Environmental Pollution 204 (2015) 124–132

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# Polychlorinated naphthalenes (PCNs) in Chinese forest soil: Will combustion become a major source?

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ARTICLE INFO

*Article history:*
Received 9 February 2015
Received in revised form
21 April 2015
Accepted 22 April 2015
Available online 14 May 2015

*Keywords:*
Chinese forest soil
Combustion-related sources
Ecotone
PCNs
SOC

ABSTRACT

We collected O- and A-horizon soil samples in 26 Chinese mountainous forests to investigate the content, spatial pattern, and potential sources of polychlorinated naphthalenes (PCNs). Spatial patterns were influenced mainly by the approximation to sources and soil organic contents. High concentrations often occurred close to populated or industrialized areas. Combustion-related activities contributed to PCN pollution. Relatively high proportions of CN-73 in northern China may be attributed to coke consumption, while CN-51 could be an indicator of biomass burning in Southwest China. There are evidences that PCNs may largely derived from unintentional production. If uncontrolled, UP-PCN (unintentionally produced PCNs) emissions could increase with industrial development. The abnormally high concentrations at Gongga and Changbai Mountains appear to be associated with the high efficient of forest filter of atmospheric contaminants at these densely forested sites. We question whether this is caused by ecotones between forests, and raise additional questions for future analyses.



## 1. Introduction

It has been suggested that forests play an important role in the global fate and distribution of POPs (persistent organic pollutants). The primary effect of forests is an increase in the net atmospheric deposition to the terrestrial environment, reducing atmospheric concentrations in forest areas and thus possibly affecting depositions in other areas (Wania and McLachlan, 2001). As a consequence, the temperature-driven geochemical circulation of POPs can be altered due to the reduction in long-range atmospheric transport (LRAT) and enhancement of vapor-pressure-dependent fractionation caused by the "forest filter effect". The reduction of POPs in the air is achieved however at the expense of soil pollution. With canopy enhanced deposition, forest soils can act as reservoir for POPs due to their strong affinity to soil organic matter; this is especially true for high-molecular-weight POPs. Chinese forests cover more than 197,290,000 ha or approximately 21.2% of the total national land area (FAO, 2005), reserving 22.56% of the national terrestrial soil organic carbon stock (Li, 2008). Because the Chinese forests are widely distributed in mountainous areas, local geographical and meteorological conditions are favorable for trapping POPs due to multiple factors, such as low temperature, high precipitation, vegetation enhanced deposition, considerable absorption capacity, and barrier effects.

PCNs (polychlorinated naphthalenes) are candidate persistent organic pollutants (POPs) under review by the Stockholm Convention, due to their potential of persistence, dioxin-like toxicity, bioaccumulation, and long-range atmospheric transport potential (Wang et al., 2012). They are ubiquitous contaminants occurring mainly in specific commercial mixtures or as by-products of industrial processes (including, in the past, the manufacturing of polychlorinated biphenyls (PCBs)) or other thermal processes (Hanari et al., 2013). There is historical evidence of industrial applications of PCN formulations in China (Hogarh et al., 2012), but the increase in the combustion indicator CNs in the top layers of the sediment core inside Jiaozhou Bay indicates that the contributions of thermal sources of CNs have increased in recent years (Pan et al.,

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http://dx.doi.org/10.1016/j.envpol.2015.04.014
0269-7491/

2012). According to regional observations, the atmospheric PCN concentrations in China were higher than those in surrounding countries or some heavily polluted areas (Hogarh et al., 2012; Lin et al., 2013). Since pronounced filtering by the forests may influence POPs with log $K_{OA}$ between 7 and 11 and log $K_{AW} > -6$ (McLachlan, 1999), it is logical to expect that will be also accumulated effectively in forest soil. Regional research on PCN accumulation in soil remains scarce. There are currently relatively few emission studies (Ba et al., 2010; Liu et al., 2010), atmospheric observations (Hogarh et al., 2012; Lin et al., 2013) and studies on soil and sediment exposure (Pan et al., 2012; Wang et al., 2012) on a local scale.

In the present study, Organic (O-horizon) and upper mineral layer (A-horizon) soil samples were collected in Chinese forests classified based meteorological, geographical, and ecological parameters. Forests were selected in locations relatively far from anthropogenic activities to provide information on background contamination, therefore reflecting the regional pollution status. The top two soil layers together account for the majority of POP storage in the forest soil (Wenzel et al., 2002; Moeckel et al., 2008), and pose a contamination risk for soil-dwelling animals and upriver aquatic systems. This is the first study to elucidate the soil contamination levels and spatial trends of PCNs in the major areas of Chinese forests. Our objective is to provide a primary outline of PCN content in Chinese mountainous forest soils, to explore whether the exposure pattern is influenced by emissions rather than environmental factors, to identify potential PCN sources, and to assess the resulting environmental risk on a national scale.

## 2. Methods

### 2.1. Sampling

The study was carried out in 26 Chinese mountain forests widely distributed over the whole country, with the exception of the Northwest area, from July 2012 to March 2013 (Figure S1). For each mountain forest, the average temperature and precipitation generally exhibited a negative and positive relationship with altitude, respectively. One to four forest soil samples were collected at different altitudes from each mountain. Sampling sites were located at areas distant from human activity (i.e., roads, villages or tourism) in nature reserves or national forest parks, differing in altitude and therefore in climate and ecosystem type. Soil samples were collected at each site using a pre-cleaned steel tool according to the vertical structure of soil layers. The O-horizon samples generally comprised five subsamples. Five pits were dug to collect the A-horizon samples. Living plant material, large roots, and any large non-organic material were removed. All soil samples were stored in polyethylene zip-bags and immediately transported in cold conditions to the laboratory. They were subsequently freeze-dried, sieved through a steel mesh, ground with agate mortar, and stored at −18 °C until further analyses. Further details of sample treatment and TOC analysis can be found elsewhere (Zheng et al., 2014).

