Characteristics and Sources of Organic Aerosol Markers in PM_{2.5}

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ABSTRACT

To investigate the molecular compositions, sources, and evolution processes of organic aerosols (OAs), PM_{2.5} samples in wintertime were collected in Jinan, a typically polluted city in the North China Plain (NCP). The concentrations of PM_{2.5}, carbonaceous species, and organic components (e.g., sugars, fatty acids, polycyclic aromatic hydrocarbons (PAHs) and oxygenated-PAHs (OPAHs)) in haze episodes were 1.8–2.7 times higher than those in clean episodes. Levoglucosan was the most abundant saccharide, which exhibited significant correlations with carbonaceous species during the whole sampling period, demonstrating that biomass burning has an important effect on the concentrations of carbonaceous species in PM_{2.5} of Jinan during wintertime. The higher ratios of both secondary OC/OC (SOC/OC) and C_{18:1}/C_{18:0} was observed during the clean days than those during haze days, implying that OAs during clean periods were more aged. The higher ratio of OPAHs/PAHs in the daytime reflected the more photochemical formation of OPAHs in the daytime. Positive matrix factorization (PMF) model proved that biomass burning was the major source of OAs during the whole sampling period. Potential source contribution function (PSCF) and concentration-weight trajectory (CWT) results indicating that Shandong Province and Beijing-Tianjing-Hebei (BTH) region made important contribution to the levels of PM_{2.5} in Jinan during the winter. Moreover, the CWT results showed that OAs during haze periods were largely originated from local and surrounding regions. These results confirmed that biomass burning can significantly influence the concentrations and chemical compositions of OAs, thereby they can affect human health and atmospheric chemistry.

Keywords: Organic aerosols, Levoglucosan, Biomass burning, PAHs, Jinan city

1 INTRODUCTION

Haze, a weather phenomenon that causes the atmosphere visibility < 10 km because of the mixed state of vapor, smoke, and suspended particles in the atmosphere (Lee *et al.*, 2014). The air pollution and severe haze events are usually observed during wintertime in Northern China due to the enhanced anthropological emissions and poor meteorological conditions (Fu *et al.*, 2008; Kong *et al.*, 2015; Wang *et al.*, 2017). For example, one month-long haze event in the begin of 2013 covered an area of more than 1.3×10^6 km² and affected more than 800 million populations (An *et al.*, 2019). Improved comprehending the physical or chemical processing which can result in the formation of haze is very essential to devise effective prevention measures (Zhang *et al.*, 2020). Previous researches have illustrated that organic components play a significant role in the haze occurrence in the NCP, especially the secondary aerosols (SOA) (Huang *et al.*, 2014; Zhou *et al.*, 2017).

OAs typically account for as much as 75% of PM_{2.5} mass in urban atmosphere and attract much public attention because of their important influence on human health, visibility, and climate change (Huang *et al.*, 2014; An *et al.*, 2019; Li *et al.*, 2019a; Ari *et al.*, 2020; Meng *et al.*, 2020). In addition, OAs can change the aerosols hygroscopic properties, because most of OAs (up to 80%)

OPEN ACCESS

Received: July 24, 2021
Revised: August 7, 2021
Accepted: August 18, 2021

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Publisher:

Taiwan Association for Aerosol
Research
ISSN: 1680-8584 print
ISSN: 2071-1409 online

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are water-soluble and play important roles in radiative forcing via affecting cloud condensation nuclei (CCN) (Meng *et al.*, 2018; Yi *et al.*, 2021). OAs are derived from multiple sources and their formation involves several atmospheric processes. For example, primary organic aerosol (POA) can be delivered directly from vehicle emissions, combustion sources, and plant emissions, whereas SOA are principally formed from the oxidation of volatile organic compounds (VOCs) (Hallquist *et al.*, 2009; Zhou *et al.*, 2017). Sugars are the relatively abundant water-soluble organic components in atmosphere, which can enter atmosphere through biomass burning, soil resuspension, and plant emissions (Wan and Yu, 2007; Li *et al.*, 2017a). Fatty acids, abundantly existing in OAs in the urban atmosphere (Oliveira *et al.*, 2007), which contribute to more than 50% of detected organic components from different emission sources (e.g., biological activities, biomass burning, and cooking activities) (Ho *et al.*, 2011; Liu *et al.*, 2019). Both PAHs and OPAHs are mostly derived from the incomplete combustion of solid fuels including fossil fuels and biomass (Wang *et al.*, 2016). Besides the direct sources, PAHs can be oxidized by atmospheric oxidants to form OPAHs (Wei *et al.*, 2012; Niu *et al.*, 2017). Recently, PAHs and OPAHs have been listed as persistent pollutants because of their high carcinogenicity and mutagenicity (Shi *et al.*, 2014; Kong *et al.*, 2015; Li *et al.*, 2019b). OPAHs are regarded as pivotal category in the reactive oxygen species (ROS) formation, which in turn can induce oxidative trauma in biological molecules (Lin *et al.*, 2015; Wang *et al.*, 2016; Niu *et al.*, 2017). High PAHs and OPAHs concentrations were widely observed in haze period during the wintertime because of the incremental consumption of fossil fuels and/or stagnant meteorology (Tan *et al.*, 2011; He *et al.*, 2014; Liu *et al.*, 2019). In sum, the molecular characteristics, concentration levels, and sources of OAs were different in diverse regions due to the complex energy structure and atmospheric environment. Therefore, it is becoming more significant to carry out a deep research on the sources and evolution processes of OAs.

