Atmospheric
Chemistry
and Physics

Characterization of organic aerosols from a Chinese megacity during winter: predominance of fossil fuel combustion

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Abstract. $PM_{2.5}$ aerosol samples were collected from the Chinese megacity of Nanjing (32.21° N, 118.73° E) during winter and analyzed for a total of 127 compounds from 12 organic compound classes. The most abundant classes of compounds were n-alkanes (mean concentration of 205 ng m^{-3}), followed by fatty acids (76.3 ng m^{-3}), polycyclic aromatic hydrocarbons (PAHs; 64.3 ng m^{-3}), anhydrosugars (56.3 ng m^{-3}), fatty alcohols (40.5 ng m^{-3}) and phthalate esters (15.2 ng m^{-3}), whereas hydroxy-/polyacids (8.33 ng m^{-3}), aromatic acids (7.35 ng m^{-3}), hopanes (4.19 ng m^{-3}), primary sugars and sugar alcohols (4.15 ng m^{-3}), lignin and resin products (2.94 ng m^{-3}), and steranes (2.46 ng m^{-3}) were less abundant. The carbon preference index of n-alkanes (0.83–1.38) indicated that they had a strong fossil fuel combustion origin. Diagnostic concentration ratios of organic tracers suggested that PAHs and hopanes originated mostly from coal burning and traffic emissions, respectively, in the Nanjing urban area. Positive matrix factorization analysis demonstrated that fossil fuel combustion was the major pollution source (28.7 %), followed by emissions from biomass burning (17.1 %), soil dust (14.5 %) and plastic burning (6.83 %) for Nanjing winter aerosols, although the contribution of secondary oxidation products (32.9 %) was the most abundant. Most of the compounds generally showed higher concentrations at nighttime compared with daytime; this was due to the accumulation process associated with inversion layers and the enhancement of emissions from heavy trucks at night. We conclude that fossil fuel combustion largely influences the winter organic aerosols in urban Nanjing. Based on the comparison of this study's results with previous research, we found that pollution levels in organic aerosols have decreased in the urban Nanjing atmosphere over the last decade.

1 Introduction

Particulate matter (PM) is comprised of a wide variety of chemical components, which are derived from a broad range of sources and processes in the atmosphere (Seinfeld and Pandis, 2006). Organic aerosol (OA) is one of the major constituents of airborne particulates, accounting for up to 70 % of the fine aerosol mass. OA can play a crucial role in the radiative forcing of the Earth and more generally in the environment (Kanakidou et al., 2005). Over the last 2 decades, more attention has been paid to identifying OA optical and cloud formation properties that link OA directly to the hydrological cycle and, in turn, to sustainability issues (Dusek et al., 2006; Riipinen et al., 2012). OA can affect the climate, air quality, human health, visibility and ecosystems on local, regional and global scales (Salma et al., 2017). Several studies have reported that OA plays an important role in both the direct and indirect aerosol forcing, affecting the Earth's radiation balance and global air quality (Cooke et al., 1999;

Lohmann et al., 2000; Jacobson, 2001; Chung and Seinfeld, 2002). The addition of organic matter (OM) to aerosol particles can make the aerosol surfaces more hydrophilic or hydrophobic based on the mixing state and aerosol composition, which subsequently modifies the cloud condensation nuclei (CCN) activity of particles. Furthermore, aerosols have a particularly strong influence on air quality (in addition to human health and climate) in urban areas due to the extensive anthropogenic emissions and favorable meteorological conditions that are generally present (Watson, 2002).

There are two major sources of atmospheric aerosols: primary emissions and secondary aerosol formation. Primary organic aerosols (POAs) are directly derived from various sources such as biomass burning, fossil fuel combustion, dust particles, microbial activity and plant material, whereas secondary organic aerosols (SOAs) are formed via the oxidation of organic species in the atmosphere. Various types of volatile organic compounds (VOCs) are emitted from natural and anthropogenic sources into the atmosphere and can be further photooxidized by OH, NO_x and O_3 to form SOA (Haque et al., 2016). Both POA and SOA can also contribute to the organic particulate matter (PM) formation in the atmosphere, which can significantly control the physicochemical properties of aerosol particles (Kanakidou et al., 2005). An understanding of the chemical characterization and the contributions of various sources of aerosol particles is essential in order to resolve the role and potential impacts of OA in the atmosphere. Moreover, as previously stated, OA poses adverse physiological effects to human health such as asthma, bronchitis, cancer and heart disease (Pope et al., 2009; Ramírez et al., 2011).

The large emissions of atmospheric particles from China have a major effect on regional and global climate changes (Huebert et al., 2003). Atmospheric pollution in China is a serious problem due to the country's rapid industrialization and urbanization. Globally, one-fourth of anthropogenic POAs originate in China (Cooke et al., 1999). Many studies have been performed to characterize inorganic aerosols from China due to the significant anthropogenic emissions involved (Wang et al., 2011; He et al., 2012; Zheng et al., 2015; Li et al., 2017); however, OAs in Chinese megacities are still poorly understood (Guo et al., 2003; Bi et al., 2003; Yao et al., 2003).

Nanjing is a highly industrialized megacity located in eastern China, which has a population of over 8 million, and suffers from a critical air pollution problem. Previous studies such as Wang et al. (2002a, b) have reported that the aerosol mass of fine particles ($< 2.5\,\mu m$) in the Nanjing atmosphere is about 2–4 times higher than that recommended by United States Environmental Protection Agency (USEPA) regulations. The average concentration of $PM_{2.5}$ in Nanjing aerosols during the sampling period for this study was $66 \pm 33\,\mu g\,m^{-3}$, whereas the Chinese National Ambient Air Quality and WHO standard levels are 35 and $25\,\mu g\,m^{-3}$, respectively (Liu et al., 2016; Shen et al., 2014); this indicates that the air quality in Nanjing is still unacceptable compared with Chinese and WHO standard levels.

The highest $PM_{2.5}$ concentrations have been observed in China during winter due to the enhancement of anthropogenic emissions from fossil fuel combustion and biomass burning in addition to unfavorable meteorological conditions, i.e., the frequent development of inversion layers (Zhang and Cao, 2015). Ma et al. (2016) also reported $PM_{2.5}$ concentrations in China from 2004–2013 and found that winter was the most polluted season. To better understand the molecular composition and sources of OAs in a Chinese urban area during winter, an aerosol sampling campaign was carried out on a night and day basis in the megacity of Nanjing from 11 December 2014 to 11 January 2015. The objective of this study was to determine more than 100 organic compounds including aliphatic lipids, sugar compounds, polycyclic aromatic hydrocarbons (PAHs), hopanes, lignin and resin products, aromatic acids, polyacids and steranes in the aerosol particles from Nanjing. The chemical characteristics, diurnal patterns and potential sources of these compounds are then discussed in comparison with previous studies conducted a decade ago.

2 Experimental

2.1 Sample collection

$PM_{2.5}$ sampling was performed from the rooftop of a six-story building at Nanjing University of Information Science and Technology, Nanjing, China, using a medium volume sampler (Laoshan, Quingdao, China) from 11 December 2014 to 11 January 2015 (Fig. 1). Daytime and nighttime sampling was conducted from 09:30 to 21:00 LT and 21:30 to 09:00 LT, respectively. A total of 62 samples were collected on prebaked ($450\,^\circ C$ for 6 h) quartz-fiber filters (80 mm) with an air flow rate of $100\,L\,min^{-1}$. After sampling, the filter samples were wrapped with aluminum foil, transported to the laboratory and stored at $-20\,^\circ C$ until the analysis.

2.2 Analysis of polar organics

Several polar organic compounds containing COOH and OH groups were analyzed by gas chromatography–mass spectrometry (GC-MS) using solvent extraction followed by a trimethylsilyl (TMS)-derivatization technique (Table S1 in the Supplement). Filter aliquots ($6.28\,cm^2$) were extracted three times with 5 mL of dichloromethane / methanol mixture (2 : 1) under ultrasonication for 10 min. The solvent extracts were filtered through quartz wool packed in a Pasteur pipette to remove all insoluble matrixes, concentrated using a rotary evaporator under vacuum and then totally dried under a gentle nitrogen stream. The dried extracts were derivatized with $50\,\mu L$ of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) plus 1 % trimethylsilyl chloride and $10\,\mu L$ of pyridine in a glass vial (1.5 mL) with a Teflon-lined screw cap

Figure 1. A map of sampling site located in Nanjing, China.

at 70 °C for 3 h. The C_{13} n-alkane (diluted in n-hexane) was used as an internal standard ($1.43 \, ng \, \mu L^{-1}$) prior to injection into the GC-MS for identification. Detailed information on the chemical analysis is interpreted elsewhere (Wang and Kawamura, 2005).

The derivatives were analyzed using a Hewlett-Packard (HP) model 6890 GC coupled to a HP model 5973 mass selective detector (MSD). The sample was injected into a splitless mode with the injector temperature at 280 °C. The GC oven temperature was set at 50 °C for 2 min, increased from 50 to 120 °C at 30 °C min^{-1}, and then increased to 300 °C at 6 °C min^{-1} with a final isothermal hold at 300 °C for 16 min. The GC separation was performed on a DB-5MS fused silica capillary column (30 m long × 0.25 mm inner diameter × 0.5 μm film thickness) with a helium carrier gas (rate 1.0 mL min^{-1}). The mass spectrometer was conducted at 70 eV in an electron impact (EI) mode with a scan range of 50–650 Daltons (Da).

