Saccharides in summer and winter PM$_{2.5}$ over Xi'an, Northwestern China: Sources, and yearly variations of biomass burning contribution to PM$_{2.5}$

Xin Wang[a,b,c], Zhenxing Shen[a,b,*], Fobang Liu[c,**], Di Lu[a], Jun Tao[d], Yali Lei[a], Qian Zhang[a], Yaling Zeng[a], Hongmei Xu[a], Yunfei Wu[e], Renjian Zhang[e], Junji Cao[b]

[a] Department of Environmental Sciences and Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[b] State Key laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710049, China
[c] Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz 55128, Germany
[d] South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou, China
[e] Key Laboratory of Regional Climate-Environment Research for Temperate East Asia, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

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ABSTRACT

Saccharides are important constituents in atmospheric aerosols but studies in northwestern China are still very limited. Here, we have measured anhydrosugars (levoglucosan, mannosan and galactosan), primary sugars (glucose, fructose, sucrose and trehalose), and sugar alcohols (arabitol, mannitol, sorbitol and inositol) in ambient PM$_{2.5}$ samples during summer and winter in Xi'an city, northwestern China. The abundance of total saccharides showed no clear seasonal variation, but apparent distinctions on the levels of the three categories and individual saccharide compounds were found. Primary sugars and particularly sucrose were dominant in summer. In contrast, levoglucosan was the predominant species in winter, contributing 60% of total saccharides. Source apportionment by positive matrix factorization revealed that airborne pollen was a major source of PM$_{2.5}$ associated-saccharides in summer, accounting for 35% of total saccharides; while biomass burning activities contributed to 60% of the winter saccharides. Furthermore, an increasing trend of biomass/biofuel burning contribution to winter PM$_{2.5}$ was observed in comparison with previous studies in Xi'an, suggesting a change in emission sources may be underway in northwestern China.

1. Introduction

Saccharides are a major class of water-soluble organic compounds (WSOC) in atmospheric aerosols. Much attention has been given to WSOC including saccharides, because they may alter the hygroscopic properties of particles and act as cloud condensation nuclei (CCN), affecting the radiative forcing of the atmosphere and climate (Chan et al., 2008; Rosenørn et al., 2006; Tang et al., 2016; Taylor et al., 2017; Xiang et al., 2017). Moreover, saccharides are relatively stable and specific in the atmosphere. Selected saccharide compounds have been proposed as tracers in several aspects, such as elucidating sources and transport pathways of atmospheric particles (Fu et al., 2012; Li et al., 2016b; Yttri et al., 2007), as well as assessing the atmospheric levels of bioaerosols (Gosselin et al., 2016; Rathnayake et al., 2017).

There are mainly three categories of saccharides in the atmosphere, i.e., anhydrosugar, sugar and sugar alcohol. Anhydrosugars including levoglucosan (LG), mannosan (MN) and galactosan (GA), are derived from the pyrolysis of cellulose and hemicellulose (Simoneit et al., 1999). They, especially LG, are good source tracers of biomass/biofuel burning (BB) attributing to their source-specific generation and atmospheric stability (Fraser and Lakshmanan, 2000; Simoneit et al., 1999). Although several studies found that coal combustion (CC) can also be a source of LG (Fabbri et al., 2009; Yan et al., 2018), resulting in an overestimation of BB sources. However, most of LG and its isomers originate from BB and thus, LG has still been used as a specific molecular marker for BB in current studies (Chen et al., 2018; Mao et al., 2018). Primary sugars mainly comprise of glucose, fructose, sucrose and trehalose (Medeiros et al., 2006). They are predominantly emitted from plant debris and pollen, but fungi and biomass burning can also contribute a minor fraction of these sugars in the atmosphere (Elbert et al., 2007; Fu et al., 2012; Medeiros and Simoneit, 2008). Sugar alcohols are derived from sugars that comprise a class of polyols. Arabitol

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and mannitol are the two typical sugar alcohols that have been widely monitored, because they can be used to identify the presence of airborne fungal spores and estimate their contribution to the mass of atmospheric aerosol particles (Bauer et al., 2008; Gosselin et al., 2016).