China, the largest developing country all over the world, has been experiencing severe air pollution in the past few years (An *et al.*, 2019; Li *et al.*, 2020; Meng *et al.*, 2020). PM_{2.5} pollution is the dominant environment issue in the NCP, which has been considered as one of the most polluted area in the world (Yang *et al.*, 2018; Li *et al.*, 2019a). As a typical industrial city, Jinan is the representative of the urban cities in the NCP. Though the overall air quality was improved in Jinan, for example, PM_{2.5} concentration decreased markedly from 204.9 $\mu\text{g m}^{-3}$ in 2012 to 114.4 $\pm$ 56.9 $\mu\text{g m}^{-3}$ in 2016 (Yang *et al.*, 2012), haze events still occurred frequently. However, previous studies in Jinan were mainly focused on the sources and characteristics of carbonaceous species and water-soluble ions (Gao *et al.*, 2011; Zhou *et al.*, 2017), while the pollution characteristics and potential source regions of OAs during the wintertime have not been fully elucidated, especially during haze events. Hence, this study will deepen our comprehending of the characteristics and source areas of PM_{2.5} in haze periods, which can further provide scientific guidance for the pollution prevention in the local and surrounding region.

2 MATERIALS AND METHODS

2.1 Aerosol Sampling

Jinan is located in the center of Shandong Province, between the Yellow River and the Mt. Tai. A PM_{2.5} sampling instrument was installed on the rooftop of the library (~30 m above the ground) in the Shandong University (Central campus, 36°40'25"N, 117°03'15"E), Jinan. The sampling site is located in a prosperous commercial street with convenient transportation and dense population, which provides the exposure information of the population to PM_{2.5} in Jinan. PM_{2.5} samples were collected from 7 to 30 January, 2016, using a medium-volume sampling instrument (KC-120H, Qingdao Laoshan Company, China) coupled with prebaked quartz fiber filters (8 h, 450°C). Each sample lasted for 11.8 h and collected from 8:00 to 19:50 for daytime or 20:00 to 7:50 of the next day for nighttime. Before and after the sampling campaign, the field blanks were collected by setting a filter onto the instrument for 15 min when the sampler was out of operation. A total of 47 (22 for daytime, 23 for nighttime, and 2 field blanks) samples were gained during the whole observation campaign. All the samples were sealed in aluminum foil bags and then stored in a freezer (-20°C) before the experimental analysis. The meteorological parameters during the observation episode were obtained from the website of platform for monitoring and analysis of air quality in China (<http://www.aqistudy.cn>).

2.2 Chemical Analysis

The analytical methods of OAs in PM_{2.5} were introduced in our previous research (Yi *et al.*, 2021). Briefly, 1/4 sample was extracted with mixed solution of methanol and dichloromethane (1:2 v/v) under ultrasonication for 15 min (thrice). Then, the samples were concentrated under vacuum states and then dried by N₂ (purity > 99.99%). At 70°C, the sample reacted with mixture of pyridine and N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) (1:5, v/v) (60 µL) for 3 h. Finally, the samples were detected using a 7890A GC coupled with 5977B MSD (Agilent). The recoveries of target organic components were from 83% to 110%.

Organic carbon (OC), elemental carbon (EC) were determined by DRI Model 2015 Carbon Analyzer with IMPROVE_A protocol (Chow *et al.*, 2007). In short, the samplers were stepwise heated to 140, 280, 480, and 580°C in pure He atmosphere to determine OC concentrations, and 580, 740, and 840°C in 98% He/2% O₂ atmosphere to test the concentrations of EC. Pyrolyzed carbon evolved from the time that the gas flow is changed from He only to 98% He/2% O₂ gas at 580°C to the time that the laser-measured filter transmittance reaches its initial value.

2.3 Backward Trajectories Analysis

The 72-hr and 100 m high air mass back-trajectories were calculated using the HYSPLIT model (<https://www.arl.noaa.gov/>). The PSCF was calculated to confirm potential source areas which contributed to the high concentrations of PM_{2.5} (Wang *et al.*, 2009). The equation can be defined as follows:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (1)$$

where n_{ij} denotes the number of endpoints cross the ij grid cell ($0.5^\circ \times 0.5^\circ$ in this study) and m_{ij} is the value where the endpoints of the trajectory concentrated in the same cell exceeding the determined threshold criterion value ($75 \mu\text{g m}^{-3}$).

