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Measurement report: Diurnal and temporal variations of sugar compounds in suburban aerosols from the northern vicinity of Beijing, China: An influence of biogenic and anthropogenic sources

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Abstract

Sugar compounds (SCs) are major water-soluble constituents in atmospheric aerosols. In this study, we investigated their molecular compositions and abundances in the northern receptor site (Mangshan) of Beijing, China, to better understand the contributions from biogenic and anthropogenic sources using a gas chromatography–mass spectrometry technique. The sampling site receives anthropogenic air mass transported by southerly winds from Beijing, while relatively clean air mass transported by northerly winds from the forest areas. Day- and nighttime variations were analyzed for anhydrosugars, primary sugars, and sugar alcohols in autumn 2007. Concentrations of overall SCs ranged from 30.8 to 875 ng m^{-3} (avg. 325 ng m^{-3}), showing diurnal variations with higher levels in daytime (351 ng m^{-3}) than nighttime (276 ng m^{-3}). Interestingly, biomass burning (BB) tracers were more abundant in nighttime than daytime, while other SCs showed different diurnal variations. Levoglucosan was found as a dominant sugar among the observed SCs, indicating an intense influence of BB over Mangshan. The levels of fungal tracers (arabitol and mannitol) were higher in daytime than nighttime, suggesting a significant transport of fungal spores and microbes to the receptor site by atmospheric transport from Beijing area. The plant emissions from Mangshan forest park significantly control the diurnal variations of glucose and fructose. The pollen tracer (sucrose) showed a clear diurnal variation, peaking in daytime due to higher ambient temperature and wind speed. We found that soil dust contributes to trehalose in daytime while microorganisms were responsible to its emissions in nighttime. The meteorological parameters (relative humidity, temperature and rainfall) significantly affect the concentrations and diurnal variations of SCs. Positive matrix factorization analysis suggested that local BB and bioaerosols transported from Beijing area were significant sources of SCs. (289)

Keywords: Anthropogenic bioaerosols, biomass burning, pollen tracer, fungal tracers, soil dust, and microbial tracers

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1. Introduction

An increased economic growth in East Asian countries causes serious emissions of anthropogenic gas and aerosols, and biomass burning (BB) products (Lin et al., 2014). The rapid urbanization and population growth also contribute to enhance the emission of organic aerosols and bioaerosols into the atmosphere, which comprised of a complex mixture of diverse molecules (Xu et al., 2011). They play essential roles in global climate changes via the modification of radiative forcing and cause a severe negative impact on human health (Fuzzi et al., 2007). Organic aerosols contain water-soluble organic compounds (WSOCs), which can act as cloud condensation nuclei (CCN) (Kanakidou et al., 2005). The BB significantly emits organic aerosols and gases into the atmosphere, controlling the air quality levels (Kanaya et al. 2013; Streets et al., 2003; Sullivan et al., 2008; Deshmukh et al., 2019a). BB is essentially a primary source of organic aerosols, affecting the earth's radiative forcing by scattering or absorbing incident solar radiation (Kanakidou et al., 2005). The BB tracers are subjected to long-range atmospheric transport, once they are emitted to the atmosphere (Verma et al., 2015). Levoglucosan is a thermal decomposition product of cellulose and hemicellulose, which is generally found as one of the major organic constituents in the BB aerosols (Simoneit et al., 1999; 2002).

SCs are ubiquitous in the atmosphere from different geographical locations including urban, forest, marine, and polar regions (Wang et al., 2006; Simoneit et al., 2004b; Burshtein et al., 2011; Fu et al., 2010; Wan et al., 2017). SCs are emitted from algae, microbes, pollen, suspended soil particle, and associated biota into the atmosphere (Carvalho et al., 2003). Winds play a vital role in the distribution of microorganisms from their source regions to receptor sites (Brown and Hovmoller, 2002). Thus, the transport of bioaerosols has been emphasized in the past studies (Yamaguchi et al., 2012). Fungi are essential microorganisms in the ecosystem, which mostly emit spores to the environment (Elbert et al., 2007). Fungal spores can travel long distances in the atmosphere (Burshtein et al., 2011). Sugar alcohols like arabitol and mannitol are emitted via the metabolism of microorganisms and fungi, thus they have been proposed as specific tracers for microbial and fungal activities (Bauer et al., 2008; Simoneit et al., 2004b). Bacteria, fungi, invertebrates, and lower plants also emit a significant amount of trehalose (Bieleski, 1995). There are several sources of sugars in the atmosphere, including higher plants and soil dust (Jaenicke, 2005). Higher plants synthesize sugars during photosynthesis, which are circulated by phloem to accumulate in root cells and developing plant sections (Pacini, 2000). Various sugars are present in terrestrial plant fruits, flowers, and plant tissues (Cowie et al., 1984).

Previous studies analyzed aerosol samples for sugar compounds (SCs) and discussed several

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factors to control their levels in the local and global atmosphere. Recently, Xu et al. (2020) examined the seasonal molecular distributions of primary biological aerosols and biomass burning aerosol samples collected from urban Beijing. They reported high levels of arabitol, mannitol, sucrose, glucose, fructose in vegetation-growing season. Kang et al. (2018) also reported higher concentrations of sugars in the urban aerosols from Beijing and suggested a large contribution of coal combustion and agriculture residue burning under stable meteorological conditions in winter and spring. Verma et al. (2015, 2018) reported thirteen years (2010-2013) observation on the remote marine aerosols from Chichijima Island. They concluded that long-range transport of organic-/bio-aerosols from East Asia significantly control the levels and compositions of SCs over the North Pacific. The above studies discussed the several factors that affect the concentrations of SCs in the aerosol samples collected from urban and remote areas. Xu et al. (2020) reported multiple sources for arabitol, mannitol, glucose, sucrose and trehalose. Verma et al. (2015, 2018) discussed the atmospheric circulations that significantly affect the seasonal concentrations of SCs.

