



# One-year characterization of organic aerosol markers in urban Beijing: Seasonal variation and spatiotemporal comparison

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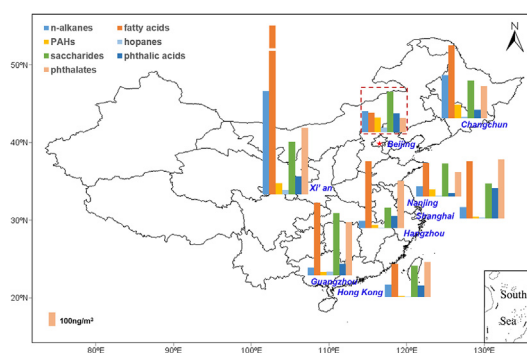
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## HIGHLIGHTS

- The levels of OA markers are 1.3–43.2 times higher in winter than in summer.
- Anthropogenic sources prevail in urban Beijing, especially in winter.
- The concentrations of OA markers are generally higher in northern China.
- The emission controls significantly alleviate the primary OA pollution.
- A long-term and geographical comparison of OA markers are provided.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Organic aerosol (OA) is a major component of fine particulate matter (PM); however, only 10%–30% of OA have been identified as individual compounds, and some are used as markers to trace the sources and formation mechanisms of OA. The temporal and spatial coverage of these OA markers nonetheless remain inadequately characterized. This study presents a year-long measurement of 92 organic markers in PM<sub>2.5</sub> samples collected at an urban site in Beijing from 2014 to 2015. Saccharides were the most abundant (340.1 ng m<sup>-3</sup>) species detected, followed by phthalic acids (283.4 ng m<sup>-3</sup>). In summer, high proportions (8%–24%) of phthalic acids, n-alkanes, fatty acids, and n-alcohols indicate dominant contributions of biogenic emission and atmospheric oxidation to OA in Beijing. In winter, when anthropogenic sources prevail, saccharides, polycyclic aromatic hydrocarbons, and hopanes are more prominent (4%–25%). The spatial distributions of these OA markers in China show higher concentrations in northern cities (mainly from coal combustion and biomass burning) than in southern cities (mainly from vehicular emission). The inter-annual variations of OA markers, except for hopanes, from 2001 to 2015 suggest significant alleviation of the primary OA pollution in Beijing, with an average reduction of 35%–89% compared with those before 2008. The diagnostic ratio analyses between OA markers indicate that contributions from coal combustion and biomass burning decreased, whereas those from vehicular emission

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increased. Increasingly large vehicle fleets have increased hopane concentrations since 2008, but the levels were 35% lower in 2015 than those in 2010–2011 because of the tightening of emission controls for vehicles. This study provides a long-term and geographical comparison (from Beijing to other locations in China and beyond) of OA markers, demonstrating the temporal and spatial variations in primary OA, and calls for more studies on secondary OA.

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## 1. Introduction

Haze pollution has become one of the most pressing environmental concerns in China in recent decades, because of its adverse effects on air quality and human health (Matus et al., 2011; Hu et al., 2015; Lin et al., 2016; Cohen et al., 2017), as well as potential implications for regional and global climates (Poschl, 2005; Wu et al., 2005; Jimenez et al., 2009). China's haze pollution is characterized by elevated concentrations of fine particulate matter (PM<sub>2.5</sub>, particles with an aerodynamic diameter of <2.5 μm) and occurs in all seasons (albeit most frequently and severely in winter), particularly in the North China Plain (NCP) (Fu et al., 2014; Long et al., 2016; An et al., 2019). Investigating the chemical composition, sources, and atmospheric evolution of PM<sub>2.5</sub> is therefore crucial for the mitigation of haze pollution.

Urban PM<sub>2.5</sub> is composed of a highly complex mixture of inorganic and organic aerosol (OA), with the latter constituting as much as 50% or more of the total PM<sub>2.5</sub> mass during haze events (Huang et al., 2014; Elser et al., 2016). The chemical composition, sources, and formation of OA are poorly understood compared with those of inorganic aerosol (Sun et al., 2016; Xu et al., 2016; Huang et al., 2019), largely due to a large chemical space with respect to functional groups, polarity, molecular weight, and structure (Jimenez et al., 2009; Nozière et al., 2015). In many environments, only 10%–30% of the OA mass has been identified as specific compounds, despite the use of sophisticated analytical techniques (Hoffmann et al., 2011). However, these identified organic components, especially the organic markers, are useful for investigating the sources, formation, and transformation of OA. For example, polycyclic aromatic hydrocarbons (PAHs), levoglucosan, hopanes, and organic acids are frequently used to apportion the sources of OA. Several major sources of PM<sub>2.5</sub> in China have been identified, including coal combustion, biomass burning, vehicular emission, cooking, and secondary formation (Wang and Kawamura, 2005; Hu et al., 2010; Guo et al., 2012; Huang et al., 2014; Tang et al., 2018). Large geographical difference in the emission sources of OA has also been observed (An et al., 2019). During severe pollution events, coal combustion is the main emission source in Beijing, whereas biomass burning is the main contributor in Xi'an (Huang et al., 2014). In addition, the formation and transformation of secondary OA (SOA) involve numerous complex chemical processes (Fuzzi et al., 2015). Certain secondary compounds are unique to specific precursors and reaction pathways. For instance, phthalic acids are formed mainly through the photochemical oxidation of aromatic compounds (Shen et al., 2018) and are considered as anthropogenic markers of SOA (Zhu et al., 2017). Studies have reported high levels of naphthalene in the urban areas of the NCP (Tao et al., 2007; Shen et al., 2018); thus, this light aromatic compound can be a potential precursor of the formation of phthalic acids (Ho et al., 2007).

The investigation of organic markers is essential for improved understanding of the sources and chemical processes of OA. However, the organic proportion in PM<sub>2.5</sub> remains inadequately characterized because of its complexity (Surratt et al., 2008; Huang et al., 2018). The synergistic effects of high emission levels from multiple sources, atmospheric oxidation, and aging processes as well as diverse meteorological conditions further complicate the OA composition. Studies have been conducted to characterize OA markers in Beijing, a typical megacity in the NCP. However, those studies focused on either limited classes of OA species in different seasons or on a variety of OA species in a single season, thus limiting our understanding in the variation of OA markers

in chemical space and temporal coverage. For example, 16 PM<sub>2.5</sub>-bound PAHs were measured to investigate their characteristics and potential sources during the summer and winter of 2014, and results showed that the concentrations in winter largely exceeded those in summer, mainly because of the residential heating in wintertime Beijing (Zhang et al., 2017). Saccharides and n-alkanes were also measured in a year-long study in Beijing, and fossil fuel combustion was found to be the main source in the heating season (Kang et al., 2018). Guo et al. (2013) and Liu et al. (2016) analyzed a series of primary OA markers in Beijing and found dominant contribution from vehicular emissions in summer and coal combustion in winter. A large portion of SOA contributing to OA was also highlighted during summer (Guo et al., 2012) and during severe pollution events in winter (Huang et al., 2014). Despite advances made over the past decades, comprehensive investigation of the OA chemical compositions, emission sources, and atmospheric processes, which vary significantly by season, is required to identify major sources and to encompass both clean and polluted periods.

In this study, one-year PM<sub>2.5</sub> samples were collected in urban Beijing from winter 2014 to winter 2015. A series of OA markers, including n-alkanes, fatty acids, n-alcohols, PAHs, hopanes, saccharides, phthalates, and phthalic acids were quantified. The main objectives were to investigate the chemical characteristics and seasonal variations of these organic compounds and to identify their potential sources. Moreover, results from this study were compared with those of studies from different years and locations to gain insights into the inter-annual variations and spatial distributions of primary and secondary OA in China.

## 2. Materials and methods

### 2.1. Sample collection

The PM<sub>2.5</sub> samples were collected on the rooftop of a building located in Haidian district (40.0°N, 116.3°E), a typical urban location in Beijing. The samples were collected every three days from December 2014 to December 2015, and a total of 112 samples were obtained. The period from March 15 to May 31, 2015, was designated as spring (SP-15,  $n = 20$ ), from June 1 to August 31, 2015, was designated as summer (SU-15,  $n = 30$ ), September 1 to November 14, 2015, was designated as autumn (AU-15,  $n = 25$ ), and December 27, 2014, to March 14, 2015, and November 15 to December 18, 2015, were designated as winter (WI-14 and WI-15,  $n = 37$ ) based on meteorological characteristics and the typical residential heating periods. The samples were collected on Whatman quartz fiber filters (20.3 cm × 25.4 cm, Whatman QM/A, Clifton, NJ, USA) over a period of 24 h using a high-volume air sampler (TE-6070 MFC, Tisch Inc., Cleveland, OH, USA) at 1.0 m<sup>3</sup> min<sup>-1</sup>. After sampling, the filter was wrapped in aluminum foil, sealed in a polyethylene bag, and stored at -20 °C until analysis.