### 2.2. Sample extraction and analysis

Approximately 20 g of prepared soil sample were spiked with $^{13}$C-*trans*-chlordane (10 ng) as surrogate, and Soxhlet extracted with dichloromethane (DCM) for 48 h. Activated copper was added to the extract to remove sulfur. The extract was then concentrated by a rotary evaporator and solvent-exchanged into hexane. The cleanup step was conducted using a multi-layer column containing anhydrous $Na_2SO_4$, neutral silica gel (3% deactivated) and neutral alumina (3% deactivated) from top to bottom, followed by a column containing 50% (w/w) sulfuric acid silica gel, florisil (2% deactivated) and neutral alumina, and finally a 6 g Biobead (SX-3) column. After concentrating to approximately 25 μL, $^{13}$C-PCB141 was added as the internal standard prior to instrumental analysis, which was performed using an Agilent 7890A gas chromatography electron capture negative-ion mass spectrometer (GC-ECNI-MS) in the selected ion monitoring (SIM) mode. A DB-5MS column (30 m × 0.25-mm i.d. × 0.25-μm film thickness) was installed to separate compounds, as described elsewhere (Wang et al., 2012). The following 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 assessed in the soil samples. Of these, CN-15, -23, -28/43, -32/48, -35, -46, -58, -61, -57, -62, -53, -59, -56, -69, -71/72, -63, -65, -75 were infrequently found above the limits of detection (LODs) in <60% of samples.

### 2.3. QA/QC

In total, 10 procedural blanks and 19-pair repeated samples were evaluated to assess contamination and stability. The LODs were calculated as a mean blank + three times the standard deviation (SD) of the target compound. CN-42, -33/34/37, -36/45, -28/43, -27/30, -51 and −49 were detected in blanks, averagely accounting for <7% of the detected values in field samples. LODs of CNs not detected in blanks were determined as the concentrations where the signal to noise ratio was equal to 3. Individual LOD values can be found in the Supporting Information (Table S1). If the quantified concentration of a compound was below the LOD (BDL), a value half of the LOD was used in the statistical treatment of the data. The surrogate recoveries for $^{13}$C-*trans*-chlordane in all samples were 85.6 ± 13.1%. The reported results were corrected according to the blanks but not the surrogate recovery values.

## 3. Results and discussion

### 3.1. Soil PCN composition and concentrations

The concentrations of individual PCNs are shown in Table S1. The ΣPCN concentrations ranged from 4.5 to 140 pg/g dw (dry weight), with an average of 26 ± 18 pg/g dw in the A-horizon. These values are lower than those reported in surface soil from the Eastern PRD (Pearl River Delta) and comparable to those from Wolong Mountain, Southwest China (Pan et al., 2013). In the O-horizon, ΣPCNs concentrations ranged from 11 to 190 pg/g dw, with an arithmetic mean of 78 ± 48 pg/g dw. These values were significantly higher than those from the A-horizon (paired sample t-test, $p < 0.01$). Although enrichment of organic contents in the O-horizon leads to accumulation of PCNs, the differences between the two soil layers in high-molecular-weight congeners remained when the results were expressed as pg per gram organic carbon. At approximately half of the sampling sites, the TOC-based concentrations of tri-CNs in the A-horizon were higher than those in the O-horizon. Moeckel et al. (2008) reported that less volatile POPs are stable in the O-horizon and credited the highest tri- and tetra-CBs in deeper soil layers with the preferential transport of lower-molecular-weight POPs in truly dissolved form. This could also explain the vertical distribution of PCNs in our results given the similar physiochemical properties of PCNs and PCBs.

The major contributors to ΣPCN concentrations were tri-CNs (~53%), followed by tetra- (~15%), penta-(~14%), hexa-(~10%), and hepta-CNs (~6%). CN-24 was the most abundant congener, with an

