: CN-75) were used as quantification standards.

2.4. QA/QC

In total, 7 field and 5 analytical blanks were used to assess the potential contamination during the experiment and field sampling. The field blanks were obtained by exposing a clean PUF disk at the sampling sites for 5 min. Only CN-14, -24 and -33/34/37 were detected in the blanks, with average values of 0.016, 0.05 and 0.01 ng/sample, respectively. There were no significant differences between the lab and field blanks or between the blanks that were taken from Pakistan and India. The instrumental detection limits (IDLs) were integrated where the signal-to-noise ratio was equal to 3, which ranged from 0.007 to 1.1 ng/sample. The method detection limits (MDLs) were defined as the average concentrations of the target compounds in the field blanks plus three times the standard deviation of CN-14, -24 and -33/34/37. The MDLs, however, were defined as IDLs of the other congeners. The surrogate recoveries for ^{13}C-trans-Chlordane in all of the samples ranged from 70.6 to 97.2%, with an average of 77.5%. The reported results were corrected by the blanks but not by the surrogate recoveries. The sampling rates of the PUF disk varied with the environmental conditions and the physicochemical properties of the target compounds. The sampling rates of the PCN congeners at another subtropical site in Pearl River Delta (Wang et al., 2012) were assessed based on a joint correction that used the active air sampling rate and the addition of depuration compounds. Here, those sampling rates were adopted to calculate the atmospheric concentrations of the PCNs due to the same passive air sampling method and similar environmental conditions. The average sampling rates were 3.0, 4.9, 8.6 and 11.6 m^3/day for the tri-, tetra-, penta-, and hexa-CNs, respectively.

3. Results and discussion

3.1. Concentrations and compositions

The air concentrations of the individual PCN congeners are listed in Table S1. The ΣPCN concentrations ranged from 4.9 to 140 pg/m^3 with an average of 28 pg/m^3 in the Indian sampling campaign, and ranged from n.d. to 31 pg/m^3 with an average of 7.8 pg/m^3 in the Pakistani campaign. The concentration levels were relatively lower than those that had been previously reported from China, and the levels of the Pakistani samples were even lower than those reported from Japan and Korea in March–May, 2008 (Hogarh et al., 2012). However, compared with the mean values of the Global Atmospheric Passive Sampling (GAPS) study in mid-December 2004 and mid-March 2005 in Eastern Europe and Asia (Lee et al., 2007), the geometric mean in India was higher than that in urban areas; however, that in Pakistan was lower than that in urban and higher than that in non-urban sites. These relationships indicate that the atmospheric PCN pollution in South Asia is comparable to other areas in Asia, but is still high worldwide.

Among the targeted compounds in the current study, CN-19, -24, -14, -33/34/37, -47, -36/45, -27/30, and -52/60 were commonly detected with a detection frequency >70%, followed by CN-42, -39, -32, -38/40, and -50, which were above the MDLs with a detection frequency >30%,

and CN-23, -28/43, -35, -46, -61, -57, -62, -53, -49, -66/67, -64/68, -69, -71/72, -63, -65, -73, and -75, which were infrequently above the MDLs with a detection frequency <30%. Overall, the tri-CNs and tetra-CNs were the major homologs in both the Indian and Pakistani air samples, and CN-24 was the dominant congener, although the average relative proportions were different (Fig. 2). The samples from Pakistan exhibited a sequence of tri-CNs (57%) > tetra-CNs (34%) > penta-CNs (7%) > hexa-CNs (1%). The dominance of the tri-CNs resembles the reported profiles in East Asia (Hogarh et al., 2012), even though the tri-CN congener profiles were only dominated by CN-14 and -24 (>90%). In India, the tri-CNs contributed ~82% on average to the ΣPCNs, followed by the tetra-CNs (~16%) and penta-CNs (~1%); these features are different from those in Asia but similar to those in Barrow (USA), Barcelona (Spain) and Alert (Canada) (Lee et al., 2007). A comparison of the homolog composition between combustion-related emission (Helm and Bidleman, 2003; Lee et al., 2005a, 2005b) and Halowax (Noma et al., 2004; Falandysz et al., 2006, 2008) showed that some Halowax types, such as 1031, 1001 and 1099, are commonly characterized by the dominance of tri-CNs, while other sources are abundant in tetra-CNs, which might induce different composition patterns. The same or similar formulations can also be enriched in tri-CNs due to different manufacturers (Falandysz et al., 2000; Yamashita et al., 2003). In addition, the average temperature was 23 °C in the Indian sites and 17 °C in the Pakistani sites during the sampling periods. Therefore, the enrichment of lighter congeners in India may also be attributed to the preferential degradation of heavier congeners (Ruzo et al., 1975) in tropical climates.

