



Polychlorinated naphthalenes (PCNs) in the surface soils of the Pearl River Delta, South China: Distribution, sources, and air-soil exchange

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ARTICLE INFO

Article history:

Received 4 May 2012

Received in revised form

3 June 2012

Accepted 5 June 2012

Keywords:

Air-soil exchange

Polychlorinated naphthalenes

Pearl River Delta

Fugacity fraction

Soil

ABSTRACT

Polychlorinated naphthalenes (PCNs) are now under review by the Stockholm Convention as a candidate for POPs for their persistence, toxicity, bioaccumulation, and long-range atmospheric transport. Data regarding PCN levels and their environmental fate are sparse in China. The PCN concentration and distribution in soils of the Pearl River Delta were reported, and the average total concentration was 59.9 ± 86.7 pg/g. Tri-CN was the dominant homologue group, and CN 24 was the most abundant congener. A gradient of PCN levels between more and less developed areas was observed. Based on fugacity fraction results, CN 51 is proposed as a possible source marker for specific combustion emissions. Air-soil exchange of PCNs was estimated by calculating the soil and air fugacity. Fugacity fraction values indicated that tri- to penta-CN were closer to equilibrium in winter and toward net volatilization in summer, while hexa-CN experienced net air-to-soil transfer in both seasons.

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1. Introduction

Under the Stockholm Convention, the release of persistent organic pollutants (POPs) needs to be eliminated or reduced for their persistence in the environment, biological accumulation throughout the food web, and negative impacts on humans and other animals (Jones and de Voogt, 1999). Due to their volatility and persistence in the air, POPs are subject to long-range atmospheric transport (LRAT) (Bailey et al., 2000). Therefore, POPs released in tropical and subtropical environments can be rapidly dispersed through the atmosphere and tend to be redistributed on a global scale (Wania and Mackay, 1995). Soil is the primary environmental reservoir for POPs in the terrestrial environment. However, soil may not be a permanent sink for these compounds, which tend to recycle continuously between the atmosphere and the terrestrial environment over long periods of time. Since the application of POPs has been banned for decades, the emission of these compounds from contaminated soils is becoming a major source of atmospheric pollution (Meijer et al., 2003a). The soil, therefore, can either be a sink for POPs to deposit or a source for POPs to release back into the atmosphere. The transport and fate of POPs in the environment are also significantly affected by the process of soil-air exchange (Meijer et al., 2003b).

PCNs are composed of naphthalene substituted with 1–8 chlorine atoms, yielding 75 possible congeners. For their potential of persistence, toxicity, bioaccumulation, and LRAT, PCNs have been targeted by the United Nations Economic Commission for Europe (UNECE) and the United Nations Environment Programme (UNEP) and are now under review by the Stockholm Convention as a candidate for POPs. Some PCN congeners are planar in structure with similar biochemical toxicity behaviour as the dioxins/furans and co-planar PCBs (Falandysz, 1998). Thus, the 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin relative potency factors (RPFs) of individual CN congeners have been estimated and used to calculate the dioxin-like toxicities of PCNs in environmental samples (Noma et al., 2004). PCNs were historically used for their thermal stability in dielectric fluids and insulators, and the worldwide commercial production of PCNs has been estimated to be around 150,000 tons (Falandysz, 1998). Although PCNs have been banned since 1977, they are still routinely observed in air (Jaward et al., 2004; Helm and Bidleman, 2005; Baek et al., 2008; Mari et al., 2008; Wang et al., 2012b; Hogarh et al., 2012) and soil (Schuhmacher et al., 2004; Nadal et al., 2007; Wyrzykowska et al., 2007). Assigning the current levels of PCNs to sources is not trivial for these compounds are still emitted from old or in-use PCN products and/or current combustions (Falandysz, 1998). Research has suggested that the contribution of combustion sources to the PCN burden in environmental media has been increasing over the past decades (Meijer et al., 2001). Although production figures for PCNs are unavailable, combustion activities such as e-waste, waste, or

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biomass open burning are ubiquitous in developing countries such as China, making PCN research especially important. However, there is a complete lack of information regarding the levels and fate of PCNs in China.