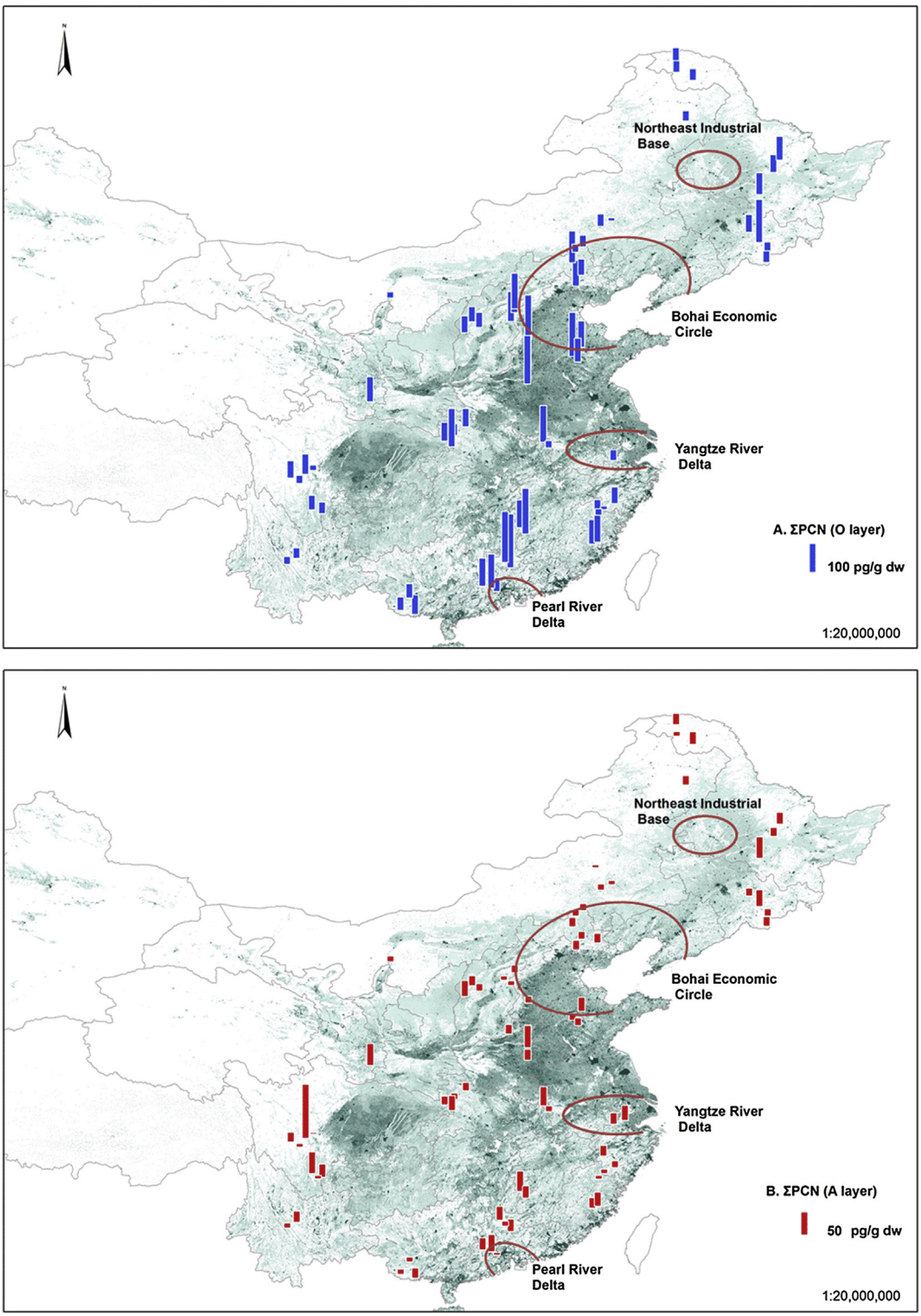


**Fig. 1.** ΣPCN concentrations (pg/g dw) in the A-horizon (A) and the O-horizon (B). The stretch values along a green color ramp indicate population density. Red lines outline four major industrial zones in China, including Northeast Industrial Base, Bohai Economic Circle, Yangtze River Delta and Pearl River Delta. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

average proportion of ~36% (Figure S2). Statistically, the relative contribution of tri-CNs in the O-horizon was lower than that in the A-horizon, while penta-CNs showed the opposite pattern (paired sample t-test, SPSS, $p < 0.01$). Given that the environmental variables for the O- and A-horizons were almost identical at each site, the observed differences are likely reflective of the relatively high mobility of light homologues. Sediment cores have shown an increased contribution of thermal sources of PCNs in recent years (Pan et al., 2012), which may have contributed to the observed differences between the two soil layers as well.

### 3.2. Spatial patterns

Fig. 1 shows the spatial pattern of ΣPCN concentrations in the O- and A-horizon. ΣPCN concentrations in the O-horizon were higher along the coastal areas, and decreased in Southwest China. The spatial pattern in the O-horizon shows some resemblance to the results of previous atmospheric monitoring in 2008 (Hogarh et al., 2012), but with a higher influence of low chlorinated congeners. The O-horizon of the forest soil is an organic horizon in which the chronological deposition of organically bound atmospheric contaminants is largely preserved (Bergknut et al., 2011). Considerably high concentration values were observed in the A-horizon at site GG2, Southwest China (Fig. 1, B). This pattern is not reflected by data from a previous atmospheric study (Hogarh et al., 2012). Unlike the O-horizon (which is more directly influenced by atmospheric deposition) exposure in the A-horizon depends on atmospheric loadings and transport and transformation processes occurring both in the A- and O- horizons. It is not surprising therefore that the exposure pattern of the deeper soil layer may not reflect directly atmospheric concentrations. After normalizing by the OC content the distribution patters on PCNs in the O- and A-horizons were similar, with relatively higher concentration levels associated to industrially developed regions (i.e., the Pearl River Delta and the Yangtze River Delta) and the petrochemical industry base (Shandong Province) (Figure S3). Population density can be regarded as indicator of human activity related sources (Hogarh et al., 2012). Elevated ΣPCN concentrations were generally detected close to areas with high population density (Figure S3). Although limited knowledge on the PCN emission inventory in China was available, it appears that the spatial pattern is controlled mainly by the proximity to potential source areas.

The relative contributions of each PCN homologues to ΣPCN are displayed in Fig. 2. The proportions of high-chlorinated CNs were elevated in both the soil layers of samples from northern China. $K_{OA}$ values increase with molecular weight of PCN homologues (Harner and Bidleman, 1998). High chlorinated CNs tend to be associated with particles in the air and are deposited in areas close to the sources. The relatively high proportions in northern China likely originate from adjacent sources. CN-66/67 and CN-73 were major contributors to hexa- and hepta-CNs, on average accounting for 45% and 57%, respectively. As suggested previously, these are indicators of thermal industrial processes (Meijer et al., 2001; Helm and Bidleman, 2003), and therefore reflect combustion-related sources of PCNs in northern China.