### 2.2. Sample preparation and analysis

A total of 92 organic compounds were identified and quantified in the PM<sub>2.5</sub> samples, including 14 PAHs, 8 hopanes, 19 n-alkanes, 22 fatty acids, 11 n-alcohols, 10 saccharides, 5 phthalates, and 3 (*o*-, *m*-, *p*-) phthalic acids (Table S1). Details of the chemical analysis are described elsewhere (Simoneit, 2004; Wang and Kawamura, 2005). In brief, a quarter (17.3 cm<sup>2</sup>) of a 47-mm punch filter was extracted

ultrasonically with a dichloromethane/methanol mixture ( $v/v = 2:1$ ) for 15 min three times. The extracts were purified by quartz wool packed in a Pasteur pipette and then concentrated to near dryness under a gentle stream of nitrogen. After the addition of 60  $\mu\text{L}$  of *N,O*-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) with trimethylsilyl chloride and pyridine, the target compounds were derivatized at 70  $^{\circ}\text{C}$  for 3 h. An Agilent 7890 gas chromatograph (GC) coupled to an Agilent 5975 mass spectrometer (MS) in a scan mode ( $m/z$  40–500) with electron impact ionization (70 eV) was used to measure the targeted compounds. GC separation was achieved using a DB-5MS capillary column (30 m  $\times$  0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness, J&W Scientific).

### 2.3. Quality control

The field blank samples were collected and analyzed, and one procedure blank was run for every 10 samples. Real ambient samples spiked with known quantities of standards were also analyzed to check for potential interference from the sample matrix. The uncertainties (RSDs) of solvent extraction are  $<10\%$  for the measured organic compounds. The recovery was calculated based on the response signals of the standards and the quantities spiked onto the blank filters. The average recoveries of all standards were  $\geq 80\%$ , except for *o*-phthalic acid (approximately 70%). The repeatability and reproducibility of the analysis were evaluated by repeating the measurements for a mixture of standards (1000  $\text{ng mL}^{-1}$ ) spiked on prebaked quartz fiber filters. Good repeatability and reproducibility were achieved with RSDs  $<15\%$ . The method detection limits were 0.04–0.1  $\text{ng m}^{-3}$  for nonpolar compounds and 0.06–0.2  $\text{ng m}^{-3}$  for polar compounds.

## 3. Results and discussion

### 3.1. Overview of organic markers and seasonal variations

Fig. 1 illustrates the seasonal variations of the measured OA markers and their fractional contributions, together with the trace gases ( $\text{SO}_2$ ,  $\text{O}_3$ ,  $\text{NO}_2$ , and  $\text{CO}$ ). The statistics of these data are summarized in the Supporting Information (SI), Table S1. The total concentrations of these OA markers ranged from 4.4  $\text{ng m}^{-3}$  to 8.4  $\mu\text{g m}^{-3}$ , with an average of 1.3  $\mu\text{g m}^{-3}$ , accounting for 1.7% of the  $\text{PM}_{2.5}$  mass. The temporal pattern of the total OA markers was consistent with that of  $\text{PM}_{2.5}$  mass, with a Spearman correlation coefficient of 0.90 ( $p < 0.005$ ). For annual averages, saccharides were the most abundant class, contributing to 26.3% of the total quantified organic mass, followed by phthalic acids (22.0%), *n*-alkanes (13.5%), fatty acids (12.7%), PAHs (9.5%), phthalates (9.1%), *n*-alcohols (4.6%), and hopanes (2.0%). From a seasonal perspective (Fig. 1a), saccharides (31%–34%) were the most abundant in spring and autumn when vegetation was blossoming and withering, respectively. Phthalic acids (24%) were the most abundant in summer, indicating a strong influence by photochemical reactions as indicated by the high  $\text{O}_3$  concentrations (average 95.3  $\mu\text{g m}^{-3}$ ). A significantly higher proportion of PAHs in winter (17%) than that in summer (1%) was consistent with the pattern for sulfur dioxide ( $\text{SO}_2$ ), indicating increased coal combustion for residential heating in Beijing and the surrounding areas in winter. Despite the large variations, similar seasonal differences in concentration occurred among individual organic classes (Fig. S1), with the lowest concentrations in summer and highest concentrations in winter (winter-to-summer ratio, WI/SU = 1.3–43.2). Compared with the WI/SU ratios of saccharides and hopanes (WI/SU = 3.9–5.3), those of PAHs were much higher (WI/SU = 31.5–42.8). However, relatively small seasonal variations (WI/SU =

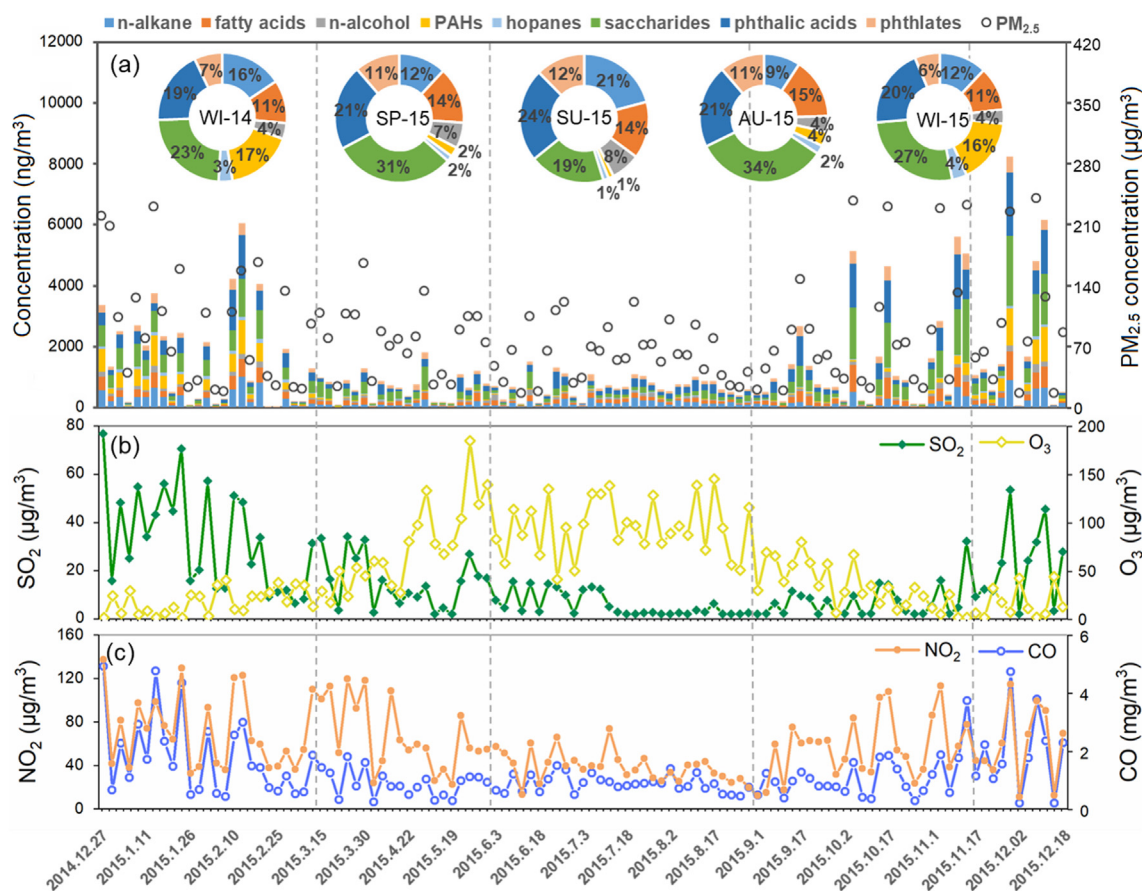


Fig. 1. Seasonal variations of the measured OA markers and their fractional contribution and  $\text{PM}_{2.5}$  concentration (a), together with  $\text{SO}_2$  and  $\text{O}_3$  (b),  $\text{NO}_2$  and  $\text{CO}$  (c) in Beijing.