In this study, we conducted the analyses of SCs in the aerosol samples collected from the northern suburb of Beijing. Beijing is one of largest polluted cities in East Asia. Its air quality deteriorates seriously due to rapid economic growth, resulting in massive emissions from vehicles and industries (Cao et al., 2014; Qiao et al., 2018; Tao et al., 2017; Wei et al., 2018; Yu et al., 2013). Here, we present comprehensive data sets of anhydrosugars, primary sugars, and sugar alcohols in the suburban aerosol samples and discuss their diurnal variations to explain the source variance following the wind patterns in day and nighttime. The positive matrix factorization (PMF) has been applied to the measured SCs in the aerosol samples to clarify the influence of local meteorology of sampling site and atmospheric transport from Beijing by southerly winds and Mangshan National Forest Park by northerly winds on the molecular distributions of SCs. Using the mass concentration ratio of levoglucosan to mannosan, we discuss the relative contribution of hard and softwood burning to the air quality of Mangshan. This study also discussed carbon contributions of SCs measured in the Mangshan aerosol samples from different sources.

2. Materials and Methods

2.1. Site description

The aerosol samples were collected near the entrance of Mangshan National Forest Park (40.28 N, 116.26 E; elevation of 187 m above sea level) from 15th September to 5th October 2007 using a high-volume air sampler (Kimoto-AS810A) (He et al. 2014, 2015). The Mangshan site is located at 40 km north of Beijing and is surrounded by urban area in the south and forest areas with

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the national park in the north (Fig. 1). The ambient temperature was higher in daytime (23.9 °C) than nighttime (12.1 °C) with an average of 17.8 °C during the campaign. The relative humidity (RH) varied significantly from 22.1% to 90.5% with an average of 51.7 % during the study period. Interestingly, a wind pattern was characterized at the sampling site. The southwest wind (69.9%) prevailed during the day, followed by northeast wind (23.4%) and southeast wind (6.2%). The northeast wind (99.5%) was dominated at night, which is consistent with the air mass back trajectories (He et al., 2014). The daytime wind from the southwest direction passed over Beijing, delivering anthropogenic air mass to Mangshan site. The northeast wind carried clean air mass from the forest area at night. The rainfall was observed at the midnight on 15th September, morning of 17th to evening 18th September, night of 26th September, and light rain lasted from October 4 to the end of the campaign (Fig. 2).

2.2. Sampling details and analytical methodologies

We collected 3-h daytime (n=26), 9-h daytime (n=12), and 15-h nighttime (n=20) samples together with four field blanks. After the sampling, filters were individually stored in a glass bottle with a Teflon-lined cap at -20 °C before analysis. Total of 58 aerosol samples were analyzed for anhydrosugars, primary sugars, and sugar alcohols (Table 1). To derivatize hydroxyl (OH) and carboxyl (COOH) groups to trimethylsilyl (TMS) ethers and esters, respectively, the extracts were reacted with 60 µl of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl (TMS) chloride in the presence of 10 µL of pyridine at 70 °C for three hours. After the reaction, n-hexane was used for dilution, and C_{13} n-alkane was added as an internal standard before GC-MS analysis. Agilent model 6890 gas chromatograph (GC) combined to Agilent model 5973 mass selective detector (MSD) was used to analyze SCs. The detailed description of GC-MS operation and identification of SCs can be found in Verma et al. (2015, 2018).

3. Results and Discussion

3.1. Ambient concentrations and diurnal variations of SCs

We detected totally ten SCs including three anhydrosugars, four primary sugars and three sugar alcohols in the Mangshan aerosol samples. Figure 3a-j showed the temporal variations of SCs in the Mangshan aerosol samples. Figure 4a-c and Table 1 show minimum, maximum and average concentrations of anhydrosugars, primary sugars and sugar alcohols with a standard deviation. The overall concentrations of SCs varied from 30.8–875 ng m^{-3} (avg. 325 ng m^{-3}). They showed distinct diurnal variations with daytime high (34.1–875 ng m^{-3}; avg. 351 ng m^{-3}) and nighttime low values

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(30.8 – 759 ng m^{-3}; avg. 276 ng m^{-3}). Interestingly, higher average concentrations of SCs were reported at Mt. Tai (daytime 640 ng m^{-3} and nighttime 799 ng m^{-3}) in the North China Plain (Fu et al., 2008) than those of the Mangshan site from this study.

The diurnal variations of SCs may be significantly influenced by the delivery of anthropogenic air masses from megacities such as Beijing, Hebei, and Tianjin, where contaminants are heavily generated by fossil fuel combustion and biomass burning. Anthropogenic aerosols emitted from urban areas are probably transported to the northern receptor site in daytime by a southerly wind. Therefore, the high levels of SCs in daytime may be related with the transport of organic and bio-aerosols from urban regions. In addition, at nighttime the wind direction is shifted to northerly, delivering comparatively clean air masses from the Mangshan National Forest area to the sampling site. Air mass from the forest may significantly contribute nighttime SCs in the Mangshan site. Although transported air mass may have mainly controlled the levels of SCs, contributions of local SCs cannot be excluded.

3.1.1. Ambient concentrations and diurnal variations of anhydrosugars

Anhydrosugars are important BB tracers because they are emitted from the pyrolysis of cellulose and hemicellulose (Simoneit et al., 1999). Concentrations of anhydrosugars ranged from 6.01 to 556 ng m^{-3} (avg. 116 ng m^{-3}), contributing 31.9% of overall SCs in the Mangshan aerosols (Table 1). Figure 3a-c shows the temporal variations of anhydrosugars. They are more abundant in nighttime (avg. 152 ng m^{-3}) than daytime (avg. 97.1 ng m^{-3}). Levoglucosan is most abundant anhydrosugar detected in Mangshan aerosols, whose concentrations are higher in nighttime (5.66–482 ng m^{-3}, avg. 132 ng m^{-3}) than daytime (1.17-418 ng m^{-3}, avg. 83.2 ng m^{-3}) (Table 1). Concentrations of galactosan are higher in nighttime (0.69-48.0 ng m^{-3}, avg. 13.0 ng m^{-3}) than daytime (0.14-45.3 ng m^{-3}, avg. 8.53 ng m^{-3}). Similarly, mannosan is more abundant in nighttime (0.53-26.1 ng m^{-3}, avg. 7.35 ng m^{-3}) than daytime (0.13-24.3 ng m^{-3}, avg. 5.37 ng m^{-3}). Levels of all anhydrosugars in Manshang are lower than those reported from Mt Tai, China (daytime, 391 ng m^{-3} and nighttime, 459 ng m^{-3}) (Fu et al., 2008).