The Pearl River Delta (PRD), which includes Hong Kong and Macao and is located in the south coast of China with an area of approximately 42,794 km², has been one of the rapidly developing regions in China over the last three decades. This region is under the strong influence of the Asian monsoon system. Previous research indicated that the transport of POPs was influenced by the Asian monsoon (Li et al., 2007), and model results also indicated that the outflow of POPs such as polycyclic aromatic hydrocarbons (PAHs) from the PRD can be transported to northern mainland China in summer, and to the South China Sea, Southeast Asian countries, and even the Pacific Ocean and beyond in winter under particular weather conditions (Lang et al., 2007). Therefore, evaluating PCN contamination in soils and the equilibrium status between air and soil in the PRD is helpful in understanding the potential impact of PCNs on nearby regions. Meanwhile, the Dongjiang River, a tributary of the Pearl River, supplies fresh water for many cities, including Guangzhou, Dongguan, Shenzhen, and Hong Kong. Highly developed industries resulting in the release of various chemicals may pose a potential pollution to the river and surrounding ecosystem.

The main objectives of this study were to elucidate the spatial trends, potential sources, and degree of contamination of PCNs in the soils from the eastern part (Dongjiang River basin) of the PRD, South China, and to assess the equilibrium status of PCNs between the air and soil.

2. Materials and methods

2.1. Sampling

Top-soils (0–5 cm, vegetation removed) at 60 sites within the eastern PRD were collected during Dec. 14th–20th of 2009 just before air sampling (Fig. 1). Each soil sample was a composite of 5 sub-samples. The samples were wrapped in aluminium foil, placed in polyethylene zip-bags and transported to the laboratory immediately. After being freezing-dried, the soil samples were ground with agate mortar, and stored at –20 °C until further analysis.

Passive air samplers (PUF) were deployed at 19 sites (Fig. 1) during two periods (Jan. – Feb. and Jul. – Aug., 2010). The analysis and calculation of PCN air concentration have been published in our previous research (Wang et al., 2012b).



Fig. 1. PUF and soil sampling locations.

2.2. Sample extraction and analysis

About 20 g freeze-dried soil sample was homogenized, spiked with surrogate standards (¹³C-trans-Chlordane, 10 ng), and Soxhlet extracted with 150 mL dichloromethane (DCM) for 48 h with activated copper to remove the sulphur. After being exchanged into hexane and reduced to approximately 1 mL, the extract was first cleaned by a column containing 50% (w/w) sulphuric acid–silica gel, and it was then purified with a multi-layer column filled with anhydrous Na₂SO₄, florisil (2% deactivated), neutral silica gel (3% deactivated) and neutral alumina (3% deactivated) from top to bottom. After being concentrated to approximately 50 µL, penta-chloronitrobenzene (PCNB) was added as the internal standard prior to instrumental analysis.

2.3. Instrumental analysis

PCNs were analyzed by gas chromatography electron capture negative-ion mass spectrometry (GC-ECNI-MS) in selected ion monitoring mode on a DB-5MS column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) with methane as the reagent gas. 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 held for 10 min. The temperatures of MSD source and quadrupoles were all 150 °C. Tri- to hexa-CNs were quantified against the technical PCN mixture Halowax1014, containing known amounts of PCN congeners (tri-CN: CN 19, 24, 14, 15, 16, 17/25, 23; tetra-CN: CN 42, 33/34/37, 47, 36/45, 28/43 27/30, 39, 32, 35, 38/40, 46; penta-CN: CN 52/60, 58, 61, 50, 51, 54, 57, 62, 53, 59, 49, 56; hexa-CN: CN 66/67, 64/68, 69, 71/72, 63, 65) (Wang et al., 2012b).