Many studies have been undertaken to characterize the atmospheric saccharides in a variety of regions and use them as indicators of major aerosol sources (Fu et al., 2012; Gosselin et al., 2016; Verma et al., 2018; Yttri et al., 2007; Zhang et al., 2007; Zhu et al., 2018). For example, Gosselin et al. (2016) compared online and offline measurements of airborne fungal spores concentrations in a semi-arid forest of North America, where they utilized arabitol and mannitol as the molecular markers to estimate the fungal spore concentrations in the offline measurements. Also, LG has been used to estimate the contribution of BB to $PM_{2.5}$ (aerodynamic diameter < 2.5 μm) and its WSOC and OC (organic carbon) content in urban sites of China (Wang et al., 2007; Yan et al., 2015; Yan et al., 2018; Zhang et al., 2007). For example, several studies have utilized LG or combined LG measurements with other chemical components analysis to estimate BB contribution to OC and $PM_{2.5}$ in Xi'an, the largest city in northwestern China located in the center of Guangzhong plain (Zhang et al., 2014; Zhang et al., 2015b; Zhu et al., 2017). This region is currently encountering severe air pollution due to rapid urbanization and industrialization and thus studies have focused on the aerosol components associated with anthropogenic emissions (Shen et al., 2008; Shen et al., 2010; Wang et al., 2018). Yet, it has been shown that emissions from biogenic and dust-related sources as well as primary biological aerosols also play important roles in the massive aerosol burden in Xi'an (Huang et al., 2014; Li et al., 2017; Shen et al., 2009). In addition, BB was commonly used for residential heating in rural or suburban areas in Xi'an in winter, that is burning maize straw in "Heated Kang", which has led to a serious pollution problem to rural and urban air (Shen et al., 2008; Shen et al., 2009; Shen et al., 2011; Sun et al., 2017). Therefore, a comprehensive field study on the molecular and seasonal variation of atmospheric saccharides may gain our understanding of the biogenic origins of aerosol particles in this region besides the anthropogenic sources. Li et al. (2016a) analyzed saccharide species and other components in total suspended particles during two haze episodes to investigate the sources and formation mechanisms of haze. However, the field studies of $PM_{2.5}$-associated saccharides are still limited in Xi'an, northwestern China.

In this study, we analyzed eleven different saccharides in $PM_{2.5}$ samples collected in Xi'an in summer and winter of 2015. Summer and winter are two seasons that may have high saccharide levels, as summer is one of the main pollen seasons and has high agricultural activities, and in winter BB was commonly used for residential heating. Here we investigated the concentration levels, seasonal variations and source profiles of atmospheric saccharides. Further, the contributions of BB to OC and $PM_{2.5}$ mass were estimated using LG as a molecular marker. Finally, the yearly contribution variations of BB to winter $PM_{2.5}$ were discussed to provide guidance for future control measures of particulate pollution.

2. Experimental

2.1. Aerosol sampling

The sampling site was located in an urban area of Xi'an (Fig. 1), surrounded by residential areas and heavy traffic roads. Aerosol sampling was conducted at the roof of a 15-m high building using a high-volume $PM_{2.5}$ sampler (Thermo, USA). The sampler was operated at a flow rate of $1.1 \pm 0.1 \, m^3 \, min^{-1}$ with a cutoff size of 2.5 μm. Details on the cutoff traceability and calibration of the $PM_{2.5}$ measurements have been described in a previous study (Aggarwal et al., 2013). Twenty-four hours samples were collected onto prebaked (800 °C, 6 h) quartz fiber filters (Whatman, UK) from June 2 to August 20, 2015, and from November 29, 2015 to January 10, 2016. A total of 60 filter samples were obtained for saccharides and other chemical components analyses.

2.2. Extraction and analysis

Filter aliquots (8.67 cm^2) were cut out from the whole filter and extracted three times with 10 mL ultrapure water by sonication for 20 min. The extracts were then filtered through a 0.45-mm microporous membrane into a clean flask, concentrated using a rotary evaporator and blown down to nearly dryness under pure nitrogen gas. Eighty microliters of N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA, Accustandard Inc) containing 1% trimethyl chlorosilane and 20 μL of pyridine were added to the extracts and reacted at 70 °C for 3 h. After the derivatization, excess BSTFA and pyridine were removed by a gentle flow of pure nitrogen gas. The derivatives were diluted by the addition of 100 μL n-hexane containing 1 ng μL^{-1} of the internal standard (hexamethylbenzene) prior to GC–MS analysis.

GC–MS analyses were performed on a Hewlette–Packard model 6890 GC coupled to Hewlette–Packard model 5975 MSD. The GC separation was achieved on a fused silica capillary column coated with HP5 (30 m × 0.25 mm × 0.25 μm). The GC operating conditions were as follows: temperature was held at 60 °C for 2 min, increased from 60 to 300 °C at a rate of 5 °C min^{-1} and held at 300 °C for 5 min. Helium was used as carrier gas at a constant flow rate of 1.0 mL min^{-1}. The sample was injected splitless with an injector temperature at 290 °C. The mass spectrometer was operated in the electron impact (EI) mode at 70 eV and scanned over the range of 33–500 amu. Individual compounds were identified by comparison of mass spectra with those of authentic standards. Compounds were quantified using selected ion peak areas and converted to compound mass using relative response factors determined by GC/MS injection of authentic standards in a concentration range of 0.1 to 100 mg L^{-1}. Field blank filters were analyzed in the same way as the real samples. No target compounds were detected in the blanks. The limits of detection (LOD) for target saccharide compounds ranged from 0.4 to 2.5 pg μL^{-1}. The mean recoveries for most of saccharide species that were spiked onto prebaked quartz fiber filters were better than 80%, while it was around 70% for mannitol.

2.3. Other chemical component analyses

The mass concentrations of $PM_{2.5}$ were determined gravimetrically using an electronic microbalance with a sensitivity of ± 1 μg (Sartorius MC5, Germany). Organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ samples were analyzed using an aerosol OC/EC analyzer (Sunset Laboratory Inc., US) following thermal/optical transmittance (TOT) method. Water-soluble potassium (K$^+$) was measured using an ion chromatograph (Dionex 500, US). Details of the chemical component analyses can refer to previous studies (Birch and Cary, 1996; Shen et al., 2014).