Biomass burning (BB) tracers showed significant positive correlations each other, i.e., levoglucosan and galactosan (r = 0.98), levoglucosan and mannosan (r = 0.97), and galactosan and mannosan (r = 0.98), suggesting their similar sources in the Mangshan aerosols (Fig. 5a-c). Figures 2 and 3 clearly show that concentrations of BB tracers decreased with increasing ambient temperature. In general BB is common for cooking and heating in East Asian countries (Verma et

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al., 2015). Hence, it is evident that increased BB activities at nighttime are associated with cool temperature (Fig. 2). The nighttime samples were collected from 18:00h to 09:00h, including peak hours of BB for cooking and space heating. Therefore, it is reasonable to detect higher abundances of BB tracers in nighttime than daytime in the Mangshan site. Warmer ambient temperature was recorded in daytime between 09h to 15h during the campaign, which is associated with declined BB activities. Kang et al. (2018) reported high levels of levoglucosan (avg. 110 ng m^{-3}) in autumn aerosols from Beijing, China. We found a significant enhancement of BB tracers in nighttime, which may be emitted mainly by local BB. However, transport from the North China Plain to the Mangshan site by northerly winds cannot be excluded (Fig. 4).

3.1.2. Ambient concentrations and diurnal variations of primary sugars

The fragment of vascular plants contains primary sugars (Medeiros et al., 2006). Concentrations of primary sugars ranged from 9.41–565 ng m^{-3} (avg. 133 ng m^{-3}) in Mangshan aerosols. Primary sugars were found as the most abundant sugars, contributing to 41.8% of the SCs (Table 1). They showed apparent diurnal variations with daytime high (avg. 166 ng m^{-3}) and nighttime low values (avg. 69.4 ng m^{-3}) (Figs. 3g-j, 4a-c). Graham et al. (2003) also reported similar diurnal variations of primary sugars for the Amazon forest aerosols.

Sucrose was found as dominant sugar among primary sugars with a concentration range of 0.02-474 ng m^{-3} (avg. 58.5 ng m^{-3}), accounting for 44% of measured primary sugars in Mangshan aerosols. Pollen was reported as dominant sources for sucrose in aerosols collected from a rural site in Texas (Jia et al., 2010). Fu et al. (2012) found high sucrose concentrations up to 1390 ng m^{-3} in the aerosols from Jeju Island, South Korea. We found a significant diurnal variation of sucrose in Mangshan aerosols with higher levels (82.9 ng m^{-3}) in daytime than nighttime (12.3 ng m^{-3}). Interestingly, significantly lower concentrations of sucrose than the Mangshan site were reported in urban aerosols from Nanjing, China, in summer (daytime, 13.2 ng m^{-3}; nighttime, 9.44 ng m^{-3}) and winter (daytime, 14.5 ng m^{-3}; nighttime, 10.9 ng m^{-3}) (Wang and Kawamura, 2005). In addition, much lower concentration of sucrose was reported for the aerosols from Mt. Hua (daytime, 3.1 ng m^{-3}; nighttime, 2.6 ng m^{-3}) in central China (Li et al., 2012). These comparisons indicate that high levels of sucrose are found in forest aerosols rather than urban and anthropogenic aerosols.

Meteorological parameters such as temperature, rainfall, wind speed, and solar radiation, are associated with the concentration levels of sucrose in the forest site. The pollen activities are significantly affected by the local meteorology (Verma et al., 2018). Interestingly, Figure 3d shows a high peak of sucrose from 02h to 15h with higher ambient temperature, whereas lower concentrations of sucrose were observed from 15h to 09h with lower ambient temperature. High daytime concentrations of sucrose might be related to the increased daytime ambient temperature, low RH, and high solar radiation. Wickmen (1994) reported that the meteorological conditions resulted in the catapulting pollen into the air and the opening of pollen-laden flower anthers, under the influence of strong daytime winds and convective activity, causing enhanced entrainment and dispersal of the particles. Pacini (2000) also reported that higher levels of sucrose in daytime coincide with higher counts of pollen, fern spore, and insect. The significant correlations of sucrose with ambient temperature (r = 0.52) and solar radiation (r = 0.55) further supported the association of meteorological parameters with the sucrose concentrations of Mangshan aerosols (Fig. 5d, e).

Five rain events were recorded during the campaign, i.e., 15th, 17th, 18th and 26th September, and 1st and 5th October (Fig. 3). Pollens are significantly settled down by wet scavenging during rain events because their sizes are large. Low sucrose concentration was found from the beginning of sampling to the morning of 20th September and from the afternoon of 26th September to the end of the sampling campaign (Fig. 3d). In addition, the increased concentrations of sucrose were found in the aerosol samples collected from 20th to 22nd September and moderate concentrations observed after 23rd to the evening of 25th September during non-precipitation events. Consequently, the pollens might be significantly scavenged from the atmosphere during wet precipitation (washout effect). The wet scavenging resulted in lower sucrose concentrations at the earlier periods, while high sucrose concentrations were found during later periods.