The organic components were determined by comparison with the retention times and mass spectra of authentic standards as well as literature and National Institute of Standards and Technology (NIST) library data of mass fragmentation patterns (Medeiros and Simoneit, 2008). The GC-MS relative response factor (RRF) of each compound was calculated using authentic standards and surrogate compounds. We performed a recovery experiment three times and acquired an average value of more than 80 % for target compounds. The field-blank filters ($n = 5$) were analyzed using the same procedures as described above. The target species were not found in the blank filters. The analytical errors based on replicate analyses ($n = 5$) were < 10 %.

2.3 Analysis of nonpolar organics

Nonpolar organics, including n-alkanes, PAHs, hopanes and steranes were analyzed using a thermal desorption gas chromatography–mass spectrometry (TD-GC-MS) technique. It should be noted that higher recoveries (> 90 %) were obtained for nonpolar organics using TD-GC-MS compared with the TMS-derivatization/GC-MS (< 70 %) technique. The filter aliquots (3 mm diameter) were cut into two pieces, placed into a TD quartz tube (78 mm long × 4 mm inner diameter) and spiked with internal standard mixture (isotope-labeled reference compounds) for quantification. The internal standards consisted of three deuterated PAHs, e.g., Nap-d_8, Ace-d_{10} and Phe-d_{10}.

Thermal desorption was performed using an Agilent GC-MS system (models 7890B/5977A). A capillary column (HP-5MS UI, 5 % biphenyl / 95 % dimethylsiloxane, 30 m long × 0.25 mm inner diameter × 0.25 μm film thickness) was used to separate the target compounds. The GC oven temperature was programmed from 35 °C (3 min) to 120 °C at 10 °C min^{-1}, ramped from 120 to 146 °C at 4 °C min^{-1} and continued to 310 °C at 8 °C min^{-1}, where it was then held at 310 °C for 16 min. The sample on the filter punch was inserted into the TD tube at the initial temperature of 35 °C before running and was manually increased up to 300 °C at 12 °C s^{-1} after the analysis began. The column flow rate was 2 mL min^{-1} and the split flow was 10 mL min^{-1} for the first 3 min, after which the column and split flow rate were then changed to 1 and 25 mL min^{-1}, respectively. The electron ionization mass spectra (70 eV) were conducted in a scan mode range of 50–650 Da. The temperatures of the ion source, quadruples and transfer line were set to 310, 150 and 310 °C, respectively.

2.4 Carbonaceous component analysis

Organic carbon (OC) and elemental carbon (EC) were measured using a Sunset Laboratory carbon analyzer following the IMPROVE (Interagency Monitoring of Protected Visual Environments) thermal–optical evolution protocol and assuming carbonate carbon to be insignificant in the sample (Boreddy et al., 2018). An area of 1.54 cm^2 of each quartz filter sample was inserted into a quartz boat inside the thermal desorption chamber of the analyzer, and then stepwise heating was performed.

A filter cut of 3.14 cm^2 of each sample was extracted with 20 mL organic-free ultrapure water (resistivity > 18.2 MΩ cm, Sartorius arium 611 UV) under ultrasonication for 30 min. The water extracts were then passed through a membrane disc filter to remove the insoluble filter matrixes and were analyzed for water-soluble organic carbon (WSOC) using a total organic carbon (TOC) analyzer (Shimadzu, TOC-Vcsh) (Boreddy et al., 2018). The analytical errors in the triplicate analyses were within 5 % for all carbonaceous components, and the concentrations reported here were corrected using the field blanks.
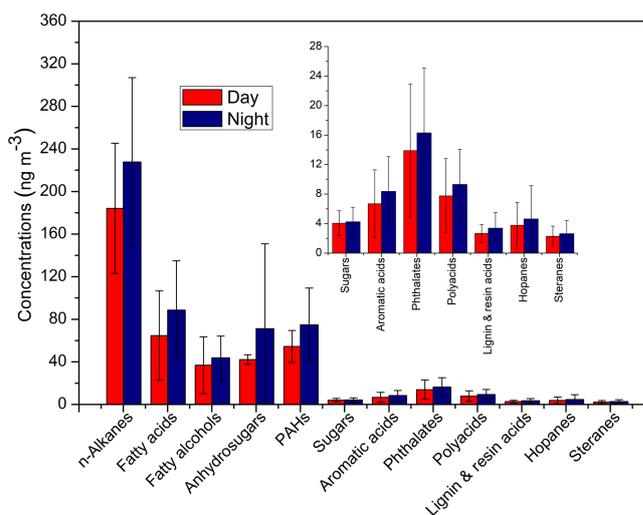
2.5 Major inorganic ion analysis

An area of $5.07\,cm^2$ of each quartz filter sample was extracted with 10.0 mL ultrapure water ($> 18.2\,\Omega$) under ultrasonication (30 min). The extract solution was filtered through a membrane disc filter (Millex-GV, Millipore) with a 0.22 μm pore size to remove insoluble materials and then analyzed for inorganic ions using ion chromatography on a Thermo Fisher Scientific ICS-5000 (USA) equipped with a gradient pump (SP), a conductivity detector/chromatography compartment (DC) and an automated sampler (AS-DV). The cations were measured by an IonPac CS12A analytical column and an IonPac CG12A guard column with an eluent of aqueous methanesulfonic acid (MSA, $30\,mM\,L^{-1}$) and a flow rate of $1\,mL\,min^{-1}$. In contrast, anions were separated on an IonPac AS11-HC analytical column and an IonPac AG11-HC guard column with an eluent of sodium hydroxide (NaOH) gradient at a flow rate of $1.5\,mL\,min^{-1}$ (0–3 min, $0.5\,mM\,L^{-1}$; 3–5 min, 0.5–$5\,mM\,L^{-1}$; 5–15 min, 5–$30\,mM\,L^{-1}$; 15–20 min $0.5\,mM\,L^{-1}$).
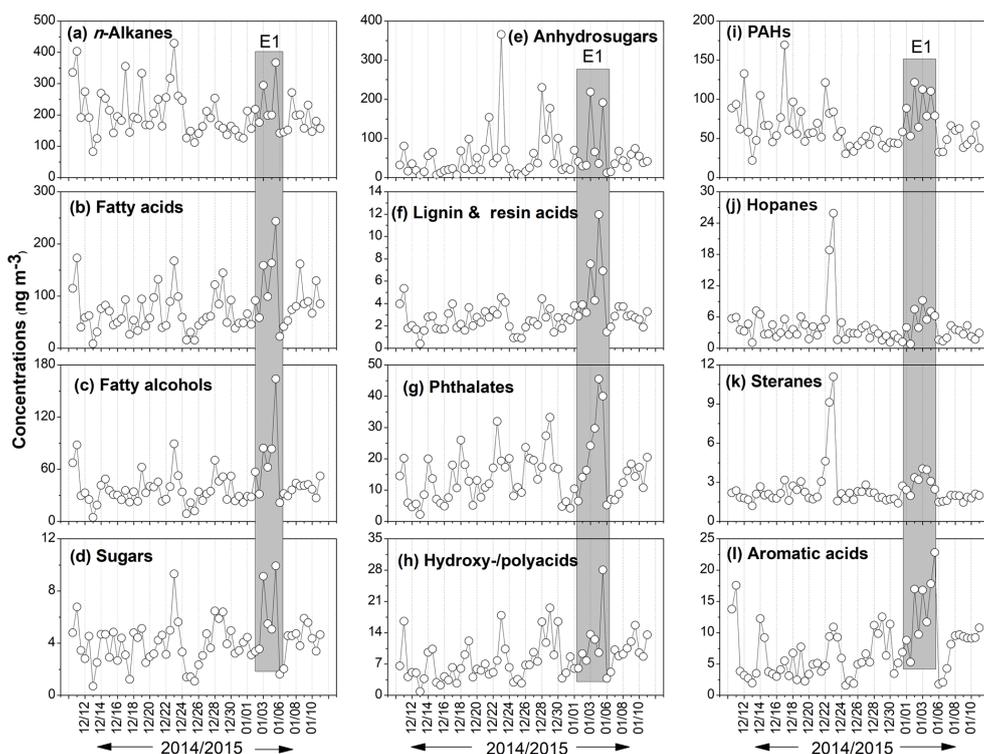

Figure 2. Concentrations of organic compound classes detected in the Nanjing aerosols. PAHs refers to polycyclic aromatic hydrocarbons. The inset panel represents the corresponding compounds for which the concentrations are low.

3 Results and discussion

3.1 Diurnal variations and meteorological conditions

No significant difference was observed between day and night for organic compounds in winter aerosols from the Nanjing urban area (Fig. 2, Tables 1 and S1). Nevertheless, concentrations of organic compounds at nighttime were slightly higher than during the day in most cases. It is notable that the planetary boundary layer height (PBLH) is generally lower at nighttime than during the day, causing higher concentrations of aerosol particles at night. Interestingly, we found high loadings of organics in a daytime sample collected on 15 December when the PBLH was high (632 m), whereas lower levels of organics were observed at nighttime on 14 December (PBLH = 82.2 m) (Figs. 3 and S1b in the Supplement).