2.4. QA/QC

In total, 8 procedural blanks and 10 repeated samples were carried out to assess the potential contamination and the repeatability of analysis. The results showed that only CN 33/34/37, 36/45, 51, 49 were detected in the laboratory blanks at average values of 10.2, 0.86, 3.8, and 4.8 pg/sample, respectively. The surrogate recoveries for ¹³C-trans-Chlordane in all of the samples were 78.1–91.2%. The reported results were all corrected by the blanks but not by the surrogate recoveries. For the PUF samples, please see the previous paper (Wang et al., 2012b).

2.5. Fugacity fraction

Meijer et al. (2003a) applied the fugacity fraction (*ff*, defined as a ratio of soil fugacity to the sum of soil fugacity and air fugacity) as an indication of the net direction of air-soil exchange. Fugacity fraction equals to 0.5 indicates equilibrium; *ff* > 0.5 indicates net volatilization from the soil into air, whereas *ff* < 0.5 indicates net transport from air to soil. The uncertainty or the propagation of errors in the calculation of *ff* reached 50% in this paper, meaning that *ff* between 0.25 and 0.75 may be considered to be equilibrium. Details of calculation of fugacity fraction and uncertainty are listed in the Supporting information (SI 1.1).

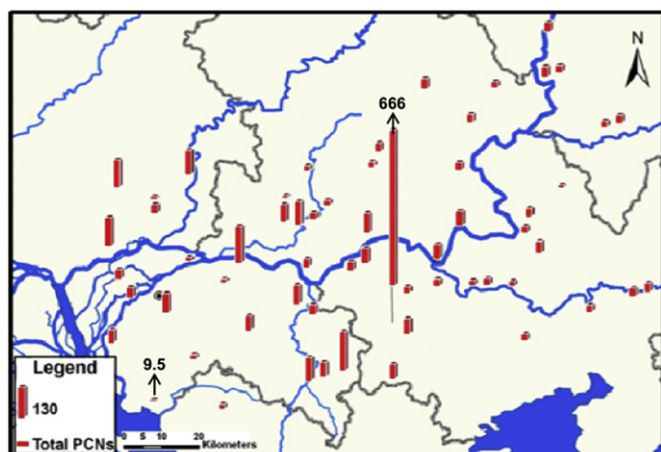
3. Results and discussion

3.1. Concentrations and distribution of PCNs in the soils

As shown in Fig. 2a, total PCN concentrations in the soil samples ranged from 9.5 to 666 with an average of 59.9 ± 86.7 pg/g. The highest concentration was discovered at site S55, a vegetable soil, while the lowest concentration was found at S10, a rural soil without any human intervention. The spatial distribution showed that most of the high PCN concentrations were located in or near Dongguan City, a highly developed and industrialized city for the electronic and toy processing businesses; while lower levels were located in the developing Huizhou City. This trend was quite similar to the PCN distribution of contemporary air samples (Wang et al., 2012b). The gradient trend of PCN concentrations from the soil of a more developed area to that of a less developed area can mainly be attributed to the proximity to primary point sources. Other environmental variables, such as meteorological factors (e.g., wind direction and speed) and/or soil properties (i.e., soil texture and organic matter content) may also play certain roles. However, the correlation between the total organic carbon (TOC) and total PCN concentrations was insignificant (*r* = –0.058, *p* = 0.658; see SI 1.2), suggesting that other factors (e.g., proximity to point sources) rather than TOC controlled the distribution of PCNs.

The concentrations of corresponding TEQ in this area according to the RPFs of individual PCN congeners summarized by Noma et al.

a PCNs (pg/g)



b TEQ (pg/g)



Fig. 2. Concentration and spatial distribution of PCNs and their corresponding TEQ (a PCNs; b TEQ).

