



Occurrence and sources of PCBs, PCNs, and HCB in the atmosphere at a regional background site in east China: Implications for combustion sources[☆]

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ABSTRACT

Multiple types of persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), and hexachlorobenzene (HCB), can be unintentionally released from combustion or thermal industrial processes, which are speculated to be the main sources of these contaminants, as they were banned on production and use since several decades ago. In this study, concentrations and sources of 40 PCBs, 39 PCNs, and HCB were analyzed in air samples collected during the period 2012–2015 at a background site in east China. Σ PCBs, Σ PCNs, and HCB were in the range of 9–341 pg/m³, 6–143 pg/m³, and 14–522 pg/m³, respectively. Seasonal characteristics with high levels in winter and low levels in summer were observed for PCNs and HCB. PCBs also exhibited slightly higher levels in winter. Source apportionment was conducted, using polycyclic aromatic hydrocarbons (PAHs) as combustion sources indicator, combined with principal component analysis (PCA) and positive matrix factorization (PMF) model. The results indicated that the legacy of past produced and used commercial PCBs was the dominant contributor (~56%) to the selected PCBs in the atmosphere in east China. PCNs were mainly emitted from combustion sources (~64%), whereas HCB almost entirely originated from combustion process (>90%).

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1. Introduction

Persistent organic pollutants (POPs) are a class of pollutants with potential of persistence, toxicity, bioaccumulation, and long-range atmospheric transport potential (Wania and Mackay, 1996; Fu et al., 2003; Han and Currell, 2017; Jones and de Voogt, 1999; Mo et al., 2018; Pozo et al., 2006). Some POPs are well known or suspected as carcinogens and mutagens that could cause serious human health effects (Alharbi et al., 2018; Jones and de Voogt, 1999; Xu et al., 2013). According to origins, POPs are divided into two

groups: (1) historical intentionally manufactured as pesticides and chemicals, which can be referred to as intentionally produced POPs (IP-POPs); (2) unintentionally formed during combustion and thermal industrial processes, which were listed as unintentionally produced POPs (UP-POPs) in the Stockholm Convention. Several kinds of POPs, such as polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), and hexachlorobenzene (HCB), share both origins.

PCBs and HCB are groups of the dirty dozen POPs. PCBs were historically manufactured for heat transfer fluids, hydraulic fluids, solvent extenders, plasticizers, flame-retardants, and dielectric fluids and were widely used in transformers and capacitors (Batterman et al., 2009; Gevao et al., 2017; Hogarh et al., 2012a). The cumulative historical global production of PCBs (from 1930s to 1993) was estimated to be 1.3 million tons, which was dominated

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by tri-, tetra- and pentachlorinated biphenyls (Breivik et al., 2002). HCB has been historically used as a pesticide and as a material for the production of pentachlorophenol and pentachlorophenol-Na (Wang et al., 2010). PCNs were historically produced as flame retardants and dielectric fluids for capacitors and also used in other industries, such as oil additives, plasticizers, and textile and paper industries (Bidleman et al., 2010). They also presented as impurities in commercial PCB mixtures. Until 1980s, the global production of PCNs was approximately 0.15 million tons (Noma et al., 2004). The intentional production and use of these commercial products, the usage and disposal of POPs-containing products, and the accidental releases caused historical emissions of these chemicals, which were persistent in the environment due to their stability.

PCBs, PCNs and HCB also can be formed during combustion and thermal industrial processes, such as domestic burning of coal and wood, production of mineral products, metal production, and waste incineration (Gong et al., 2017; Lee et al., 2005; Liu et al., 2014; Liu et al., 2013b), in analogous to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs). Lee et al. (2005) estimated the emission factors of PCBs from domestic combustion of coal and wood to be approximately 1000 ng/kg fuel, which was one order of magnitude higher than PCNs and PCDD/Fs. Emission factors for PCBs from several industrial thermal processes in China were estimated to be in the range of 10–5000 µg/t, which was comparable to PCNs (Liu et al., 2014; Liu et al., 2013b). Emission factors for HCB ranged from 1 mg/t to 40,000 mg/t in the metallurgical industry (Gong et al., 2017). Although emission factors for PCBs, PCNs, and HCB from combustion-related processes were not as high as that for PAHs, the emission amounts of these contaminants are unneglectable.

Since the ban on production and use of commercial products, primary emissions of PCBs, PCNs, and HCB directly from intentional sources showed decreasing trends (Anttila et al., 2016; Braune and Muir, 2017; McGoldrick et al., 2018; Xu et al., 2018). Re-emissions from POPs sinks (such as soil and sediment) or other contaminated compartments were recognized to be controlling POPs levels in the atmosphere (Xu et al., 2018; Zhao et al., 2017). However, ongoing emissions from combustion and thermal industrial processes constantly input these contaminants into the environment. A prediction of PCBs emission trends in China indicated that PCBs from unintentional sources will become a major contributor in the near future (Zhao et al., 2017). Therefore, combustion-related sources likely play an increasingly important role for POPs in the environment. However, recent studies mostly focused on predicting emission inventories or describing the influence of combustion sources qualitatively. Relatively few studies have elucidated the contribution of combustion sources to POPs based on atmospheric observational data.