We observed one episode (E1) from 2 to 5 January, during which $PM_{2.5}$ and all organic compounds showed similar temporal variations with high loadings (Fig. 3). Notably, NO_2 showed high concentration during E1, whereas relative humidity (RH) and ozone (O_3) levels were not high (Fig. S1). Our results suggest that NO_2 influences the organic molecular compositions in urban aerosols. It is noteworthy that the major source of NO_2 is vehicular exhaust (Kendrick et al., 2015); however, coal combustion can also emit NO_x into the atmosphere (Chang et al., 2018). Previous studies have also reported that NO_x could affect SOA formation (Kanakidou et al., 2005; Zhang et al., 2015; Mochizuki et al., 2015). Moreover, PAHs, hopanes and steranes showed another episode on 23 and 24 December 2014, most likely due to a coal combustion event. It should be noted that higher RH (81–88 %) and $PM_{2.5}$ levels (152–226 μg m^{-3}) caused a

reduction in visibility on 29 December (1.7 km), 10 January (1.8 km) and 11 January (1.6 km), which might have been due to haze formation. It is remarkable that the levels of organics were not high during these periods (Figs. 3 and S1). These results imply that NO_2 derived from fossil fuel combustion plays an important role in the formation of OAs in the atmosphere in Nanjing.

3.2 Carbonaceous components

The results of the OC, EC and WSOC analyses are shown in Table 1. The respective values of OC and EC were found to be 8.76–40.0 μg m^{-3} (mean 18.6 μg m^{-3}) and 2.41–30.3 μg m^{-3} (mean 8.25 μg m^{-3}) at daytime, and 2.98–40.1 μg m^{-3} (mean 19.1 μg m^{-3}) and 0.87–22.9 μg m^{-3} (mean 8.86 μg m^{-3}) at nighttime. We found that the day and night variations of OC and EC were not significant. The mass ratio of OC to EC (OC/EC) is often used to characterize fossil fuel and biomass burning emissions. Several investigators have used OC/EC ratios to classify the sources of carbonaceous aerosols (Ram et al., 2008; Sandradewi et al., 2008; Saarikoski et al., 2008). A higher OC/EC ratio implies that the major source of carbonaceous species is biomass burning, whereas lower ratios are characteristic of emissions from fossil fuel combustion. Sandradewi et al. (2008) documented an average OC/EC ratio of 1.1 for vehicular emissions and 7.3 for wood burning emissions. Saarikoski et al. (2008) reported OC/EC ratios of 0.71 for vehicular emissions and 6.6 for biomass burning. Furthermore, Watson et al. (2001) proposed OC/EC ratios of 1.1 for vehicular emissions, 2.7 for coal combustion and 9.0 for biomass burning emissions. The OC/EC ratios in this study ranged from 1.30 to 3.80 with a mean value of 2.40, which is comparable to the abovemen-

Figure 3. Temporal variations in the concentrations of organic compound classes detected in the Nanjing urban aerosols.

tioned values for coal combustion and vehicular emissions. These results suggest that fossil fuel combustion is the major source of carbonaceous aerosols in urban Nanjing.

OC/EC ratios are also used to differentiate the relative contribution of primary vs. secondary sources: high OC/EC ratios (> 2.0) have been reported for aerosols with significant SOA contributions (Kunwar and Kawamura, 2014; Pani et al., 2017). The OC/EC ratio in this study was 2.40 on average, suggesting the significant contribution of SOA in Nanjing aerosols, which is consistent with positive matrix factorization (PMF) results (see Sect. 3.4). The concentration range of WSOC was 5.52–$26.6\,\mu g\,m^{-3}$ (mean $11.7\,\mu g\,m^{-3}$) at daytime and 2.51–$20.2\,\mu g\,m^{-3}$ (mean $11.8\,\mu g\,m^{-3}$) at night. The WSOC/OC ratio is often used to discuss SOA formation via the photochemical aging of atmospheric aerosol particles. WSOC/OC ratios exceeding 0.4 indicate aged aerosols with a significant contribution from SOA (Boreddy et al., 2018). The average WSOC/OC ratio of 0.64 in the present study indicated that OAs in Nanjing were relatively aged. Moreover, air mass back trajectories also indicated that some air masses originated from polluted regions over North China, suggesting SOA formation during long-range transport (Fig. S5).

3.3 Organic molecular compositions

We detected 12 organic compound classes, including sugars, lignin and resin acids, fatty acids, fatty alcohols, n-alkanes, PAHs, hopanes, steranes, glycerol and polyacids, phthalate

esters, and aromatic acids in the aerosol samples from Nanjing. The total concentrations of organics were $424\,ng\,m^{-3}$ at daytime and $555\,ng\,m^{-3}$ at nighttime on average with the predominance of n-alkanes followed by fatty acids, PAHs, anhydrosugars, fatty alcohols, phthalate esters, glycerol and polyacids, aromatic acids, sugars, hopanes, lignin and resin acids, and steranes (Fig. 2). Table S1 shows the values of the identified organic compounds. Levoglucosan was the dominant species followed by C_{16} and C_{24} fatty acids, and C_{29} n-alkane (Table S1).

3.3.1 Aliphatic lipid components

The lipid compounds, e.g., fatty acids, fatty alcohols and n-alkanes mainly originate from marine or microbial detritus, terrestrial higher plant waxes and fossil fuel combustion. Homologues of n-alkanes (C_{13}–C_{39}) were detected at higher concentrations at nighttime (74.8–$535\,ng\,m^{-3}$, mean value of $228\,ng\,m^{-3}$) than during daytime (97.6–$497\,ng\,m^{-3}$, mean value of $184\,ng\,m^{-3}$) with a maximum at C_{29} ($14.0\,ng\,m^{-3}$ during daytime and $17.9\,ng\,m^{-3}$ during nighttime) in Nanjing aerosols (Tables 1 and S1, Fig. 4a). These concentrations are comparable to those reported from urban cities in Hong Kong ($195\,ng\,m^{-3}$) and Shanghai ($259\,ng\,m^{-3}$) (Wang et al., 2006), but much higher than the western North Pacific region (0.11–$14.1\,ng\,m^{-3}$; Kawamura et al., 2003). Concentration levels of n-alkanes in this study are not significantly different from previous studies in Nanjing (112–$265\,ng\,m^{-3}$,

Table 1. Mean concentrations of identified organic compound classes ($\mathrm{ng\,m^{-3}}$) and carbonaceous components ($\mathrm{\mu g\,m^{-3}}$) in the atmospheric aerosol samples ($PM_{2.5}$) from Nanjing, China.

| Compounds	Daytime				Nighttime			
	Mean	Min[a]	Max[b]	SD[c]	Mean	Min[a]	Max[b]	SD[c]
n-Alkanes	177	96.1	467	76.6	218	74.4	500	89.3
Plant wax alkanes	15.5	1.12	56.2	11.2	17.6	0	62.1	14.2
Fatty acids	66.8	14.3	254	47.9	91.3	8.57	252	59.2
Fatty alcohols	36.9	7.30	165	29.9	43.8	4.61	129	26.7
Anhydrosugars	42.3	5.8	191	40.9	71.2	5.71	367	80.1
Sugars	3.44	0.78	8.89	1.75	3.43	0.59	8.49	1.81
Phthalate esters	13.9	2.66	40.0	10.1	16.3	3.80	51.8	11.1
Glycerol and polyacids	7.78	1.59	29.7	6.17	9.30	2.54	23.1	5.79
Aromatic acids	6.70	1.53	23.1	4.69	8.37	1.99	18.4	4.83
Lignin and resin products	2.68	0.84	6.96	1.29	3.39	0.75	14.3	2.70
PAHs	54.5	29.5	106	17.8	74.8	21.7	223	43.8
Hopanes	3.79	0.07	20.8	4.15	4.64	0.13	26.1	5.31
Steranes	2.29	1.13	9.15	1.56	2.65	1.08	11.1	1.92
Total organics	434	163	1378	254	565	126	1686	347
OC	18.6	8.76	40.0	8.44	19.1	2.98	40.1	8.53
EC	8.25	2.41	30.3	5.46	8.86	8.86	8.86	8.86
WSOC	11.7	5.52	26.6	4.68	18.1	1.51	34.4	8.92
OC/EC	2.47	1.30	3.69	0.54	2.36	1.51	3.76	0.56
WSOC/OC	0.58	0.42	0.78	0.10	0.55	0.40	0.70	0.08

[a] Minimum. [b] Maximum. [c] Standard deviation. (OC refers to organic carbon, EC refers to elemental carbon and WSOC refers to water-soluble organic carbon.)

mean value of $172\,\mathrm{ng\,m^{-3}}$ during daytime; $61.0\text{–}503\,\mathrm{ng\,m^{-3}}$ and a mean value of $278\,\mathrm{ng\,m^{-3}}$ at nighttime; Table 2; Wang and Kawamura, 2005).