PCNs exhibit dioxin-like toxicities due to their structural similarity to dioxins. Given that we found relatively high ΣPCN concentrations adjacent to densely populated areas (Fig. 1A), it is necessary to evaluate the resulting health impact. The overall PCN toxic equivalent quantity (PCN-TEQ value) is the sum of the product of 2,3,7,8-tetrachlorodibenzo-p-dioxin relative potency factors (RPF) of individual CNs and its corresponding soil concentrations. Based on the RPFs of the individual PCN congeners (including CN 35, 38/40, 50, 54, 56, 57, 63, 66/67, 64/68, 69, 71/72, 73) (Noma et al., 2004), the PCN-corresponding TEQ (toxic equivalency) values were estimated and plotted in Fig. 3. The TEQ values were generally high in the O-horizon, ranging from 0.04 to 110 fg/g dw (27 ± 27 fg/g dw), compared to 0.002 to 43 fg/g dw (7.5 ± 7.5 fg/g dw) in the A-horizon. The highest TEQ was observed at JG3. Relatively high TEQ values often occurred in Eastern and Central China, which are densely populated regions. However, not all the densely populated areas were characterized by a high PCN-related health risk.

If compared with the concentration distribution map in Fig. 1, the risk in the southeastern coastal province was relatively low even though the ΣPCN concentrations in this area were in the same range. Similarly, the risk was moderate at site GG2 because this area despite having the highest recorded ΣPCN concentration presented a higher contribution of less toxic tri-CNs. Overall, CN-66/67, -73 and −64/68 were the major contributors to the total PCN-corresponding TEQ, on average accounting for ~36%, 35% and ~17% of the total TEQ, respectively. CN-66/67 and −73 are combustion indicators (Meijer et al., 2001), suggesting that thermal sources are major contributors to the PCN-related health risk in China.

### 3.3. Influence of environmental factors

Another important factor influencing PCN concentrations is organic matter, due to its lipophilic properties. The overall correlation coefficient between ΣPCN and TOC was 0.56 ($p < 0.01$). The correlation was significant ($r = 0.37$, $p < 0.01$) in the A-horizon but non-significant in the O-horizon. The concentrations of individual homologue groups were regressed against TOC to investigate the influence of organic matter (Figure S4). A significant relationship was observed for tri-, tetra- and penta-CNs in the A-horizon. Generally, the concentrations increased with TOC, and the TOC-dependence was stronger for lighter than for heavier homologues. Similar trends of PCBs in soils from Norway and the United Kingdom have been interpreted as evidence that more volatile compounds are moving towards equilibrium with the organic matter burden of the soil compartment (Meijer et al., 2002). In the O-horizon, PCN concentrations were found to correlate with neither TOC nor other environmental factors, but tri-, tetra- and penta-CNs were significantly influenced by annual average precipitation ($r = 0.27, 0.35, 0.36$) if the concentration of each homologue was expressed on a pg/g C basis (Figure S5). As discussed above, the O-horizon was subject to atmospheric deposition even though POPs in this layer were partially depleted. The atmospheric influence decreased with increasing soil depth, and only tetra-CN in the A-horizon was significantly correlated with rainfall ($r = 0.28$).

### 3.4. Potential sources

Principal component analysis (PCA) facilitates identification of the major influencing factors in complex multivariated datasets. Individual common detected congeners (defined as detection rate > 70%) were normalized to mass percent contributions to ΣPCN and then processed in the PCA analysis. Three PCs were retained. PC1, PC2 and PC3 explained 29.2%, 13.1% and 8.6% of the total variation in the O-horizon, and 24.7%, 11.7% and 8.4% in the A-horizon, respectively. As reported by previous atmospheric study, PCN sources were somewhat evenly distributed across China (Hogarh et al., 2012). The extracted components accounted for only half of the total variance, suggesting that the substantial residual factors are at present unexplained. PC1 can be considered to represent combustion sources, because some combustion-related congeners (CN-39, 52/60, -50, -54 and −66/67) showed elevated loadings (>0.8) oriented along the positive axis. PC2 was loaded with light congeners, such as CN-19 and -14 (Figure S6). PC1 impacted mainly northern China, which is characterized by intense domestic energy combustion and heavy industry. Interestingly, the loading of CN-51 on PC1 was lower than that of other combustion-related penta-homologues (CN-52/60 and −54). A previous study on soil PCNs conducted in PRD reported that CN-51 levels were higher in the less industrialized areas than the highly industrialized areas compared to CN-54, possibly due to heating or biomass burning rather than industrial processes (Wang et al., 2012). Similarly, we frequently found high proportions of CN-51 in Southwest China (Figure S7), which has fewer industries, suggesting that soil PCN levels in China reflect multiple combustion sources.