(2004) are displayed in Fig. 2b. The PCN corresponding TEQ (including CN 35, 38/40, 50, 54, 56, 57, 63, 66/67, 64/68, 69, 71/72) ranged from 0.2 to 62.8 fg/g (Mean = 13.0 ± 12.9 fg/g). The highest TEQ was discovered at site S16, a vegetable soil, and the lowest TEQ was found at S27, a wood soil. Similar to the PCN distribution, TEQ values were also discovered to be higher in or near the northeast part of Dongguan City suggesting that it was source area of PCNs.

Few papers have paid attention to PCN pollution in soils so far. The total PCN concentrations in soils from the eastern PRD were lower than those in soils collected before the 1990s from the UK (Meijer et al., 2001), but were comparable to those in soils (32–180 pg/g, 2002; 17–142 pg/g, 2005) from Catalonia, Spain (Schuhmacher et al., 2004; Nadal et al., 2007).

3.2. Congener profiles and source indicators of PCNs in the soils

The homologue distribution and congener profile for the environmental sample may be of great help to qualitatively elucidate the sources that contributed to PCN contamination at a specific site. The most frequently detected PCN congeners (found at >90% of all sites) are listed as follow: 3-Cl: CN 24; 4-Cl: CN 42, 33/34/37, 47, 36/45, 28/43, 27/30, 39; 5-Cl: CN 52/60, 50, 51, 54, 49; 6-Cl: CN 66/67, 63. As shown in Fig. 3a, the congener with the largest contribution to the total PCNs is CN 24 (20.4%). CN 24 has been considered to be

associated with coal and wood combustion (Lee et al., 2005), implying a significant input of coal and wood burning in the study area. The average homologue mass percentage distribution (tri- to hexa-CNs) for all of the samples is 34% for tri-CNs, 30% for tetra-CNs, 23% for penta-CNs, and 13% for hexa-CNs. As expected, tri-CNs was the most dominant homologue group since CN 24 was the most abundant congener. The trend that the contribution of PCN homologue groups to total PCNs decreased with the increasing number of chlorine atoms was in agreement with the results of our previous research on air and deposition in this area (Wang et al., 2012a, 2012b). Meanwhile, the compositions of tri-, tetra-, penta-, and hexa-CNs in contemporaneous deposition and air samples were 54%, 17%, 17%, 12%, and 72%, 20%, 6%, 2%, respectively (Wang et al., 2012a, 2012b). The low chlorinated PCNs (total of tri- and tetra-CNs) presented higher percentages in the air samples than in the deposition and soil samples, consistent with their higher volatility. This also confirmed that “light” PCN congeners have greater LRAT ability than “heavy” congeners.

Combustion-related PCN congeners (PCNs_{comb}, such as CN 17/25, 36/45, 39, 35, 50, 52/60, 51, 54, and 66/67), which had been discovered to be minor or absent in the Halowaxes mixtures (Yamashita et al., 2000; Imagawa and Lee, 2001; Meijer et al., 2001; Helm and Bidleman, 2003), were rich in their own homologue groups in the soil samples (Fig. 3b). The contributions of combustion-related PCNs to their own groups (tri-_{comb}/tri-, tetra-_{comb}/tetra-, penta-_{comb}/penta-, and hexa-_{comb}/hexa-CNs) averaged 12%, 18%, 60%, 36%, respectively, while the sum fraction of those congeners to total PCNs (PCNs_{comb}/total PCNs) was 25%. As reported (Lee et al., 2007), the fractions for Halowaxes (Noma et al., 2004) are below 11%, while those for combustion fly ashes (Helm and Bidleman, 2003) (e.g., municipal/medical waste incineration, and iron sintering) are no less than 50%. The percentage in our study area (25%) is below 50% but is much higher than 11%, indicating that both historical emissions and combustion sources contributed to the PCN burden in soils within the PRD. Since technical PCNs have been banned for decades, combustion emissions may become more and more important.