Biogenic n-alkanes showed stronger odd/even carbon number predominance with a carbon preference index (CPI) of > 5, whereas for anthropogenic n-alkanes the CPI value is usually close to unity (Simoneit et al., 1991a, 2004c). CPI values obtained in this study ranged from 1.18 to 1.32 (mean 1.28) at daytime and 1.10 to 1.37 (1.24) at nighttime, which is close to unity. This result suggests that the major contributor of n-alkanes is anthropogenic activity such as fossil fuel combustion, with less contribution from higher plants in Nanjing aerosols. The present CPI values are similar to those from other Chinese urban areas (mean 1.16; Wang et al., 2006) and Tokyo (1.10–2.80, mean 1.50; Kawamura et al., 1995). On the contrary, higher CPI values have been reported for Mt. Tai (4.60; Fu et al., 2008) and Chichijima aerosols (4.50; Kawamura et al., 2003), where n-alkanes mainly originated from terrestrial higher plant waxes. Plant wax-derived n-alkanes are estimated as the excess of odd homologues minus adjacent even homologues (Simoneit et al., 1991b, 2004c), and are attributable to vascular plant waxes (Tables 1 and S1). Concentration ranges of higher plant wax-derived n-alkanes were $2.12\text{–}48.1\,\mathrm{ng\,m^{-3}}$ (mean $15.5\,\mathrm{ng\,m^{-3}}$) at daytime and $0.86\text{–}58.9\,\mathrm{ng\,m^{-3}}$ (mean $17.6\,\mathrm{ng\,m^{-3}}$) at night, both of which are much lower than to-

tal n-alkanes, indicating that n-alkanes in the Nanjing urban area are derived mainly from fossil fuel combustion.

A homologous series of $C_{12:0}\text{–}C_{32:0}$ saturated fatty acids, including two unsaturated fatty acids ($C_{18:1}$ and $C_{18:2}$), were identified in Nanjing samples. The values of total fatty acids ranged from 14.3 to $254\,\mathrm{ng\,m^{-3}}$ (mean $66.8\,\mathrm{ng\,m^{-3}}$) during daytime, whereas they ranged from 8.59 to $252\,\mathrm{ng\,m^{-3}}$ (mean $91.3\,\mathrm{ng\,m^{-3}}$) at night. It is notable that fatty acids are less abundant than n-alkanes in Nanjing samples (Fig. 2). The molecular distributions of fatty acids show a strong even carbon number predominance with C_{max} at $C_{16:0}$ and $C_{24:0}$ (Table S1 and Fig. 4b). CPI values of fatty acids are found to be 5.41 in daytime samples and 5.52 in nighttime samples. A similar distribution pattern has been proposed for marine and continental aerosols (Mochida et al., 2002; Kawamura et al., 2003; Fu et al., 2008). Lower molecular weight (LMW) fatty acids ($< C_{20:0}$) originate from various sources, e.g., vascular plants, microbial sources and marine phytoplankton, whereas high molecular weight (HMW) fatty acids ($> C_{20:0}$) are derived from terrestrial higher plant waxes (Kawamura et al., 2003; Kolattukudy, 1976; Simoneit, 1978). Biomass burning, motor vehicles and cooking can also be important sources of fatty acids in urban areas (Fu et al., 2010). The value of $C_{18:1}$ was observed to be lower during the day than at nighttime, suggesting an en-
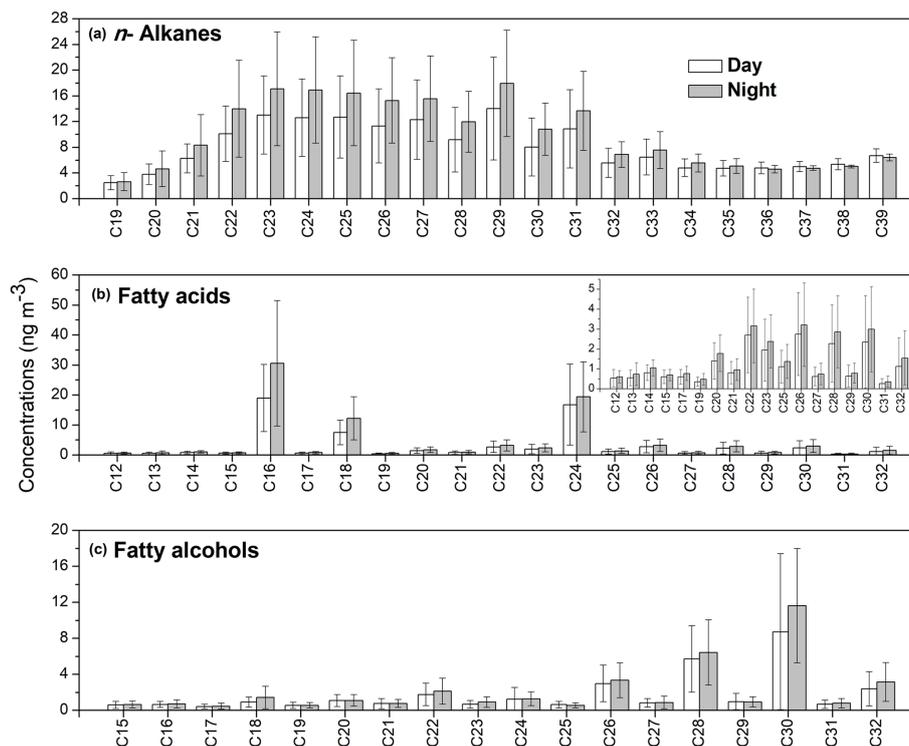
Figure 4. Molecular distributions of **(a)** n-alkanes, **(b)** fatty acids and **(c)** fatty alcohols in PM$_{2.5}$ aerosols collected from Nanjing, China. The inset panel in **(b)** represents the correspondence carbon of fatty alcohols for which the concentrations are low.

Table 2. Comparisons of the average concentrations (ng m^{-3}) of organic tracers in Nanjing aerosols with those measured during the 2004–2005 winter period.

Compounds	This study		2004–2005	
	Daytime	Nighttime	Daytime	Nighttime
n-Alkanes[a]	177	218	172	278
Plant wax alkanes[a]	15.5	17.6	18.8	20.6
Fatty acids[a]	66.8	91.3	245	338
Fatty alcohols[a]	36.9	43.8	74.5	120
Levoglucosan[a]	42.3	71.2	238	297
Sugars[a]	3.44	3.43	59	53
Phthalate esters[b]	13.9	16.3	158	181
Glycerol and polyacids[a]	7.78	9.30	41.4	41.8
Aromatic acids[a]	6.70	8.37		Not detected
Lignin and resin products[a]	2.68	3.39	16.0	35.1
PAHs[b]	54.5	74.8	69	104
Hopanes[b]	3.79	4.64	7.3	9.9
Steranes[a]	2.29	2.65		Not detected
Total organics	434	565	1108	1502

[a] Wang and Kawamura, 2005; [b] Wang et al., 2007a.

hanced emission to the atmosphere at night and a higher oxidation rate during daytime (Kawamura and Gagosian, 1987).

Concentration ranges of C$_{12}$–C$_{34}$ fatty alcohols were 7.30–165 ng m^{-3} (mean 36.9 ng m^{-3}) during daytime and 4.61–129 ng m^{-3} (mean 43.8 ng m^{-3}) at nighttime (Table S1

and Fig. 2). Their molecular distributions are characterized by a strong even-to-odd carbon number predominance with C$_{max}$ at C$_{28}$ or C$_{30}$ (Fig. 4c). We found that the CPI values of fatty alcohols in Nanjing aerosols (2.56–10.3, mean value of 5.22 at daytime; 3.06–15.5, mean value of 6.32 at

nighttime) are lower than those of aerosols from Chennai, India (9.75 ± 2.94; Fu et al., 2010) and Mt. Tai, China (CPIs 7.95–66.5, mean value of 25.6 at daytime; 12.2–53.4, mean value of 22.8 at nighttime; Fu et al., 2008). HMW fatty alcohols ($> C_{20}$) are dominant in terrestrial higher plants, soils and loess deposits, whereas LMW fatty alcohols ($< C_{20}$) are dominant in marine biota and soil microbes (Simoneit et al., 1991b). Moreover, a large amount of fatty alcohols in addition to fatty acids and n-alkanes can also be derived from biomass burning (Simoneit, 2002). A positive correlation was observed between fatty alcohols and levoglucosan ($r = 0.60$, $p < 0.001$), indicating that fatty alcohols partly originate from biomass burning in Nanjing winter aerosols (Fig. S2c). This conclusion is further supported by the factors resolved by PMF analysis, where a high loading of fatty alcohols was found with the biomass burning tracer levoglucosan.

3.3.2 Biomass burning tracers

Levoglucosan, galactosan and mannosan belong to a class of anhydrosugars that are produced by the pyrolysis of cellulose and hemi-cellulose (Simoneit, 2002). Levoglucosan is a unique tracer of biomass burning, and has been reported in urban (Wang et al., 2006; Fu et al., 2010; Yttri et al., 2007), marine (Simoneit et al., 2004b; Ding et al., 2013) and polar regions (Stohl et al., 2007; Fu et al., 2009). Levoglucosan is a relatively stable species in atmospheric aerosols and may be transported long distances (Mochida et al., 2010). We found that levoglucosan is one of the most abundant single tracers among all of the identified compounds in the present study, with a concentration range of 4.79–179 ng m^{-3} (mean 38.4 ng m^{-3}) during daytime and 4.96–354 ng m^{-3} (mean 66.0 ng m^{-3}) at night (Tables 1 and S1, Fig. 5a), although the values are lower than previous results reported in Nanjing (Wang and Kawamura, 2005).