1.3–2.4) were observed for phthalic acids, n-alkanes, phthalates, fatty acids, and n-alcohols. The concentrations of PAHs and hopanes (with average values of 317.1 and 56.3 ng m<sup>-3</sup>, respectively) were higher in winter than in summer (9.1 and 9.5 ng m<sup>-3</sup>, respectively) ( $p < 0.001$ ) due to increased emissions from fossil fuel combustion in winter (Saha et al., 2012; Wang et al., 2017). Transport of saccharides from biomass burning in the surrounding rural areas of Beijing (Li et al., 2019) could be the reason for higher saccharide concentrations in winter (466.6 ng m<sup>-3</sup>) than those in summer (132.0 ng m<sup>-3</sup>) ( $p = 0.001$ ). The average concentrations of fatty acids and n-alcohols in summer (96.9 and 51.5 ng m<sup>-3</sup>, respectively) were comparable to those in winter (207.6 and 72.3 ng m<sup>-3</sup>, respectively) ( $p = 0.163$ ), which might be due to relatively stable emissions, such as cooking emissions for fatty acids and plant wax for n-alcohols.

### 3.2. n-Alkanes, fatty acids, and n-alcohols

Both anthropogenic and biogenic sources can produce n-alkanes. Specifically, fossil fuel combustion is a major source of low-molecular-weight (LMW) n-alkanes ( $\leq C_{26}$ ) (Vasconcellos et al., 2011), and terrestrial higher plant wax is the main source of high-molecular-weight (HMW) n-alkanes ( $> C_{26}$ ) (Kawamura et al., 2003). Biomass burning has also been reported to emit HMW n-alkanes (Schauer et al., 2001; Yadav et al., 2013). The molecular distributions of n-alkanes ( $C_{18}$ – $C_{36}$ ) in Beijing are shown in Fig. S2a. The predominant odd-to-even carbon numbers and distinct unimodal patterns were observed in all seasons. In particular, the LMW n-alkanes were relatively abundant in winter, dominated by  $C_{23}$  (31.3 ng m<sup>-3</sup>) and  $C_{25}$  (27.3 ng m<sup>-3</sup>); the concentrations of the HMW n-alkanes were elevated in summer, with a greater abundance of  $C_{32}$  (19.6 ng m<sup>-3</sup>) and  $C_{34}$  (19.7 ng m<sup>-3</sup>). The enhancement of the LMW n-alkanes in winter suggests elevated contribution from fossil fuel combustion in winter, whereas biogenic sources are likely the major contributor to n-alkanes in summer because of the dominance of HMW n-alkanes.

The carbon preference index (CPI) of n-alkanes, calculated as  $CPI = 2 \sum C_{19}-C_{35} / (\sum C_{18}-C_{34} + \sum C_{20}-C_{36})$ , is also an useful indicator of emission sources. The annual CPI average of 1.2 (range 0.2–2.8) is within the range of averages reported by studies in other Chinese cities (1.1–2.0) (Wang and Kawamura, 2005; Ho et al., 2011; Huang et al., 2012; Wang et al., 2016; Hong et al., 2017; Zhang et al., 2018). The average CPI value in winter was 1.1, which is close to 1.0 (indicating fossil fuel combustion) and higher than the values in spring (1.6), summer (1.2), and autumn (1.3). In addition, the wintertime CPI in this study was higher than the values for southern cities in China ( $> 1.3$ ) (Wang and Kawamura, 2005; Huang et al., 2012; Feng et al., 2015; Hong et al., 2017), further reflecting the large contribution from coal combustion in wintertime Beijing. The average contributions of plant wax-related n-alkanes (Wax%) show similar seasonal variations to those of CPI, with the minimum value in winter. The annual average (13.7%) of Wax% was lower than the values observed in other southern cities such as Guangzhou (14.7%) (Wang et al., 2016), Nanjing (24.4%) (Wang and Kawamura, 2005), and Shanghai (47.5%) (Hong et al., 2017) due to the lower temperatures and vegetation coverage in Beijing compared with southern cities.

LMW fatty acids ( $< C_{20}$ ) are closely related to biomass burning, fossil fuel combustion, and meat cooking; HMW fatty acids ( $\geq C_{20}$ ) are emitted directly from the surface of higher terrestrial plants (Simoneit, 2004; Fu et al., 2012a; Boreddy et al., 2018). The molecular distributions of fatty acids ( $C_{12}$ – $C_{32}$ ) measured in Beijing were characterized by strong predominance of even carbon numbers and dominance of LMW fatty acids (predominance with  $C_{max}$  at  $C_{16:0}$  and  $C_{18:0}$ , note that the first figure is C-number and the second is the number of double bonds) in all seasons (Fig. S2b), which resembles the distributions reported in other urban areas of Guangzhou, Shenzhen, and Hong Kong (Ho et al., 2011; Huang et al., 2012). The dominance of LMW fatty acids highlights the contributions from anthropogenic sources in urban areas. This is

largely different from the distributions of fatty acids observed in mountainous (Fu et al., 2008) and remote marine areas (Kawamura et al., 2003) with a bimodal pattern of  $C_{max}$  at  $C_{16:0}$  and  $C_{24:0}$  due to large biogenic emissions. In addition, the HMW n-alcohols ( $C_{22}$ – $C_{32}$ ), mainly  $C_{28}$  (13.8 ng m<sup>-3</sup>) and  $C_{30}$  (18.0 ng m<sup>-3</sup>), which are typical biomarkers emitted from terrestrial higher plant wax (Fu et al., 2008; Boreddy et al., 2018), were also detected in this study (Fig. S2c).

The fatty acid ratio  $C_{18:0}/C_{16:0}$  can be used as a qualitative measure for source identification (Rogge et al., 2006).  $C_{18:0}/C_{16:0}$  ratios lower than 0.25 indicate vegetation combustion, wood smoke, and waxy leaf emissions; ratios between 0.25 and 0.50 indicate fossil fuel combustion; and ratios between 0.50 and 1.00 indicate cooking emissions and road dust (Ren et al., 2016). In this study, the range of the  $C_{18:0}/C_{16:0}$  ratio was 0.62–0.94 (average 0.76) in spring, 0.50–1.24 (0.81) in summer, 0.59–0.99 (0.74) in autumn, and 0.55–0.90 (0.70) in winter. Although the average ratio of  $C_{18:0}/C_{16:0}$  was the lowest in winter compared with those in other seasons, the ranges in all the seasons were between 0.5 and 1.0, suggesting that the main sources of fatty acids were cooking emissions and road dust. In addition to saturated fatty acids, an unsaturated fatty acid ( $C_{18:1}$ ) was also detected. Unsaturated fatty acids are notable precursors of SOA because of their rapid oxidation and aging (Tyagi et al., 2016). Therefore, the  $C_{18:1}/C_{18:0}$  ratio has been widely used to estimate the reactivity and aging of OA in the atmosphere (Bendle et al., 2007; Boreddy et al., 2018). In this study, the average ratios of  $C_{18:1}/C_{18:0}$  in spring (0.08) and summer (0.06) were much lower than those in autumn (0.12) and winter (0.17), suggesting that unsaturated fatty acids were depleted by enhanced aging degree due to high ambient temperature and radiation in spring and summer. However, cooking, biomass burning, and vehicular emissions may contribute greatly to unsaturated fatty acids during autumn and winter.