3.2. Potential sources

Coal and wood combustion, Halowax, industrial thermal processes and PCB-associated emission could be sources of atmospheric PCNs. The comparison of homolog distribution, ΣPCNs/ΣPCBs ratios, combustion indicator congeners, and other statistical analyses have been widely applied to distinguish between those potential sources (Jaward et al., 2004; Lee et al., 2005a, 2005b). There was no biomass burning during the Indian sampling campaign and some in adjacent areas during the Pakistani sampling campaign (http://firefly.geog.umd.edu/firemap/); therefore, the potential contribution should be limited in Pakistan. In Indian samples, the average concentrations of ΣPCNs were approximately two orders of magnitude lower than those of polychlorinated biphenyls (PCBs), which rules out the association between PCNs and PCBs as was suggested by (Gevao et al., 2000). (Wang et al., 2012) suggested that CN-17/25, 36/45, 27/30, 39, 35, 52/60, 50, 51, 54, and 66/67 were relatively minor or absent in the Halowaxes and PCB technical mixtures compared with incineration and other industrial thermal processes and, thus, can be used to distinguish between those sources. CN-35 and -66/67, which is relatively high in Halowax PCN or Aroclor PCB mixtures, were generally below MDL (SI). CN- 17/25, 36/45, 27/30, 39, 52/60, 50, 51, and 54 were frequently detected. The contributions of total these combustion-related congeners (tri-CNs to hexa-CNs) to ΣPCNs ($\Sigma PCN_{com}/\Sigma PCNs$) > 0.5 was estimated as the combustion emission, while <0.11 was Halowax (Lee et al., 2007). The sampling sites in the present study were located in urban and rural areas where the influence of sources commonly exceed that of environmental processes, so the effect of preferential photodegradation on $\Sigma PCN_{com}/\Sigma PCNs$ ratio was not considered. The ratio ranged from 0 to 0.37, with an average of 0.05. Five samples from Punjab (PK-01, -04, -07, -08 and -09) and one from Kolkata (KL-17) were detected with a $\Sigma PCN_{com}/\Sigma PCNs$ ratio larger than 0.11, suggesting that the major sources of PCNs were the re-emission of Halowax, and some sites were also influenced by combustion processes. A Pearson correlation analysis also confirmed this assumption (Table 1). The congeners had many non-detectable values that might lead to spurious correlations, so the correlation coefficients between the congeners with >70% of the samples above the MDLs were calculated (Table 1). Significant correlations occurred for most of the CNs, except for CN-52/60 with CN-19 and CN-14. CN-52 represents combustion-related emission while the other CNs might represent Halowax, indicating the existence of Halowax and combustion sources in the study area.

3.3. Spatial distribution

The spatial distribution of the ΣPCNs is illustrated in Fig. 1. The PCNs were ubiquitous in the target areas, and the local distribution is generally impacted by the proximity to potential sources. Some sites that were close to industrial clusters exhibited high ΣPCN concentrations, while others found less contamination. As discussed above, Halowax and industrial combustion-related activities were the sources of the PCNs. An intercity variation of the atmospheric PCNs can be expected due to the difference in the industrial and energy structures and productions. Kolkata and Mumbai in India and the Kalashah Kaku industrial zone in Pakistan are home to many industrial units, including electronics, machinery, chemicals, printing, leathers, textiles, mining, cement, pharmaceuticals, and other industrial factories. The economy in Chennai is based on light and high-tech industries, health care and financial services. Differences in the atmospheric levels of the PCNs can be expected and were statistically compared by an ANOVA analysis (SPSS 17.0). The significant differences ($p < 0.05$) are discussed in the following sections.