Levoglucosan could account for up to 90 % of total sugars in Chinese urban aerosols (Wang et al., 2006). The contribution of levoglucosan to OC and WSOC was 0.02–0.51 % (mean 0.09 %) and 0.03–0.57 % (mean 0.13 %) during daytime and 0.02–0.48 % (mean 0.13 %) and 0.03–0.78 % (mean 0.22 %) at nighttime, respectively. Galactosan and mannosan were also detected in the aerosol samples. The amount of galactosan was found to be 0.65–7.47 ng m^{-3} (mean 2.26 ng m^{-3}) during daytime and 0.48–7.75 ng m^{-3} (mean 3.13 ng m^{-3}) at nighttime, whereas those of mannosan were 0.36–4.30 ng m^{-3} (mean 1.62 ng m^{-3}) during daytime and 0.27–5.73 ng m^{-3} (mean 2.06 ng m^{-3}) at nighttime (Table S1 and Fig. 5a). Levoglucosan showed similar temporal trends and strong correlations with galactosan ($r = 0.87$, $p < 0.001$) and mannosan ($r = 0.84$, $p < 0.001$) (Fig. S2a). It should be noted that the levoglucosan level in this study was 4–6 times lower than that of a previous study in Nanjing (Table 2; Wang and Kawamura, 2005). This result implies
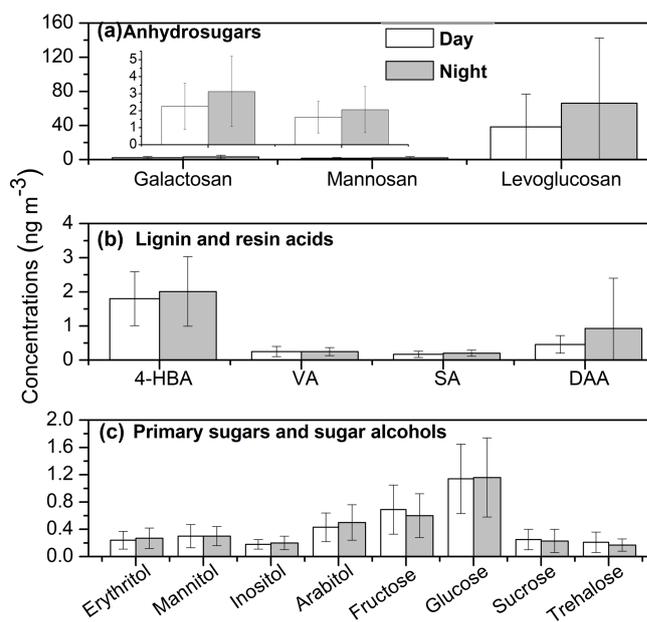
Figure 5. Molecular distributions of **(a)** anhydrosugars, **(b)** lignin and resin acids and **(c)** sugars/sugar alcohols in Nanjing aerosols. (4-HBA refers to 4-hydroxybenzoic acid, VA refers to vanillic acid, SA refers to syringic acid and DAA refers to dehydroabietic acid).

that winter biomass burning emissions have decreased significantly over the last decade in the Nanjing area.

We detected four lignin and resin products, i.e., 4-hydroxybenzoic, vanillic, syringic and dehydroabietic acids, which have been used as biomass burning tracers (Simoneit et al., 2004c). Lignin is a wood polymer, which can produce phenolic acids during burning, whereas dehydroabietic acid is more specific to conifer resin (Simoneit, 2002). We found that 4-hydroxybenzoic acid was dominant among all lignin and resin products identified in Nanjing samples (Fig. 5b). The concentration ranges of 4-hydroxybenzoic, vanillic and syringic acids in day and nighttime samples were 0.65–4.31 ng m^{-3} (mean 1.80 ng m^{-3}) and 0.62–4.96 ng m^{-3} (mean 2.01 ng m^{-3}), 0.04–0.92 ng m^{-3} (mean 0.25 ng m^{-3}) and 0.08–0.66 ng m^{-3} (mean 0.25 ng m^{-3}), and 0.04–0.57 ng m^{-3} (mean 0.17 ng m^{-3}) and 0.05–0.43 ng m^{-3} (mean 0.20 ng m^{-3}), respectively. The value of dehydroabietic acid was observed to be 0.11–1.16 ng m^{-3} (mean 0.46 ng m^{-3}) during daytime and 0.00–8.29 ng m^{-3} (mean 0.93 ng m^{-3}) at nighttime. The levels of lignin and resin acids in this study were 1–10 orders of magnitude lower than those from India (Fu et al., 2010) and China (Wang et al., 2006). Lignin products showed strong correlations with levoglucosan ($r = 0.60$–0.72, $p < 0.001$), suggesting similar sources and origins. In contrast, there is no correlation of dehydroabietic acid with levoglucosan ($r = 0.07$), indicating a different source of dehydroabietic acid in Nanjing aerosols. The low concentrations of dehydroabietic acid imply that bo-

real conifer forest fires are not important for the Nanjing aerosols.

3.3.3 Primary sugars and sugar alcohols

Sugar compounds are considered to be tracers for primary biological aerosol particles, which are water-soluble and thus contribute to WSOC in aerosol particles (Elbert et al., 2007; Medeiros et al., 2006; Yttri et al., 2007). Four primary sugars (glucose, fructose, trehalose and sucrose) and four sugar alcohols (erythritol, arabitol, mannitol and inositol) were identified in the aerosol samples from Nanjing. The sugar compounds are generated from microorganisms (pollen, fungi and bacteria), plants, flowers, the resuspension of surface soil and unpaved road dust (Graham et al., 2003; Simoneit et al., 2004a; Yttri et al., 2007). They can also originate from biomass burning. Total concentrations of primary sugars measured were 0.78–7.02 ng m^{-3} (mean 2.90 ng m^{-3}) at daytime and 0.50–6.58 ng m^{-3} (mean 2.98 ng m^{-3}) at nighttime, whereas those of sugar alcohols were 0.30–2.90 ng m^{-3} (mean 1.16 ng m^{-3}) during daytime and 0.19–2.75 ng m^{-3} (mean 1.27 ng m^{-3}) at nighttime.

Most primary sugars exhibited higher concentrations at daytime than at night, except for glucose (Fig. 5c). Graham et al. (2003) proposed that fructose and glucose along with sucrose are emitted as fern spores, pollen and other "giant" bioaerosol particles during daytime. Glucose showed a significant correlation with levoglucosan ($r = 0.75$, $p < 0.001$; Fig. S2d), indicating that it is associated with biomass burning, which may explain the high levels of glucose at nighttime, whereas other primary sugars only showed weak correlations with levoglucosan ($r = 0.05–0.09$). Biomass burning as a source of glucose has also been proposed by Fu et al. (2008). Trehalose is mostly derived from microorganisms such as bacteria, fungi and yeast as well as to a lesser degree from higher plants and invertebrates (Medeiros et al., 2006). It is also considered to be a product of unpaved road dust and the resuspension of surface soil (Simoneit et al., 2004b; Wang and Kawamura, 2005).

On the contrary, all sugar alcohols showed higher concentrations at nighttime than during the day, whereas the scenario was reversed for primary sugars. Significant correlations were observed between sugar alcohols and levoglucosan ($r = 0.51–0.75$, $p < 0.001$), suggesting a contribution from biomass burning to primary bioaerosol particles, which could explain their higher concentrations at nighttime. Previous articles have proposed that a huge amount of sugars and sugar alcohols can be emitted via the combustion of green vegetation from temperate forests (Medeiros and Simoneit, 2008). The sugar polyols are mainly produced from microbial sources, e.g., fungi and bacteria. They can also be released from the bark of trees, leaves and branches. The values of sugar compounds in this study are lower than values reported from other Chinese urban areas (Wang et al., 2006).

3.3.4 Polycyclic aromatic hydrocarbons (PAHs)

PAHs have severe negative effects on human health due to their genotoxicity and carcinogenicity. These aromatic compounds are mainly emitted from anthropogenic activities, including biomass burning, coal combustion, vehicular emissions and natural gas combustion. PAHs showed a weak positive correlation with levoglucosan ($r = 0.20$), suggesting that there is no serious contribution from biomass burning activities to PAHs in Nanjing aerosols. A total of seventeen PAHs were identified in the Nanjing samples with concentrations ranging from 29.5 to 106 ng m^{-3} (mean 54.5 ng m^{-3}) at daytime and 21.7–223 ng m^{-3} (mean 72.5 ng m^{-3}) at nighttime (Tables 1 and S1, Fig. 2). The higher concentrations of PAHs at nighttime might be due to the lower dispersion of the boundary layer at night (Fig. 6a). Furthermore, household coal combustion significantly contributes to the air quality in China during winter (Kerimray et al., 2017). Dropping nighttime temperatures due to a cold weather, especially in rural areas, result in the use of a large amount of coal for house heating. Furthermore, heavy-duty trucks, which are only permitted by the local government to work at night, as well as coal combustion would also contribute to higher concentrations of PAHs in the nighttime air. Our values are 3–4 times higher than those found in Hong Kong (14 ng m^{-3}) but lower than those in Beijing winter aerosols (208 ng m^{-3}) (Wang et al., 2006). Fluoranthene was found as a dominant PAH (mean 8.24 ng m^{-3}) in Nanjing aerosol samples followed by chrysene (mean 6.72 ng m^{-3}), pyrene (mean 6.42 ng m^{-3}) and benzo(b)fluoranthene (BbF; mean 5.85 ng m^{-3}) (Fig. 6a).