### 3.3. Saccharides, hopanes, phthalic acids, and phthalates

Seasonal molecular distributions of saccharides in Beijing are displayed in Fig. S3a. Anhydrosugars, particularly levoglucosan, are predominant pyrolysis products of cellulose and are widely used as markers of biomass burning (Kang et al., 2018; Wang et al., 2018). Levoglucosan was the most abundant saccharide measured in this study, with an annual average concentration of 208.3 ng m<sup>-3</sup>, which is approximately 8–63 times higher than those of other saccharide species. Much higher proportions of levoglucosan in saccharides were observed in autumn and winter (78.6%–84.8%) than in spring and summer (36.8%–38.9%) (Fig. S3b), in line with other studies that showed biomass burning for residential cooking and heating to be a notable source of saccharides in Beijing and its surrounding areas (Zheng et al., 2017). Sugar alcohols can be found in the degradation products of fungal spores, algae, and soil biota (Caseiro et al., 2007; Burshtein et al., 2011) and are widespread in branches and leaves (Yan et al., 2019). Arabitol was the dominant sugar alcohol, with an annual average of 8.5 ng m<sup>-3</sup>, followed by mannitol (7.0 ng m<sup>-3</sup>) and inositol (3.3 ng m<sup>-3</sup>). The concentrations of sugar alcohols were higher in autumn (24.3 ng m<sup>-3</sup>) than in other seasons (15.3–19.8 ng m<sup>-3</sup>), probably due to enhanced vegetation decomposition and subsequently increased fungal population. Yang et al. (2012) found that the amount of arabitol derived from fungal spores increased greatly in PM<sub>2.5</sub> as a result of biomass burning. A close correlation between sugar alcohols and levoglucosan ( $r > 0.60$ ,  $p < 0.001$ ) in autumn and winter was also found in this study, suggesting that sugar alcohols in fine particles may also originate from biomass burning for heating or cooking in Beijing and surrounding areas, consistent with another study (Kang et al., 2018). Primary sugars, including glucose, fructose, sucrose, and trehalose, are also reportedly emitted from plant materials, including pollen, fruits, leaves, and their fragments (Fu et al., 2012b), as well as biomass burning emission (Nolte et al., 2001). Glucose was the dominant primary sugar during four seasons, with an annual average of 27.8 ng m<sup>-3</sup>. In addition, these four primary sugars showed similar seasonal variations, with

higher concentrations in spring (average  $82.2 \text{ ng m}^{-3}$ ) and autumn ( $82.5 \text{ ng m}^{-3}$ ) than those in summer ( $53.9 \text{ ng m}^{-3}$ ) and winter ( $57.6 \text{ ng m}^{-3}$ ), likely due to the vegetation blossoms in spring and plant decomposition in autumn (Burshtein et al., 2011). Pollen detritus could also contribute to the enhancement of primary sugars in spring (Yttri et al., 2007). Therefore, besides biomass burning, biogenic emission may also partly contribute to the increased concentrations of primary sugars during spring and autumn.

Hopanes are detected in vehicle exhausts from unburned lubricating oil residues and are therefore widely used as markers of traffic emissions (Feng et al., 2015; Han et al., 2018). The concentrations of hopanes were 4–6 times higher in winter than in other seasons. Among the detected hopanes,  $17\alpha(\text{H}),21\beta(\text{H})$ -30-norhopane ( $\text{C}_{29}\alpha\beta$ ) was the most abundant, with an annual average concentration of  $7.6 \text{ ng m}^{-3}$ , and  $17\beta(\text{H}),21\alpha(\text{H})$ -30-norhopane ( $\text{C}_{29}\beta\alpha$ ,  $5.5 \text{ ng m}^{-3}$ ) was the second most abundant. The seasonal average molecular distributions of hopanes in all seasons (Fig. S4) are similar to the source profiles of hopanes in vehicular emissions (Saha et al., 2017), indicating that vehicular emissions in Beijing are a major source of hopanes throughout the year. However, a higher abundance of  $\beta$  isomers (i.e.,  $\text{C}_{29}\beta\alpha$  and  $\text{C}_{30}\beta\alpha$ ) in coal combustion emissions than in vehicular emissions has been reported (Saha et al., 2012). Higher contributions of  $\text{C}_{29}\beta\alpha$  (20.9%) and  $\text{C}_{30}\beta\alpha$  (9.9%) to hopanes were also observed in this study. Therefore, the contribution from coal combustion to hopanes should be considered in areas with coal as a residential energy source.

Three phthalic acids (*o*-, *m*-, and *p*- isomer) were detected; *o*-isomer was the most abundant, with an annual average value of  $150.2 \text{ ng m}^{-3}$ , *p*-isomer ( $123.8 \text{ ng m}^{-3}$ ) was less abundant, and *m*-isomer ( $7.1 \text{ ng m}^{-3}$ ) was the least abundant. The isomer distribution was similar to that measured in many cities (Ho et al., 2007, 2011), but was different from that in Chengdu, central China, where *p*-isomer was the most abundant phthalic acid (Li et al., 2015), due to the differences in their specific sources. It is reported that *p*-phthalic acid is mainly from primary sources, including incomplete combustion processes and off-gassing of plasticizers from plastics (Fu et al., 2010; Kawamura and Pavuluri, 2010), while *o*-phthalic acid can be formed by secondary reactions of aromatic compounds (Kawamura and Yasui, 2005; Zhang et al.,

2010). For example, naphthalene and benzo[*a*]anthracene, which are reported to be abundant in Beijing (Lin et al., 2015; Gao and Ji, 2018), are precursors of phthalic acids (Ho et al., 2007). In this study, a strong correlation ( $r^2 = 0.60$ ,  $p < 0.05$ ) between *o*-phthalic acid and benzo[*a*]anthracene was observed in summer, suggesting the formation of *o*-phthalic acid from the oxidation of benzo[*a*]anthracene or other PAHs with similar emission sources.

High concentrations of phthalates were observed in autumn (average  $169.1 \text{ ng m}^{-3}$ ) and winter ( $128.7 \text{ ng m}^{-3}$ ) because increased temperature promotes the evaporation of semi-volatile phthalates from indoor materials, such as wallpaper, flooring, food packages, plastic film, and electronics (Wang et al., 2015b). However, the concentrations of phthalates measured in this study (annual average of  $117.7 \text{ ng m}^{-3}$ ) were much lower than those in indoor environments (range  $774.6$ – $2050.7 \text{ ng m}^{-3}$ ) (Song et al., 2015; Sampath et al., 2017), suggesting that phthalates in the atmosphere might be transported from indoor environments, as reported in other studies (Shi et al., 2012; Kim et al., 2013). Among the phthalates measured, bis (2-ethylhexyl) phthalate and di-*n*-butyl phthalate were the prominent species (annual averages of  $69.1$  and  $39.4 \text{ ng m}^{-3}$ , respectively) during the whole year because of their widespread usage as additives in polyvinyl chlorides (PVCs) and in the manufacturing of various polymers (Guo and Kannan, 2011; Li et al., 2018).

### 3.4. Spatial distribution and inter-annual variation

Fig. 2 shows the spatial distributions of annual concentrations of n-alkanes, fatty acids, PAHs, hopanes, saccharides, phthalic acids, and phthalates from this study and the literature (Wang and Kawamura, 2005; Feng et al., 2006; Wang et al., 2006; Ho et al., 2007; Wan and Yu, 2007; Wang et al., 2007; He et al., 2014; Feng et al., 2015; Wang et al., 2015a; Li et al., 2016; Wang et al., 2016; Hong et al., 2017; Wang et al., 2017; Wang et al., 2018). The concentrations of these organic markers in China are generally higher in northern cities than in southern cities, reflecting more severe particulate air pollution in northern China. The differences in spatial distributions among these organic markers suggest potential differences in emission sources, formation

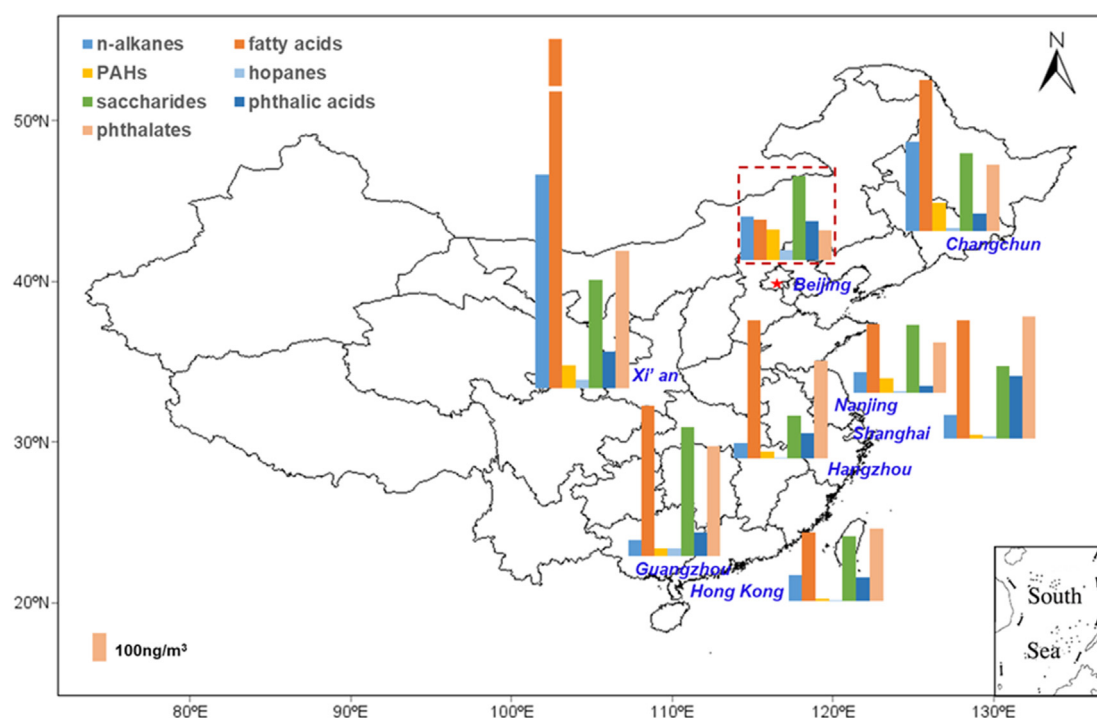


Fig. 2. Spatial distribution of OA markers in major cities of China.