3.3.1. Punjab province, Pakistan

The average ΣPCN concentration in the Punjab Province was significantly lower than that in Kolkata and Mumbai. PCN-24, the major contributor to the ΣPCNs, was the lowest in the Punjabi samples. Some congeners, such as CN-15, -23, -28/43, -32, -35, -46, -61 and -75, were below the detection limits. The CN-19, -24 and -42 concentrations were lower than those in Kolkata and Mumbai. The levels of other compounds (such as CN-14, -47, -36/45, - 27/30 and 50) were significantly lower than those in Mumbai. Despite the low average levels, CN-51, -57 and -73 were the highest in the PK-09 site. The PK-09 site was a densely populated town near the Kalashah Kaku industrial zone. Another site (PK-05) close to that industrial zone exhibited elevated atmospheric PCN concentrations, and other samples from sited that are relatively distant from the Kalashah Kaku area were characterized by low concentration levels. Compared with the Indian samples, the relative distance between the sampling sites and the potential source (Kalashah Kaku)

Table 1
Correlation matrix for some PCNs. The data represent the Pearson correlation coefficients between two congeners.

	CN-19	CN-24	CN-14	CN-33/34/37	CN-47	CN-36/45	CN-27/30	CN-52/60
CN-19	1	.614**	.778**	.729**	.807**	.720**	.599**	.281
CN-24	.614**	1	.603**	.569**	.570**	.591**	.588**	.313*
CN-14	.778**	.603**	1	.710**	.897**	.744**	.519**	.127
CN-33/34/37	.729**	.569**	.710**	1	.864**	.933**	.796**	.639**
CN-47	.807**	.570**	.897**	.864**	1	.902**	.700**	.445**
CN-36/45	.720**	.591**	.744**	.933**	.902**	1	.899**	.672**
CN-27/30	.599**	.588**	.519**	.796**	.700**	.899**	1	.687**
CN-52/60	.281	.313*	.127	.639**	.445**	.672**	.687**	1

** $p < 0.01$.

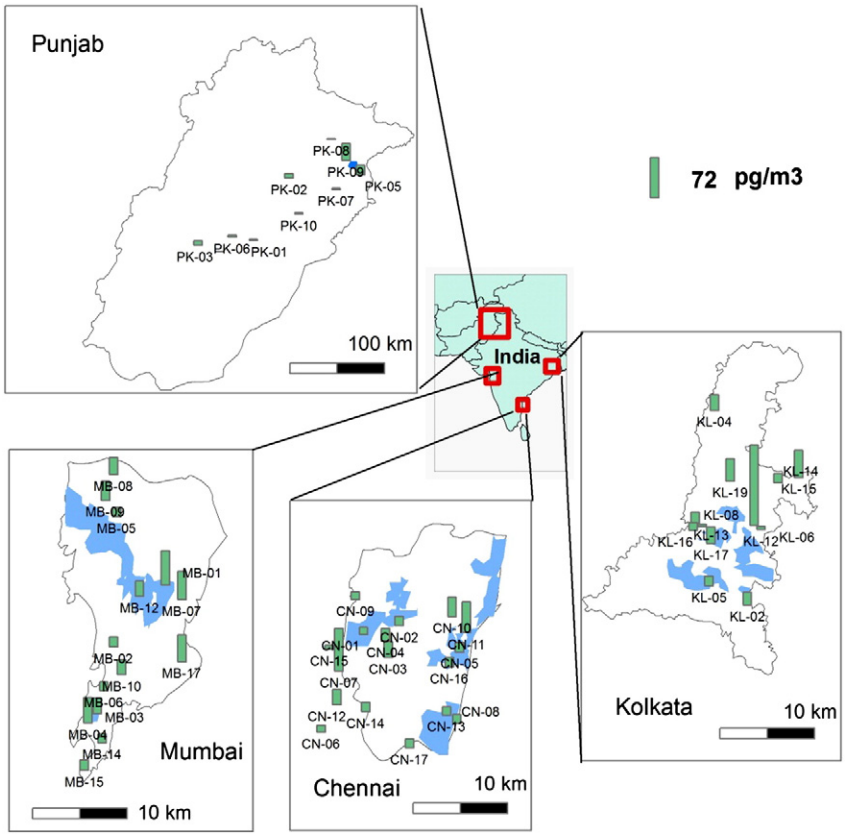

Fig. 1. Spatial distributions of atmospheric ΣPCNs at sampling sites in India and Pakistan. Blue areas represent the industrial clusters in the Punjab Province, Mumbai, Chennai and Kolkata, respectively.