Concentration-weight trajectory (CWT) analysis has an advantage to distinguish the pollutants level of different trajectories (Wei *et al.*, 2019). The CWT can be calculated as:

$$C_{ij} = \frac{\sum_{l=1}^M C_l \tau_{ijl}}{\sum_{l=1}^M \tau_{ijl}} \quad (2)$$

where C_{ij} is the mean weight concentration on the grid cell ij , C_l is the concentration corresponding to trajectory l arriving grid ij , τ_{ijl} is the detention time of trajectory l in grid cell ij . In this study, both the PSCF and CWT algorithms were calculated using the MeteoinfoMap software with TrajStat plugins (Wang *et al.*, 2009), which had been proved as an effective approach to determining the potential source areas of pollutant (Wei *et al.*, 2019).

3 RESULTS AND DISCUSSION

3.1 General Descriptions of Carbonaceous Species in PM_{2.5}

The temporal variations of PM_{2.5}, OC and EC are presented in Fig. 1 along with the temperature (T), relative humidity (RH), and wind speed (WS). The mean concentrations of PM_{2.5} during the whole sampling campaign was $114.4 \pm 56.9 \mu\text{g m}^{-3}$, being higher than those in the corresponding period in Beijing ($54.3 \mu\text{g m}^{-3}$), Tianjin ($60.8 \mu\text{g m}^{-3}$), and Shijiazhuang ($104.6 \mu\text{g m}^{-3}$) in Northern China (<http://www.aqistudy.cn>), suggesting that air pollution in Jinan was severe. It is noteworthy that the concentration of PM_{2.5} decreased by 44.2% compared to those reported in 2012 ($204.9 \mu\text{g m}^{-3}$) (Yang *et al.*, 2012), suggesting that the air quality in Jinan has become better in recent ten years, although the city still experienced severe air pollution. The difference (t test, $p > 0.05$) on PM_{2.5} concentrations between day ($112.7 \pm 55.4 \mu\text{g m}^{-3}$) and night ($116.0 \pm 58.3 \mu\text{g m}^{-3}$) in the whole sampling period was negligible, indicating the minor impact of boundary layer heights.

Fig. 1. Temporal variation of meteorological parameters (e.g., T, RH, and wind speed), the concentrations of PM_{2.5} and organic compounds during the whole sampling period.

According to WHO, the air quality guideline value is $25 \mu\text{g m}^{-3}$ for 24-hr mean concentration (<http://www.who.int>). However, the daily PM_{2.5} concentration higher than $25 \mu\text{g m}^{-3}$ was only observed in one sample in this study. Thus, the haze day was defined as the PM_{2.5} concentration larger than the $75 \mu\text{g m}^{-3}$ (Chinese National Ambient Air Quality Standard, Grade II, (NAAQS)), while the clean day was defined as the PM_{2.5} concentration lower than $75 \mu\text{g m}^{-3}$. A total of 45 samples were collected in Jinan, including 13 clean days and 32 haze days. PM_{2.5} during haze periods was $139.7 \pm 47.2 \mu\text{g m}^{-3}$, which was 2.7 times higher than that ($52.0 \pm 16.5 \mu\text{g m}^{-3}$) during clean periods. As a reliable primary combustion emission tracer (Zhang *et al.*, 2021), CO exhibited strong positive correlations ($R^2 = 0.77$) (Fig. S1) with PM_{2.5} concentration. The concentration of CO increased dramatically from $1.1 \pm 0.3 \text{ mg m}^{-3}$ during clean periods to $2.2 \pm 0.6 \text{ mg m}^{-3}$ during haze periods, suggesting the significant effect of primary combustion on the haze formation in winter. The PM_{2.5} concentration decreased dramatically by 61.6 % when a snowfall event occurred in the beginning of Clean2 period (21–22 January, 2016), which could attributed to the removal effect of wet deposition. The value was similar to the result about the effect of rain in Jinan (14%–55%) (Tian *et al.*, 2021). Therefore, the more severe PM_{2.5} pollution in haze periods can be attributed to the stagnant meteorological and the enhanced emission of air pollutants (Table 1 and Fig. 1).

EC is directly emitted from the incomplete combustion of fossil fuels and biomass (Shi *et al.*, 2021). OC is not only from the primary emissions, but also is from the atmospheric chemical reactions (Zhang *et al.*, 2014). A strong correlation between OC and EC ($R^2 = 0.70$, Fig. 2) has been found in this study, suggesting that both species had similar emission sources. As depicted in Fig. 1, the OC and EC concentrations, and OC/EC ratios did not exhibit significant difference (*t* test, $P < 0.01$) between day and night. The OC and EC average concentrations in Jinan in haze periods were 1.8 times more (30.6 ± 9.6 ; $9.4 \pm 2.8 \mu\text{g m}^{-3}$) than those (17.2 ± 5.8 ; $5.1 \pm 1.8 \mu\text{g m}^{-3}$) in clean days. Previous studies confirmed that OC/EC ratios in the aerosols emitted from biomass burning, coal combustion, and vehicles, were 9.0, 2.7, and 1.1, respectively (Li *et al.*, 2014). The mean OC/EC ratio was 3.3 ± 0.7 in haze days, which was slightly lower than that (3.6 ± 1.5) in clean days, indicating that coal combustion was an important contributor in the atmosphere of Jinan. In addition, the higher OC/EC ratios in clean periods were mainly because of the enhanced formation of SOA. The OC/EC ratio can be applied to distinguish the presence of the secondary

Table 1. Concentrations of organic compounds and meteorological parameters in the wintertime atmosphere of Jinan in 2016.