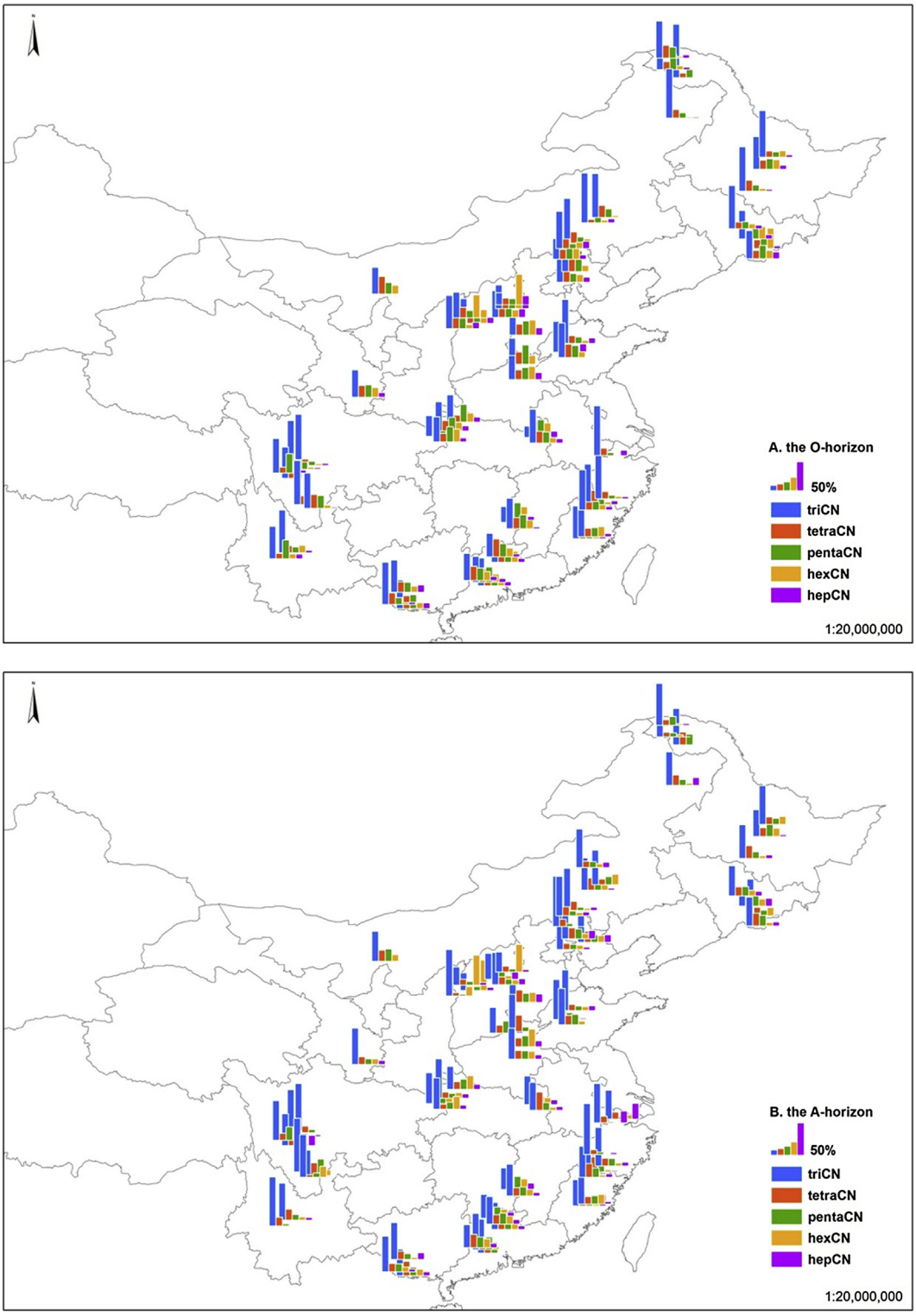


**Fig. 2.** Composition patterns of PCNs in the O-horizon (A) and A-horizon (B).

Homologue profiles are easily distorted by environmental processes (Hogarh et al., 2012), therefore, the average contributions of combustion-related PCNs to their own homologue groups (tri-comb/tri-, tetra-comb/tetra-, penta-comb/penta-, and hexa-comb/hexa-CNs) were applied as chemical signatures to identify potential sources. Table 1 summarizes the average ratios of several combustion indicators (CN-17/25, 36/45, 39, 35, 52/60, 50, 51, 54, 66/67) to their homologue groups in Halowax formulations (Noma et al., 2004; Falandysz et al., 2006a, 2006b) and fly ashes of combustion sources (Helm and Bidleman, 2003; Lee et al., 2005). The average tri-comb/tri-, tetra-comb/tetra-, penta-comb/penta-, and hexa-comb/hexa-CNs ratios were ~12%, 33%, 72% and 42%,