3.3. Fugacity fractions

Air concentrations of PCNs based on passive air sampling were published in our previous research (Wang et al., 2012b) and are summarized in S1 Table S1. For certain POPs, soil has been reported to act as a significant repository, primitively absorbing the substance from the atmosphere during heavy discharge periods and releasing it slowly back to the atmosphere during later light discharge periods or even after banishment (Harner et al., 1995). Though PCNs are no longer commercially produced, they are still emitted from many other sources, leading to the necessity of study of air-soil equilibrium status. The fugacity fractions (*ff*) of different PCN homologue groups (tri- to penta-CNs) and some selected PCN congeners for specific air sampling sites are shown in Fig. 4. The hypothesis that the alteration of PCN levels in soils is negligible has been considered for the soil samples were collected a few days before the passive air samples were collected (10 days for winter, six months for summer). For each PUF site, the seasonal air concentrations and the average concentration of 2–5 soil samples from around the site were used to calculate the *ff* values. The average values for PCN homologue groups in the air are listed in Table S1, and the average values for TOC and PCN homologue groups in the soils are listed in Table S2. More details of the air concentrations of PCNs have been presented in our previous research (Wang et al., 2012b).

The *ff* values shown in Fig. 4a were based on the arithmetic mean of the PCN congeners within the same homologue group, for

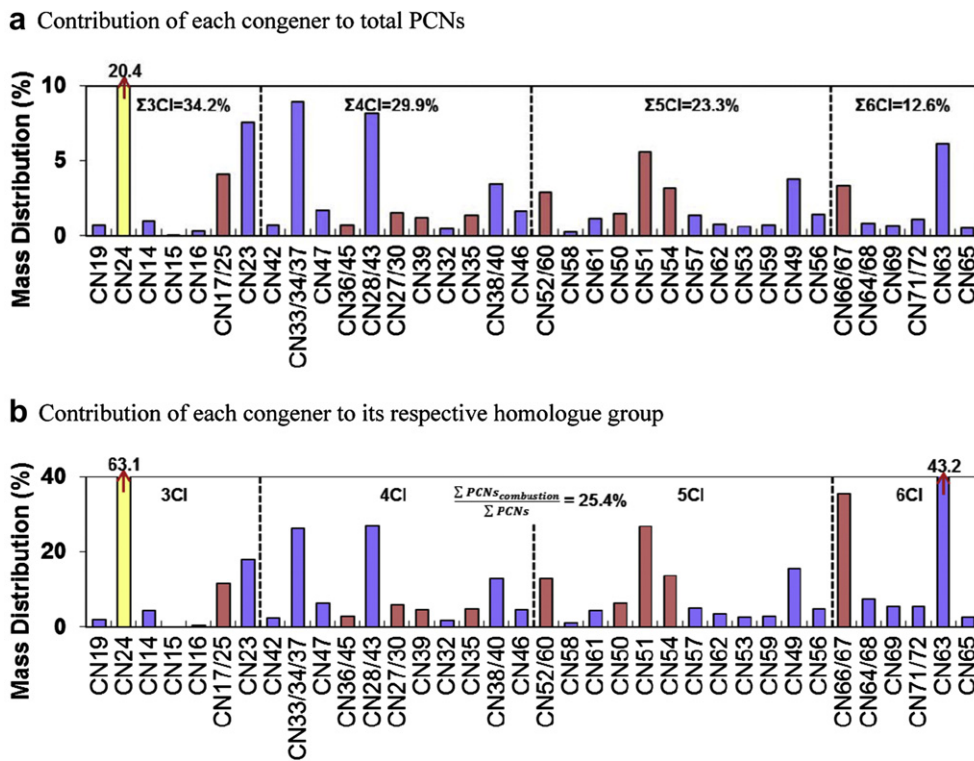


Fig. 3. Contribution of each congener to total PCNs (a) and to its respective homologue group (b) based on the average values for all of the soil samples (The red bars represent the combustion-related congeners, while the yellow one represents CN 24. The equations represent the contribution of each homologue group to total PCNs. The combustion PCNs used in the formula included CN 17/25, 36/45, 27/30, 39, 35, 52/60, 50, 51, 54, 66/67, but CN 24.). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