mechanisms, or influencing factors. For n-alkanes, the average concentrations were approximately 4–9 times higher in Xi'an ( $864.0 \text{ ng m}^{-3}$ ) and Changchun ( $353.0 \text{ ng m}^{-3}$ ) than in other cities. The average concentrations of fatty acids decreased in the order of Xi'an ( $1663.0 \text{ ng m}^{-3}$ ) > Guangzhou, Changchun, Hangzhou, and Shanghai ( $463.0\text{--}740.0 \text{ ng m}^{-3}$ ) > Nanjing and Hong Kong ( $274.0\text{--}277.0 \text{ ng m}^{-3}$ ) > Beijing ( $164.3 \text{ ng m}^{-3}$ ) (Table S2). The abundant fatty acids in Xi'an may be partly attributed to the high level of suspended soil dust coated with organic matter (Wang et al., 2006). The spatial distribution of phthalates is largely similar to that of fatty acids, with the highest level in Xi'an ( $554.0 \text{ ng m}^{-3}$ ) and the lowest in Beijing ( $117.7 \text{ ng m}^{-3}$ ). The spatial distributions of hopanes and saccharides are also observed to be similar despite their different origins (i.e., hopanes from fossil fuel combustion versus saccharides from biomass burning). Specifically, the concentrations of hopanes and saccharides were higher in Guangzhou ( $30.9$  and  $514.0 \text{ ng m}^{-3}$ , respectively) and Xi'an ( $31.9$  and  $463.2 \text{ ng m}^{-3}$ , respectively) and lower in Hangzhou ( $2.8$  and  $171.0 \text{ ng m}^{-3}$ , respectively) and Hong Kong ( $2.4$  and  $258.0 \text{ ng m}^{-3}$ , respectively). This observation indicates that both fossil fuel combustion and biomass burning are influential in Guangzhou and Xi'an, two cities with different topographies and landforms. The concentrations of PAHs and phthalic acids, however, exhibited different spatial distributions, with the highest values in Beijing ( $123.2$  and  $157.3 \text{ ng m}^{-3}$ ), indicating increased emissions of PAHs from coal combustion and the formation of phthalic acids from the oxidation of PAHs.

Fig. 3 shows the inter-annual variations of these organic markers measured in Beijing during summer and winter from 2001 to 2015 in this study and in related studies (He et al., 2006; Huang et al., 2006; Wang et al., 2006; Ho et al., 2007; Wang et al., 2009; Zhou et al., 2009; Guo et al., 2013; Li et al., 2013b; Lin et al., 2015; Yan et al., 2015; Zhang et al., 2015; Liang et al., 2016; Yang et al., 2016; Kang et al., 2018; Ren et al., 2018; Zhao et al., 2018). Most of the organic markers exhibit low concentrations in summer and high concentrations in winter, except for phthalates, saccharides, and fatty acids. The high concentrations of phthalates in summer in 2003–2004 are likely due to extensive use of plastic products that emit phthalates at high temperatures (Sampath et al., 2017; Li et al., 2018). The field burning of crop residues occurred frequently from July to August in 2003–2004 and

released copious pollutants into the atmosphere (Li et al., 2007), leading to high concentrations of saccharides. The origin of fatty acids is ubiquitous from biogenic sources (Simoneit and Mazurek, 1989). Therefore, high concentrations of fatty acids were recorded in summer from 2003 to 2004, probably as a result of increased terrestrial biogenic activity. From 2001 to 2015, the lowest summertime concentrations of these compounds were observed during the 2008 Beijing Olympic Games, and the lowest wintertime concentrations were observed during the Asia-Pacific Economic Cooperation summit in 2014. During these two events, aggressive and strict air pollution control measures were implemented in Beijing and its surrounding regions, such as temporary industrial shut-down and the “odd-even vehicular ban” policy. The peak concentrations of n-alkanes, fatty acids, and PAHs occurred between 2003 and 2007, with averages of  $543.9$ ,  $472.0$ , and  $44.0 \text{ ng m}^{-3}$  in summer and  $1299.7$ ,  $463.6$ , and  $1317.0 \text{ ng m}^{-3}$  in winter, respectively (Table S3). The average concentrations of these three compounds after 2008 decreased by 35%–69% in summer and by 45%–66% in winter compared with those before 2008. From 2003 to 2015, the concentration of phthalates decreased by 79% from  $402.0$  to  $86.1 \text{ ng m}^{-3}$  in summer and by 28% from  $178.0$  to  $128.7 \text{ ng m}^{-3}$  in winter because of restrictions on the production and use of phthalates (Wang et al., 2006; Yang et al., 2016; Ren et al., 2018). Similarly, a significant decreasing trend was also observed for saccharides, with an 89% decrease in summer and a 35% decrease in winter, as a result of the implementation of control measures in the field burning of crop residue. By contrast, the average concentrations of hopanes after 2008 were twice as high as those before 2008, closely related to the increases in vehicular fleet numbers at the rate of 20%–25% per year (China Statistical Yearbook, 2011). However, the hopane concentrations in 2015 ( $8.7 \text{ ng m}^{-3}$  in summer and  $56.3 \text{ ng m}^{-3}$  in winter) were lower than those in 2010–2011 ( $17.9$  and  $68.6 \text{ ng m}^{-3}$ ) because of the effective emission controls for vehicles from national standards IV to V (equal to European vehicular emission standards). In addition, higher concentrations of phthalic acids were measured in 2008–2015, within the range of  $25.7\text{--}103.2 \text{ ng m}^{-3}$  in summer and  $43.4\text{--}218.3 \text{ ng m}^{-3}$  in winter, revealing increases of 83% and 13% relative to the values in 2003. The reduction of primary pollutants provides more favorable atmospheric conditions for the formation of secondary pollutants, such as less shielded solar radiation and more abundant oxidants, potentially causing phthalic acid formation to

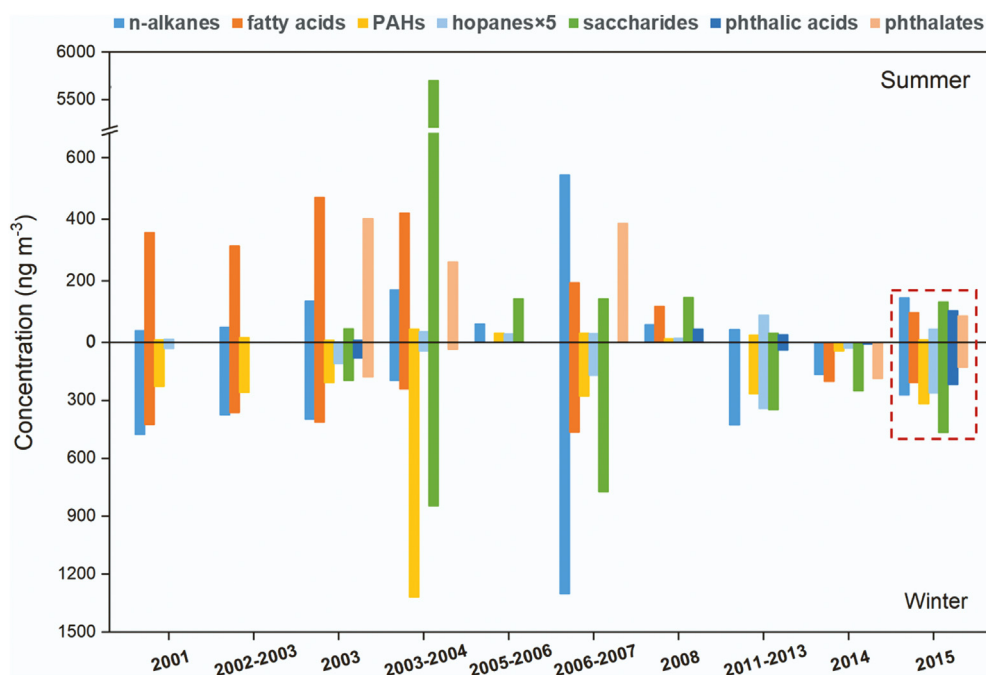


Fig. 3. Inter-annual variation of OA markers in Beijing from 2001 to 2015.