The concentrations of glucose ranged from 1.86 to 297 ng m^{-3} (avg. 40.0 ng m^{-3}). Similarly, a wide range of fructose (1.72-117 ng m^{-3}, avg. 20.1 ng m^{-3}) was observed in Mangshan aerosols (Table 1). The levels of glucose are equivalent to that (50.1 ng m^{-3}) reported from the Howland Experimental Forest site in USA (Medeiros et al., 2006). The high concentrations of these sugars suggested that they might be associated with pollen/fern spores, insects, and other plant materials from the background forest region. The nectars and fruits of subtropical and tropical plants are reported as key sources for these primary sugars (Baker et al., 1998). Several studies have reported lichens and soil dust as major sources of both primary sugars (Dahlman et al., 2003; Nolte et al., 2001). The local vegetation and autumn decay of vascular plant leaves in the Mangshan forest might have contributed to high levels of these primary sugars.

Glucose and fructose showed significant diurnal variations, whose concentrations were higher in daytime (44.2 ng m^{-3} and 23.9 ng m^{-3}, respectively) than nighttime (32.0 ng m^{-3} and 12.8

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ng m^{-3}, respectively) in Mangshan aerosols (Fig. 3e, f; 4b, c; Table 1). Similar diurnal variations but lower concentrations were reported in Mt. Hua aerosols collected from the Guanzhong Plain, central China in January (daytime 6.2 ng m^{-3} and 6.3 ng m^{-3}, respectively; nighttime 4.8 ng m^{-3} and 4.5 ng m^{-3}, respectively), during a typical burning season of biofuel and coal for house heating (Li et al., 2012). Similar trends of glucose and fructose were reported in urban Nanjing aerosols (daytime 16.9 ng m^{-3} and 18.9 ng m^{-3}, respectively, and nighttime 21.6 ng m^{-3} and 30.9 ng m^{-3}, respectively) (Wang and Kawamura, 2005). On the other hand, higher concentrations with different diurnal variations (daytime 49.5 ng m^{-3} and 16.7 ng m^{-3}, respectively; nighttime, 74.7 ng m^{-3} and 21.3 ng m^{-3}, respectively) have been reported for Mt. Tai aerosols collected from the North China Plain (Fu et al., 2008). Interestingly, both primary sugars were significantly enriched in forest aerosol samples compared to urban aerosols.

The vegetation and pollen/fern spores from the local forest area of Mangshan significantly contributed to the high levels of glucose and fructose. The Mangshan site is located at the northern receptor of anthropogenic air mass from megacities by southerly winds. However, the southerly winds also cover the major area of the vegetation region, including the northeast direction (23.4%) in daytime (He et al., 2014), which may transport the primary sugars (glucose and fructose) abundantly to the Mangshan site. Although the wind direction shifted to northeasterly (99.5%) in nighttime, sugar emissions from the vegetation sources may have decreased due to lower ambient temperature, which may be a possible reason for low levels of glucose and fructose in nighttime aerosols at Mangshan site.

Trehalose in the environment is significantly controlled by the activities of bacteria, fungal spores, yeast, algae, invertebrates, and plant species as well as suspended soil particles (Verma et al., 2018). The concentrations of trehalose ranged from 0.06 to 39.5 ng m^{-3} (avg. 14.3 ng m^{-3}, see Table 1), which are lower than those of TSP samples collected from urban Guangzhou during summer (67.8 ng m^{-3}) and autumn (42.7 ng m^{-3}) (Ma et al., 2009). Interestingly, higher trehalose concentrations have been reported in urban (29 ng m^{-3}) and suburban (27 ng m^{-3} and 30 ng m^{-3}) aerosol samples than rural aerosols in Norway (3.8 ng m^{-3}) (Yttri et al., 2007). The above results emphasizes that fungi and microbes associated with anthropogenic and bioaerosols, which are vigorously emitted in the urban and suburban areas, may be responsible for the high levels of trehalose (Verma et al., 2018).

Trehalose showed insignificant diurnal variation, whose concentrations ranged from 0.06–34.4 ng m^{-3} (avg. 15.3 ng m^{-3}) in daytime and 0.87–39.5 ng m^{-3} (avg. 12.3 ng m^{-3}) in nighttime (Fig. 4b, c). The similar levels of trehalose in day- and nighttime indicated its multiple sources in the Mangshan aerosols. The southerly winds might transport anthropogenic aerosols associated with microorganisms, which emit trehalose at nighttime due to low temperature and high RH. Interestingly, the nighttime concentration of trehalose was significantly covaried with arabitol and mannitol (r = 0.76 and 0.85, respectively) (Fig. 5f, g), suggesting that fungal and microbial species contributed to trehalose in nighttime. The metabolic activities of microorganisms increase in autumn with favorable metrological conditions to emit trehalose (Verma et al. 2018). In addition, Hackl et al. (2000) found trehalose as dominant sugar in spring aerosols and proposed it as a tracer for soil dust particles. Daytime wind transports soil particles from the urban area due to the active building constructions. The transported soil particles may contribute to the high levels of trehalose in daytime at the receptor site of Mangshan. The trehalose concentration was significantly correlated with Ca (r = 0.82) in daytime, indicating a significant contribution of soil dust to the site (Figs. 3g, 5h).

3.1.3. Ambient concentrations and diurnal variations of sugar alcohols

The concentrations of sugar alcohols ranged from 8.53–259 ng m^{-3} (avg. 75.8 ng m^{-3}), contributing 26.4% of total SCs in Mangshan aerosols (Table 1). Sugar alcohols showed distinct diurnal variations, with daytime high (avg. 87.4 ng m^{-3}) and nighttime low (avg. 53.7 ng m^{-3}) concentrations. The sugar alcohols are emitted by the metabolic activities of fungi and microbes into the atmosphere (Filippo et al., 2013). The mannitol and arabitol are key components of fungal spores, and thus they are termed as fungal tracers (Bieleski, 1995). Mannitol was found as a dominant sugar alcohol in the Mangshan aerosols, whose concentrations ranged from 4.19–182 ng m^{-3} (avg. 44.1 ng m^{-3}) followed by arabitol (3.89–72.2 ng m^{-3}, avg. 29.1 ng m^{-3}). The inositol was found as a minor sugar alcohol with an average concentration of 2.62 ng m^{-3}. During precipitation events, concentrations of arabitol, mannitol, and inositol decreased (Fig. 3h-j). Interestingly, their concentrations increased gradually after the end of precipitation, following the increases in ambient temperature and RH (Figs. 2, 3h-j).