was long, leading to atmospheric dispersion and possibly reducing the average concentrations of PCNs in the sampling campaign of Pakistan. Another important feature of the Pakistani PCNs in the air was that the contributions of high molecular weight congeners represented a relatively high proportion of the ΣPCNs. The penta-CNs and hexa-CNs accounted for more than 10% and 1% of all of the PCNs at some sites, respectively (Fig. 3). At those sites, the ratios of $\Sigma PCN_{com}/\Sigma PCNs$ exceeded 0.11 (Fig. 4). The highest ratio occurred at a less-polluted agricultural site (PK-04) where the industrial activities and coal consumption were limited. The satellite data showed that some fire spots occurred in the southern and eastern areas of the sampling sites in Pakistan. The biomass burning might induce relatively high proportions of combustion-related congeners, although its influence on the ΣPCN concentrations in the air was of minor importance.

3.3.2. Chennai

Chennai's economy based high-tech industries, so the pollution was relatively low. The levels of CN- 42 in Chennai were lower than those in Kolkata, and those of CN-14, 33/34/37, 47, 36/45, 28/43, 27/30, 39 and 38/40 were lower than those in Mumbai. CN-23, 38/40, 35, 46 and the penta-CNs and hexa-CNs, except for CN-52/60, 50 and 51, were below the MDLs in the Chennai samples. However, not only were the concentrations of CN-24 higher than in Pakistan and comparable to Kolkata and Mumbai, but also the relative contribution to the ΣPCNs was the highest in Chennai. CN-24 is an indicator of coal and wood combustion (Lee et al., 2005a, 2005b). The levels of coal consumption in Chennai were second to those in Kolkata and Mumbai, which should have led to a relatively low proportion of CN-24. The opposite observation suggests that the atmospheric PCNs in Chennai were largely associated with technical mixtures and industrial production. The PCN compositions are illustrated in Fig. 4. The congener profile in Chennai was also significantly different from that in other areas. The average proportion of tri-CNs to ΣPCNs was approximately 90%, which was the highest among the reported percentages by PAS. The ratio of $\Sigma PCN_{com}/\Sigma PCNs$ ranged from 0.01 to 0.06 within the fraction range of the Halowax. Considering that the average air temperature remained constant during the Indian sampling campaign, the composition differentiation should be associated with the Halowax that is dominated by the tri-CNs and/or the photodegradation of the high molecular weight congeners (Orlikowska et al., 2009; Wyrzykowska et al., 2009).

3.3.3. Kolkata

Kolkata and Mumbai were characterized by relatively high PCN concentrations. As Fig. 1 illustrates, the highest level was monitored in the KL-06 site. The KL-06 site is located in an industrial area with cement, chemical, textile, metal, printing and leather factories. Although the sample was taken in a residential area, the influence of the adjacent industries led to the highest concentrations of CN-19, 14, 24, 15, 23, 33/34/37, 47, 36/45, 35, 38/40, 46, and 75 in this study. The concentration of CN-75 reached levels as high as 3.7 pg/m^3, even though the PUF disks capture only a part of the high molecular weight compounds (Melymuk et al., 2011). The relative fraction of CN-75 was high in cement kiln and Halowax 1051 emission (Helm and Bidleman, 2003), possibly implicating those sources at KL-06. Unlike the other sites in Kolkata, KL-17 was characterized by the low proportion of tri-CNs and high proportions of tetra-CNs, hexa-CNs and penta-CNs. The concentrations of CN-52/60, 61 and 66/67 were the highest in this study, and the $\Sigma PCN_{com}/\Sigma PCNs$ ratio was 0.12. This site was located among metal factories (Chakravorty et al., 2003), which suggests combustion-related emission. In addition to industrial activities, coal and wood combustion have been identified as other important sources of PCNs (Lee et al., 2005a, 2005b). The fossil fuel energy consumption in Kolkata was