increase, especially in summer. However, the formation of SOA is extremely complicated and is affected by many factors, such as precursors, ambient humidity, and particle acidity (Ziemann and Atkinson, 2012; Kirkby et al., 2016; Shrivastava et al., 2017). Therefore, more efforts are required to evaluate the effects of emission controls on inter-annual variations in SOA formation.

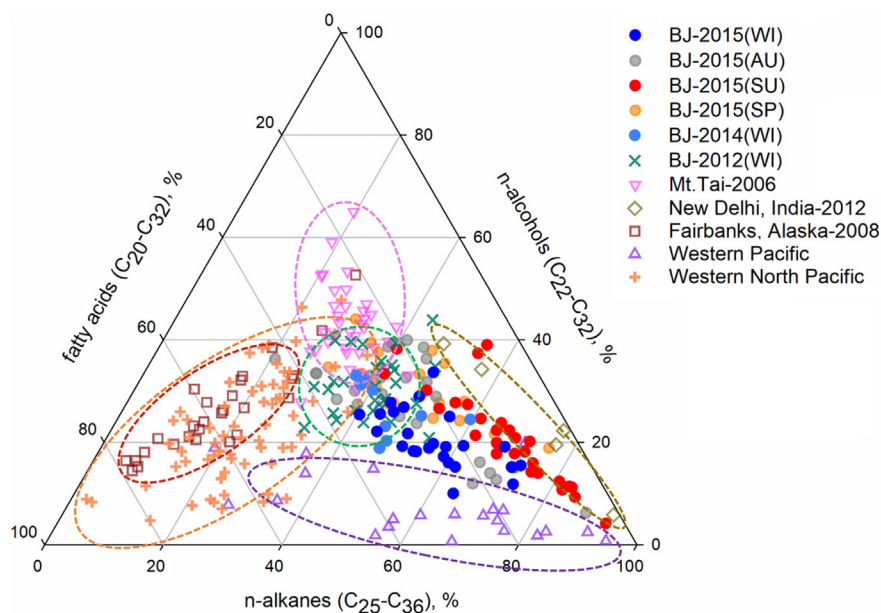
The abundances (%) of n-alkanes ( $C_{25-36}$ ), fatty acids ( $C_{20-32}$ ), and n-alcohols ( $C_{22-32}$ ) relative to the sum of the three terrestrial biomarker classes are plotted in the triangular diagram displayed in Fig. 4. A greater abundance of n-alkanes (40.2%–92.0%) was noted in summer, whereas a greater abundance of fatty acids (11.4%–34.1%) and n-alcohols (8.3%–33.2%) was observed in winter, demonstrating a clear seasonal variation in their component distribution. A possible explanation is the greater effect from biogenic sources on n-alkanes in summer, while more obvious on fatty acids and n-alcohols in winter. Results from this study are also compared with those of studies in different locations. As seen in Fig. 4, the distribution of abundance for the biomarker classes in this study (especially in autumn and winter) overlaps with that in Beijing in the winter of 2012 (Ren et al., 2016) and is also close to the distributions of abundance at the mountainous site affected by biomass burning (Fu et al., 2008), suggesting a contribution from biomass burning. However, the distribution of these three classes of biomarkers in Beijing is different from those in marine regions (Kawamura et al., 2003; Bendle et al., 2007) and other foreign cities (including New Delhi, India and Fairbanks, Alaska) (Kang et al., 2016; Boreddy et al., 2018), implying differences in the sources of terrestrial OA in different regions.

### 3.5. Specific ratios of selected species

The possible sources of PAHs in the atmosphere can be distinguished according to the concentrations of certain species and the characteristic ratios (Akyuz and Cabuk, 2010; Tobiszewski and Namiesnik, 2012; Gao and Ji, 2018). Many studies have used the molecular diagnostic ratios of PAH concentrations to identify petrogenic sources from oil spills and pyrogenic sources from incomplete combustion of fossil fuels (Pies et al., 2008; Katsoyiannis et al., 2011; Lin et al., 2015; Saha et al., 2017). Fig. 5 depicts the seasonal distributions of the four ratios for anthracene/(anthracene + phenanthrene) ( $(\text{Ant}/(\text{Ant} + \text{Phe}))$ ), benz(a)

anthracene/(benz(a)anthracene + chrysene) ( $(\text{BaA}/(\text{BaA} + \text{Chr}))$ ), fluoranthene/(fluoranthene + pyrene) ( $(\text{Fla}/(\text{Fla} + \text{Pyr}))$ ), and indeno (123-cd) pyrene/(indeno (123-cd) pyrene + benzo(ghi) perylene) ( $(\text{IcdP}/(\text{IcdP} + \text{BghiP}))$ ). The ratios in summer and winter are clearly distinct, demonstrating the seasonal difference in the sources of PAHs. The average ratios of  $\text{Ant}/(\text{Ant} + \text{Phe})$ ,  $\text{BaA}/(\text{BaA} + \text{Chr})$ ,  $\text{Fla}/(\text{Fla} + \text{Pyr})$ , and  $\text{IcdP}/(\text{IcdP} + \text{BghiP})$  were 0.35, 0.32, 0.51, and 0.47 in summer and 0.16, 0.47, 0.53, and 0.62 in winter, respectively. Comparing these ratios measured in Beijing with those measured in different source samples (Yunker et al., 2002; Sheesley et al., 2003; He et al., 2008; Yu and Yu, 2011), as shown in Fig. 5 and Table S4, coal combustion, biomass (wood, grass, and straw) burning, and vehicular emissions might exert largely different influences on the PAH concentrations in Beijing in different seasons. The pyrogenic sources (coal combustion and biomass burning) are dominant for PAHs in winter, and petrogenic sources (vehicular emissions) dominate in summer.

The PAH-specific ratios measured in this study agree with those measured in previous years in Beijing (Li et al., 2013b; Lin et al., 2015; Zhang et al., 2017; Song et al., 2019). These results indicate higher contributions to PAHs from vehicular emissions in summer and from coal combustion and biomass burning in winter. However, the ratios of  $\text{BaA}/(\text{BaA} + \text{Chr})$  and  $\text{Fla}/(\text{Fla} + \text{Pyr})$  in 2014–2015 were lower than the ratios before 2014 (Li et al., 2013b; Lin et al., 2015), indicating a reduced contribution from coal combustion and biomass burning and an increased contribution from vehicular emissions. This is consistent with the changes in local energy structure, namely the decreased use of coal and biomass for residential heating (Guo et al., 2013; Tang et al., 2018). Moreover, when compared with the results from other cities, including Xi'an, Hangzhou, Nanjing, and Guangzhou (Wang et al., 2007; Feng et al., 2015; Wang et al., 2016, 2017), the ratios of  $\text{Ant}/(\text{Ant} + \text{Phe})$ ,  $\text{BaA}/(\text{BaA} + \text{Chr})$ ,  $\text{Fla}/(\text{Fla} + \text{Pyr})$ , and  $\text{IcdP}/(\text{IcdP} + \text{BghiP})$  in all cities exhibit similar seasonal variations. Specifically, the summertime ratios are closer to the ratios from petrogenic sources than the wintertime ratios are. Nevertheless, these ratios also exhibit spatial differences. For example, the ratios in Beijing and Xi'an are similar in both summer and winter, and both are similar to the ratios from pyrogenic sources, indicating that coal combustion and biomass burning contribute greatly to PAHs in northern China. By contrast, the ratios in Hangzhou, Nanjing, and Guangzhou are more similar to the ratios



**Fig. 4.** Triangular plot of relative abundance of terrestrial biomarkers: n-alkanes ( $C_{25-36}$ ), fatty acids ( $C_{20-32}$ ), and n-alcohols ( $C_{22-32}$ ) in different seasons in Beijing during 2014 to 2015, Beijing in 2012 (Ren et al., 2016), mountain site (Fu et al., 2008), New Delhi, India (Kang et al., 2016), Fairbanks, Alaska (Boreddy et al., 2018) and marine regions (Kawamura et al., 2003; Bendle et al., 2007).