2.4. PCA and PMF receptor models

Multivariate analytical tools based on principle component analysis (PCA) and positive matrix factorization (PMF), were applied for the identification of emission sources to atmospheric saccharides. PCA aims at reducing a large set of original variables to a small set of factors that still contains most of the information. In this study, PCA was performed on the un-normalized concentrations of all saccharides using SPSS (IBM SPSS Statistics, version 19.0). Factors with eigenvalues > 1 were extracted and rotated using varimax method.

The PMF model (EPA PMF 5.0) was used to resolve potential sources and apportion their contribution to atmospheric levels of saccharides. PMF model has been proved to be a useful approach for verifying sources of atmospheric aerosols and gaseous pollutants (Kim et al., 2003; Ling et al., 2011; Paatero and Tapper, 1994). A detailed description of the PMF application on source apportionment can be found in EPA PMF 5.0 Fundamentals and User Guide (https://www.epa.gov/sites/production/files/2015-02/documents/pmf_5.0_user_guide.pdf).
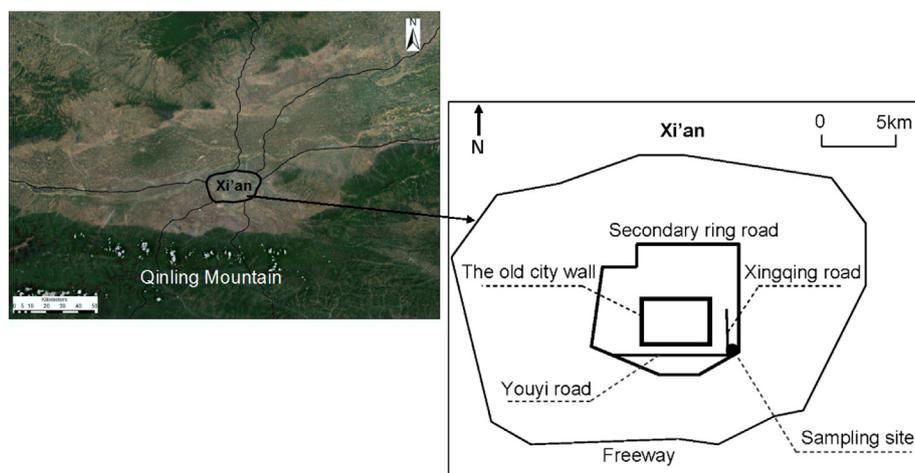
Fig. 1. Location of the sampling site in Xi'an.

The measurement uncertainty of 20% of the measured values of saccharide compounds was used for error estimates (30% uncertainty was used for mannitol). Half of the LOD was used for the value below the detection limit and their overall uncertainties were set at 5/6 of the LOD. PMF model was run with 4–7 factors and with random seeds. The 6-factor was considered to be the optimal one, based on the Q values (the weighted least-squares of difference between the observations and the model) and the interpretable factors identified by PMF. All the scaled residuals were between −4 and 4 with > 90% of them between ± 3. Although lower Q values and scaled residuals could be obtained when adding more factors, it did not result in much improvement to interpret the factor profiles based on the references for sources of atmospheric saccharides (Liang et al., 2016; Verma et al., 2018).

3. Results and discussion

3.1. Concentrations of saccharides in summer and winter PM$_{2.5}$

Table 1 and Fig. 2 (a) show the concentration levels of 11 measured saccharides in summer and winter. The mean concentration of total saccharides during the study period was 436.2 ± 115.6 ng m^{-3}, with a range of 244.8–713.9 ng m^{-3}. This result was higher than the values at an urban site of Shanghai (283.2 ng m^{-3}) (Li et al., 2016b) and a suburban site of Hongkong (258 ng m^{-3}) (Wan and Yu, 2007), but was comparable to that (386.9 ng m^{-3}) of Beijing urban PM$_{2.5}$ samples collected in 2013 (Yan et al., 2015). Interestingly, Liang et al. (2016)

Table 1
Concentrations of saccharides in PM$_{2.5}$ of Xi'an during summer and winter 2015.