As one of the most economically developed regions in China, east China, especially the Yangtze River Delta (YRD) economic hub, experiences a heavy burden of POPs (Yang et al., 2012). Additionally, east China exhibits a subtropical monsoon climate that can be influenced by air masses transported from Southeast Asia in summer and from north China in winter. Therefore, the Ningbo Atmospheric Environment Observatory (NAEO, 29°40.8'N, 121°37'E, 550 m ASL) in east China, which is located close to the East China Sea and in the southern part of the YRD, was selected as a regional background site to monitor POPs, including PCBs, PCNs, and HCB. The sampling site has been described elsewhere (Liu et al., 2013a; Mao et al., 2019). Air samples were collected at NAEO from August 2012 to August 2015 in this study.

Although four inadvertently produced non-Aroclor PCBs were identified as the predominant congeners in the atmosphere at NAEO according to our previous study (Mao et al., 2019), the

influence of unintentional sources to Aroclor PCB congeners (which can also be produced inadvertently from combustion and thermal industrial processes) were still indeterminate. Therefore, 40 selected PCBs (including typical Aroclor congeners, indicator PCBs, and dioxin-like PCBs) were discussed in this study, along with 39 PCNs and HCB. This work sought to determine the contribution of combustion sources to Aroclor PCBs, PCNs, and HCB in east China. PAHs, primarily originated from the incomplete combustion process, exhibit similar persistence and long-range transport potency with PCBs, PCNs and HCB. Accordingly, PAHs could serve as a potential chemical indicator of combustion sources. Consequently, source apportionment were conducted for selected PCBs, PCNs, and HCB, using PAHs as combustion sources indicator, combined with principal component analysis (PCA) and positive matrix factorization (PMF) model.

2. Materials and methods

2.1. Sampling

The sampling site, NAEO is located on a rural mountaintop in Zhejiang Province. It is regional background site on the transport route of air masses. Air samples were collected about once (successive 24 h) a week at NAEO by a high volume air sampler (XTrust Instruments Co., Shanghai, 201600, China) fitted with polyurethane foam plugs (PUFs, 6.5 cm diameter, 7.5 cm length), operating at 300 L/min. One from about each fortnight samples from August 2012 to August 2015 (74 samples) were used in this study.

2.2. Sample pretreatment and analysis

Details are described in Text S1 in the Supplementary Material (SM). Briefly, each sample was spiked with PCB30, PCB198, and 2, 4, 5, 6-tetrachloro m-xylene (TCmX), and perdeuterated PAHs as surrogates and extracted for 24 h with dichloromethane (DCM). The extracts were purified on a neutral silica gel column. After the quantification of PAHs, the samples were further purified with 50% sulfuric acid silica gel column. Agilent 7890/7000 GC-MS/MS, and an Agilent 7890/5975 GC-MS were used to quantify PCBs, HCB, and PCNs, respectively.

2.3. Quality control and quality assurance (QC/QA)

QC/QA was performed through running laboratory and field blanks, calculating method detection limit (MDL) and instrument detection limit (IDL), calculating percent recovery of surrogate chemicals. In this study, five laboratory and three field blanks were extracted and analyzed as normal samples using the same solvent and analytical procedure to assess any contamination during the experiment procedures. The MDLs of each analyte, which are listed in Tables S3–S5, were calculated through analyte levels in blank samples or the IDL. The average recoveries were $71 \pm 8\%$, $103 \pm 15\%$, and $65 \pm 7\%$ for PCB 30, PCB198, and TCmX, respectively. Details of QC/QA are given in Text S1 in the MS. All reported values were corrected using the recoveries and the mean of blanks.

2.4. Air mass back trajectories

Five-day backward trajectories were calculated using National Oceanic and Atmospheric Administration's (NOAA) HYSPLIT model (<http://ready.arl.noaa.gov/HYSPLIT.php>). The National Centers for Environmental Prediction and the National Center for Atmospheric Research (NCEP/NCAR) reanalysis meteorological data were used as the input. All trajectories ended at the sampling site (29°40.8'N,

121°37'E) were calculated at an interval of 6 h with an arrival height of 550 m ASL (above sea level) for each sampling day of the campaign period (from 2012 to 2015). Then trajectory cluster analysis was utilized to group all the resulted trajectories into distinct transport patterns according to their speed, direction, origins, altitudes, transport patterns and meteorological conditions, using the HYSPLIT 4 clustering tool which applied the hierarchical cluster method. Clustering started by assuming each trajectory to be a cluster (i.e., there are N trajectories and N clusters). In each iteration, the cluster number was reduced by one as two clusters are merged together. Every combination was assessed and the two clusters combined are those that result in the lowest increase in total spatial variance (TSV). This process continues until only one cluster remains. Further description was illustrated in HYSPLIT-4 User's Guide-Version 4. In this study, the resulting trajectories were firstly separated in to four groups according seasons. Clustering was carried out on each data set individually and the optimum number of clusters was chosen in each case by visual identification of the TSV plots. The results are presented in Fig. S4.

2.5. Data and statistical analysis

Statistical analyses were carried out using the software of SPSS 23 (SPSS Inc., Chicago, IL, USA). Values below the MDLs were replaced by MDL/2 during statistical analyses. Pearson correlations were used to determine significant correlations between PAHs and other analytes (PCBs, PCNs, and HCB). Correlation coefficients are listed in Tables S6–S7 in the SM. Principle component analysis (PCA) was applied to investigate relationships within the data. In the PCA, the PCBs and PCNs + HCB data, combined with PAHs, in summer and other seasons were employed to establish possible combustion source character. PCA results are listed in Tables S8 and S9 in the MS.