	Daytime (n = 22)	Nighttime (n = 23)	Clean periods (n = 13)	Haze periods (n = 32)	Total (n = 45)
<i>I. Meteorological parameters and gas pollutants</i>					
T	-4.2 ± 4.7	-4.2 ± 4.6	-6.6 ± 4.8	-1.0 ± 3.6	-2.6 ± 4.8
RH	52.5 ± 15.6	53.3 ± 15.7	48.2 ± 17.2	47.9 ± 16.7	48.0 ± 16.9
WS	3.7 ± 0.7	3.7 ± 0.8	4.0 ± 1.1	3.5 ± 1.0	3.6 ± 1.1
NO ₂ ($\mu\text{g m}^{-3}$)	68.4 ± 22.7	69.0 ± 22.4	38.2 ± 12.7	78.8 ± 19.9	67.1 ± 25.9
CO (mg m^{-3})	1.8 ± 0.8	1.9 ± 0.7	1.1 ± 0.3	2.2 ± 0.6	1.9 ± 0.7
<i>II. Organic species (ng m^{-3})</i>					
Levogluconan	140 ± 75.5	136 ± 69.7	69.1 ± 25.3	166 ± 66.8	138 ± 72.6
anhydrosugars	176 ± 98.7	172 ± 90.6	85.4 ± 30.7	210 ± 88.0	174 ± 94.7
Primary sugars	17.9 ± 14.0	13.8 ± 7.8	16.8 ± 17.6	15.4 ± 7.6	15.8 ± 11.5
Sugar alcohols	6.3 ± 2.4	5.2 ± 1.9	4.8 ± 2.8	6.1 ± 1.8	5.7 ± 2.2
Saccharides	200 ± 101	191 ± 95.2	107 ± 35.8	231 ± 92.5	195 ± 98.1
C _{18:0}	264 ± 118	235 ± 119	150 ± 56	290 ± 115	249 ± 119
C _{18:1}	80.3 ± 58.0	124 ± 132	33.1 ± 17.7	131 ± 112	103 ± 105
LFAs	497 ± 233	496 ± 304	266 ± 89.3	590 ± 265	496 ± 271
HFAs	696 ± 371	657 ± 372	312 ± 108	824 ± 338	676 ± 372
Fatty acids	1193 ± 590	1152 ± 644	578 ± 189	1414 ± 567	1172 ± 618
PAHs	54.6 ± 39.9	56.2 ± 32.1	32.8 ± 8.7	64.6 ± 38.9	55.4 ± 36.2
OPAHs	81.0 ± 54.7	78.8 ± 47.2	48.3 ± 16.3	92.7 ± 54.6	79.9 ± 51.0
<i>III. Other species ($\mu\text{g m}^{-3}$)</i>					
PM _{2.5}	113 ± 55.4	116 ± 58.3	52.0 ± 16.5	140 ± 47.2	114 ± 56.9
OC	27.9 ± 11.1	26.1 ± 10.0	17.2 ± 5.1	30.6 ± 9.4	26.9 ± 10.6
EC	8.3 ± 3.3	8.1 ± 3.1	5.1 ± 1.8	9.4 ± 2.8	8.2 ± 3.2
OC/EC	3.4 ± 0.7	3.4 ± 1.1	3.6 ± 1.5	3.3 ± 0.7	3.4 ± 1.0

organic carbon (SOC) when the ratio exceeds 2.0 (Yang *et al.*, 2012). The ratios of OC/EC fluctuated between 2.4 and 7.6, with an average of 3.4 ± 1.0 in the whole sampling period, indicating that large amounts of SOC were likely formed in Jinan. In this study, the concentration of SOC was estimated using the following Eq. (3) (Wang *et al.*, 2010):

$$\text{SOC} = \text{OC} - \text{EC} \times (\text{OC/EC})_{\min} \quad (3)$$

where $(\text{OC/EC})_{\min}$ refers to the minimum value of detected OC/EC during the sampling period. The SOC concentrations were $5.1 \mu\text{g m}^{-3}$ and $7.9 \mu\text{g m}^{-3}$ in clean and haze days, accounting for 29.5% and 25.7% of the OC, respectively, implying that the SOC was an important contributor of PM_{2.5} in Jinan and the secondary pollution was more serious in clean periods. A previous study in Handan of China during the wintertime haze events also found that the relative abundance of SOC in ambient aerosol increased with the decreased PM_{2.5} concentrations (Yang *et al.*, 2018), largely because the high density of particles in the troposphere blocked solar radiation from reaching the ground layer and reduced the SOC generation rate (Tian *et al.*, 2014).