| Species	Summer (n = 30)		Winter (n = 30)	
	Mean (ng m^{-3})	Range (ng m^{-3})	Mean (ng m^{-3})	Range (ng m^{-3})
Levoglucosan	100.4	60.2–217.7	268.5	110.1–481.9
Mannosan	5.6	3.3–12.0	15.3	6.4–28.7
Galactosan	6.3	3.8–13.6	18.0	7.5–33.6
Fructose	33.9	9.5–73.4	26.0	10.2–40.9
Glucose	60.5	16.1–151.6	42.0	11.2–152.7
Sucrose	134.3	26.8–374.7	13.7	6.3–23.7
Trehalose	21.7	6.2–52.9	11.0	6.5–21.8
Arabitol	10.6	1.6–23.9	8.9	1.8–26.3
Manitol	15.5	5.9–36.2	15.1	6.6–29.0
Sorbitol	13.8	5.9–30.4	17.7	5.9–36.4
Inositol	17.6	6.2–37.5	16.0	6.0–55.8
Total	420.2	280.1–668.9	452.2	244.8–713.9
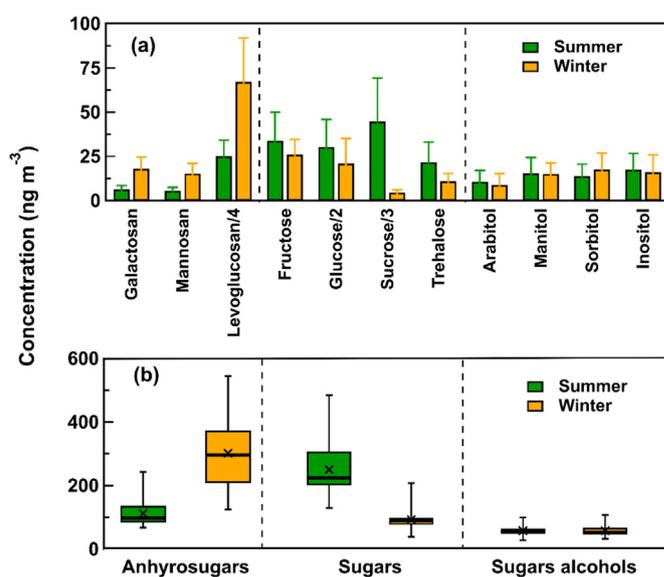
Fig. 2. (a) Mean concentrations of individual saccharide compounds in summer and winter. The error bars denote the standard deviation. (b) Box and whisker plots of three saccharide categories concentrations in summer and winter. The boxes represent the 25th percentile (lower edge), median (solid line), mean (X mark), and 75th percentile. The whiskers represent the minimum and maximum.

reported an annual mean value of total saccharides of 600.0 ± 399.1 ng m^{-3} in the same urban region of Beijing, in which the PM$_{2.5}$ samples were collected in 2010–2011. The main difference between the studies of Yan et al. (2015) and Liang et al. (2016) was on the LG level, which was about 169 ng m^{-3} higher in the study of Liang et al. (2016). Nevertheless, the high saccharide concentrations in Xi'an and Beijing were both mainly due to a high level of LG. This indicates BB emissions was a serious issue in such regions and could be an important factor responsible for the severe particulate pollution in the northern and northwestern China.

It was noticed that the difference of total saccharide concentrations between summer (420.2 ± 108.0 ng m^{-3}) and winter (452.2 ± 122.4 ng m^{-3}) was small in Xi'an, as shown in Table 1. However, the contribution from individual saccharides (Fig. 2(a)) as well as the three categories (Fig. 2(b)), i.e., anhydrosugar, sugar and sugar alcohol, displayed a distinct variation between summer and winter. For example, anhydrosugar accounted for 67% of total saccharides in winter while it was only 27% in summer. All the measured

anhydrosugars in winter, including LG, MN and GA, showed about three times higher than those in summer. The LG concentration was the highest among all the measured saccharides in winter, which is consistent with the previous results for particulate matter in Xi'an (Li et al., 2014). This should be mainly due to that biofuels such as crop residues and fuel wood were used for residential heating in winter in northwestern China (Wang et al., 2006; Zhang et al., 2014). In addition, the meteorological conditions during winter in Xi'an were characterized by stagnation with a low inversion layer (Zhang et al., 2014), which were not favored for the dilution and diffusion of atmospheric particles. Nevertheless, this result indicated a higher impact of BB on $PM_{2.5}$ levels in winter. Primary sugars including two monosaccharides (glucose and fructose) and two disaccharides (sucrose and trehalose), exhibited an inverse seasonal pattern with higher concentrations in summer. The portion of primary sugars in total saccharides was 60% in summer, which was much higher than that (20%) in winter. Sucrose even accounted for the highest concentration among all the measured saccharides. The concentration of sucrose was one order of magnitude higher in summer than winter. Summer is one of the main pollen seasons in northwestern China while winter is not due to low temperature (Liu et al., 2010). Thus, the much higher sucrose level in summer could be associated with substantial pollen emissions, since sucrose is a dominant component in airborne pollen grains (Verma et al., 2018). Other sources such as vegetation and agricultural activities are also more abundant in summer, resulting in the higher ambient levels of primary sugars. Sugar alcohols accounted for the least portion (13%) in both summer and winter and the mean concentrations were almost equal in these two seasons. Besides, the individual sugar alcohol compounds also had very close values between summer and winter. Note that although the sugar alcohol levels were similar between summer and winter, considering the meteorological conditions in winter intensifying the accumulation of ambient particles, our result might still indicate more emissions of sugar alcohols in summer.

3.2. Source apportionment of saccharides

Table 2 shows the PCA results of varimax rotated factor matrix. Four factors were extracted, explaining over 80% of total variance. The first factor (F1), dominated by LG, MN and GA, explained 34% of the variance. F2 had moderate to high positive loadings of sucrose, trehalose and fructose. This factor accounted for the variance of 15%. F3 was highly loaded with glucose and inositol with 14% variance. F4 with a variance of 11%, was correlated with arabitol, mannitol and sorbitol.

The aim of PCA is to explain the maximum variability of original dataset with a minimum number of factors (Li et al., 2016b). Thus, a factor may contain more than one emission sources. To better

Table 2
PCA results of varimax rotated factor matrix for the 11 saccharides in $PM_{2.5}$ from Xi'an.