Positive matrix factorization (PMF) has often been used for the source apportionment of POPs (Assefa et al., 2014; Bzdusek et al., 2006; Sundqvist et al., 2010). In this study, EPA PMF 5.0 software was used for source apportionments of PCBs, PCNs and HCB in gas phase. Prior to analysis, PCBs with detection frequencies below 50% were excluded and 28 congeners (or coeluting congener groups) in 74 samples were retained (28 × 74). An uncertainty of 15% was adopted for data points above the MDL. Undetectable values (null values) were replaced with values of MDL/2, and an uncertainty of 166% was assigned (Praipipat et al., 2013; Rodenburg and Meng, 2013). For analysis of PCNs and HCB, 38 PCNs, along with HCB and the sum concentration of PAHs (Σ PAHs) were included in the data set. An uncertainty of 20% was adopted for PAHs (Fang et al., 2016). Uncertainties of PCNs and HCB were assigned to be the same set with PCBs. Each PMF model was run 20 times requesting 4–9 factors with random seeds. Finally, a four-factor solution was determined to be optimal for PCBs and a five-factor solution was determined for the combined PCNs + HCB + Σ PAHs data set. These solutions gave the most stable result and produced Q values (both robust and true) close to the theoretical Q value.

3. Results and discussion

3.1. Concentrations and compositions of POPs

Although POPs were quantified in both gas and particle phase, contents in particles were deemed negligible as they were far lower than that in gas phase. Therefore, the analysis and discussion of this study were focused on selected POPs in gas phase only. The gas phase concentrations of POPs are summarized in Table 1, with details in Tables S3–S5 in the SM.

Table 1
Summarized concentrations of selected POPs in gas phase.

Contaminants	Min	Max	Mean ± Std
PCBs, pg/m³			
Di-CBs	1.1	34	10 ± 7.5
Tri-CBs	4.9	136	56 ± 29
Tetra-CBs	2.4	136	58 ± 36
Penta-CBs	0.25	38	16 ± 10
Hexa-CBs	0.03	17	4.2 ± 3.1
Hepta-CBs	<MDL	4.4	0.55 ± 0.67
Octa-CBs	<MDL	0.23	0.01 ± 0.03
Σ_{40}PCBs	9.0	341	145 ± 80
PCNs, pg/m³			
Tri-CN	2.3	116	27 ± 22
Tetra-CN	1.0	18	7.4 ± 3.8
Penta-CN	0.72	14	3.7 ± 2.5
Hexa-CN	0.02	3.2	0.67 ± 0.50
Hepta-CN	<MDL	0.60	0.10 ± 0.10
Octa-CN	<MDL	0.06	0.02 ± 0.01
Σ_{39}PCN	5.9	143	38 ± 27
HCB, pg/m³			
HCB	14	522	132 ± 117
PAHs, ng/m³			
Σ_{15}PAHs	1.3	44	15 ± 9.2

3.1.1. PCBs

The concentration of total PCBs (sum of 40 PCBs, Σ_{40} PCBs) ranged from 9.0 to 341 pg/m³, with an average value of 145 ± 80 pg/m³. The average concentration of Σ indicator PCBs (represents the sum concentrations of PCB28, PCB52, PCB101, PCB118, PCB138, PCB153, and PCB180) was 43 ± 22 pg/m³, accounting for ~30% of Σ_{40} PCBs. It was higher than those measured in central and southwest China (<39 pg/m³ and 0.80 pg/m³, respectively) (Wang et al., 2016b; Zhan et al., 2017). The total concentration of PCBs was much lower than that observed in Vietnam (136–1518 pg/m³) and India (1000–9560 pg/m³) (Chakraborty et al., 2013; Wang et al., 2016a), but slightly higher than levels in Japan, Singapore, and South Korea (7–247 pg/m³, 5–31 pg/m³, and 12–84 pg/m³, respectively) (Jaward et al., 2005). The PCBs profile was dominated by low molecular weight congeners, such as PCB28, PCB31, PCB18, PCB52 + 73, and PCB8+5. Average contributions of homologue groups to the total PCBs concentrations ranked as the following order: tri-CBs (~40% of Σ PCBs) > tetra-CBs (~38% of Σ PCBs) > penta-CBs (~10% of Σ PCBs) > di-CBs (~8% of Σ PCBs) > hexa-, hepta-, and octa-CBs. This pattern was inconsistent with the production and consumption history of PCBs in China, where 90% PCBs products were tri-CBs and 10% were penta-CBs (Liu et al., 2016). The high levels of tetra-CBs might be attributed to other sources that differed from commercial products or the effect of long-range atmospheric transport from other countries and areas.

3.1.2. PCNs

The sum concentration of measured 39 PCNs (Σ_{39} PCNs) varied from 5.9 to 143 pg/m³ with an average concentration of 38 ± 27 pg/m³. It was a slightly lower than that conducted across China (61 ± 6 pg/m³), but higher than that in Japan (9.5 ± 1.5 pg/m³) and Korea (16 ± 2.4 pg/m³) (Hogarh et al., 2012a). PCN24 and 17/25 contributed most to the concentration of Σ PCNs, accounting for ~37% and 14% of Σ PCNs, respectively. The most abundant homologue group was tri-CN, comprising ~65% of Σ PCNs, followed by tetra-CN (~22% of Σ PCNs) and penta-CN (~11% of Σ PCNs), while the heavier groups (hexa-CN to octa-CN) had a lower contribution (~2% of Σ PCNs). The composition profile agreed with those observed in other areas such as Japan, Korea, Ghana, India, and Pakistan, in which tri-CN and tetra-CN were the most abundant homologues, comprising more than 80% of Σ PCNs (Hogarh et al., 2012a; Hogarh et al., 2012b; Xu et al., 2014). The homologue

profile in this study differed significantly from the distributions of Howlax1014, a widely manufactured commercial product which was dominated by penta-, hexa-, and tetra-CN_s (Noma et al., 2004). However, similar patterns with a high tri-CN_s abundance were found and reported in emissions from coal and wood combustion (Lee et al., 2005), as well as industrial thermal processes (Liu et al., 2015a; Liu et al., 2015b).