3.2 Concentrations and Variations of Organic Molecular Composition

3.2.1 Saccharides

Ten kinds of sugar were determined in PM_{2.5} in Jinan (Fig. 3(a)). The total sugars concentrations were $107.0 \pm 35.8 \text{ ng m}^{-3}$ and $231.3 \pm 92.5 \text{ ng m}^{-3}$ in clean days and haze days, respectively (Table 1). As an important indicator of biomass burning, levoglucosan was observed to be the dominant sugar (Table 1). The levoglucosan concentration in haze days ($165.6 \pm 66.8 \text{ ng m}^{-3}$) was 2.4 higher than that ($69.1 \pm 25.3 \text{ ng m}^{-3}$) in clean days, contributed to 71.6% and 64.6% of the detected saccharides, respectively. The higher concentration and relative contributions of levoglucosan were largely because of the enhanced biomass burning activities in the surrounding regions and adverse meteorological conditions (Fig. S2). Levoglucosan exhibited close correlations with OC

Fig. 2. Liner regressions of OC, EC, and major organic components in PM_{2.5}.

and EC ($R^2 > 0.50$, Fig. 2), suggested the important role of biomass burning in the concentrations of carbonaceous species in Jinan. As the isomers of levoglucosan, galactosan and mannosan also can be proposed as the key tracers for biomass burning (Li *et al.*, 2012; Yi *et al.*, 2021). In this study, both species were robustly correlated with levoglucosan ($R^2 > 0.80$). As shown in Fig. 1, the three kinds of anhydrosugars concentrations were highest in haze periods, again indicating that the aerosols in haze days was greatly affected by biomass burning. Previous researches have confirmed that the ratio of levoglucosan/mannosan (L/M) was lower (3–7) for softwood burning and higher (> 10) for hardwood and crop residue burning (Fu *et al.*, 2014; Zhang *et al.*, 2015). In the whole sampling period, L/M ratios varied from 5.8 to 23.1 with an average of 10.8, implying that the aerosols from biomass burning were closely related to the combination of softwood, hardwood, and/or crop residue burning.

The relative abundance of both primary sugars and sugar alcohols in total saccharides was 15.7% in Jinan aerosols (Fig. 3(a)). As shown in Fig 3, the dominant primary saccharide was glucose. Glucose was originated from multiple sources such as resuspension of surface soil, biomass burning, and biological particles. In this study, glucose did not show any correlation with levoglucosan ($R^2 < 0.01$), confirmed the minor effect of biomass burning on glucose. Trehalose is a good tracer for dust emissions from Gobi areas, because it is only abundant in highly desiccation-tolerant plants (Wang *et al.*, 2012). The trehalose concentration during the haze periods ($0.7 \pm 0.2 \text{ ng m}^{-3}$) was around one half of that ($1.3 \pm 1.4 \text{ ng m}^{-3}$) during the clean periods, indicating that the atmospheric pollutants in haze days were less influenced by long-distance transport from Gobi deserts. Sucrose is the predominant constituent of airborne pollen grains (Fu *et al.*, 2012), which exerts a major influence on plant flowering process. The concentration of sucrose was much higher in daytime ($2.5 \pm 1.9 \text{ ng m}^{-3}$) than that in nighttime ($1.5 \pm 0.7 \text{ ng m}^{-3}$), indicating the stronger biological activities during daytime than nighttime.

Fig. 3. Difference in the concentrations of (a) saccharides, (b) fatty acids, (c) PAHs, and (d) OPAHs in PM_{2.5} between during clean and haze periods.

3.2.2 Fatty acids

As shown in Table 1 and Fig. 3(b), fatty acids (C_{10:0}–C_{18:0}, C_{18:1}, C_{19:0}–C_{32:0}) were the predominant species in the detected organic compounds. The average concentrations of all fatty acids were $1172.1 \pm 618.3 \text{ ng m}^{-3}$ during the entire observation period. The fatty acids concentration was 2.4 times higher in haze days ($1413.5 \pm 566.9 \text{ ng m}^{-3}$) than that ($578.0 \pm 189.2 \text{ ng m}^{-3}$) in clean days. The saturated fatty acids had maxima at C_{18:0} and C_{24:0} and exhibited a robust even carbon number dominance. Low molecular weight (LMW) fatty acids (C_{10:0}–C_{19:0}) are largely from cooking activity, plants, and microbe, whereas high molecular weight (HMW) fatty acids (C_{20:0}–C_{32:0}) are mostly originated from terrestrial higher plant waxes (Fu *et al.*, 2008; Li *et al.*, 2013; Liu *et al.*, 2019). Carbon preference index (CPI, the concentration ratios of even/odd carbon for C₂₀–C₃₀ fatty acids) is a reliable method to distinguish anthropogenic or biogenic sources (Fu *et al.*, 2008). The CPI value near to one can be regarded as the fossil fuel combustion source, but the value higher than five can be proposed to be largely originated from higher plant wax emissions (Fan *et al.*, 2020). The CPI values were 3.2 in clean days and 2.8 in haze days, reflecting that the fatty acids were influenced by fossil fuel combustion source in the aerosols of Jinan. Previous research on field burning of crop residues found that the concentration of fatty acids was significantly enhanced in biomass burning period (Li *et al.*, 2019a). Fatty acids concentration presented a robust correlation ($R^2 = 0.83$) with levoglucosan in all samples (Fig. 2), implied the important contributor of biomass burning on the concentration of fatty acids. C_{18:1} is unstable and prone to photochemical degradation comparing to C_{18:0}, so the C_{18:1}/C_{18:0} ratio is used to evaluate the level of oxidation (Wang *et al.*, 2006). Two times higher of the ratio (0.45 ± 0.24) in haze days was observed than that (0.22 ± 0.09) in clean days, indicating that the photochemical degradation of unsaturated fatty acids was enhanced in clean periods.