	F1	F2	F3	F4
Levoglucosan	0.975	−0.091	−0.035	0.106
Mannosan	0.975	−0.089	−0.036	0.113
Galactosan	0.976	−0.101	−0.039	0.102
Fructose	−0.002	0.828	0.196	−0.136
Glucose	−0.213	−0.069	0.831	−0.081
Sucrose	−0.611	0.523	0.047	0.088
Trehalose	−0.276	0.775	−0.154	0.143
Arabitol	0.007	0.208	0.317	0.537
Manitol	0.112	0.041	−0.050	0.748
Sorbitol	0.067	−0.163	−0.127	0.742
Inositol	0.100	0.113	0.857	0.045
Initial eigenvalues	3.77	1.66	1.53	1.20
% of variance	34.25	15.12	13.89	10.86

Factor loadings > 0.5 are in bold. Only factors with eigenvalues > 1 are presented.

understand the contribution of possible sources to atmospheric saccharides, a PMF analysis was also utilized in this study. Fig. 3 shows the source profiles obtained by the PMF model. Each profile was identified by some typical molecular tracers as well as by comparing with several source profiles reported for atmospheric saccharides in previous studies (Fu et al., 2012; Li et al., 2016b; Verma et al., 2018). Factor 1 was considered as BB, as it was dominated by LG (64%), MN (65%) and GA (65%), which have been generally associated with BB (Nolte et al., 2001; Simoneit et al., 1999). Factor 2 has high levels of sugar alcohol compounds, i.e., arabitol (73%), mannitol (58%), sorbitol (61%) and inositol (53%). Arabitol and mannitol are common energy storage substances in fungal spores and are considered as good tracers for the quantification of airborne fungal spores (Bauer et al., 2008; Gosselin et al., 2016). Thus, we considered this factor to represent a source of fungal spores. It should be noted that glucose (11%) and fructose (28%) showed non-ignorable fractions in Factor 2. These results suggest that fungal spores can contribute partly to these hexose sugars in the atmosphere, which is consistent with the findings in previous studies (Elbert et al., 2007; Fu et al., 2012). Factor 3 is characterized by the dominance of sucrose (74%). Sucrose has been regarded as a tracer of pollen because it is the dominant sugar component in the phloem of plants and plays an important role in developing flower buds (Bieleski, 1995; Fu et al., 2012). Thus, this factor refers to airborne pollen. Factor 4 mainly consisted of trehalose (54%), mannitol (28%), sucrose (23%) and sorbitol (19%). These saccharide compounds were all detected in the suspended soil particles and associated microbiota (e.g., fungi, bacteria and algae) (Rogge et al., 2007; Simoneit et al., 2004). In particular, previous studies (Hackl et al., 2000; Kumar et al., 2017) proposed that trehalose can be used as a tracer of soil dust emission to the atmosphere. Hence, this factor was attributed to soil microbiota. Factor 5 was dominated by glucose (63%), followed by inositol (27%). Glucose is a major soluble carbohydrate in the bark and leaves of plants (Fu et al., 2012). Inositol can also be emitted from plant debris and pollens (Verma et al., 2018). Therefore, this factor refers to a vegetation source. Factor 6 was loaded with fructose (51%), trehalose (30%), inositol (19%), levoglucosan (14%), mannosan (14%), and galactosan (14%). Since the main emission sources of fructose and inositol, trehalose, and the three anhydrosugars were plant debris (Verma et al., 2018), soil biota and BB, respectively, this factor was likely associated with mixed sources contributing from vegetation, microbiota, and BB. Note that the relatively small number of samples (n = 60) input into the PMF model may not provide the most representative results of source profiles, but previous studies have shown that the PMF source apportionment results from similar numbers (n = 47 or 73) were still fairly robust (Fu et al., 2012; Mao et al., 2018).