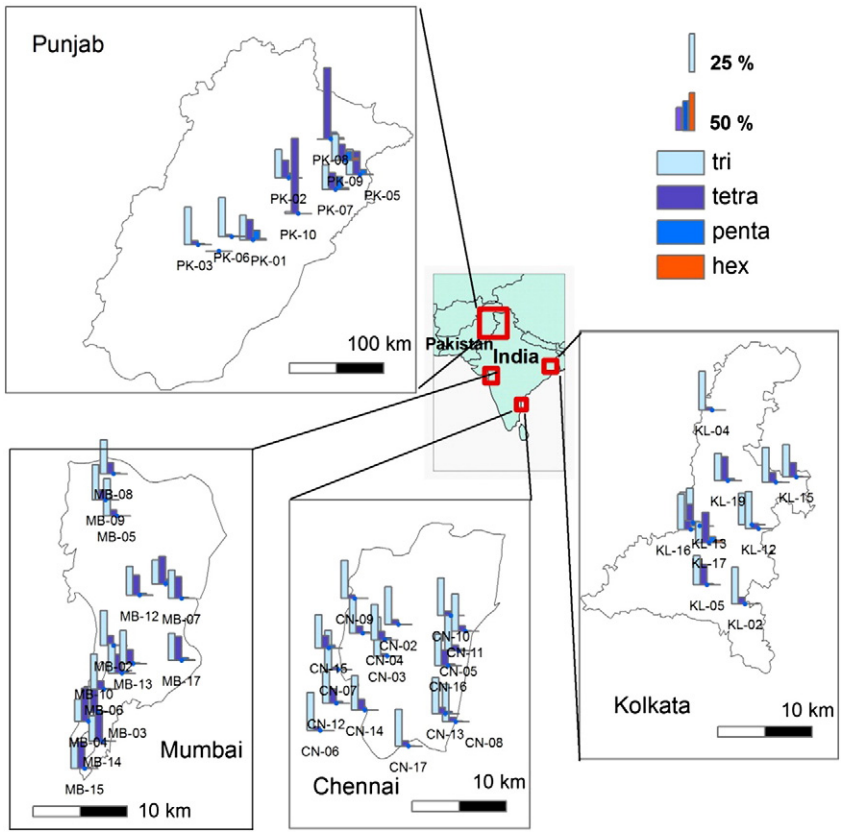

Fig. 2. Spatial distributions of compositional patterns of the PCN homologs.

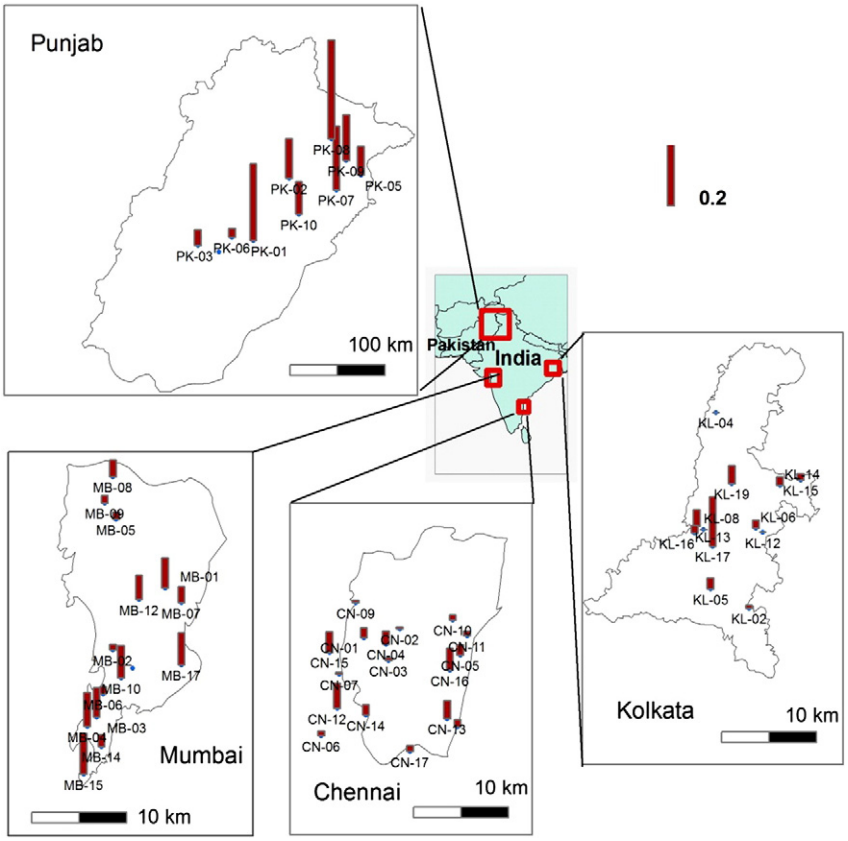

Fig. 3. Contribution of combustion-related PCNs to the ΣPCNs. Combustion-related congeners refer to CN- 17/25, 36/45, 27/30, 39, 35, 52/60, 50, 51, 54, and 66/67. This figure presents the fractional contribution of combustion-related PCNs.