3.1.3. HCB

The HCB concentration was in the range of 14–522 pg/m³ with an average value of 132 ± 117 pg/m³. The value was comparable to that measured at background site in central China (17–477 pg/m³) (Zhan et al., 2017), lower than that in southwest China (270 ± 100 pg/m³) (Xu et al., 2011), but higher than that in northwest China (38 pg/m³) (Cheng et al., 2007). It also higher than that in some east Asia counties such as Japan, Singapore, and South Korea (14–95 pg/m³, 9–25 pg/m³, and 26–136 pg/m³, respectively) (Jaward et al., 2005). Although HCB has never been used as a pesticide in China, it can be released as a trace contaminant from production and application of other pesticides and chemicals. Moreover, HCB can originate from incomplete combustion processes. Atmospheric HCB in China has been reported more related with the combustion sources (Liu et al., 2009).

3.1.4. PAHs

PAHs are primarily generated from incomplete combustion

process. They thus can be used as indicators of combustion sources when analyze sources of PCBs, PCNs, and HCB. The sum of the measured 15 PAHs (each PAHs was listed in Table S5 in SM) in gas phase was in the range of 1.3–44 ng/m³, with a mean value of 15 ± 9.2 ng/m³. It was slightly lower than that in north China (a background site in Shandong Province with an average of 19 ng/m³) (Zhu et al., 2014), but much higher than those observed in East Asia, such as Japan (average of 0.67 ng/m³) (Tang et al., 2015) and Korea (average of 2.9 ng/m³) (Kim et al., 2012).

3.2. Seasonal variations of selected POPs

Concentration time-series of PCBs, PCNs, and HCB from August 2012 to August 2015 are plotted in Fig. 1. ΣPAHs is also depicted for comparison. Concentration ranges of the target groups in different seasons are shown in Fig. S5. The tri-CBs was at a slightly higher level in winter with comparable levels for other seasons. The tetra-CBs and penta-CBs were observed with slightly lower levels during spring and elevated levels in winter. The result was inconsistent with observations that identified the highest PCBs levels in summer or warm seasons (Estellano et al., 2017; Galbán-Malagón et al., 2013; Kurt-Karakus et al., 2018). Seasonal variations with the following descending order were observed for all PCNs homologues as well as PAHs: winter (December to February) > fall (September to November) > spring (March to May) > summer (June to August). HCB also reached highest average level in winter and the lowest in