PAHs can be further photooxidized to form SOA, i.e., phthalic acid in the atmosphere (Zhang et al., 2016). Ding et al. (2007) proposed that PAHs could be degraded during long-range transport. Therefore, the ratios of PAH isomer pairs can be used to interpret the chemical aging of PAHs in the atmosphere. Benzo[a]anthracene (BaA) and benzo(a)pyrene (BaP) are expected to be degraded more easily than their isomers during transportation due to their higher reactivity. Thus, lower ratios ($<$ 1.0) of benzo[a]anthracene (BaA) / chrysene (Chry) and benzo(a)pyrene (BaP) / benzo(e)pyrene (BeP) indicate relatively more photochemical processing of PAHs. In this study, the ratios of BaA / Chry and BaP / BeP were calculated to be 0.79 and 0.88, respectively; these values imply that the PAHs of Nanjing aerosols were aged due to the atmospheric transportation from long distances.

Characteristic ratios of PAHs are indicative of their specific sources. Previous studies (Wang et al., 2007a, 2009; Bi et al., 2005) have pointed out that the concentration ratios of indeno(1,2,3-cd)pyrene to benzo(ghi)perylene (IP / BghiP), and benzo(ghi)perylene to benz(e)pyrene (BghiP / BeP), are indicative of different emission sources (Table 3). Ratios of IP / BghiP around 0.22, 0.50 and 1.3 are attributable to gasoline, diesel and coal combustion sources, respectively. Conversely, a BghiP / BeP ratio of 2.0 indicates vehicle ex-
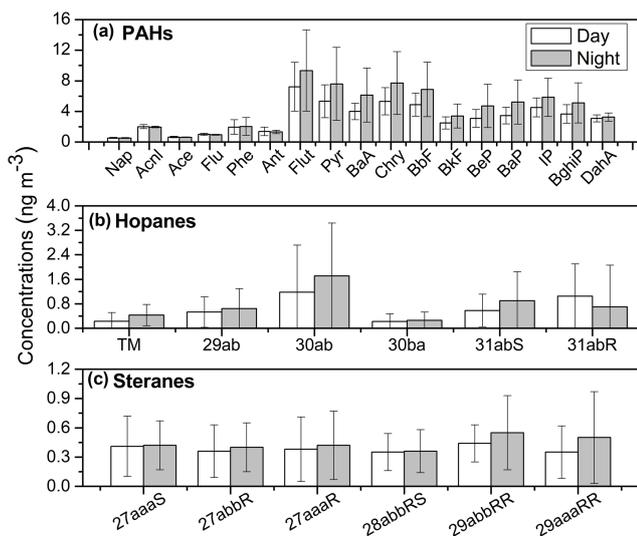
Figure 6. Molecular distributions of **(a)** PAHs, **(b)** hopanes and **(c)** steranes in winter aerosols from Nanjing, China. (The abbreviation of the PAHs listed are as follows: Nap – napthalene; Acnl – acenaphthylene; Ace – acenapthene; Flu – fluorene; Phe – phenanthrene; Ant – anthracene; Flut – fluoranthene; Pyr – pyrene; BaA – benzo(a)anthracene; Chry – chrysene; BbF – benzo(b)fluoranthene; BkF – benzo(k)fluoranthene; BeP – benzo(e)pyrene; BaP – benzo(a)pyrene; IP – indeno(1,2,3-cd)pyrene; BghiP – benzo(ghi)perylene; and DahA – Dibenzo(a,h)anthracene. TM refers to 17α(H)-22,29,30-Trisnorhopane.

haust and 0.8 indicates coal combustion emissions (Grimmer et al., 1983; Ohura et al., 2004). Furthermore, fluoranthene / (fluoranthene + pyrene) (Flut / (Flut + Pyr)) ratios of 0.46–0.56 indicate vehicular emissions, especially from catalytic converter-equipped automobiles (0.44), whereas IP / (BghiP + IP) ratios of 0.18, 0.37 and 0.56 represent vehicle emissions, diesel emissions, and coal combustion, respectively (Bi et al., 2005).

In this study, we found the ratios of IP / BghiP, Bghi / Bep, Flut / (Flut + Pyr) and IP / (IP + BghiP) to be 1.23, 1.17, 0.56 and 0.55, respectively. These ratios are closer to those of coal burning emissions than vehicle exhausts, and imply that the PAH components in Nanjing winter aerosols are mainly derived from coal combustion. The PAH compositions reported in our study are different from those found in Sacramento (Kleeman et al., 2008), Los Angeles and London (Finlayson-Pitts and Pitts Jr., 2000), where BghiP / BeP ratios were 5.6, 3.5 and 1.7, respectively, and vehicular emissions were the major PAH source. The PAH concentrations in Nanjing aerosols found in this study are lower than those found in a previous study of Nanjing samples collected in 2004 (Table 2; Wang et al., 2007a) and one-fourth of those collected during a study in 2001 (214 ng m^{-3}; Yang et al., 2005), which indicates that the local air quality in Nanjing has improved since 2001.

3.3.5 Hopanes and steranes

Hopane and sterane isomers are considered to be biomarkers of fossil fuel emissions, which belong to the higher boiling fraction of crude oil and are more resistant to degradation than n-alkanes. These isomers are found in high concentrations and originate from the crude oil and engine oil, which means that they consequently occur in vehicle exhaust from unburned lubricating oil residues and road dust (Ding et al., 2009). Six hopane compounds were identified in the Nanjing urban samples (Table S1) with higher levels at nighttime (0.13–26.1 ng m^{-3}, mean 4.16 ng m^{-3}) and lower levels at daytime (0.09–20.8 ng m^{-3}, mean 3.78 ng m^{-3}) (Fig. 2). The concentrations of hopane in the present study are comparable with those from other Chinese cities and Tokyo (0.7–15 ng m^{-3}; 5.5 ng m^{-3}; Wang et al., 2006). Wang et al. (2009) reported that concentrations of hopanes in the urban samples were 2 orders of magnitude higher than those in mountain samples, whereas hopanes were not detectable in marine samples.

The diagnostic ratios of hopanes can differentiate their sources (Table 3). 17α(H)-21β(H)-$29-$norhopane (C$_{29}\alpha\beta$)/17α(H)-21β(H)-hopane (C$_{30}\alpha\beta$) ratios of 0.59–0.66, 0.42, and 0.58–2.0 denote gasoline, diesel and coal burning emissions, respectively (Rogge et al., 1993a; Oros and Simoneit, 2000). In addition, ratios of 17α(H)-21β(H)-22S-homohopane/(17α(H)-21β(H)-22S-homohopane + 17α(H)-21β(H)-22R-homohopane) [C$_{31}\alpha\beta$S/(C$_{31}\alpha\beta$S + C$_{31}\alpha\beta$R)] ranging from 0.60 to 0.62, 0.50, and 0.05 to 0.37 indicate gasoline, diesel and coal burning emissions, respectively (Rogge et al., 1993a; Oros and Simoneit, 2000). We observed that concentration ratios of C$_{29}\alpha\beta$/C$_{30}\alpha\beta$ and C$_{31}\alpha\beta$S/(C$_{31}\alpha\beta$S + C$_{31}\alpha\beta$R) in this study are 0.58 and 0.48, respectively, which are closer to those of vehicular emissions than coal combustion. Thus, hopanes in Nanjing aerosol are predominantly emitted from traffic emissions due to the rapid increase in the use of automobiles in Chinese megacities.

A series of steranes were also identified in the present study. Concentration ranges of total steranes were 1.14–9.16 ng m^{-3} (mean 2.29 ng m^{-3}) during daytime and 1.09–11.1 ng m^{-3} (mean 2.64 ng m^{-3}) during nighttime. The diurnal distribution patterns of steranes showed remarkable similarity to hopanes. A strong correlation coefficient was also observed between steranes and hopanes ($r = 0.94$, $p < 0.001$), indicating similar emission sources (Fig. S3d). This is reasonable because homologues of hopanes and steranes are very stable and have similar atmospheric fates (Ding et al., 2009). In contrast, PAHs showed positive correlations with hopanes and steranes with a lower correlation coefficient ($r = 0.42$, $p < 0.001$), indicating somewhat similar sources.

Table 3. Diagnostic concentration ratios of biomarkers for source identification from fossil fuel combustions including gasoline and diesel cars.

	Present study		Gasoline		Diesel	Coal
	Daytime	Nighttime	Non-catalyst	Catalyst		
IP / BghiP	1.26	1.19	0.22[a]		0.50[a]	1.3[a]
BghiP / Bep	1.21	1.13	2.0[b]			0.8[b]
Flut / (Flut + IP)	0.57	0.56	0.46–0.56[c]	0.44[c]		
IP / (IP + BghiP)	0.56	0.54	0.18[c]		0.37[c]	0.56[c]
$C_{29}\alpha\beta/C_{30}\alpha\beta$	0.65	0.51	0.59[d]	0.66[d]	0.42[d]	0.58–2.0[e]
$C_{31}\alpha\beta S/(C_{31}\alpha\beta S + C_{31}\alpha\beta R)$	0.39	0.57	0.60[d]	0.62[d]	0.50[d]	0.05–0.37[e]

[a] Grimmer et al. (1983). [b] Ohura et al. (2004). [c] Bi et al. (2005). [d] Rogge et al. (1993a). [e] Oros and Simoneit (2000).