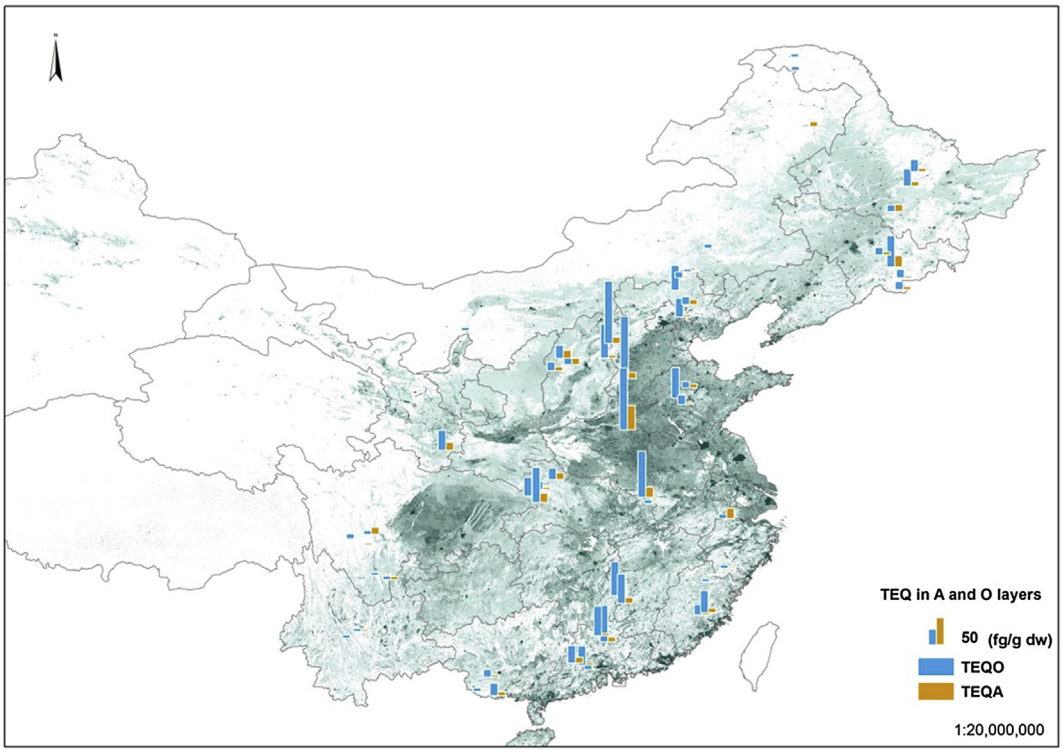


**Fig. 3.** TEQ values in the A- and O-horizon samples. The stretch values along a color ramp indicate population density.

**Table 1**
The average proportions of combustion-related PCNs to their own homologue groups of different sources (%).

| Source | Tri-CNs | Tetra-CNs | Penta-CNs | Hexa-CNs |
|---|---|---|---|---|
| Halowax1000[a] | 3 | 12 | 14 | 2 |
| Halowax1001[a] | 3 | 14 | 21 | 3 |
| Halowax1013[a] | 1 | 11 | 10 | 3 |
| Halowax1014[a] | 2 | 10 | 16 | 3 |
| Halowax1031[a] | 4 | 13 | 14 | 3 |
| Halowax1051[a] | 5 | 12 | 05 | 15 |
| Halowax1099[a] | 3 | 14 | 13 | 4 |
| Halowax1031[b] | 0 | 13 | 14 | 3 |
| Halowax1000[b] | 3 | 13 | 10 | 0 |
| Halowax1001[b] | 2 | 14 | 15 | 3 |
| Halowax1013[b] | 1 | 11 | 11 | 3 |
| Halowax1014[b] | 2 | 10 | 15 | 3 |
| Halowax1099[b] | 2 | 14 | 11 | 4 |
| Koppers 1970s[c] | 3 | 38 | 47 | 21 |
| A7020287 Accu[c] | 0 | 39 | 100 | 26 |
| Analabs[c] | | | | 30 |
| J296H Foxboro[c] | 6 | 16 | 12 | 15 |
| B127[c] | | 44 | 50 | 25 |
| 8796[c] | | 52 | 47 | 2 |
| Housecoal combustion[d] | 24 | 39 | 36 | 0.58 |
| Hardwood combustion[d] | 10 | 41 | 34 | 19 |
| Municipal waste incinerator[e] | 28 | 63 | 85 | 68 |
| Cement kiln[e] | 0 | 60 | 52 | 56 |
| IRON sintering[e] | 49 | 65 | 60 | 21 |
| Medical waster[e] | 32 | 51 | 91 | 83 |
| O horizon of forest soil[f] | 9 | 41 | 74 | 49 |
| A horizon of forest soil[f] | 12 | 33 | 72 | 42 |

[a] Noma et al., 2004.
[b] Falandysz et al., 2006a, 2006b.
[c] Falandysz et al., 2006a, 2006b.
[d] Lee et al., 2005.
[e] Helm and Bidleman 2003.
[f] This study.

respectively, in the A-horizon, and ~9%, 41%, 74%, 49%, respectively, in the O-horizon. These values are significantly higher than those of technical mixtures in Table 1, except for Halowax 1051, suggesting combustion-related sources. Halowax 1051 almost exclusively contains CN-73, 74 and 75. In this study, these three congeners contributed only a minor proportion of ΣPCN. Additionally, CN-73, a compound emitted not only from Halowax 1051 (Falandysz et al., 2006a, 2006b), but also from metallurgical facilities (Ba et al., 2010), coking industry (Liu et al., 2010), municipal solid waste incineration and e-waste recycling (Lin et al., 2013) in China, was significantly correlated with the combustion indicators noted above ($r = 0.38–0.69$). As stated above, it often occurred in relatively high proportions in northern China, which is characterized by high coke combustion (Figure S8). The profiles of O-horizon soil samples close to this area were also similar to previous reports in coke plants (Liu et al., 2010) (Figure S9). This suggests a relation to sources associated to this process rather than commercial formula (namely, Halowax 1051). Given the high variations of the diagnostic ratios (Table 1), it is difficult to attribute the forest soil PCNs in China to a single combustion-related source.

The intimate connection between POP concentrations and TOC may lead to a pseudo-correlation when exploring the impact of other factors by means of bivariate correlation analysis. Partial correlation can be used to assess the co-variation of PCNs and PCBs in cases where the influence of TOC is eliminated. A significant partial correlation was observed between the ΣPCN and ΣPCB concentrations in the O- and A-horizons ($r = 0.63$ and 0.24, respectively, using TOC as the controlling factor), indicating similar sources and environmental behaviors. The correlation between atmospheric ΣPCN concentrations and ΣPCB was reported to be non-significant at Chinese sites in 2008 (Hogarh et al., 2012), although this does not mean that our results contradict previous observations. A recent emission inventory suggests that PCBs emissions from the cement, steel, and coking industries (which