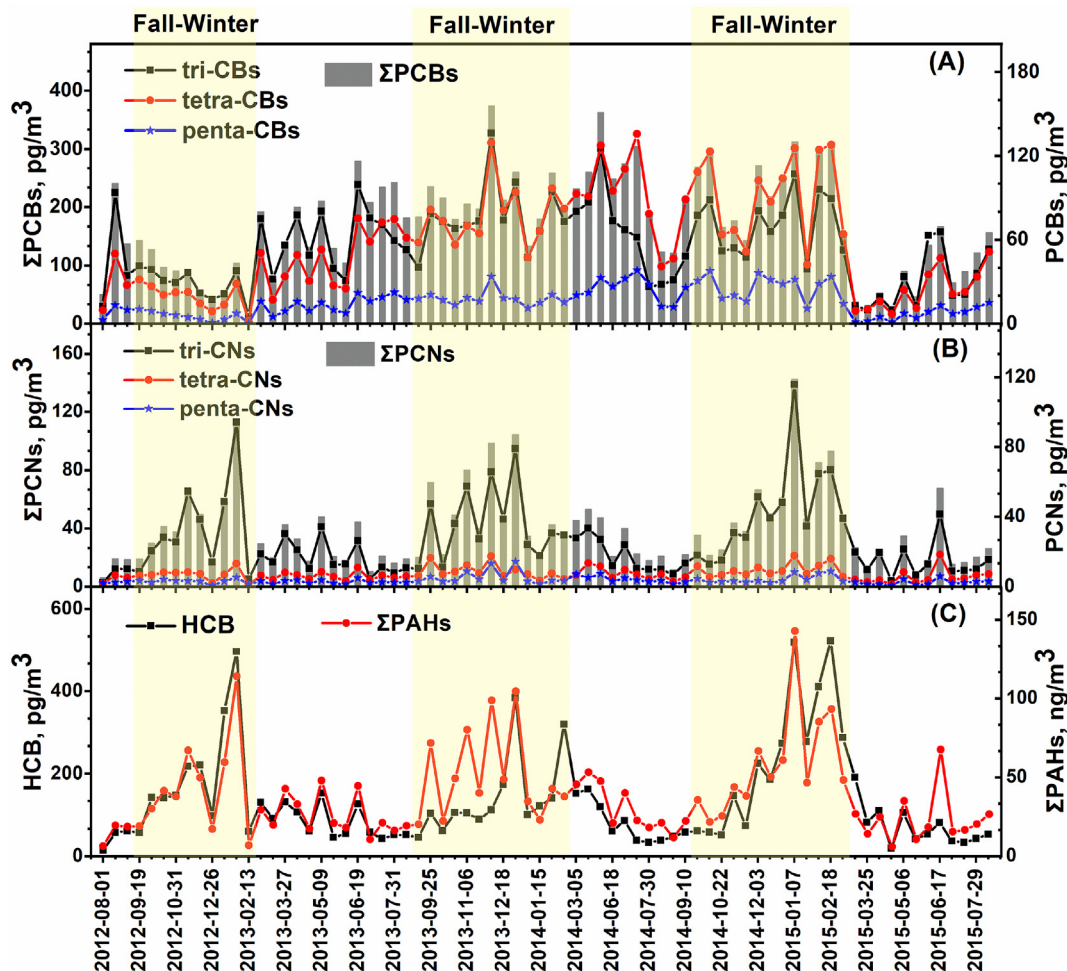


Fig. 1. Concentration time-series of selected POPs from 2012 to 2015.

summer. PCNs and HCB exhibited contrary seasonality with the temperature variation.

Seasonal variability is known to be mostly attributed to climatic changes (e.g., temperature changes or the monsoon-controlled air masses transport) or anthropogenic activities. Generally, ambient temperature was recognized to be the major influence factor for seasonality due to the temperature-dependent volatilization process. However, PCBs, PCNs, and HCB in this study showed less temperature dependence. According to five-day backward trajectories, air masses originated from or passed over north China in spring, fall, and winter, while from the marine areas during summer. However, more biofuel and fossil fuel were used for household heating during winter, especially in north China. The similar seasonality of PCNs, HCB, and PAHs with high levels in winter and low levels in summer might be attributed to the long-range transport of combustion-related emissions. The high concentration levels of PCBs in winter may also be influenced by the transport of increased pollutants in cold seasons.

3.3. Correlation analysis

Correlations between target chemicals may indicate common origins and atmospheric processes. PAHs primarily originated from incomplete combustion process. Therefore, correlations with PAHs may indicate the influence of combustion sources on PCBs, PCNs, and HCB. According Pearson correlation coefficients (Tables S6–S7), most PCBs displayed weak correlations with PAHs, might indicating the less influence of combustion sources.

However, most PCN congeners and HCB showed significant correlations with PAHs, especially the correlations between tri-CN, tetra-CN, and HCB versus Flu, Phe, Ant, and Fla. For example, PCN17/25, 16, 15, 23 36/45, and 27/30 were significantly correlated with Phe ($r > 0.80$, $P < 001$). HCB, PCN14, PCN 24, and PCN 49 presented good correlations with Flu ($r > 0.80$, $P < 001$). Some PCN congeners like PCN17/25, 36/45, 27/30, 39, 35, 52/60, 50, 51, 54, and 66/67 have frequently been recognized as combustion-related congeners (PCNs_{com}) and indicators during source apportionment of PCNs (Lee et al., 2007; Li et al., 2016; Li et al., 2017; Wang et al., 2012). All of these congeners (except PCN51) were strongly correlated with PAHs. The strong relationship between PCNs and HCB versus PAHs suggest that these contaminants may have originated from the same sources. However, contaminants from the same regions may also exhibit good correlations between each other. For example, PCNs, HCB and PAHs showed the same low levels in summer when air masses originated from the marine areas, with the same high levels being observed in winter when air masses originated from north China. The same seasonal trend caused by air masses transport may also result in the strong relationship between contaminants. To eliminate any ambiguity, correlation analysis for contaminants in different seasons were conducted via PCA.

During summer (i.e., when air masses originated from marine areas), the PCBs along with PAHs data set retained two components, respectively explaining 58.4% and 14.8% of the variation in the combined data set. The loading plots of the results are presented in Fig. 2(A). Component 1 presented high loadings of most