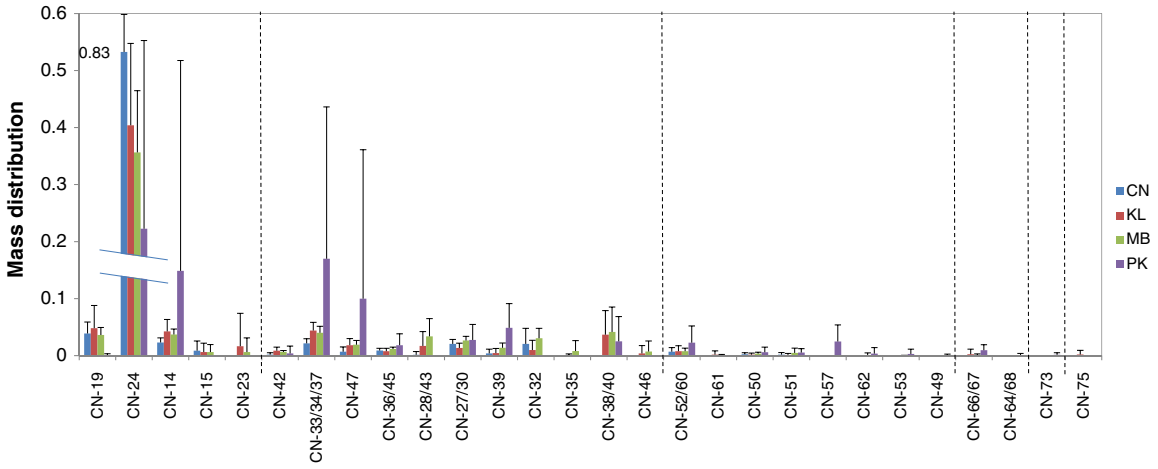

Fig. 4. Mass distributions of individual congeners of the PCNs in Chennai, Kolkata, Mumbai and the Punjab Province.

more intense than that in Mumbai and Chennai (Reddy and Venkataraman, 2002). However, the combustion indicators were not significantly higher in Kolkata than in the other sampling sites in India. The average percentages of CN-24 and -50, indicators of coal combustion (Lee et al., 2005a, 2005b), were even lower than those in Chennai, suggesting that the emission of coal combustion was not the major contributor to atmospheric PCNs in Kolkata. On the other hand, the correlation results between congeners with >70% samples above the MDLs exhibited another pattern in Kolkata. CN-52/60 showed no connection with the other congeners, while the association of other congeners except for CN-52/60 became strong ($r = 0.8–0.9$). Therefore, the Halowax and industrial thermal processes could be the main sources of the PCNs in Kolkata.

3.3.4. Mumbai

The concentration levels and composition of the PCNs in Mumbai were similar to those in Kolkata. Some combustion indicators (CN-36/45, 39 and 50) in Mumbai were significantly higher than those in Chennai and Pakistan. The MB-01 site was characterized by the highest concentrations of CN-28/43 and 53, the MB-04 site by CN-35 and 62, and the MB-17 site by 27/30, 39, 32 and 50. Compared with the mass distribution of the individual congeners from the Halowax and industrial thermal processes (Helm and Bidleman, 2003), the percentage of some congeners such as CN-53, 27/30 and 62 was similar to that from combustion sources, and other congeners were close to those from different Halowax series. Unlike the situation in Kolkata, CN-52/60 significantly correlated with other major congeners in the air ($r = 0.6–0.9$), although the correlation coefficients between the other congeners decreased to some extent, also indicating multiple sources in Mumbai. The $\Sigma PCN_{com}/\Sigma PCNs$ ratio varied from 0.01 to 0.1 in Mumbai, inferring Halowax pollution. Among all the Halowax series, Halowax 1014 and 1013 are enriched in CN-52/60. It is unclear which type of Halowax was applied in Mumbai, but the present observations may identify industrial processes and tri- and penta-CN-enriched Halowax as major sources.