The pie charts in Fig. 3(b) show the contribution of each source to total saccharides. A clear seasonal source variation was found between summer and winter. Note that since the mean concentrations of total saccharides were very close between summer and winter, the following comparisons of contribution ratios also reflect the comparisons of absolute concentrations. In summer, airborne pollen (34.8%) was found as the dominant contributor to total saccharides, whereas, the pollen contribution (0.5%) was negligible in winter. This was owing to that summer is one of the main pollen seasons in Xi'an but there were very limited blooming periods in winter (Liu et al., 2010). Similarly, a higher vegetation contribution in summer (15.1%) than winter (4.3%) possibly corresponds to more active local vegetation and agricultural activity in summer. The contribution from soil microbiota in summer (15.0%) was slightly higher than that in winter (9.3%), which can be due to the increased resuspension of soil particles during agricultural activity. In contrast, BB contributed the highest with an average contribution of 60.8% in winter, while it was only 10.4%, accounting for the lowest contribution in summer. The contribution from fungal spores showed no significant variation between summer (9.5%) and winter (8.9%), suggesting the saccharide emissions from fungi was relatively stable. The mixed factor involving of vegetation, soil microbiota and biomass
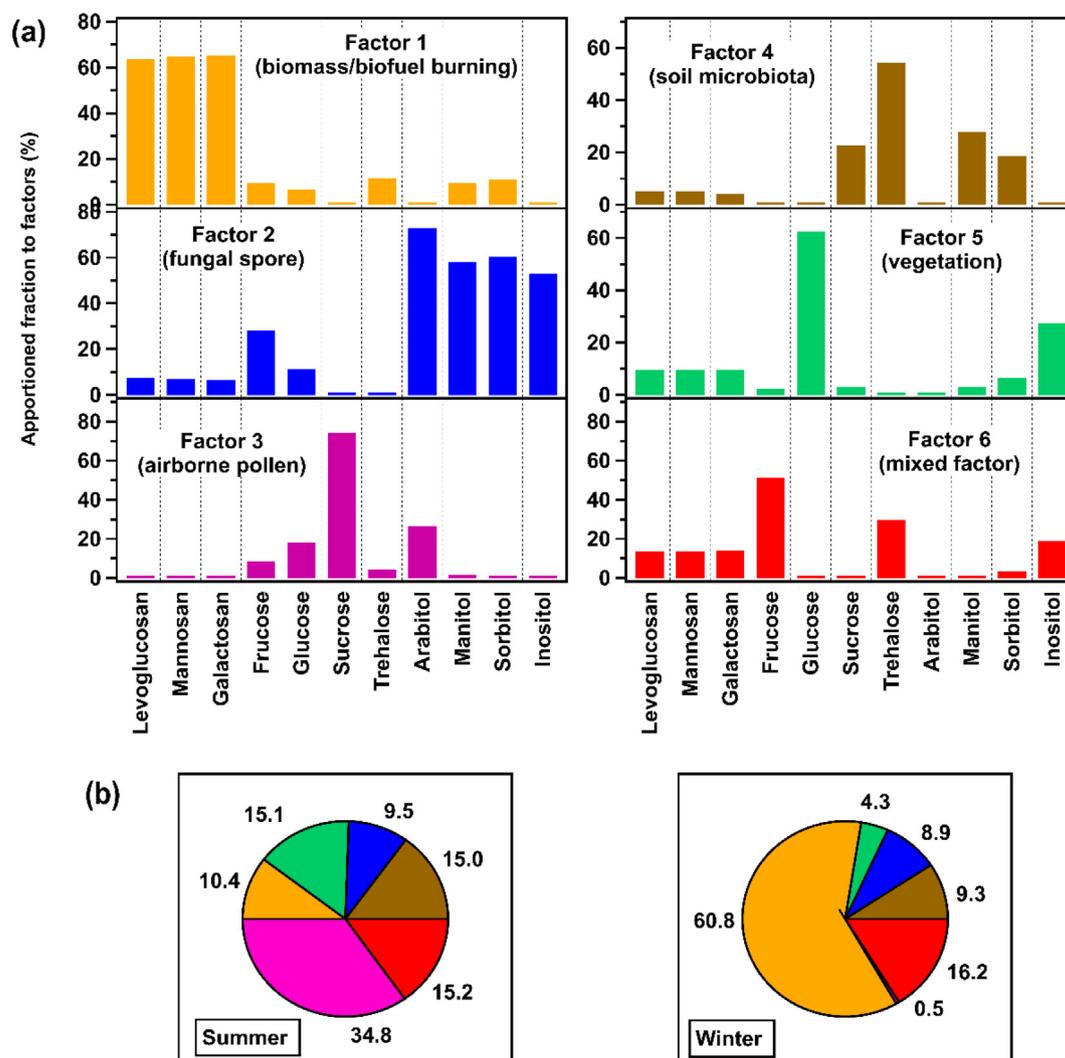
Fig. 3. (a) Factor profile obtained by positive matrix factorization (PMF) analysis. (b) Source contribution of the six factors to the total saccharides in PM$_{2.5}$ of Xi'an in summer and winter.

burning also showed no clear seasonal variation. But since the apportionment of each sub-factor to this mixed factor was unknown, no further discussion is present here.

3.3. Contribution of biomass burning to OC and PM$_{2.5}$

Besides the importance of understanding the biogenic emission sources of atmospheric saccharides, some saccharide molecular markers such as arabitol, mannitol, and LG, on the other hand, can be used to estimate the contribution of specific sources to the aerosol particle mass (Gosselin et al., 2016; Wang et al., 2007; Yan et al., 2015). Since BB is one of the major sources responsible for the severe PM$_{2.5}$ pollution in northern and northwestern China (Zhang et al., 2018; Zong et al., 2018), several studies have utilized LG to estimate the contribution of BB to OC and PM$_{2.5}$ (Chen et al., 2018; Wang et al., 2007; Yan et al., 2015; Zhang et al., 2014). However, in a recent study, Yan et al. (2018) showed that CC is a non-negligible source of ambient LG during wintertime in Beijing and the BB sources could be overestimated if using LG as a source marker in the northern China. But they also demonstrated that the ratios of LG to its two isomers, MN and GA, differ between CC and BB emissions. On the basis of their study, to examine if the LG was mostly emitted from BB or not, we first correlated LG with potassium ion (K$^+$, another well-known BB tracer) and its two isomers. The results are shown in Fig.4. LG was highly correlated with K$^+$ (R^2 = 0.8),