3.3.6 Phthalates

Phthalates are common additives widely used as a softener or plasticizer in polyvinylchloride (PVC) and synthetic polymers, respectively. They can be emitted into the atmosphere via the evaporation process due to their weak bonding in the polymer. Phthalates have potential negative health effects due to their endocrine disrupting and carcinogenic properties (Sidhu et al., 2005). It is necessary to carefully consider phthalates as toxic components in the aerosol particles; however, few studies have reported their atmospheric distribution over China (Fu et al., 2008; Wang et al., 2006, 2007a). Four phthalate esters, i.e., diethyl (DEP), di-iso-butyl (DiBP), di-n-butyl (DnBP) and di-(2-ethylhexyl) (DEHP) phthalates were characterized in this study with total concentrations of 13.9 ng m^{-3} (range from 2.66 to 40.0 ng m^{-3}) during daytime and 16.3 ng m^{-3} (range from 3.79 to 51.8 ng m^{-3}) at nighttime (Fig. 7a). DnBP (mean 8.07 ng m^{-3}) was the dominant tracer, followed by DEHP (mean 4.00 ng m^{-3}) , DiBP (mean 2.59 ng m^{-3}) and DEP (mean 0.14 ng m^{-3}). The levels of phthalates in this study are 4–20 times lower than those that were proposed in other Chinese megacities in 2006 (Wang et al., 2006), although they are comparable to those observed in Paris, France (8.2 ng m^{-3}; Teil et al., 2006), Sweden (3.7 ng m^{-3}; Thuren and Larsson, 1990), and Texas, USA (2.1 ng m^{-3}; Weschler, 1984).

The evaporation of phthalates can be accelerated under high ambient temperature conditions. The higher values of phthalates found in Nanjing aerosols at nighttime compared with daytime values is the opposite behavior to that seen with respect to Mt. Tai aerosols (Fu et al., 2008) due to the decreased PBLH at nighttime. Moreover, there was no significant difference in temperature between day and night during the campaign in Nanjing (Fig. S1). Significant correlations were found between DEP and DiBP ($r = 0.85$, $p < 0.001$) as well as DiBP and DnBP ($r = 0.87$, $p < 0.001$; Fig. S4a and b), suggesting that these compounds are commonly used as plasticisers in China and are released into the atmosphere in the same way. It should be noted that the concentration level of phthalates in this study was 1–2 orders of magni-
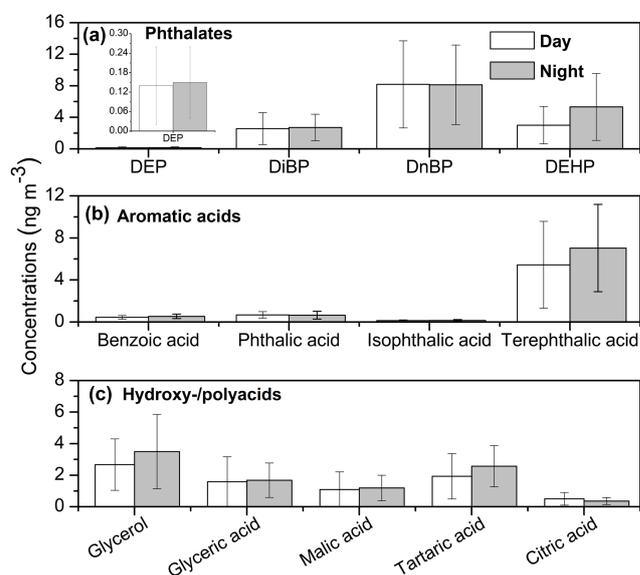
Figure 7. Molecular distributions of **(a)** phthalates, **(b)** aromatic acids and **(c)** hydroxy-/polyacids in Nanjing aerosols (DEP refers to diethyl phthalate, DiBP refers to di-iso-butyl phthalate, DnBP refers to di-n-butyl phthalate and DEHP refers to di-(2-ethylhexyl) phthalate).

tude lower than those found in Nanjing aerosols collected in 2004 (mean 230 ng m^{-3}; Wang et al., 2007a), suggesting a significant improvement in the local air quality in Nanjing regarding plastic emission.

3.3.7 Aromatic acids

We detected benzoic acid and three phthalic acids in the urban aerosols from Nanjing with total concentrations of 6.70 ng m^{-3} (1.53–23.1 ng m^{-3}) during daytime and 8.37 ng m^{-3} (1.99–18.5 ng m^{-3}) at night (Fig. 7b). These acids can play a significant role in increasing the formation of new particles in the atmosphere (Zhang et al., 2004). Benzoic acid ranged from 0.17 to 0.95 ng m^{-3} (mean 0.45 ng m^{-3}) at daytime and from 0.24 to 1.22 ng m^{-3} (mean 0.54 ng m^{-3}) at

night (Table S1), which is 1 and 4 orders of magnitude lower than the concentration in summertime aerosol at Mt. Tai and wintertime aerosol in tropical India, respectively (Fu et al., 2008, 2010). Benzoic acid is primarily emitted from automobiles (Rogge et al., 1993b; Kawamura et al., 2000) but has also been proposed as a secondary component via the photooxidation of several aromatic hydrocarbons (Fu et al., 2010).

Total phthalic acids varied from 1.40 to 21.9 ng m^{-3} (mean 6.25 ng m^{-3}) during daytime and 1.76 to 16.8 ng m^{-3} (mean 7.83 ng m^{-3}) during nighttime. Their concentrations were lower than those found during aircraft measurements over China in summer (17 ± 13 ng m^{-3}; Wang et al., 2007b) but higher than measurements from the northwestern Pacific (mean 1.5 ng m^{-3}; Simoneit et al., 2004a). The molecular distributions of phthalic acids showed the dominance of terephthalic acid (Fig. 7b), which accounted for 82 % of total aromatic acids in the Nanjing samples. Phthalic acids are SOA products produced from several PAHs (Oliveira et al., 2007; Fine et al., 2004). It is noteworthy that PAHs mostly produce phthalic acids over the North China Plain (Fu et al., 2008). Terephthalic acid can also be derived from burning plastics (Fu et al., 2010).

Aromatic acids showed positive correlations with four- and five-ring PAHs ($r = 0.56$, $p < 0.001$) and phthalates ($r = 0.71$, $p < 0.001$) (Fig. S3c), suggesting that they are primarily derived from PAHs. Furthermore, aromatic acids showed significant correlations with oxidation products of polyacids ($r = 0.83$, $p < 0.001$; Fig. S4c), indicating that the secondary oxidation process is a major source of aromatic acids. However, higher concentrations of aromatic acids at nighttime may not be explained by photochemical oxidation. We propose two explanations for the high level of SOA products at nighttime: (1) SOA products are formed during long-range atmospheric transport that is consistent with aged PAHs in the aerosols as discussed above (Sect. 3.3.4); (2) NO$_x$ can play an important role in oxidizing PAHs at night when the NO$_x$ concentration is high (Offenberg et al., 2007; Henze et al., 2008). However, further studies are needed to justify the influence of NO$_x$ on the atmosphere in Nanjing.

3.3.8 Hydroxy-/polyacids

Glycerol and several polyacids were identified in all of the samples from Nanjing (Table S1). Glycerol is a primary product of a metabolic reaction of soil organisms, whereas polyacids are produced secondarily by the photooxidation of organic precursors (Simoneit et al., 2004c). Glycerol did not show a significant correlation with polyacids ($r = 0.21$–0.38), implying that the two have different sources (i.e., primary and secondary). Kawamura and Ikushima(1993) and Matsunaga et al. (1999) reported that malic acid is a photooxidation product of succinic acid, which is one of the photooxidation products of biogenic unsaturated fatty acids (BUFAs) in the atmosphere. Moreover, SOA tracers, including malic

and tartaric acids, are produced by the photochemical oxidation of isoprene (Claeys et al., 2004).

The concentration range of glycerol was 0.66–5.99 ng m^{-3} (mean 2.67 ng m^{-3}) during daytime and 0.73–8.72 ng m^{-3} (mean 3.50 ng m^{-3}) at night. Glycerol is a dominant component in this group (Table S1 and Fig. 7c), which is consistent with the previous report regarding Nanjing aerosol from the 2004–2005 period, whereas the present concentration level is lower than that reported (Wang and Kawamura, 2005). Concentrations ranges of total polyacids were 1.21–23.5 ng m^{-3} (mean 5.1 ng m^{-3}) during daytime and 2.05–11.2 ng m^{-3} (mean 5.80 ng m^{-3}) at night, among which tartaric acid (mean 2.18 ng m^{-3}) was dominant (Fig. 7c). Tartaric acid presented a positive correlation with levoglucosan ($r = 0.75$, $p < 0.001$; Fig. S2b), suggesting the influence of biomass burning. Significant correlations were found among all polyacids ($r = 0.50$–0.75, $p < 0.001$), indicating similar source or formation pathway. Polyacids showed a strong correlation with WSOC ($r = 0.85$, $p < 0.001$; Fig. S4d), indicating their water-soluble and hygroscopic nature in addition to their possible influence on the CCN activity of aerosol particles. It should be noted that secondary oxidation products are formed during long-range atmospheric transport, which could explain the high values of polyacids at night. This result is consistent with the high WSOC/OC ratio in Nanjing aerosols (see Sect. 3.2) as well as the air mass back trajectories (Fig. S5).