Significantly low levels of mannitol and arabitol were reported for remote sites, including the North Pacific (0.01-0.23 ng m^{-3} and 0.01-0.19 ng m^{-3}) and North Atlantic (0.01-0.06 ng m^{-3} and 0.006-0.07 ng m^{-3}) (Fu et al., 2011). These remote locations are far away from the continent and anthropogenic activities. The moderate levels of mannitol and arabitol compared to the Mangshan

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site were reported at Gosan, Jeju Island (11 ng m^{-3} and 12 ng m^{-3}, respectively) (Fu et al., 2012), Cape Hedo, Okinawa Island (13.0 ng m^{-3} and 12.3 ng m^{-3}, respectively) (Zhu et al., 2015) and Chichijima Island (18.2 ng m^{-3} and 15.8 ng m^{-3}, respectively) (Verma et al., 2018) in autumn. These islands are situated in the outflow region of East Asia with the emissions of bio- and anthropogenic aerosols from megacities. These continental sources might affect the levels of trehalose, arabitol, and mannitol over the remote ocean (Verma et al., 2018).

Mannitol and arabitol showed a strong correlation (r = 0.81) (Fig. 5i), suggesting similar sources of both sugar alcohols in the Mangshan site. The significant diurnal co-variance of mannitol and arabitol is characterized by higher concentrations in daytime (51.7 ng m^{-3} and 32.5 ng m^{-3}, respectively) than nighttime (29.6 ng m^{-3} and 22.5 ng m^{-3}, respectively) (Fig. 4b, c). The lower concentrations than Mangshan were reported for aerosol samples from Mt. Tai in the North China Plain in daytime (77.8 ng m^{-3} and 52.5 ng m^{-3}, respectively) and nighttime (83.9 ng m^{-3} and 56.4 ng m^{-3}, respectively) (Fu et al., 2008). Additionally, the diurnal variations of fungal tracers may be significantly influenced by local meteorological parameters. RH well correlated with mannitol (r = 0.57) and arabitol (r = 0.69) (Fig. 5j, k). The temporal trends of arabitol, mannitol and inositol correlated with RH. Therefore, we hypothesized that increased daytime concentrations of arabitol and mannitol (Fig. 3h, i) are associated with increased emissions of yeast and fungal spores that are transported from megacities to the receptor site. On the other hand, lower concentrations can be explained by clean air mass delivered by mountain breeze from the Mangshan National Forest area in nighttime.

3.2. Positive matrix factorization (PMF) analysis

To investigate the source apportionment of SCs, positive matrix factorization (PMF) analysis was performed for the studied aerosol samples using tracer compounds for anhydrosugars, primary sugars and sugar alcohols. The PMF analysis resulted five interpretable factors, which reproduced more than 95% of SCs. Paatero et al. (2002) and Zhou et al. (2004) discussed the determination and applications of PMF in details. Figures 6 and 7 show the factor profile resolved by PMF analysis of the Mangshan aerosol samples. The percentages of each component are summed for factors 1 to 5 to be calculated as 100%.

Factor 1 is characterized by high contribution of glucose (80.2%) followed by fructose (69.6%), mannitol (24.8%) and inositol (15.1%) (Fig. 6a). Glucose and fructose are highly water-soluble SCs that are present in the leaves and bark of plants (Graham et al., 2003). High

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concentrations of glucose and fructose have been reported in vascular plants and phytoplankton by Cowie and Hegdes (1984). The dominant glucose and fructose in the Mangshan aerosol samples collected in autumn are rational as leaf senescence and decay result both primary sugars being released into the atmosphere during the fall season. We found an excellent correlation between glucose and fructose (r = 0.94) in the Mangshan aerosols (Fig. 5l), indicating the similar vegetation sources for both sugar species in autumn (Baker et al., 1998; Burshtein et al., 2011; Pacini, 2000). The SCs emitted from vegetation during the campaign significantly contributed to factor 1. Therefore, factor 1 can be termed as a vegetation factor due to the high abundances of both sugar species.

Factor 2 is dominated by high loading of trehalose (80.2%), followed by mannitol (29.7%), galactosan (19.8%), and arabitol (18.2%) (Fig. 6b). The contribution of trehalose to soil dust has been reported in several studies from different locations around the world, suggesting trehalose as a tracer for the surface soil (Jia et al., 2010; Medeiros et al., 2006). In addition, previous studies reported that bacteria and other microbes in the soil are also an important source for trehalose (Rogge et al., 2007). The significant contributions of arabitol and mannitol indicated microbial sources of trehalose for factor 2. Trehalose is significantly correlated with fungal spore tracers such as arabitol (r=0.58) and mannitol (r=0.58), and Ca (r=0.70) (Fig. 5m-o); the latter is a primary soil dust tracer. The above discussions suggest multiple sources of trehalose. Therefore, factor 2 can be termed as microbial and soil dust factor.

Factor 3 is characterized by levoglucosan (82.2%), galactosan (77%), and mannosan (73.6%) (Fig. 6c). Previous studies have reported that these sugars are associated with BB aerosols (Simoneit, 2002). The PMF results are very well supported by the fact that anhydrosugars are associated with BB in the Mangshan site. Factor 4 is dominated by high loading of sucrose (90%), followed by inositol (36.9%) and fructose (11.7%) (Fig. 6d). Sucrose, fructose and inositol are associated with airborne pollen spores so that factor 4 is termed as pollen factor (Pacini, 2000; Verma et al., 2018). Sucrose plays a crucial role in the plant blossoming process because it is the dominant sugar compound of pollen grains (Pacini, 2000).