3.2.3 PAHs and OPAHs

Concentrations and variations of PAHs and OPAHs in different periods

PAHs are mainly derived from the incomplete combustions of biomass and fossil fuels (Li *et al.*, 2017b; Liu *et al.*, 2019; Yi *et al.*, 2021). The total concentrations of 14 kinds of PAHs fluctuated between 18.3 and 152.8 ng m⁻³ (average: 55.4 ± 36.2 ng m⁻³), which was comparable to the observed in Beijing (53.8 ng m⁻³) and Xi'an (87 ng m⁻³), but was 79.1 times more than that in Qinghai Lake (0.7 ± 0.5 ng m⁻³) (Li *et al.*, 2013) and was 61.6 times more than that on Mt. Tai (0.9 ± 0.6 ng m⁻³) of China (Yi *et al.*, 2021). In addition, the PAHs concentration reported in this article was also higher than the southern cities such as Guangzhou (23.7 ± 18.4 ng m⁻³) (Li *et al.*, 2006) and Nanchang (22.5 ± 8.5 ng m⁻³) (Liu *et al.*, 2016). High values of PAHs in Jinan could be attributed to the enhanced coal combustion for heating in winter (Wang *et al.*, 2006). The PAHs concentration exhibited a strong correlation with levoglucosan ($R^2 = 0.74$, Fig. 2), which suggested that biomass burning was key source of PAHs in Jinan. The low temperature (−3°C) (Fig. 1) in the winter could favor the gaseous PAHs partitioning into particle phase (Qiao *et al.*, 2014; Liu *et al.*, 2019). Fluoranthene (Flu) was the most abundant PAHs, followed by benzo(b)fluoranthene (BbF), and chrysene (Chr) (Fig. 3(c)). The ratio of BaP/BeP could be employed to illustrate whether the aerosols are freshly emitted (higher than one) or aged (lower than one) (Li *et al.*, 2019b). In this study, the average BaP/BeP ratio was 0.79 ± 0.09, manifesting that PAHs in the PM_{2.5} samples had undergone an aging process. The total concentration of PAHs (64.6 ± 38.9 ng m⁻³) during haze periods was 1.9 times more than that (34.4 ± 8.7 ng m⁻³) during clean periods because of the effects of both enhanced emissions of human activities and unfavorable meteorological conditions. As shown in Fig. 4, 4-ring was the dominant PAHs, followed by 6-ring and 3-ring (or 5-ring) during clean periods (or haze periods). LMW PAHs (3-ring and 4-ring) principally come from the coal and biomass combustion, while HMW PAHs (5-ring and 6-ring) were primarily originated from the vehicle exhausts (Yi *et al.*, 2021). LMW PAHs accounted for 61.0% and 55.7% of the total PAHs concentration during clean and haze periods, respectively. The dominance of LMW PAHs illustrated the significant contribution of biomass and coal combustions to PAHs in this study. In addition, a possible mechanism for the dominance of LMW PAHs was that LMW PAHs under low temperatures condition were readily assembled in the particulate phase and lower boundary layer (Yi *et al.*, 2021). The mean temperature in haze periods (−1.0°C) was higher than that in clean periods (−6.6°C). Thus, the higher LMW/HMW PAHs ratio (1.5 ± 0.3) in clean days was obtained than that (1.2 ± 0.2) in haze days, again confirming that the lower temperature conditions favored the LMW PAHs transferring into particle phase due to the cold-trapping of PAHs. The driving role of gas-particle partitioning of PAHs was supported by the good correlation of T with HMW PAHs/LMW PAHs ratios ($R^2 = 0.49$) (Fig. S3).