their values were almost similar with each other (Standard deviation: 0.002–0.2, with several exceptions such as CN51). Congeners with the concentrations under the MDL were not considered when calculating this mean *ff* values. Since the *ff* values for hexa-CNs in both seasons were ≤ 0.4 at all sites (Table S3), the values are not presented in this figure. Generally, the *ff* of different homologue groups varied considerably between sites, from <0.01 to 0.98, and displayed a decrease with the degree of chlorination. Moreover, the *ff* values showed a significant seasonal variation, and non-equilibrium was established. The *ff*, especially for low chlorinated PCNs, decreased during the cold winter and increased during the hot summer. The *ff* values of tri- to penta-CNs exceeded or were close to 0.5 at all of the sites in the summer, and were almost all below 0.5 in the winter. However, the seasonal variability for hexa-CNs was negligible, with the *ff* approaching 0, indicating strong net air-to-soil gaseous transfer for both seasons (Table S3). Almost all of the PCNs were transferred from the air to the soil in the winter in the eastern PRD. In the summer, the status of penta-CNs was closer to equilibrium, while the tendencies of tri-CNs and tetra-CNs were toward net volatilization. Even taking the uncertainty of *ff* (± 0.25) into consideration, tri- to penta-CNs were mainly close to equilibrium, with a deposition trend in the winter and a volatilization trend in the summer, while hexa-CNs were still deposited in both seasons. Consequently, soil acts as a sink for high molecular weight PCNs (penta- and hexa-) during the winter and as a secondary source for low molecular weight PCNs (tri- and tetra-) to the air especially, but not exclusively, during the summer. Since soils were only collected during the winter, we also calculated the summer *ff* values using 80% of the soil concentrations in case the volatile trends of PCNs were overestimated, especially for low molecular weight congeners (Table S4). The results showed that the variations in the summer *ff* based on 100% and 80% soil concentrations were

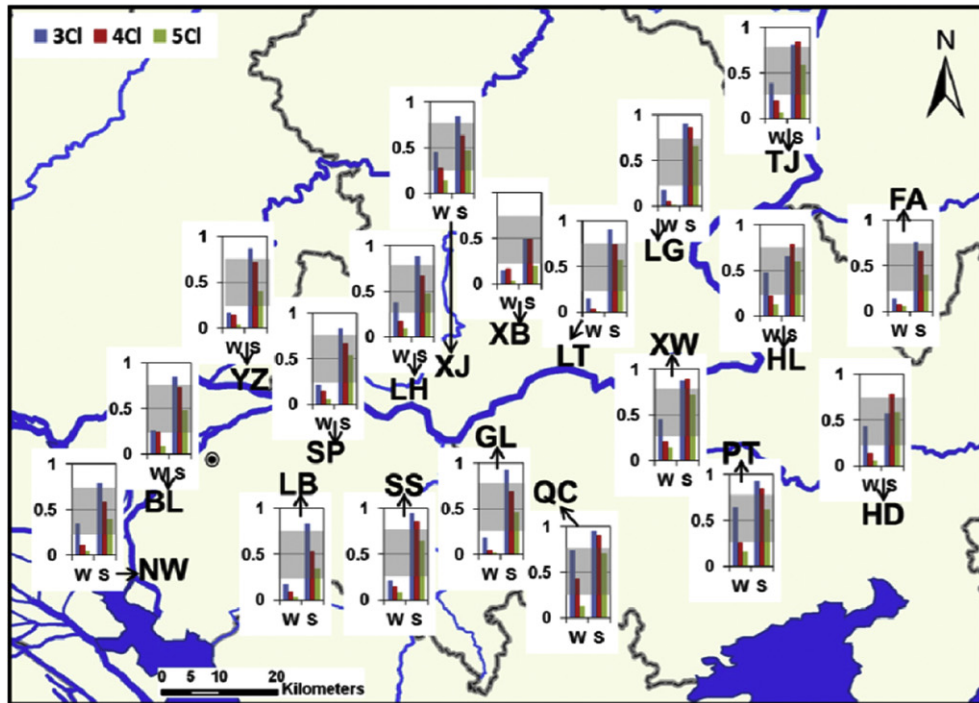
slight, with deviations of 0.01–0.04, which were not wide enough to alter the exchange status of PCNs. This calculation also verified the seasonal changes, because the loss of PCN levels in soils can barely reach 20%. In addition, the seasonal variation of *ff* for the PCNs was in agreement with previous studies of OCPs and PCBs (Bidleman and Leone, 2004; Ruzickova et al., 2008). Low temperatures will cause an increased magnitude of the air-to-soil transport and reduce re-volatilization, whereas high temperatures have the opposite effect. Obviously, meteorological conditions, the physicochemical properties of the contaminants in question, heterogeneity of soil properties (e.g., organic matter content, moisture), and the presence of a crop canopy will also result in great spatial and seasonal variations in PCN concentrations in the air and soils, causing differences in *ff* values (Cousins et al., 1999; Ruzickova et al., 2008). Regarding spatial variation, the status of the individual PCN homologue groups was almost consistent in the whole study area except at several special sites, such as the QC site, where the highest *ff* values (tri- to hexa-) were discovered.