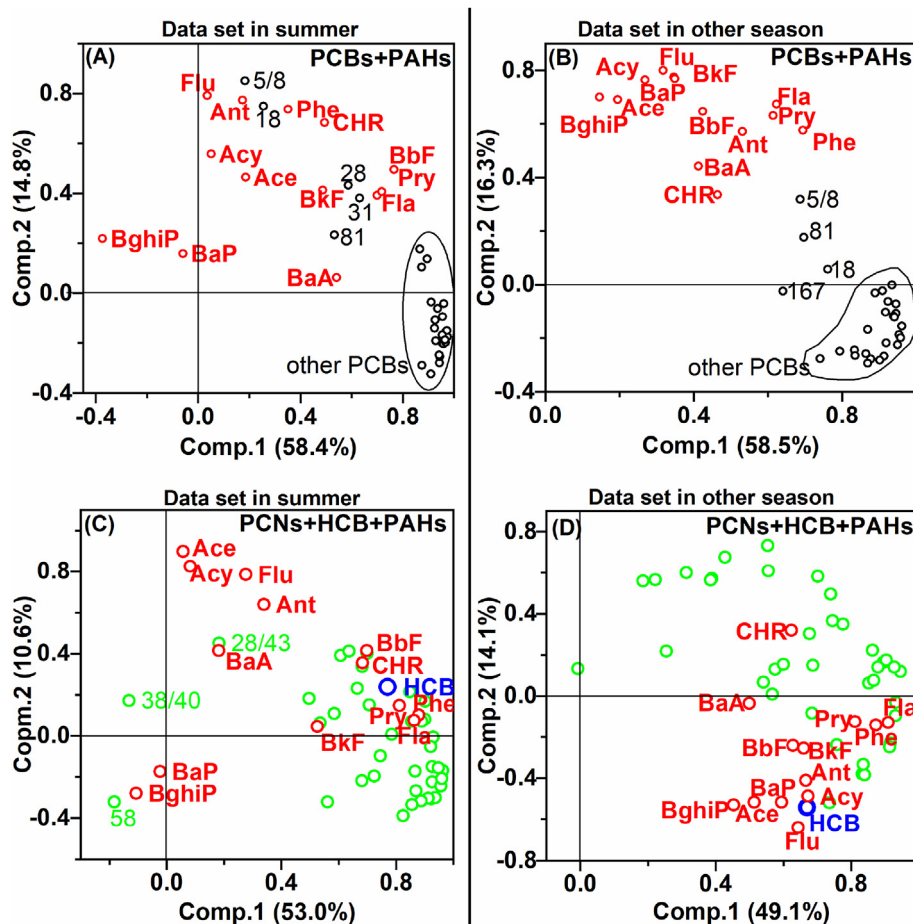


Fig. 2. Loading plots of principal component analysis for PCBs (black), PCNs (green), HCB (blue), plus PAHs (red) in gas phase for that from different seasons (summer or other seasons). Numbers on the right of the small circle represent IUPAC No. of PCB or PCN congeners. Detailed data are listed in Tables S8–S9. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

PCB congeners. Only few PCBs, such as PCB18, 5 + 8, 28, and 31, along with Flu, Ant, Phe, and Chr showed relatively high loadings on Component 2. In other seasons (i.e., when air masses originated from the north of the mainland), PCBs apparently separated from PAHs according to the PCA result as presented in Fig. 2(B). The loadings of PCBs were at high levels on Component 1 (explaining 58.5% of the variation), while PAHs were higher on Component 2 (explaining 16.3% of the variation). The results indicated that PCBs and PAHs mainly originated from different sources, regardless of the air mass origins.

The PCA results on data set of PCNs, HCB and PAHs for different seasons are presented in Fig. 2(C) and (D). Most PCN congeners hardly separated from PAHs, especially Phe, Pry, Fla, and Chr, whether air masses originated from marine areas or the north of mainland, suggesting the strong relationship and common sources between these contaminants. Compared with PCNs, the loading distribution of HCB was more similar to that of PAHs, especially during seasons when air masses originated from the north of mainland. HCB and PAHs (e.g., Phe, Acy, Flu, Fla, and Pry) showed moderate and positive loadings on Component 1 (Fig. 2(C) and (D)), suggesting that HCB largely originated from combustion sources.

3.4. Contribution of combustion sources to POPs

3.4.1. PCBs

PMF was used for source apportionment of PCBs. The congener profiles of the resolved four factors are shown in Fig. 3(A), with comparisons to other sources. To identify these factors, the $\cos\theta$ similarity metric was used for assessing the association of PCB congener profiles between each PMF factor versus individual source patterns.

In China, trichlorobiphenyl (#1 PCB) and pentachlorobiphenyl (#2 PCB) are two major PCBs commercial products, which have been reported to be similar to Aroclor 1242 and 1254, respectively. Although the production of commercial PCBs has been banned for

decades in China, volatilization of PCBs from ongoing use of PCB-containing products has still been a major source. Additionally, a large number of imported capacitors containing PCBs have also brought a variety of commercial products to China (Xu et al., 2018). Therefore, the four resolved factors were compared with Aroclor mixtures. Congener profiles of six main Aroclor products were obtained from Frame et al. (1996), and then rescaled to match the congeners selected in the PMF analysis.

Additionally, unintentional emission and e-waste recycling activities were other two major sources of PCBs. Among the industries, steel production, cement production, and incineration were reported to be the three major contributors to unintentionally produced PCBs in China (Cui et al., 2013; Sun et al., 2016; Zhao et al., 2017). PCBs have also been reported to be released as byproducts from domestic burning of coal and wood (Lee et al., 2005), which are typically fuels used for household heating in China. Therefore, steel production, cement production, waste incineration, coal and wood burning were identified as major unintentional sources and compared with the PMF factors. Moreover, China has been reported as one of the largest globally importer and recycler country of e-waste (Breivik et al., 2014). Thus, the impact of e-waste recycling activities on PCBs in the study area cannot be neglected. PCBs emission profiles from steel plants, cement plants and municipal solid waste incineration, and domestic burning of coal and wood were obtained from emission factors reported by Odabasi et al. (2009), Ishikawa et al. (2007), Ikononou et al. (2002), and Lee et al. (2005), respectively. The congener profile emitted from e-waste recycling activities was conducted according to air PCBs concentrations at an e-waste recycling site reported by Wang et al. (2016c). The obtained profiles were then rescaled to match the congeners selected in the PMF analysis.

According to the $\cos\theta$ values, Factor 1 showed the highest similarity with the profiles of Aroclor 1242 ($\cos\theta = 0.99$, $n = 28$). Factor 2 was displayed much resemblance to Aroclor 1248 ($\cos\theta = 0.96$, $n = 28$). Factor 3 was similar to PCBs profiles in air at the e-waste