3.4 Source apportionment of organic aerosols using PMF

Positive matrix factorization (PMF5.0, USEPA) analysis was performed in this study in order to better understand the sources of the identified components. It is a statistical source apportionment model widely used to verify underlying covariance among chemical parameters (Paatero and Tapper, 1994; Jaeckels et al., 2007). Detailed information regarding the PMF model can be found elsewhere (Paatero, 1997; Paatero and Tapper, 1994). The PMF model was applied to apportion ambient PM to motor vehicle and wood combustion emission, SOA, and two-point sources using organic molecular markers (Jaeckels et al., 2007). This model has also been extensively used for identifying source profiles and source contributions of PM-based elemental and organic marker data (Song et al., 2001; Buzcu et al., 2003; Jaeckels et al., 2007; Jia et al., 2010). The analytical errors estimated for the measured values of chemical species in PMF analysis are 10 %. The detected organic compound classes were subjected to source apportionment evaluation to carry out the classification of sources using the model. PMF model application resolved five source factors based on Q values that contributed to ambient PM$_{2.5}$ in this study. OC, EC and some inorganic ions were also used to investigate possible different sources. We used PM$_{2.5}$ as the sum of total variables during the model convergence. Figure 8 shows composition source
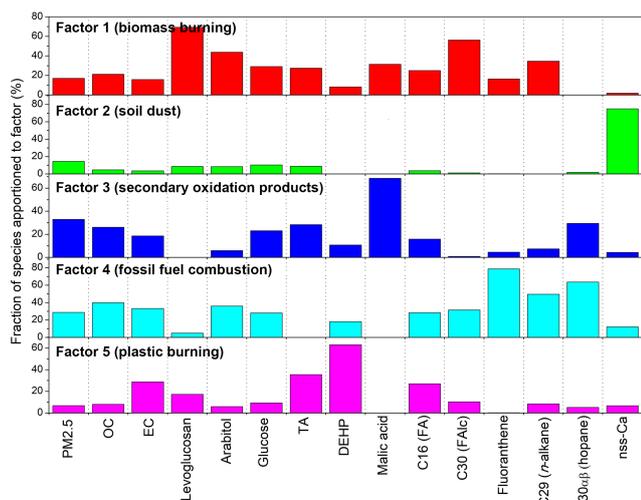
Figure 8. Composition profiles (percentage of the total of each species) for the five factors resolved using a PMF based on data from Nanjing winter aerosols from 11 December 2014 to 11 January 2015. (TA refers to terephthalic acid, DEHP refers to di-(2-ethylhexyl) phthalate, FA refers to fatty acid and FAlc refers to fatty alcohol.)

profiles for the five factors resolved by PMF analysis, where Factor 3 is a dominant source.

Factor 1 is dominated by levoglucosan (69 %) followed by fatty alcohol (C_{30}) (56 %), arabitol (44 %) and n-alkane (C_{29}) (34 %). Factor 1 is associated with biomass burning, as levoglucosan is a specific tracer of biomass burning. Moreover, fatty alcohols, fatty acids, n-alkanes and sugar compounds can also be emitted from biomass burning. Biomass materials, including rice and wheat straws and cotton stems, are widely used for domestic cooking in rural areas around Nanjing, particularly in the evening. Therefore, particles from biomass burning are abundantly released into the atmosphere and then transported to the Nanjing urban area. This idea is consistent with the high loadings of biomass burning tracers during nighttime.

Factor 2 is enriched (75 %) by the non-sea-salt fraction of calcium (nss-Ca^{2+}), suggesting that the component is associated with soil dust for which nss-Ca^{2+} is a specific tracer (Athanasopoulou et al., 2010; Brahney et al., 2013). The infrastructure in many urban areas in China is currently undergoing construction, which can produce dust particles that are largely emitted into the atmosphere. Factor 3 is attributed to secondary oxidation products because the dominant species in this source profile is malic acid (69 %), which is a secondary oxidation product as described above (see Sect. 3.3.8).

Factor 4 was abundantly loaded by fluoranthene (79 %), $C_{30}\alpha\beta$ (64 %) and C_{29} (50 %) which are representative PAHs, hopanes and n-alkanes, respectively, implying that this factor originated from fossil fuel combustion. It should be noted that n-alkanes also showed a loading in Factor 1,

suggesting that n-alkanes are partly associated with biomass burning. PAHs can be emitted from fossil fuel combustion and biomass burning activities. However, we observed that PAHs are mainly derived from fossil fuel combustion in Nanjing (see Sect. 3.3.4). Furthermore, n-alkanes can originate from fossil fuel combustion and higher plant waxes, although fossil fuel was the dominant source for n-alkanes in Nanjing aerosols (see Sect. 3.3.1). Hopanes are emitted from the vehicular exhaust as well as coal burning. Low-quality coals are extensively used in urban and rural areas in China for cooking and house heating. Many power plants in Chinese cities also used a large amount of coal to produce energy. The use of vehicles has also increased severely in China, and can emit hopanes into the atmosphere. Factor 5 is dominated by di-(2-ethylhexyl) phthalate (DEHP) (63 %) followed by terephthalic acid (35 %), which can be associated with plastic burning. Terephthalic acid is a secondary oxidation product and can also be emitted from the open burning of plastics as discussed above.

PMF results can be further utilized to calculate the relative contributions of sources to the amount of ambient OC or $PM_{2.5}$ using a multiple linear regression between the isolated factor strengths and measured OC or $PM_{2.5}$ (Song et al., 2001). Results of this analysis are presented in Fig. 9, where source contributions to $PM_{2.5}$ are calculated. Fossil fuel combustion was the dominant source (28.7 %), considering the primary source, followed by emissions of biomass burning (17.1 %), soil dust (14.5 %) and plastic burning (6.83 %) during the study period. However, secondary oxidation products showed the highest contribution (32.9 %) to $PM_{2.5}$ in Nanjing which was most likely due to long-range atmospheric transport. These results indicate that fossil fuel combustion is an important contributor to Nanjing aerosol during winter. Wang and Kawamura (2005) reported that fossil fuel combustion (52 %) was the largest contributor to total organics followed by biomass burning (14 %) and SOA (10 %) from Nanjing, whereas coal combustion was found to contribute 39.5 % to $PM_{2.1}$ in Nanjing in 2010 (Chen et al., 2015). Gao et al. (2013) pointed out that coal combustion was the dominant (58 %) contributor to $PM_{2.5}$ followed by biomass burning (31 %) and vehicular emissions (11 %) in the Pearl River Delta region (two urban, two suburban and two rural sites) for samples collected in 2009. The comparison of current results with previous studies implies that the contribution of fossil fuel combustion and biomass burning emissions in China have decreased significantly over the past decade. However, pollution levels in China are still severe compared with the National and WHO standards as discussed above (Sect. 1).

4 Summary and conclusions

We collected $PM_{2.5}$ aerosol samples during winter 2014–2015 from Nanjing, an urban area located in eastern China.
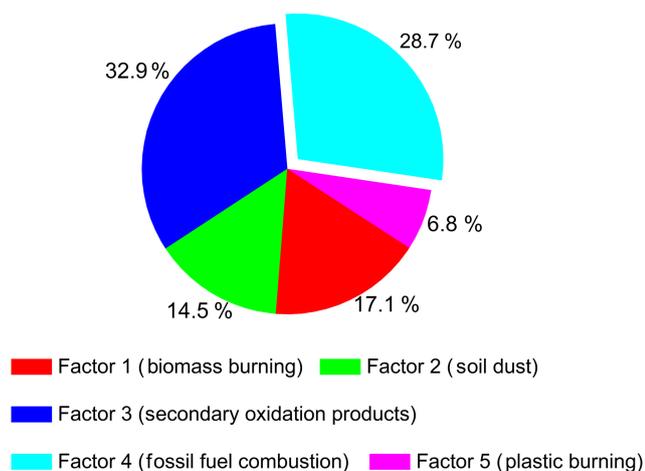
Figure 9. Pie diagram showing the estimated source contributions of five factors resolved by PMF to the $PM_{2.5}$ in Nanjing aerosols.

A total of 12 organic compound classes were identified in the aerosol samples, with *n*-alkanes being the dominant compound class, followed by fatty acids, PAHs, anhydrosugars, fatty alcohols and phthalate esters. The concentrations of organic compounds were slightly higher in nighttime samples due to the lower PBLH and higher emissions from heavy-duty trucks as well as coal and biomass burning during the night.

The molecular signature of *n*-alkanes with a weak odd-carbon number predominance and a maxima of C_{29} (mean CPI: 1.18) implies significant emissions from fossil fuel combustion. On the contrary, microbial and plant waxes are the major source of fatty acids and fatty alcohols in this study. Fatty alcohols are also significantly emitted from biomass burning. The biomass burning tracer, levoglucosan was the dominant species among the detected compounds. Levoglucosan and other biomass burning tracers mainly originated from domestic cooking and heating during the study period. Concentrations of secondary oxidation products, including aromatic acids and polyacids, reached a maximum during nighttime possibly due to the influence of NO_x or long-range atmospheric transport.

The diagnostic ratios of the tracer compounds suggest that coal burning is the major source of PAHs, whereas hopanes are abundantly emitted from traffic emissions into the Nanjing atmosphere. PMF analysis demonstrated that secondary oxidation products are the dominant contributor (32.9 %) to $PM_{2.5}$, whereas fossil fuel combustion is an important source (28.7 %) in Nanjing winter aerosols. The concentrations of organic tracers in this study are lower than those previously reported in Nanjing aerosols collected in 2004–2005. The air quality in Nanjing may have improved over last decade; however, fossil fuel combustion emissions have not decreased to a satisfactory level and still control the composition of wintertime OAs in Nanjing's atmosphere.

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