For the reason that a strong south wind prevails in the summer, the lower-chlorinated PCNs released from soils in the PRD during hot period may transport to northern China (Lang et al., 2007). According to the global distillation hypothesis or cold condensation hypothesis (Wania and Mackay, 1993, 1996), the PCNs released from the low-latitude PRD region may even transport to the high-latitude areas of the northern hemisphere (Lang et al., 2007).

3.4. Possible source marker for special combustion emissions

It is interesting that the equilibrium status of different PCN congeners was also discovered to be site-specific, even within the same homologue group, as was the case for penta-CN 51 and 54 (Fig. 4b). The *ff* values for CN 54 were quite similar to the average *ff*

a PCN homologue groups



b PCN congeners

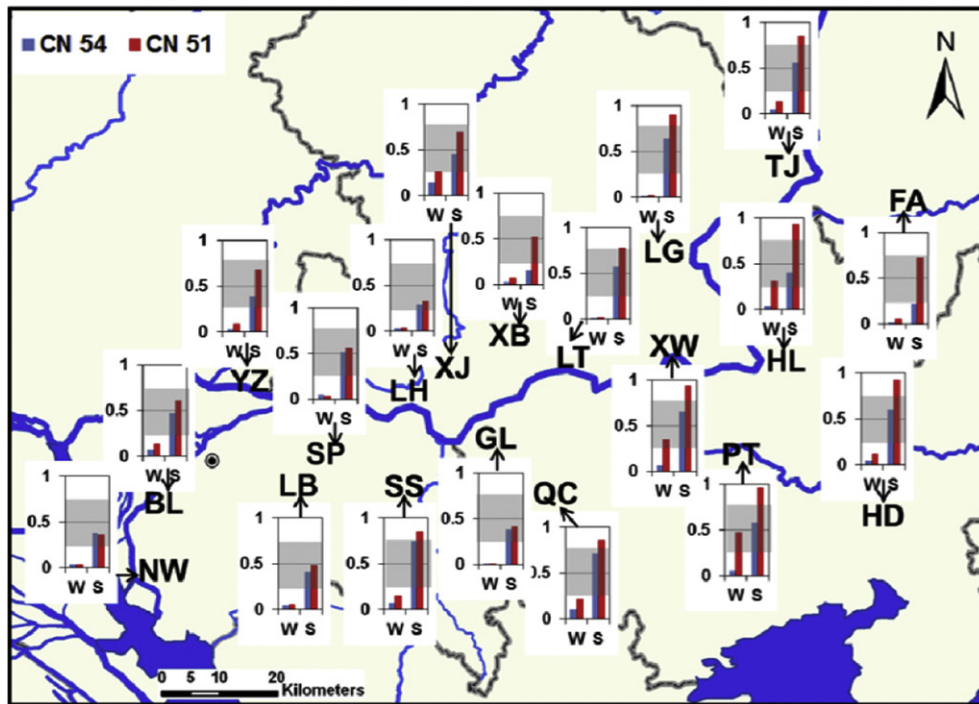


Fig. 4. Site-specific and seasonal variability in the fugacity fractions (*ff*) for the lower chlorinated PCNs (a) and special PCN congeners (b). (Bars within the shadow between 0.25 and 0.75 are considered to be in equilibrium).

values for the penta-CN group shown in Fig. 4a, while the *ff* values for CN 51 were extraordinarily higher than the rest of the penta-CN especially in the summer. CN 51 and 54 are both referred to as “combustion markers” and are associated with many similar thermal processes, e.g., municipal waste incineration (MWI) (Iino et al., 2001; Helm and Bidleman, 2003; Jansson et al., 2008).

However, their spatial distributions were quite different (Fig. 4b), implying that these two PCN congeners originate from different combustion sources other than the similar processes. In highly industrialized areas, such as NW, BL, LB, SP, LH, SS, the *ff* values of CN51 and 54 were comparable. Whereas CN 51 was oversaturated in the soil relative to the air, resulting in net soil-to-air transfer in

the summer, in contrast to CN 54 in the less developed areas (e.g., HL, TJ, FA, PT, HD), suggesting that the sources of CN 51 in those areas may be different from the sources of CN 54. The higher *ff* values for CN 51 in the less developed areas suggested that the abundance of this congener in the soil relative to the air may be due to the seasonal reduction of atmospheric emission from special thermal processes (e.g., heating or biomass burning) in the summer. The lower *ff* values for other combustion-indicator congeners may reflect continuous atmospheric emissions from other common combustion processes such as incineration. Meanwhile, the concentration ratios of CN 54/CN 