suggesting that LG was most likely from BB sources. The ratios (the regression slopes) of LG with MN and GA are 17.5 and 15.0. These values are in the range of that from crop straw and wood burning samples but much higher than that from coal burning samples (LG/GA of 9.5, LG/MN of 8.3) (Yan et al., 2018). Furthermore, the ratios of LG to OC (LG/OC, μg C μg^{-1}C) and LG to PM$_{2.5}$ (LG/PM$_{2.5}$, μg μg^{-1}) were almost equal for OC and PM$_{2.5}$ mass emitted from crop straw and wood combustion in China (Yan et al., 2018), i.e., LG/OC of 0.018 ± 0.012 and 0.018 ± 0.013, and LG/PM$_{2.5}$ of 0.020 ± 0.015 and 0.020 ± 0.016 for crop straw and wood burning products, respectively. Therefore, LG/OC of 0.018 and LG/PM$_{2.5}$ of 0.020 were utilized to estimate the BB contribution to OC and PM$_{2.5}$ in this study. Calculations were based on the following equations:

$$BB/OC = \frac{(LG/OC)_{ambient}}{(LG/OC)_{source}} \tag{1}$$

$$BB/PM_{2.5} = \frac{(LG/PM_{2.5})_{ambient}}{(LG/PM_{2.5})_{source}} \tag{2}$$

Results show that the contributions of BB to OC and PM$_{2.5}$ were similar in between summer and winter, as displayed in Fig.5. The values of BB/OC and BB/PM$_{2.5}$ were (28.9 ± 2.4) % and (12.2 ± 1.4) % in summer, and (32.4 ± 1.4) % and (16.0 ± 0.9) % in winter. Note that much higher LG concentrations suggested more emissions from biomass burning in winter but this did not correspond to higher BB/OC and BB/
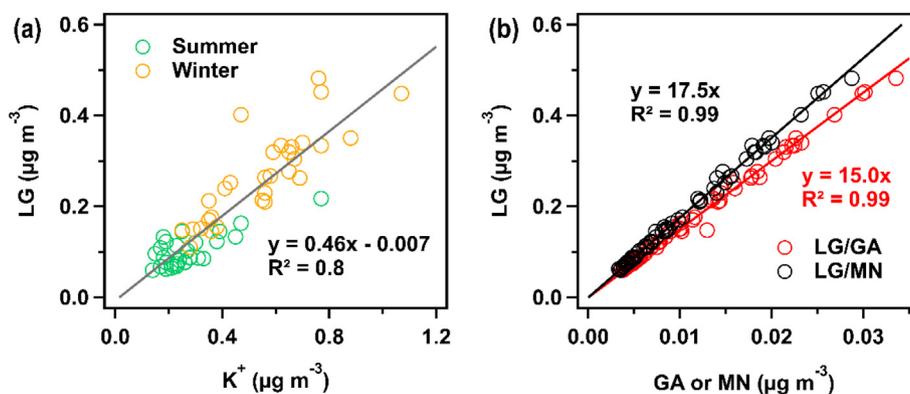
Fig. 4. (a) Correlations between levoglucosan (LG) and potassium ion (K^+). (b) Correlations between LG and its two isomers (galactosan, GA; mannosan, MN) during the sampling period.
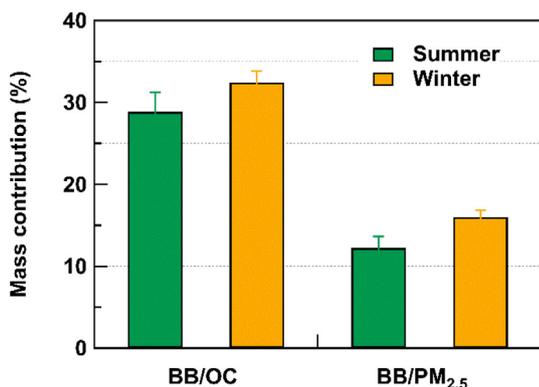

Fig. 5. Contribution of biomass burning (BB) to organic carbon (OC) and $PM_{2.5}$ mass concentrations.

$PM_{2.5}$, as the OC and $PM_{2.5}$ mass concentrations were much higher in winter (20.4 and 85.0 $\mu g\, m^{-3}$) than in summer (9.1 and 47.5 $\mu g\, m^{-3}$) as well. In contrast, our results indicate that BB was an important emission source and its contributions to OC and $PM_{2.5}$ were relatively constant in summer and winter.