Factor 5 is characterized by a higher contribution of arabitol (61.5%) than mannitol (39.3%) and inositol (15.3%) (Fig. 6e). Sugar species that contribute to factor 5 are associated with fungal spores (Bauer et al., 2008). Arabitol and mannitol are considered as suitable tracers for fungal activities (Medeiros et al., 2006). Therefore, factor 5 is termed as a fungal factor due to the high loading of arabitol and mannitol. Overall, the average contributions of each factor to measured SCs were estimated by PMF analyses (Fig. 7), in which BB was found to account 27% of measured SCs.

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The vegetation and microbial plus soil dust sources equally contribute (21%) to total SCs. The fungal spores and pollen spores contribute 16% and 15% of total SCs, respectively. Finally, biomass burning emissions from the local areas and megacities via long-range atmospheric transport were identified as a severe source for the Mangshan aerosols.

3.3. Contributions of sugar compounds to WSOC and OC

The mean carbon content of measured sugar compounds varied from 14.1-371 ng m^{-3} (av. 145 ng m^{-3}) in daytime and 12.8-322 ng m^{-3} (av. 117 ng m^{-3}) in nighttime, accounting for 0.83% and 0.91% of OC, respectively (Fig. 8a, b). The mean carbon contents of anhydrosugars showed clear diurnal variation with higher values in nighttime (67.1 ng m^{-3}) than daytime (42.7 ng m^{-3}), accounting for 0.43 % and 0.22 % of OC, respectively. These results suggest that biomass burning significantly contributed to Mangshan aerosols. However, the carbon contents of primary sugars showed opposite diurnal variations; higher (68.5 ng m^{-3}) in daytime than nighttime (28.3 ng m^{-3}) accounting for 0.41 % and 0.28 % of OC, respectively. (Fig. 8a, b). This study suggests that the daytime emissions of primary sugars from local vegetation and the decay of plant leaf in forest significantly contribute to OC. We found lower levels of sugar alcohols in daytime (34.6 ng m^{-3}) and nighttime (21.3 ng m^{-3}), accounting for 0.20 % and 0.19 % of OC, respectively. This result indicates multiple carbon sources of sugar alcohols in day and night. In addition, contributions of anhydrosugars, primary sugars, and sugar alcohols to WSOC were similar to those of OC in Mangshan aerosols.

Based on the PMF analysis, we found five sources for SCs measured in Mangshan aerosols. The following tracer compounds were used to calculate carbon contents: biomass burning (i.e., levoglucosan, galactosan, mannosan; BB-C), vegetation (glucose, fructose; VG-C), fungi (arabitol, mannitol; FG-C), pollen (sucrose; PL-C) and microbial/soil (trehalose; MbS-C) (Fig. 8c, d). Among the five sources, BB-C was found as the largest contributor to Mangshan aerosols (36.7%) followed by FG-C (23.7%), VG-C (19.7%), PL-C (14.2%), and MbS-C (4.84%). In addition, BB in nighttime accounted for 1.38% and 0.43% of WSOC and OC, respectively (Fig. 8c, d), although the levels are lower in daytime (0.57% and 0.22%, respectively). The BB for cooking and space heating are very common in central China (Verma et al., 2015), which should increase the nighttime levels of BB-C at the Mangshan site. However, the emissions from VG-C and FG-C sources are similar during day and nighttime for the Mangshan aerosols. PL-C accounted for 0.20 % and 0.07 % of OC in daytime and nighttime, respectively. Higher pollen activities are key sources for the daytime high levels of PL-C in the forest site (Verma et al., 2018).

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3.4. Contribution of levoglucosan to OC and WSOC

We calculated the mass concentration ratio of levoglucosan to OC (Lev/OC) and WSOC (Lev/WSOC) to evaluate the contribution of BB and anthropogenic emissions to Mangshan aerosols. Fossil fuel combustion and BB primarily emit WSOC and OC. They are also secondarily produced by photochemical oxidation of volatile organic compounds in the atmosphere (Wang et al., 2005; Huang et al., 2006; Deshmukh et al., 2019b). The coal combustion and vehicle exhaust can highly contribute to the levels of OC and WSOC in aerosols (Xu et al., 2020). Levoglucosan, a dominant constituent of BB products has been considered as an excellent tracer of BB (Kuo et al., 2011).

Lev/OC average ratio (5.69×10^{-3}) was lower than Lev/WSOC (1.66×10^{-2}) in Mangshan samples (Fig. 9a). Interestingly, we found a strong diurnal variation of Lev/OC and Lev/WSOC ratios in the nighttime samples. The average ratios are higher in nighttime (Lev/OC: 8.48×10^{-3}, Lev/WSOC: 2.70×10^{-2}) than daytime (Lev/OC: 4.21×10^{-3}, Lev/WSOC: 1.11×10^{-2}) (Fig. 9b, c). These results indicate that BB contributed substantially to organic carbon in the nighttime aerosols. Our results also denote that secondary production of OC and WSOC from BB-derived organic precursors was crucial during nighttime at the Mangshan site. We presume that the nighttime contribution of BB in the site is due to the cooking and space heating in central China at night. Moreover, the correlations of levoglucosan with OC and WSOC are stronger in nighttime ($r = 0.81$ and 0.70, respectively) than daytime ($r = 0.45$ and 0.40, respectively), indicating the dominance of BB-derived organic carbon during nighttime in the Mangshan aerosol samples.

In addition, water-soluble organic compounds are derived from various emission sources. We propose that secondary organic aerosols can constitute a significant fraction of WSOC and OC in daytime Mangshan aerosols. The photochemical oxidation of organic precursors emitted by fossil fuel combustion of industries and vehicular exhausts also contributes to WSOC and OC in daytime (He et al., 2015), suggesting that emissions from the urban Beijing area may significantly influence the daytime levels of Mangshan aerosols. He et al. (2015) suggested a possible contribution of photochemical formation of secondary organic aerosols to atmospheric WSOC and OC in central China. Nevertheless, the photochemical degradation of levoglucosan by OH radicals under ultraviolet radiations and high temperatures (Hennigan et al., 2010) might play a key role for the lower ratios of Lev/OC and Lev/WSOC in daytime than nighttime in the Mangshan aerosols.