51 in the soils showed that CN 51 levels were also higher in the less industrialized areas than the highly industrialized areas compared to CN 54 (Fig. S1), suggesting that this congener has other sources besides industrial processes. The higher air concentrations of CN 51 in winter than in summer relative to CN 54 also indicated that the sources of CN 51 mainly emerged during cold periods, which confirmed our previous hypothesis that this congener was associated with special thermal processes such as heating or biomass burning. Similar observations that concentrations of CN 51 and 54 were comparable in urban areas but different in background areas were also obtained in the Global Atmospheric Passive Sampling (GAPS) Study by Lee et al. (2007). However, this hypothesis needs much further studies in the future.

4. Conclusions

After being released into the environment, chemicals always strive to establish equilibrium among media, such as air and soil. However, this equilibrium is a dynamic balance that may change in response to a variety of environmental factors, such as temperature. As a heterogeneous environmental compartment, soil also has a range of properties that may control the fate of those chemicals. Certain soils from the PRD have been heavily polluted by PCNs, according to the present research. The PCN pattern showed that both combustion and historical emission are sources of PCNs in the soils of the PRD. The air-soil equilibrium status of PCNs varied widely with season and location in the study area. Generally, lower chlorinated PCN congeners had a stronger tendency to escape from soil to the air than higher congeners. Seasonally, soil acted as a sink for high molecular weight PCNs, especially in the winter, while it tended to be a secondary source for low molecular weight PCNs released into the air in the summer. The difference in the distributions of concentrations and *ff* values of CN 51 compared to other combustion-related congeners suggested that it is a possible source marker for special combustion emissions such as biomass burning. The results implied a potential risk of PCN emissions from the PRD area to northern mainland China during hot periods, which requires further and deeper research.

Acknowledgements

This study was supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (KZCX2-YW-Q02-01) and the National Natural Science Foundation of China (No. 41125014 and 40821003).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.envpol.2012.06.008>.

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