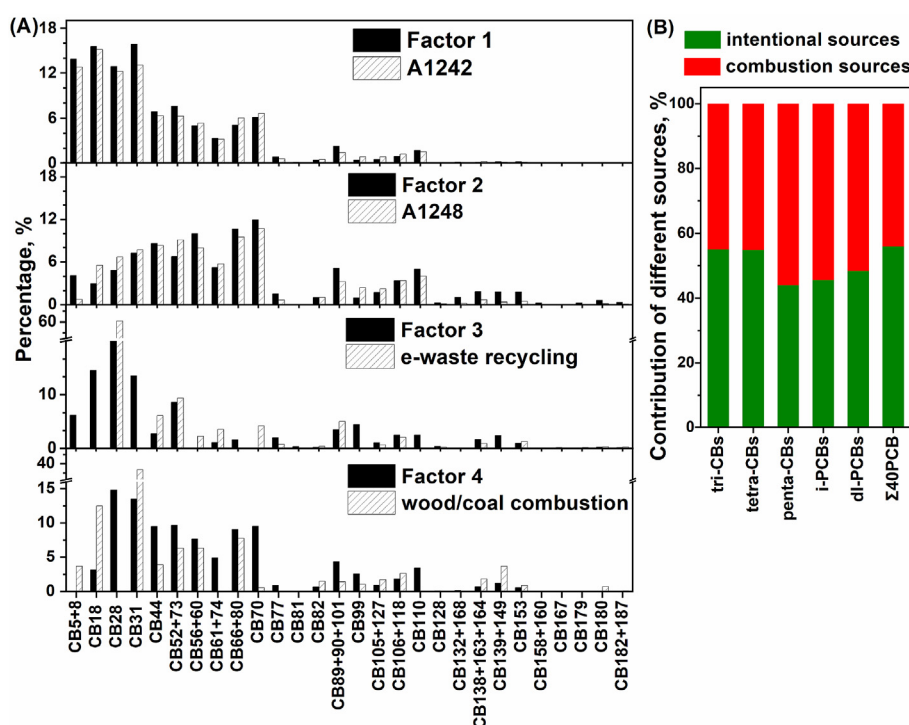


Fig. 3. Source apportionment of selected PCBs based on PMF: (A) PCBs profiles of PMF factors and different sources; (B) Contributions of different sources to PCBs.

recycling site ($\cos\theta = 0.98$, $n = 18$). Factor 4 showed high similarity with the profiles of emissions from wood and coal combustion ($\cos\theta = 0.93$, $n = 19$). Consequently, Factor 1 was attributed to Aroclor 1242. Factor 2 was used to represent Aroclor 1248. Factor 3 represented the emission from e-waste recycling activities. Factor 4 was characterized as wood/coal combustion. For the four resolved PCBs sources, emissions from Aroclor mixtures (Factor 1 and Factor 2), undoubtedly intentional sources, contributed ~56% (43% for Factor 1 and 13% for Factor 2) of all sources to Σ PCBs. Emission from e-waste recycling activities (Factor 3) was comprising ~13% of the concentration of Σ PCBs. Wood/coal combustion (Factor 4) showed a contribution of ~31% to Σ PCBs. Both Factor 3 and 4 were attributed to combustion-related sources, contributing ~44% to Σ PCBs. The result was consistent with the PCBs emission inventories in China predicted by Cui et al. (2015) and Zhao et al. (2017), which indicated that the intentionally produced PCBs were dominant in the atmosphere but the increasing emissions of unintentionally produced PCBs should be a cause for concern.

3.4.2. PCNs

As reported, the concentration ratio of Σ PCNs_{com} (the sum of combustion-related congeners) to Σ PCN could suggest the contribution of combustion sources to PCNs (Cetin, 2016; Lee et al., 2007; Mahmood et al., 2014). PCN51 was excluded in the PCNs_{com} because of the weak correlation with PAHs, thus only PCN 17/25, 36/45, 27/30, 39, 35, 52/60, 50, 54, and 66/67 were calculated as combustion indicators and a value of 0.28 ± 0.07 (0.16–0.42) was conducted for

Σ PCNs_{com}/ Σ PCNs in this study. The value of Σ PCNs_{com}/ Σ PCNs < 0.11 was identified as re-emission from Halowax mixtures in a previous study, while a ratio in the range of 0.5–0.75 suggested combustion sources such as waste incinerations, cement kiln, and iron sintering (Lee et al., 2007). The ratio in the range of 0.11–0.5 was considered as the results of combined effects of Halowax mixtures and combustion-related sources (Li et al., 2017; Wang et al., 2012). However, Σ PCNs_{com}/ Σ PCNs ratios of 0.34 and 0.35 were derived respectively for household coal and hardwood combustion according to Lee et al. (2005). The derived ratio in our study was within the typical range of combined effects of Halowax mixtures and combustion-related sources. It is noteworthy that only reported combustion-related congeners were considered when calculate the Σ PCNs_{com}/ Σ PCNs ratio. However, some non-reported PCNs_{com} congeners showed significant correlations with PAHs as mentioned above. For example, PCN16 significantly correlated with Phe ($r > 0.80$, $P < 0.01$). The dominant congener PCN24, as well as some other tri-CN (e.g., PCN14, 19, and 15), also showed strong correlations with PAHs. These congeners should be recognized as combustion-related. Therefore, the actual Σ PCNs_{com}/ Σ PCNs ratio in atmosphere should be higher (more closely to ratios conducted from combustion-related sources), indicating the predominance of combustion sources.