3.4. Annual contribution trend of biomass burning to $PM_{2.5}$ in Xi'an

The results in this study were also compared with the reported values obtained by other methods. For example, Xu et al. (2016) analyzed selected chemical species and apportioned the source contribution of BB to $PM_{2.5}$ using PMF model. In another study by Huang et al. (2014), they estimated the BB contributions to organic aerosol and $PM_{2.5}$ by combing aerosol mass spectrometry measurements with the correction of species-dependent extraction efficiencies during a severe winter haze period. Based on these previous studies, we summarized the annual contribution trend of BB to winter $PM_{2.5}$ in Xi'an from 2006 to 2015, as given in Fig.6. Mean $BB/PM_{2.5}$ of ~6% were shown for wintertime $PM_{2.5}$ of inter-annual sampling during 2006–2010 (Xu et al., 2016), where the mean $PM_{2.5}$ concentrations were ~(200 ± 100) $\mu g\, m^{-3}$. During the wintertime of 2013, the $BB/PM_{2.5}$ was ~9% when $PM_{2.5}$ was in a range of 150–200 $\mu g\, m^{-3}$, and increased to 11% when $PM_{2.5}$ was in a lower range of 100–150 $\mu g\, m^{-3}$ (Huang et al., 2014). It should also be noted that in the study of Huang et al. (2014), the $BB/PM_{2.5}$ was only estimated to be 4 to 5% during the severe haze days ($PM_{2.5}$ > 300 $\mu g\, m^{-3}$), which may be due to an increase of other contributions such as dust-related sources and secondary aerosol species (Zhang et al., 2015a). In this study, the $PM_{2.5}$ concentration was (85 ± 21) $\mu g\, m^{-3}$ during wintertime of 2015, and the $BB/PM_{2.5}$ was estimated to be ~16%. Thus, overall the contribution of BB to wintertime $PM_{2.5}$ in Xi'an increased gradually year by year with decreasing
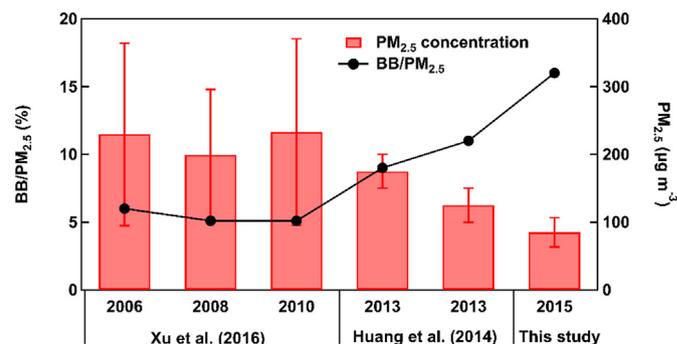

Fig. 6. The annual trend of BB contribution to winter $PM_{2.5}$ (left y-axis) and the corresponding $PM_{2.5}$ concentrations (right y-axis) in Xi'an during 2006–2015. The error bars of $PM_{2.5}$ concentrations in Xu et al. (2016) and this study represent the standard deviations of all the collected $PM_{2.5}$ samples. The bottom and top lines of the error bars in Huang et al. (2014) represent the minimum and maximum values of the classified $PM_{2.5}$ concentrations.

$PM_{2.5}$ concentrations, regardless of the different calculation methods. Indeed, one of the local policies to resolve air pollution in recent years was to reduce coal consumption. As a result, the contribution of coal combustion to $PM_{2.5}$ was reduced (Xu et al., 2016), while the relative contribution of BB increased. Interestingly, by converting to the absolute contribution, we found the BB contribution to $PM_{2.5}$ was stable from 2006 to 2015, accounting for ~13 $\mu g\, m^{-3}$ of $PM_{2.5}$ mass concentration. Yet the World Health Organization (WHO) air quality guildline for $PM_{2.5}$ was 10 $\mu g\, m^{-3}$ of annual average and 25 $\mu g\, m^{-3}$ of daily average (World Health Organization, 2005). Thus, our result suggests that except for reducing coal usage, much concern should also be given to biomass and biofuel consumption, in order to improve the air quality in wintertime of northwestern China. For example, Sun et al. (2018) reported that using the secondary air supply advanced stove can reduce the $PM_{2.5}$ emissions more effectively (7.7% reduction in $PM_{2.5}$ in normal conditions in winter) in comparison with the "Heated Kang". Therefore, clean heating in winter is suggested to be conducted in the future, such as using high efficiency advance stove rather than the traditional smoldering of "Heated Kang", or using clear fuels such as natural gas and electricity for heating in rural areas.

4. Conclusions

In this study, atmospheric saccharide compounds of summer and winter $PM_{2.5}$ in an urban area of Xi'an have been measured. The mean concentrations of total saccharides were very close between summer and winter. However, the contribution from the three categories and individual saccharide compounds were remarkably distinct in these two seasons. Summer was dominated with sugar species, particularly

sucrose, while anhydrosugar was the predominant group and levoglucosan contributed around 60% of total saccharides in winter. Results of PMF analysis also revealed specific sources of saccharide compounds during different seasons. The emissions from airborne pollen contributed 35% of total saccharides in summer; in contrast, 60% of total saccharides were derived from biomass burning activities in winter.

Furthermore, the average contribution from biomass burning to $PM_{2.5}$ in Xi'an was estimated to be 12% in summer and 16.0% in winter. In a comparison with previous studies, we found the biomass burning contribution increased from ~6% to 16% with a stable absolute contribution of $13 \, \mu g \, m^{-3}$ for wintertime $PM_{2.5}$ over the past few years, signifying the importance of controlling biomass burning emissions for the purpose of reducing the severe air pollution in winter. Our results therefore suggest that, effective strategies need to be taken to control emissions from biomass/biofuel combustion, besides the ongoing project of changing coal to natural gas for residential heating. Moreover, enforced measures may result in a changing face of urban air pollution (Lewis, 2018; McDonald et al., 2018) and thus, more studies need to be carried out to investigate contribution changes of biomass/biofuel burning as well as other emission sources, which may result from China's air pollution control policies.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

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