unintentionally produce PCBs, namely, UP-PCBs) were responsible for atmospheric PCB concentrations in Chinese rural areas. These sources are often located in rural areas close to, but not within, populated urban centers (Cui et al., 2013). These industries may also release PCNs (referred as UP-PCN here.) (Table 1), leading to the correlation between ΣPCN and ΣPCB. Conversely, UP-PCBs were not a major PCB sources in urban areas, therefore identifying a relation with the results from the 2008 study (in which most sampling sites were located in urban areas) is difficult. Cui et al. (2013) suggested that UP-PCB emissions are a major source of PCBs in China and were responsible for the increase in PCBs in Chinese air as a whole since the 2000s. We argue here that the situation would be similar for UP-PCN. In the present study, in fact, the average contributions of combustion-related PCNs to their own homologue groups in the O-horizon were higher than those in the A-horizon, with the exception of tri-comb/tri-CNs. Given that the cement industry also yields low tri-comb/tri-CNs ratios (Table 1), this difference suggests a general increasing contribution of thermal processes to PCN pollution on a regional scale. Many unintentional processes, such as combustion, industrial production and other activities, will induce POPs into the environment as by-products. As the Stockholm Convention emphasized, unintentionally produced POPs (UP-POPs) have contributed to China's growing distress concerning POPs. This study further confirms that UP-POPs have become a dominant source in some regions and their controls are of critical need to alleviate pollution of POPs in China.

### 3.5. Outliers

Cold-trapping of POPs in mountainous areas has been reported to be a result of altitudinal gradients of temperature, wind, rainfall, snow, and fog (Daly and Wania, 2005). Due to the complexity of sources in China and small elevation differences in each mountainous area, the observed elevation gradients of PCNs were inconsistent among sampled mountains (Figs. 3 and 4, S10–S14). Among the mountains with four sampling sites, PCN concentrations were correlated positively with altitude in Shennongjia (SN) (Figure S10), but negatively in the Jiugong (JG) and Longquan (LQ) Mountains (Figure S11 and S12). The altitudinal trends in other mountains were difficult to decipher due to the scarcity of samples.

Pan et al. 2014 observed that the concentrations of penta- and hexa-CNs were positively correlated with altitude, while tri-CNs showed a negative correlation in the Wolong high mountain area, eastern Tibet-Qinghai Plateau. At the Gongga (GG) sites, situated ~100 km to the east of Wolong Mountain, the concentrations of high-molecular-weight homologue groups also increased with increasing altitudes in the O-horizon, but the trend was disturbed by high concentrations at 2700 m regardless of normalization to dry weight or TOC (GG2 site, 2700 m, Fig. 4). In addition, the concentration of each PCN homologue at GG2 in the A-horizon was higher than those in the O-horizon, which differs from the results of a previous study that reported enriched levels of high-chlorinated compounds in the O-horizon (Moeckel et al., 2008), as well as a vertical distribution of PCNs at other sites. Our sampling sites were located in areas distant from human activities, minimizing the potential influence of point sources. A previous study on soil properties in Gongga Mountain reported that soil organic matter and the C:N ratio peaked at an elevation of 2700 m, which is a transition area (ecotone) between deciduous broad-leaved and coniferous forest zones (Wang et al., 2004). The dissolved organic carbon (DOC) at surrounding areas (the elevation of 2800 m) was also elevated, especially in the deep soil layer (Li et al., 2013). A high soil absorption ability and reduced microbial activities (high C:N ratio) favor the accumulation of POPs at the GG2 site. Downward transport associated with dissolved organic matter leads to leaching of more hydrophobic compounds, which may explain the elevated concentrations of high-chlorinated PCNs with low mobility in the A-horizon at this site.

It is interesting to note that the ecotone between dark conifer forest and *Betula ermanii* forest in Changbai Mountain was located in 1790 m a.s.l. (Yu et al., 2004), close to the altitude where elevated PCN (Fig. 5), PCBs and organochlorine pesticides (Wan et al., 2010) concentrations were recorded. The type and quantity of return plant residue, temperature and moisture in a mixed forest results in high soil organic matter concentrations (Li et al., 2013). However, the TOC content is independent from POP deposition (Aichner et al.,