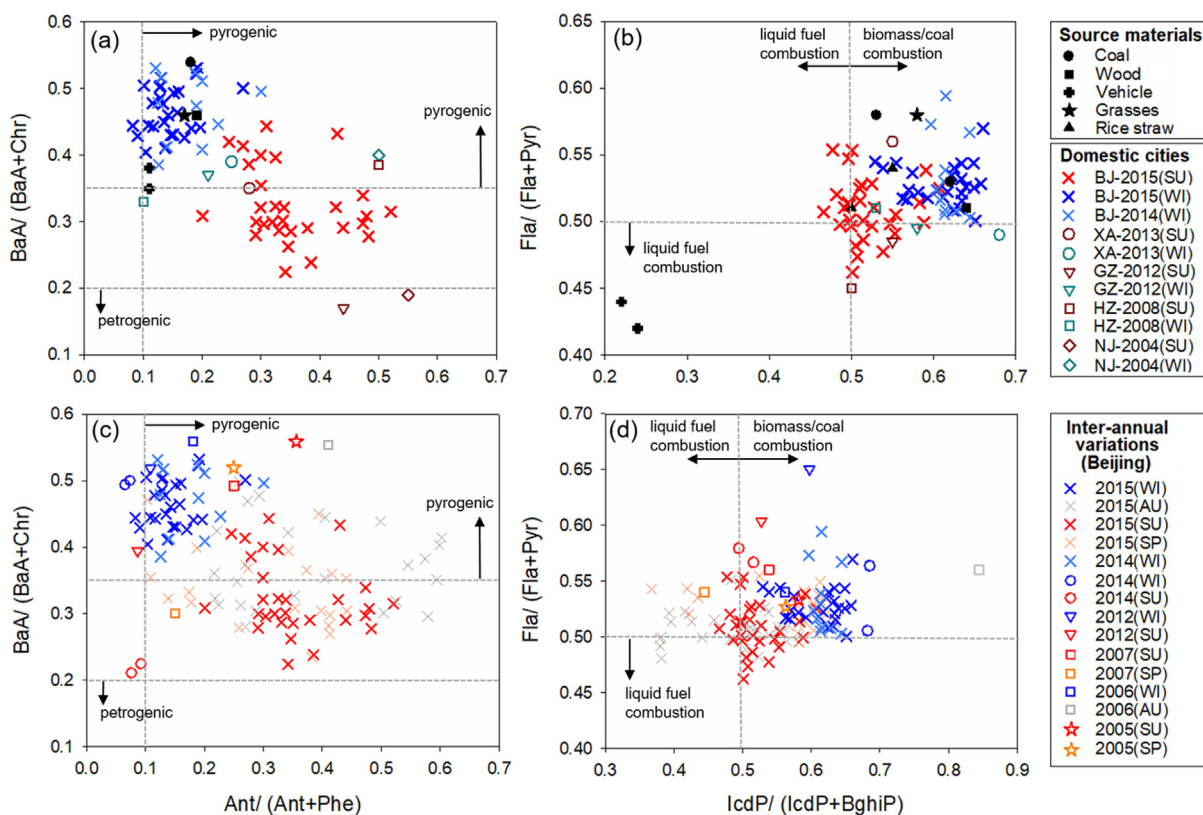


Fig. 5. Spatial distribution and inter-annual variation of Ant/(Ant+Phe), BaA/(BaA + Chr) (a, c) and IcdP/(IcdP+BghiP), Fla/(Fla + Pyr) (b, d) in different seasons.

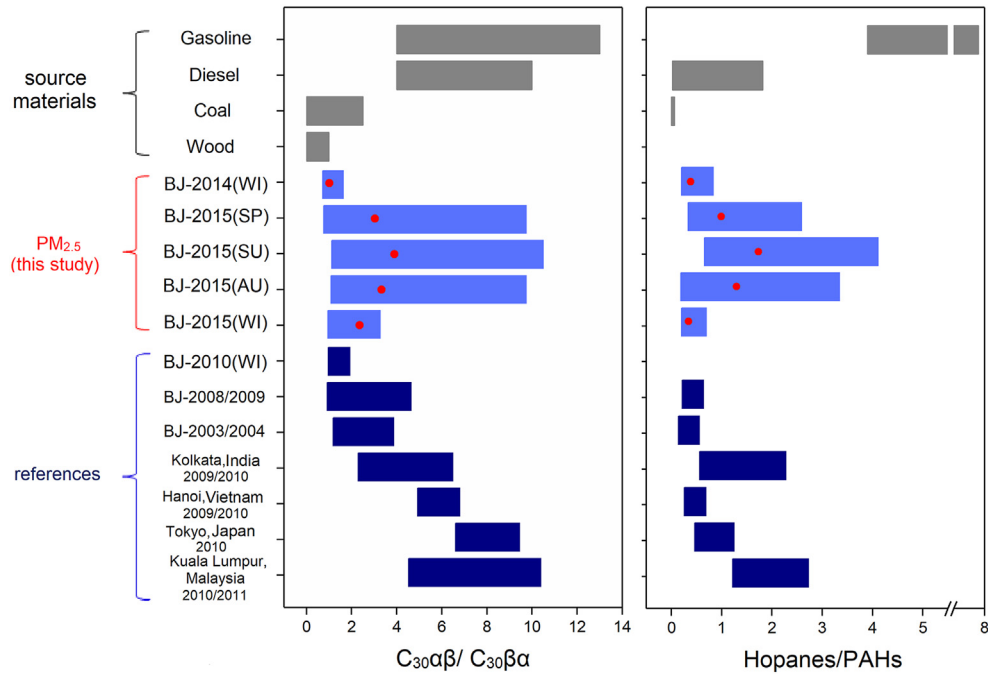
from petrogenic sources in both summer and winter, highlighting the prominent contribution of vehicular emissions to PAHs in southern China.

The ratios of  $C_{30}\alpha\beta/C_{30}\beta\alpha$  and hopanes/PAHs further reveal the relative contributions from coal combustion, wood burning, or vehicular emission (gasoline or diesel) (Saha et al., 2012). Fig. 6 shows the ratios measured in various seasons together with the ratios from other studies and from different source samples (Saha et al., 2012). The ratios of  $C_{30}\alpha\beta/C_{30}\beta\alpha$  in winter are within the range for coal combustion and wood burning, and the ratios of hopanes/PAHs in winter are close to the range for coal combustion. By contrast, the ratios of  $C_{30}\alpha\beta/C_{30}\beta\alpha$  in non-heating seasons overlap mostly with the ratios from diesel and gasoline emissions. These results demonstrate the major contribution to hopanes from coal combustion and wood burning in winter and the large contribution from vehicular emissions in non-heating seasons. Regarding inter-annual variation, the  $C_{30}\alpha\beta/C_{30}\beta\alpha$  ratios in winter 2014–2015 were similar to those measured in winter 2010–2011 (Zhang et al., 2015). However, the annual ratios of  $C_{30}\alpha\beta/C_{30}\beta\alpha$  in 2014–2015 (0.7–10.5) reached the ratios for vehicular emissions and far exceeded those in 2008–2009 (1.2–4.1) (Zhou et al., 2008) and 2003–2004 (0.9–4.7) (Saha et al., 2017), indicating an increasing contribution from vehicular emissions in recent years. Similar conclusions may be drawn from the comparison of hopane/PAH ratios (Fig. 6). Compared with results from other cities (Saha et al., 2017), the  $C_{30}\alpha\beta/C_{30}\beta\alpha$  ratios in this study resemble those in Kolkata, India (2.3–6.5), within the range for coal combustion and vehicular emissions; however, they differ from those in Hanoi, Vietnam; Tokyo, Japan; and Kuala Lumpur, Malaysia (4.9–10.4), which are closer to the range for vehicular emissions.