3.3.5. Other trends

The urban–rural trend was investigated by statistical comparison. The significant differences in the urban and non-urban sites can only be found in CN-33/34/37 and -52/60, possibly because most of the sampling sites were generally located in urbanized or industrialized areas. Although they may not be directly exposed to sources, the regional pollution still influences those samples. Another feature in the present study was that the concentrations of CN-19, 24, 36/45, 27/30, 52/60, 50, 51, etc. in residential areas were significantly higher than those in agricultural sites. In India, many worker clusters are located near factories (Chakravorty et al., 2003); therefore, the residential samples might become polluted.

3.4. Potential toxicity

Due to the structural similarity to dioxins, the PCNs exhibit dioxin-like toxicities. (Noma et al., 2004) have summarized the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin relative potency factors (RPFs) of the individual PCN congeners. Therefore, the PCN-corresponding TEQ (toxic equivalency) values were estimated and plotted in Fig. S1. The total TEQ ranged from 0 to 3.0 fg/m^3 (PK-09) with an average of 0.09 fg/m^3, considerably lower than in urbanized areas such as the Dongjiang River basin (Wang et al., 2012), Toronto (Helm and Bidleman, 2003) and Chicago (Harner and Bidleman, 1997), and comparable to some remote sites (Lee et al., 2005a, 2005b). The TEQ values at most sites were <0.1 fg/m^3, except for KL-17; MB-01, -12, and -17; and PK-05, -07 and -09. Those sites with high TEQs were generally located in industrial areas. As expected, the TEQ values in Kolkata and Mumbai were relatively high. The Pakistani samples were characterized with relatively high proportions of hexa-CNs with high RPF values. Although the ΣPCNs in the air were low, the adverse effect was the opposite. The TEQ values in Chennai were ≤0.01 fg/m^3, indicating that the PCN-related health impact can be ignored in Chennai, although those compounds can be detected in the air. Assuming that an adult with a body weight of 60 kg inhales 15 m^3 air per day, the daily intake of dioxin toxicity at the site with the highest TEQ value would be 0.75 fg TEQ/kg body weight/day, much lower than the tolerable daily intake dose (1–4 pg TEQ/kg body weight/day) that is suggested by the WHO (van Leeuwen et al., 2000). These results suggest that the potential toxicity that is induced by the inspiration of atmospheric PCNs was insignificant in South Asia.

4. Conclusions

In the present study, two sampling campaigns were conducted in India and Pakistan to monitor the atmospheric PCN status in South Asia. The monitored levels were relatively lower than those reported in China, but still considerably higher than in other sites worldwide. Among all of the PCNs, CN-24 was the dominant congener in the air. The tri-CNs and tetra-CNs contributed to the major proportion of ΣPCNs in both the Indian and Pakistani samples. The average percentage of tri-CNs in India was among the highest in the world. The $\Sigma PCN_{com}/\Sigma PCNs$ ratios and correlation analyses indicate that the major source of the PCNs was the re-emission of Halowax, and some sites were also influenced by combustion processes. However, the complexity, sources

and environmental processes may alter the composition features, making it difficult to identify the source type. Spatially, the average ΣPCN concentrations in the Punjab Province and Chennai were lower than those in Kolkata and Mumbai. In Punjab, the proportions of the tri-CNs were relatively low, and the $\Sigma PCN_{com}/\Sigma PCNs$ ratios were high. The emissions from the Kalashah Kaku industrial zone and the biomass burning might introduce PCN pollution to adjacent sites. Chennai was characterized by the highest percentage of tri-CNs in the present study. Technical mixtures, such as tri-CN-dominated Halowax, were identified as the major source in Chennai, but the congener patterns did not resemble the homolog pattern in previous reports. The combined pollution from the Halowax series and/or environmental processes may play an important role in that area. In Kolkata, the combustion indicators suggest that industrial thermal emission contributed a considerable proportion of the atmospheric PCNs. It is also worth noting that the contribution of coal combustion was of minor importance, despite the fact that a large amount of coal has been consumed in Kolkata. Mumbai is also influenced by industrial and technical sources, but the compositional pattern indicates tri- and penta-CN-enriched Halowax emission. However, the present study cannot explain the dominance of the tri-CNs in all three Indian cities, suggesting that further work should be conducted in tropical areas to investigate the sources and fates of PCNs. A positive result is that the PRFs of tri-CNs were low; therefore, the potential health impact was generally comparable to non-urban sites worldwide. Only some sites with a high relative abundant of high molecular weight congeners should be of concern.

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