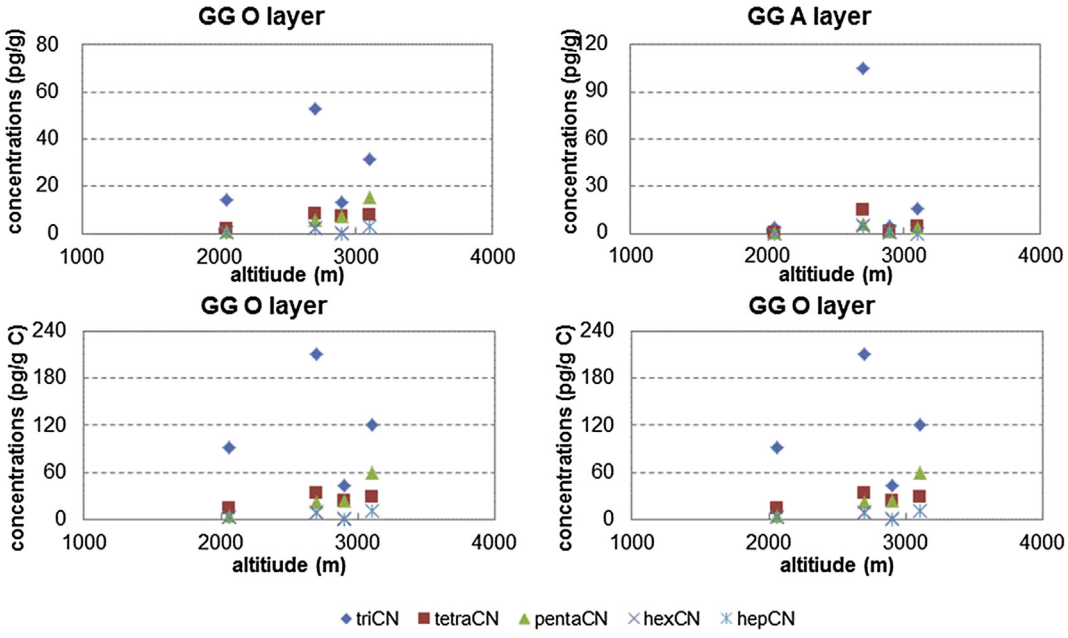


**Fig. 4.** Latitudinal trends of PCN homologue groups at Gongga Mountain in the A- and O-horizons.

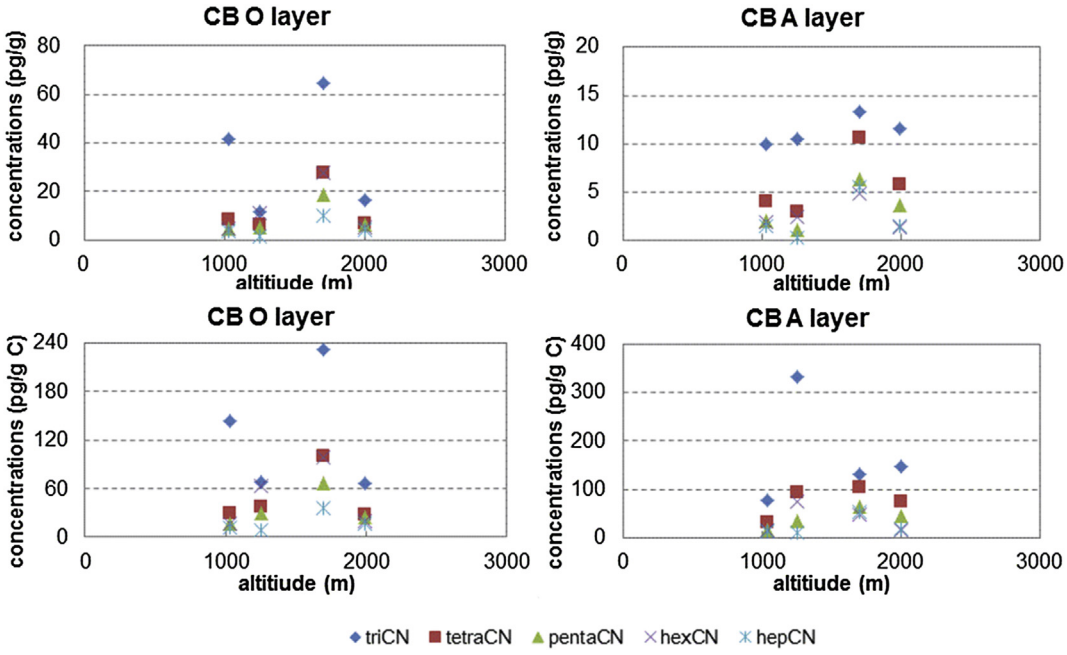


**Fig. 5.** Latitudinal trends of PCN homologue groups at Changbai Mountain in the A- and O-horizons.

2013). The elevated TOC-based concentrations in the O-horizon suggests that other factors, such as microbial activities, soil properties or deposition rates, may contribute to the trend. Nizzetto et al. (2006) also suggested that deposition behaviors vary substantially among forest ecosystem types. The role of forests and the dynamics of POPs in these environments have not been sufficiently investigated to date. Additionally, the extent to which they affect the fate of POPs on a regional or global scale remains largely uncertain. The high storage ability of POPs in these forest soils exceeded expectations, highlighting the need for further investigations to fully understand the behavior of POPs in forest ecosystems.

## 4. Conclusions

PCNs were measured in the O- and A-horizon soil samples collected in Chinese forest from July 2012 to March 2013. High chlorinated-CNs were enriched in the O-horizon while low chlorinated ones preferentially transported to the A-horizon. After normalization on OC content relatively high concentrations of PCNs were found in developed region or areas with presence of petrochemical industries, indicating the importance of source emission. Relatively high TEQ values often occurred in those developed areas with dense population, except southeastern coastal. Source emission and SOM are the major factors influencing PCN in Chinese forest surface soil. Although it is difficult to identify specific source of PCNs, both combustion indicators and PCA analysis suggest the contribution of thermal processes, such as industrial processes and biomass burning. Relatively high proportions of CN-73 in northern China could be an indicator of coke-related sources of PCNs. Unintentional industrial activities lead to the significant correlations between PCNs and PCBs. Due to restriction on intentionally produced POPs, development in China will possibly cause higher releases UP-PCN in the future if no emission control measure will be set in place. In this study, abnormally high PCNs concentrations were recorded at some outliers in the middle altitude of Gongga Mountain, possibly associated with high amounts of SOM accumulated in ectone. Less microbial activities and high DOC may also favors accumulation. Similar pattern was observed at the ecotone in Changbai Mountain, but mixed forest does not necessarily mean high concentrations of PCNs in other mountains. No matter how the large accumulation ability occurred, our observation indicates that the storage of POPs in some particular forest soil may exceed our expectations.

## Acknowledgment

This work is supported by the National Scientific Foundation of China (Nos. 41125014, 41390240 and 41403103). LN contribution was supported by the National Sustainability Programme of the Czech Ministry of Education, Youth and Sports (LO1214) and the RECETOX Research Infrastructure (LM2011028). We are grateful to Dr. Haijian Bin, Dr. Ruijie Zhang for their assistance in field sampling.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2015.04.014.

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