3.5. Mass concentration ratios of levoglucosan/mannosan

The mass concentration ratios of levoglucosan and mannosan (Lev/Man) were calculated to better characterize the emissions sources of BB tracers (softwood vs. hardwood) in the Mangshan

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site. Figure 10 represents the variations of Lev/Man ratios for overall, day- and nighttime periods. The Lev/Man ratios have been used to distinguish the burning of hardwood (angiosperm) and softwood (gymnosperm) in the ice core record from the Russian Far East (Kawamura et al., 2012). Hardwood contains 55–65% of cellulose and 20–30% hemicellulose (Klemm et al., 2005). Levoglucosan and mannosan are derived from thermal decomposition of cellulose and hemicelluloses, respectively (Simoneit, 2002). Levoglucosan is thermally more stable than mannosan and galactosan (Kuo et al., 2011). Hence, lower Lev/Man ratio is associated with softwood burning whereas higher ratio with hardwood burning (Engling et al., 2006, 2009). However, we found insignificant diurnal variations of Lev/Man ratios between night (9.33-25.9, avg. 15.8) and day (0.90-23.3, avg. 13.6) in Mangshan. Interestingly, wheat straws and lignite are used in China for domestic cooking and house heating. Such biofuel combustion might also contribute to the high levels of levoglucosan and mannosan in the Mangshan aerosols.

Likewise, comparable Lev/Man ratios (9–13 for PM_{10} and 10–13 for $PM_{2.5}$) were reported for aerosol samples from Tanzania, where wood and charcoal are primary fuels used for domestic cooking and heating (Mkoma and Kawamura, 2013). Slightly higher Lev/Man ratios were observed in springtime (15–40) aerosols from Jeju Island (Simoneit et al., 2004b). Engling et al. (2013) reported a high Lev/Man ratio (40) for aerosol samples from south-central Taiwan. Furthermore, a high Lev/Man ratio (46) was reported in field burning for wheat straw (Fu et al., 2008). Tsai et al. (2013) reported low Lev/Man ratios of 5.73-7.69 and 14.1-14.9 for urban/industrial aerosols during non-episodic pollution and episodic pollution events, respectively. The low Lev/Man ratios for urban aerosols are reasonable because biofuel and coal are often used for industrial purposes, while biomass burning is more common in rural and suburban areas for household heating and cooking.

In addition, there are several biomass combustion studies by chambers and controlled field experiments. Iinuma et al. (2007) reported lower Lev/Man ratios for the burning of conifer (4, 6.5, 4.7) than savanna grasses (21.7, 22.7). High Lev/Man ratios were reported for rice straw burning (41.6) (Sheesley et al., 2003) and for cereal straw burning (55.7) (Zhang et al., 2007). Similarly, Schmidl et al. (2008) reported lower Lev/Man ratios (3–5) for softwood than hardwood (14–15) burning by a laboratory chamber experiment. Engling et al. (2009) found higher Lev/Man ratios of 40–55 in the controlled field burning of cereal and rice straws. Tsai et al. (2010) reported Lev/Man ratio of 12.5 for fresh sandalwood burning and 13.5 for aged sandalwood burning. As discussed above, it is not easy to differentiate hardwood and softwood burning base on Lev/Man ratios because several studies reported a high Lev/Man ratio for both softwood and hardwood burning. Thus, there may exist some other factors that significantly control the Lev/Man ratios.

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Additionally, Kuo et al. (2011) reported a significant effect of burning temperature on the emissions of levoglucosan and mannosan: they observed higher levels of levoglucosan at high temperature. The mannosan production increases up to 200 °C. Compared to low-temperature smoldering, higher emissions of levoglucosan was observed during high-temperature flaming (Gao et al., 2003). Engling et al. (2006) reported higher Lev/Man ratios for the flaming (27.5-52.3) than smoldering (2.43-3.08). Notably, higher temperatures (≥300 °C) and longer combustion time may result in higher Lev/Man ratios (Kuo et al., 2011). The variations of Lev/Man ratios in the Mangshan aerosols may be significantly influenced by several parameters such as burning temperature associated with the flaming or smoldering process, duration of biomass burning, and hardwood or softwood burning. In spite of the above discussions, moderate Lev/Man ratios in autumn aerosols from Mangshan suggest that softwood burning contributes to the levels of levoglucosan and mannosan. However, the contribution of a hardwood burning from house heating associated with the smoldering process or low temperature could not be excluded.

4. Summary and Conclusions

Anhydrosugars, primary sugars and sugar alcohols were detected with distinct diurnal variations in suburban aerosol samples collected at the Mangshan site in the northern vicinity of Beijing. The wind patterns indicate that daytime air masses were transported from urban Beijing to Mangshan, while nighttime air masses were delivered from the Mangshan National Forest Park. Daytime air masses from urban Beijing significantly influence the air quality of northern forest region. The aerosol concentrations were characterized by the peaks of anhydrosugars in daytime. Levoglucosan was observed as a dominant anhydrosugar among sugar compounds (SCs) due to potential biomass burning (BB) in Mangshan. Levoglucosan showed clear diurnal variation with higher concentrations in nighttime than daytime. BB for cooking and space heating significantly contributed to the high levels of levoglucosan at the suburban site.

Sucrose was found as the second most abundant sugar with higher concentrations in daytime. These results suggested a significant influence of enhanced ambient temperature and solar radiation for the pollen rupture in daytime. The insignificant diurnal variation of trehalose indicated multiple sources, i.e., microbial activities at night due to high RH, while soil dust particles transported from Beijing areas due to a southerly wind in daytime. The maximum concentrations of sugar alcohols were observed in daytime. Arabitol and mannitol are delivered from fungal and microbial sources in daytime due to favorable meteorological conditions (high RH and temperature). PMF analyses concluded that local BB and long-range transport of bioaerosols from Beijing seriously affected the air quality of the Mangshan site. The mean contribution of BB tracers to OC was estimated to be 0.43% in nighttime due to domestic cooking and space heating in central China. Although the levels are lower (0.22%) in daytime, Lev/Man ratios obtained in the aerosols suggest that low temperature or smoldering burning of softwood/hardwood was the main source.