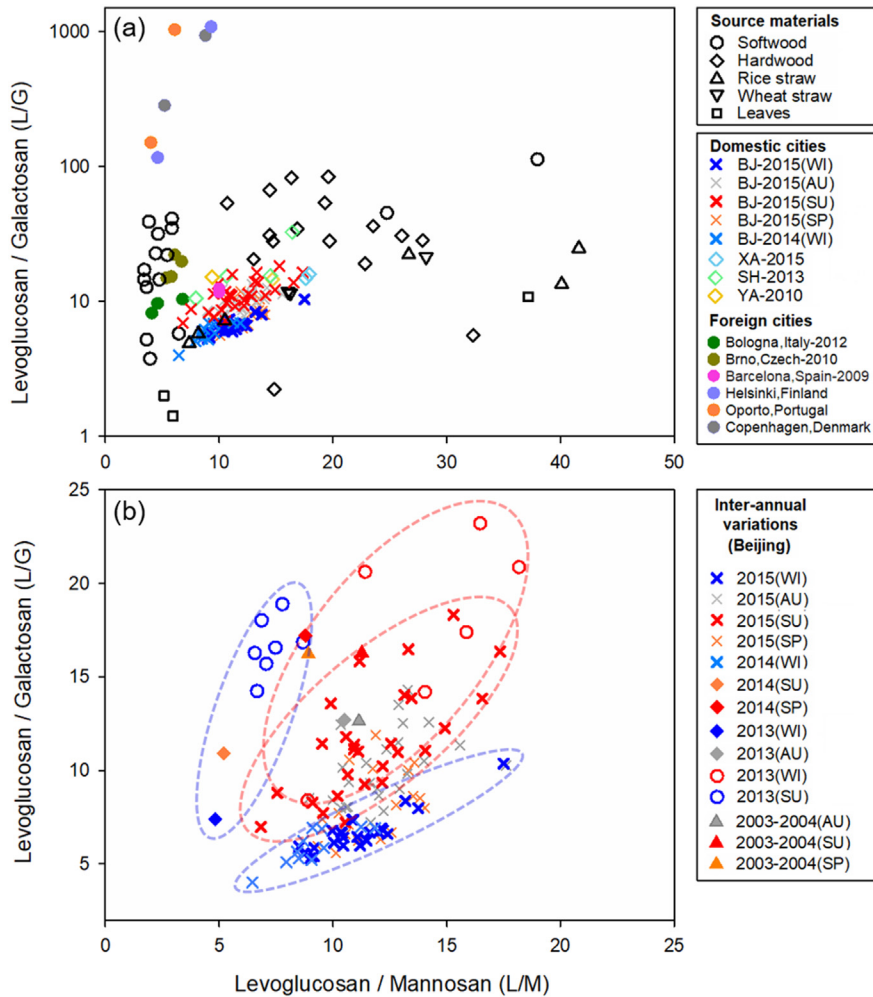
The concentration ratios of levoglucosan to mannosan (L/M) and of levoglucosan to galactosan (L/G) have been used to identify the type of biomass burned, such as softwood, hardwood, crop residues, or leaves. As shown in Fig. 7a, the L/M and L/G ratios ranged from 6.1 to

17.6 (average 11.4) and 4.0 to 18.3 (average 8.9), respectively, which are within the ranges for softwood, hardwood, and crop residue burning. Zhou et al. (2017) reported that maize stalks, wheat straws, and hardwood were often burned in rural areas surrounding Beijing for cooking and heating. Yan et al. (2015) also found that the burning of softwoods and needles contributed to the presence of saccharides in Beijing. Therefore, hardwood, crop residues, and softwood could be the important types of biomass burned in Beijing and the surrounding areas. Nevertheless, the seasonal differences in the L/M and L/G ratios are significant. The wintertime L/M ratios (6.3–17.5) are similar to the summertime L/M ratios (6.8–17.4), but the wintertime L/G ratios (5.3–10.4) are smaller than the summertime L/G ratios (7.0–18.3). The two ratios in winter overlap with the ratios from the burning of rice and wheat straw, suggesting that saccharides are most often produced by crop burning for daily heating and cooking in winter. The inter-annual comparison in Beijing shows that the L/M and L/G ratios in summer 2014–2015 overlap mostly with data in 2003–2004 and 2013–2014 (Yan et al., 2015; Kang et al., 2018). However, in winter 2014–2015, the L/G ratios were lower but the L/M ratios were higher than those in previous years (Yan et al., 2015; Kang et al., 2018). This indicates that crop residue burning was a prevalent source of saccharides in winter 2014–2015, whereas softwood burning was a prevalent source before 2014. In addition, data in Beijing, Xi'an (Wang et al., 2018), Ya'an (Li et al., 2013a), and Shanghai (Du et al., 2015) overlap, indicating that similar types of biomass are burned in these areas. Moreover, the L/G and L/M ratios in Beijing also resemble the ratios in Barcelona, Spain, but largely differ from those in other European cities. In these other cities, including Helsinki, Finland, Oporto, Portugal, Copenhagen, Denmark, and in particular Bologna, Italy (L/M ratio of 5.2 and L/G ratio of 9.4) (Pietrogrande et al., 2014) and Brno, the Czech Republic (L/M ratio of 6.0 and L/G ratio of 18.0) (Mikuška et al., 2017), the data are much closer to those for softwood burning (Caseiro and Oliveira, 2012; Reche et al., 2012).





**Fig. 6.** Comparison of the  $C_{30\alpha\beta}/C_{30\beta\alpha}$  and hopanes/PAHs ratios (red dots: averages) in different seasons in Beijing with those of source materials (Saha et al., 2012) and other studies (Zhou et al., 2009; Zhang et al., 2015; Saha et al., 2017).



**Fig. 7.** Spatial distribution (a) and inter-annual variation (b) of the levoglucosan/galactosan (L/G) and levoglucosan/mannosan (L/M) ratios in different seasons.

#### 4. Conclusion

In a year-long sampling campaign, 92 organic markers were measured at an urban site in Beijing. Saccharides were the most abundant species ( $340.1 \text{ ng m}^{-3}$ ) among all of the detected organic markers, followed by phthalic acids ( $283.4 \text{ ng m}^{-3}$ ). From a seasonal perspective, phthalic acids, n-alkanes, fatty acids, and n-alcohols accounted for a higher proportion of OA mass in summer, indicating the dominance of biogenic emission and atmospheric oxidation. By contrast, saccharides, PAHs, and hopanes were more prominent in winter, when anthropogenic sources contribute the most to OA. Spatial distributions of organic markers indicate that the concentrations of organic markers are generally higher in northern China than in southern China. The analysis on diagnostic ratios indicates that coal combustion and biomass burning are the primary sources in northern China, whereas vehicular emissions are the dominant source in southern China. In addition, the mixture of softwood, hardwood, and crop residue are the main types of biomass burned in China, unlike in some European cities, where softwood burning is more prevalent. The inter-annual variations of organic markers from 2001 to 2015 suggest the significant alleviation of the primary OA (except hopanes) pollution in Beijing, with an average reduction of 35%–89% compared with those before 2008. The results of diagnostic ratio analyses between OA markers indicate a reduced contribution of coal combustion and biomass burning but an increased contribution from vehicular emissions. The increase in vehicle fleets may account for the increase in hopane concentrations since 2008, but a 35% reduction was observed in 2015 compared with in 2010–2011 as a result of tightening emission controls for vehicles. For SOA markers, however, because of their high complexity, further research must be conducted to evaluate the effects of emission controls on inter-annual variations.

#### Data availability

Raw data used in this study are archived at the Institute of Earth Environment, Chinese Academy of Sciences, and are available on request by contacting the corresponding author.

#### CRediT authorship contribution statement

**Ting Wang:** Conceptualization, Formal analysis, Data curation, Methodology, Writing - original draft, Writing - review & editing. **Ru-Jin Huang:** Conceptualization, Formal analysis, Data curation, Methodology, Writing - original draft, Writing - review & editing. **Yongjie Li:** Writing - review & editing. **Qi Chen:** Writing - review & editing. **Yang Chen:** Writing - review & editing. **Lu Yang:** Writing - review & editing. **Jie Guo:** Writing - review & editing. **Haiyan Ni:** Writing - review & editing. **Thorsten Hoffmann:** Writing - review & editing. **Xinming Wang:** Writing - review & editing. **Bixian Mai:** Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.140689>.

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