During the PMF analysis, five factors were resolved as shown in Fig. 4(A). All factors except Factor 2 and Factor 4 had loadings of PAHs, which can be used as an indicator of combustion sources. Therefore, Factor 1, Factor 3, and Factor 5 were characterized as

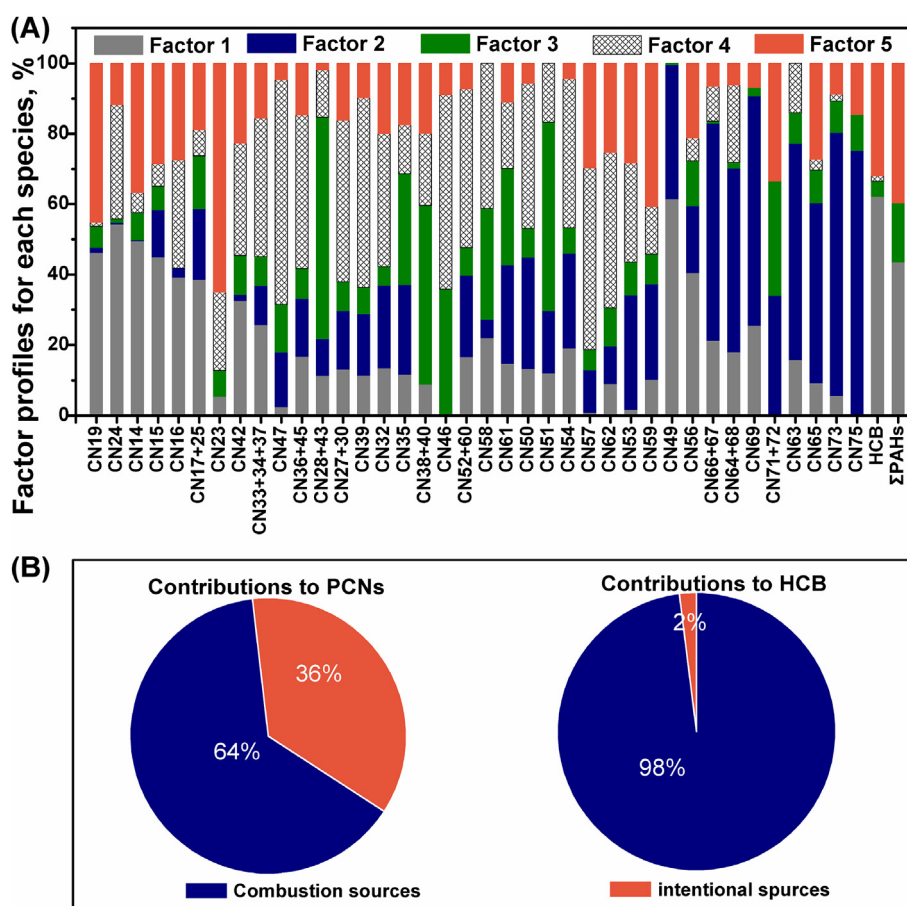


Fig. 4. Source apportionment of PCNs and HCB based on PMF: (A) Factor profiles for each species; (B) Contributions of different sources to PCNs and HCB.

combustion sources, including combustion or industrial thermal process. Factor 2 and Factor 4 explained zero of the variability in the concentration of PAHs, suggesting other sources unrelated with combustion, such as the legacy of historical intentionally produced commercial products. Thus Factor 2 and Factor 4 were referred to intentional sources. The average contributions of each source to Σ PCNs were plotted in Fig. 4(B). Accordingly, combustion sources (Factor 1, 3, and 5) contributed ~64% to the concentration of Σ PCNs. The results suggested that combustion sources have become the dominant source of PCNs in the atmosphere in east China.

3.4.3. HCB

According to the result of the PMF analysis, the atmospheric HCB in this study almost entirely originated from the combustion sources. The manufacturing and application of pesticides and chemicals, as well as combustion and industry thermal processes were attributed to be the major sources of HCB in the environment. However, the result of this study indicated that combustion sources are controlling HCB burdens in the atmosphere. This is consistent with the global HCB emission inventory, which suggested that emissions of HCB from combustion-related and thermal processes were much higher than that from pesticides and chemicals production and application (Bailey, 2001). Similarly, a recently revised HCB release inventory in China also revealed that releases from production and use of consumer goods were overwhelmed by combustion-related and thermal sources (Chen et al., 2019).

4. Conclusion

PCBs, PCNs, and HCB were measured in air samples collected at a regional background site in east China from August 2012 to August 2015. PAHs were also analyzed as an indicator of combustion sources. PCBs were dominated by tri-CBs and tetra-CBs, followed by penta-CBs. The tri- and tetra-homologues were enriched in air samples, constituting over 80% of Σ PCNs. Seasonal characteristics with high levels in winter and low levels in summer were observed for PCNs and HCB, which might be attributed to the influence of long-range transport. PCBs were also at a slightly high levels in winter. PCBs displayed weak correlations with PAHs, indicating the less influence of combustion sources. The significant correlations between PCNs, HCB and PAHs suggested the common sources such as combustion or thermal industrial process emissions. According to the source apportionment of PCBs by the PMF model, the legacy of past produced and used commercial PCBs were dominant in the atmospheric PCBs in east China. Both combustion indicators and PMF analysis suggested that PCNs were mainly emitted from combustion sources, while HCB almost entirely originated from combustion sources.

Declaration of competing interest

The authors declare that they have no conflict of interest.

CRediT authorship contribution statement

Shuduan Mao: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. **Gan Zhang:** Conceptualization, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Jun Li:** Writing - review & editing, Supervision. **Xiaofei Geng:** Validation, Data curation. **Jiaqi Wang:** Investigation, Resources. **Shizhen Zhao:** Formal analysis. **Zhineng Cheng:** Resources, Data curation. **Yue Xu:** Writing - review & editing. **Qilu Li:** Writing - review & editing. **Yan Wang:** Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2020.114267>.

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