The mean concentration of total seven OPAHs was 79.9 ± 51.0 ng m⁻³ in the entire sampling episodes (Fig. 3(d)). 5,12-Naphthacenequinone (NAQ, 36.3%) was observed as the most abundant OPAHs, followed by 9,10-anthraquinone (ANTQ) (26.3%), and 1-naphthaldehyde (NAD) (11.9%) in all the day and night samples. The OPAHs concentration in Jinan was higher than in Guangzhou and Xi'an, China (Wei *et al.*, 2012; Wang *et al.*, 2016). The high OPAHs concentrations observed in North China could be attributed to the increased fuel combustions during the heating periods (Li *et al.*, 2015). The higher emission factor of OPAHs from the combustion of biomass fuels in

Fig. 4. Distribution of ring number of PAHs in PM_{2.5} collected in Jinan during (a) clean periods and (b) haze periods.

residential stoves was obtained than that from the solid fuel combustions and motor vehicle exhausts (Shen *et al.*, 2013; Li *et al.*, 2015; Shen *et al.*, 2015). As shown in Fig. 2, OPAHs exhibited a strong correlation with levoglucosan ($R^2 = 0.75$), which indicated that biomass burning significantly contributed to OPAHs in Jinan. Moreover, OPAHs presented robust correlation with PAHs ($R^2 = 0.94$) (Fig. 2), suggesting that OPAHs were either co-emitted with PAHs or derived from the secondary formation by radical reactions with PAHs in the environment. Around two times more OPAHs concentration ($92.7 \pm 54.6 \text{ ng m}^{-3}$) in haze periods was obtained than that ($48.3 \pm 16.3 \text{ ng m}^{-3}$) in clean periods. The values of OPAHs/parent-PAHs (PPAHs) can elucidate the secondary formation level of OPAHs from related PPAHs (Bandowe and Nkansah, 2016). Unlike above discussions of other atmosphere oxidation indicator (e.g., SOC/OC, $C_{18:1}/C_{18:0}$), the ratios of OPAHs/PAHs between clean and haze periods were equivalent (6.3) (Fig. S4). The mass ratio of OPAHs/PAHs in daytime (7.3 ± 1.4) was higher than that in nighttime (5.4 ± 1.5), which implied more photochemical formation of daytime OPAHs due to the stronger solar radiation and higher temperature. Previous studies have proved that the BaAQ/BaA and ANTQ/ANT ratios were in the range of 0.03–0.16 and 0.14–0.89, respectively, indicating that they were freshly emitted from the combustion sources (Shen *et al.*, 2011; Shen *et al.*, 2012; Wang *et al.*, 2016). The average values of BaAQ/BaA and ANTQ/ANT were 0.8 ± 0.2 and 40.7 ± 9.3 , respectively, illustrating that the secondary production of OPAHs had essential effect on the aerosols in Jinan.

Sources apportionment of PAHs by diagnostic ratios

The ratios of Ant/(Ant + Phe), Flu/(Flu + Pyr), BaA/(BaA + Chr), and InP/(InP + BghiP) were calculated to differentiate different sources of PAHs (Fig. 5). The mass ratio of Ant/(Ant + Phe) higher than 0.1 is from the fossil fuel combustion, and the opposite is characteristic of petroleum (Wang *et al.*, 2008; Yi *et al.*, 2021). The ratio of Ant/(Ant + Phe) ranged from 0.07 to 0.17, implying that petroleum (e.g., oil spill and volatilization) and fossil fuel combustions were the major

Fig. 5. Diagnostic ratios for the emissions sources of PAHs. (a) Ant/(Ant + Phe) and Flu/(Flu + Pyr); (b) BaA/(BaA + Chr) and InP/(InP + BghiP).

sources of PAHs in Jinan. The ratio of Flu/(Flu + Pyr) was in the scope of 0.53 to 0.61, suggested the important contribution of biomass burning or coal combustion. The BaA/(BaA+Chr) ratio varied from 0.26 to 0.46, falling into the scopes of diesel (0.38–0.64) and gasoline (0.22–0.55) emissions (Shi *et al.*, 2014). The ratio of InP/(InP + BghiP) is reported as 0.18, 0.38 and 0.50 for gasoline, diesel and mixture of coal and biomass combustion (Liu *et al.*, 2019). The ratios fluctuated from 0.54 to 0.60, implying that PAHs were mainly from combustions of coal and biomass. Based on above analysis, we concluded that biomass burning and coal combustions were the dominant sources of PAHs in the Jinan aerosols, despite a sharp rise in vehicle emissions in recent years. Thus, the Jinan government should do their best great efforts to reduce the consumption of coal and biomass to decrease urban PAHs concentrations.

3.3 Sources Appointment

3.3.1 PMF

To quantitatively estimate the sources of target organic components in PM_{2.5} in different episodes, PMF model was chosen in this study. Detailed introduce about PMF model has been published in a previous article (Manousakas *et al.*, 2017). Fig. 6 illustrates the factor profiles resolved by the model for Jinan city.

In clean periods, the first factor was dominated by levoglucosan, followed by LMW and HMW fatty acids. Levoglucosan was a key tracer for biomass burning. Fatty acids also exhibited good correlation with levoglucosan as discussed above. Therefore, Factor 1 could be identified as biomass burning source, and the relative contribution of which was 45.1% in clean periods. Factor 2 was characterized by the high level of glucose. Glucose is mostly derived from soil resuspend and biological activities. Thus, Factor 2 could be defined as soil and plant emissions, accounting for 32.1%. Factor 3 was dominated by LMW PAHs, HMW PAHs and OPAHs. PAHs and OPAHs are largely from the anthropogenic emissions (e.g., vehicle emissions and coal combustions), and OPAHs were mainly originated from secondary oxidation as discussed above. Thus, Factor 3 can be regarded as the combustions of fossil fuels and secondary formation, accounting for 22.8%.

In haze periods, Factor1 was dominated by EC, levoglucosan and fatty acids, which can be

Fig. 6. Results of PMF for organic aerosols during (a) clean periods and (b) haze periods in PM_{2.5} in Jinan.

considered as biomass burning. The higher values of LMW PAHs, HMW PAHs and OPAHs were obtained in Factor 2, which could be regarded as fossil fuel combustions and the secondary formation. Factor 3 was characterized by high contribution of glucose, which can be regarded as soil and plant emissions. The relative contribution in haze periods in Jinan was 49.1% for biomass burning (Factor 1), 33.9% for fossil fuel combustions (Factor 2), and 16.9% for soil and plant emissions (Factor 3). These results again demonstrated the significant effect of biomass burning on the Jinan aerosols.

3.3.2 PSCF and CWT

Spatial distributions of potential source areas of $PM_{2.5}$ and its major organic components in Jinan during winter are illustrated in Fig. 7. The darker colors represented the heavier contribution weight of the areas. The relatively high PSCF values for $PM_{2.5}$ were largely distributed in the surrounding areas of the sampling site (Fig. 7(a)), such as Shandong Province and the BTH region, which indicated that air masses from these regions exerted an important influence on the haze occurrence in this region. The weaker PSCF values were distributed in Inner Mongolia and northern of Henan Province, suggesting that the effect of long-distance transport on $PM_{2.5}$ was minor. The calculated CWT values also supported the result of PSCF. For $PM_{2.5}$, the high CWT values (above $80 \mu g m^{-3}$) were observed in the BTH region and Shandong Province (Fig. 7(b)), indicating that the $PM_{2.5}$ in Jinan city were principally derived from the surrounding regions.

Fig. 7. (a) PSCF and (b) CWT values and spatial distribution of $PM_{2.5}$ during the whole sampling period. CWT values and spatial distribution of (c) EC, (d) levoglucosan, (e) fatty acids and (f) PAHs in haze periods.

Potential source regions of the major organic components in PM_{2.5} during haze periods determined by the CWT model were listed in Figs. 7(c–f). During haze periods, the high CWT values for EC, levoglucosan, fatty acids and PAHs were mainly distributed in the Shandong Province. Several studies of source apportionment have used PSCF and CWT values to conclude that the Shandong Province was the major source region of EC and PM_{2.5} (Kim *et al.*, 2018). As shown in Fig. 7(d), Shandong Province can be regarded as an important potential area for biomass burning in Northern China on account of high CWT values for levoglucosan. In general, the PSCF and CWT model indicated that Shandong Province was the important potential source region of organic compounds and PM_{2.5} in Jinan.

4 CONCLUSIONS

In recent years, China has suffered severe air pollution, especially in the NCP. To investigate the characteristic of PM_{2.5} pollution and the potential formation processes, PM_{2.5} samples were collected in Jinan, which is a typical polluted city in NCP. A total of 48 kinds of PM_{2.5}-bound organic components including 10 saccharides, 24 fatty acids, and 14 PAHs during a wintertime haze period were analyzed. The PM_{2.5} concentration in haze periods ($139.7 \pm 47.2 \mu\text{g m}^{-3}$) was 1.9 times higher than the NAAQS, Grade II limit ($75 \mu\text{g m}^{-3}$), implying that Jinan was facing severe PM_{2.5} pollution in wintertime. The ratios of OC/EC and correlation analysis implied that OC was principally from the mixture of biomass burning and coal combustions. During haze days, the concentrations of saccharides, fatty acids and PAHs significantly increased, and those species were robustly correlated with levoglucosan ($R^2 > 0.7$), suggesting that OAs in Jinan during the winter were highly affected by biomass burning. The C_{18:1}/C_{18:0} ratio in clean days (0.45 ± 0.24) was higher than that in haze days (0.22 ± 0.09), suggesting that the aerosols were more oxidized in clean periods. Based on the results of PMF model, three source factors were identified. During clean periods, biomass burning (45.1%) was the most dominant source, followed by soil and plant emissions (32.1%), and fossil fuel combustion and secondary formation (22.8%). However, the dominant source of OAs was biomass burning (49.1%) during haze periods, followed by fossil fuel combustion and secondary formation (33.9%), and soil and plant emissions (16.9%). High PSCF and CWT values indicated that Shandong Province and BTH region were the major potential source regions of PM_{2.5}. In addition, the CWT results showed that Shandong Province was the major source area of OAs in haze periods. Therefore, this study has an important contribution to understand the pollution characteristic and sources of Jinan aerosols, which can in turn deepen our comprehending of regional pollution in North China.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (Grant Nos. 41505112 and 41702373), the Natural Science Foundation of Shandong Province (Grant No. ZR2020MD113), and the Open Funds of State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences (Grant No. SKLLQG2020).

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at <https://doi.org/10.4209/aaqr.210180>

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