SCs were recognized as a significant component of aerosols from Mangshan, northern suburbs of Beijing. SCs can influence the air quality and possibly climate because they are essential components of organic aerosols on a global scale. This study of SCs at Mangshan demonstrates that ambient levels of SCs are highly sensitive to the emissions of anthropogenic and biogenic aerosols. Higher contribution of BB product (levoglucosan) to SCs showed a significant BB activity around the Mangshan site in north China.

Data availability. Raw data are available on request by contacting the corresponding author.

Author contributions. This research was designed YK, KK and ZW. Laboratory measurements were performed by FY with a support of PF. The paper was prepared by SKV and KK.

Competing interests. The authors declare that they have no conflict of interest.

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Figure Captions

Figure 1. Geographical location of Mangshan, China. The map was downloaded from © Google Maps 2019.

Figure 2. The meteorological parameters at Mangshan during sampling periods.

Figure. 3. Temporal variations in the concentrations (ng m^{-3}) of sugar compounds in the Mangshan aerosol samples collected for September-October 2007.

Figure 4. Concentrations (ng m^{-3}) of sugar compound (a) overall, (b) daytime and (c) nighttime in aerosol samples from Mangshan during autumn 2007 (The error bars denote the standard deviation).

Figure 5. Linear regression analysis between mass of sugar components (a) levoglucosan and galactosan, (b) levoglucosan and mannosan, (c) galactosan and mannosan, (d) sucrose and ambient temperature, (e) sucrose and solar radiation, (f) trehalose and arabitol at nighttime, (g) trehalose and mannitol at nighttime, (h) trehalose and Ca^{2+} at daytime, (i) arabitol and mannitol, (j) relative humidity and arabitol, (k) relatinve humidity and mannitol, (l) glucose and fructose, (m) trehalose and arabitol, (n) trehalose and mannitol, and (o) trehalose and Ca^{2+} in the aerosol samples collected from Mangshan, China.

Figure 6. PMF analyses of sugar compounds in Mangshan aerosols based on the autumn 2007 data set.

Figure 7. Source contributions to sugar compounds from various sources based on PMF analyses.

Figure 8. The concentrations and relative contributions of the carbon content of anhydrosugars (AS-C), primary sugars (PS-C) and sugar-alcohols (SA-C) to the carbon concentrations of measured sugar compounds (SCs-C), water-soluble organic carbon (WSOC) and organic carbon (OC) fraction of Mangshan aerosols (a = daytime and b = nighttime). The concentrations and relative contribution of the carbon content of five sources of sugar compounds to total sugar compounds measured, WSOC and OC fraction of Mangshan aerosols (c = daytime and d = nighttime).

Figure 9. Mass concentrations ratio of levoglucosan (Lev) to organic carbon (OC) and water soluble organic carbon (WSOC) in the Mangshan aerosol samples for autumn 2007.

Figure 10. Average levoglucosan to mannosan ratios (Lev/Man) in the Mangshan aerosol samples for autumn 2007.

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Fig. 1.

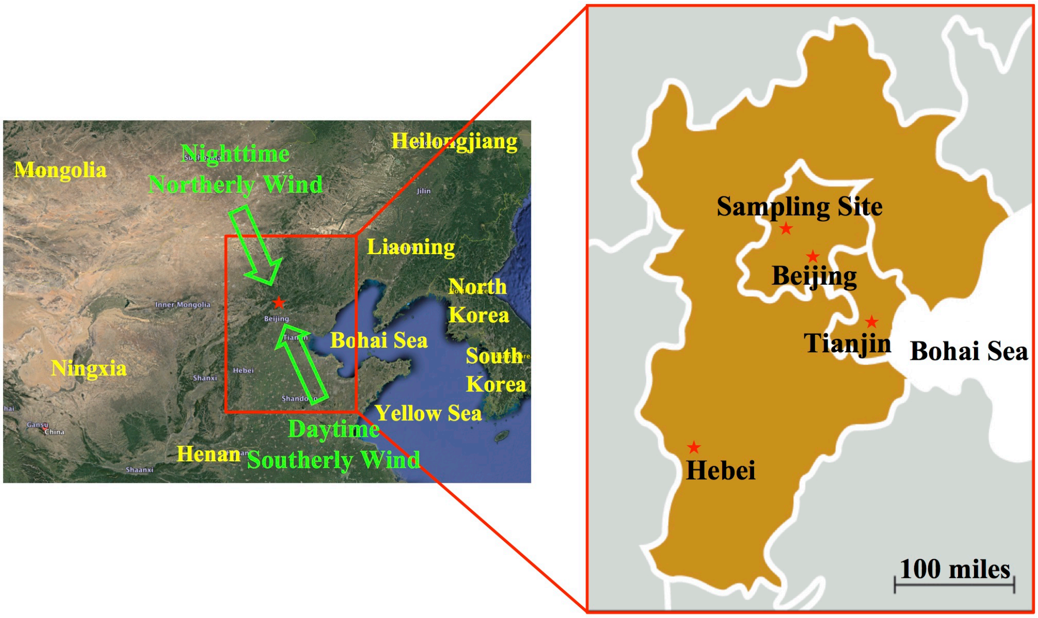

Fig. 2.

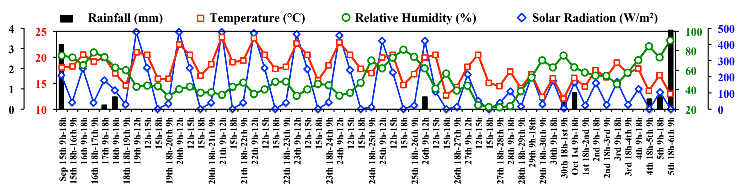

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Fig. 3.

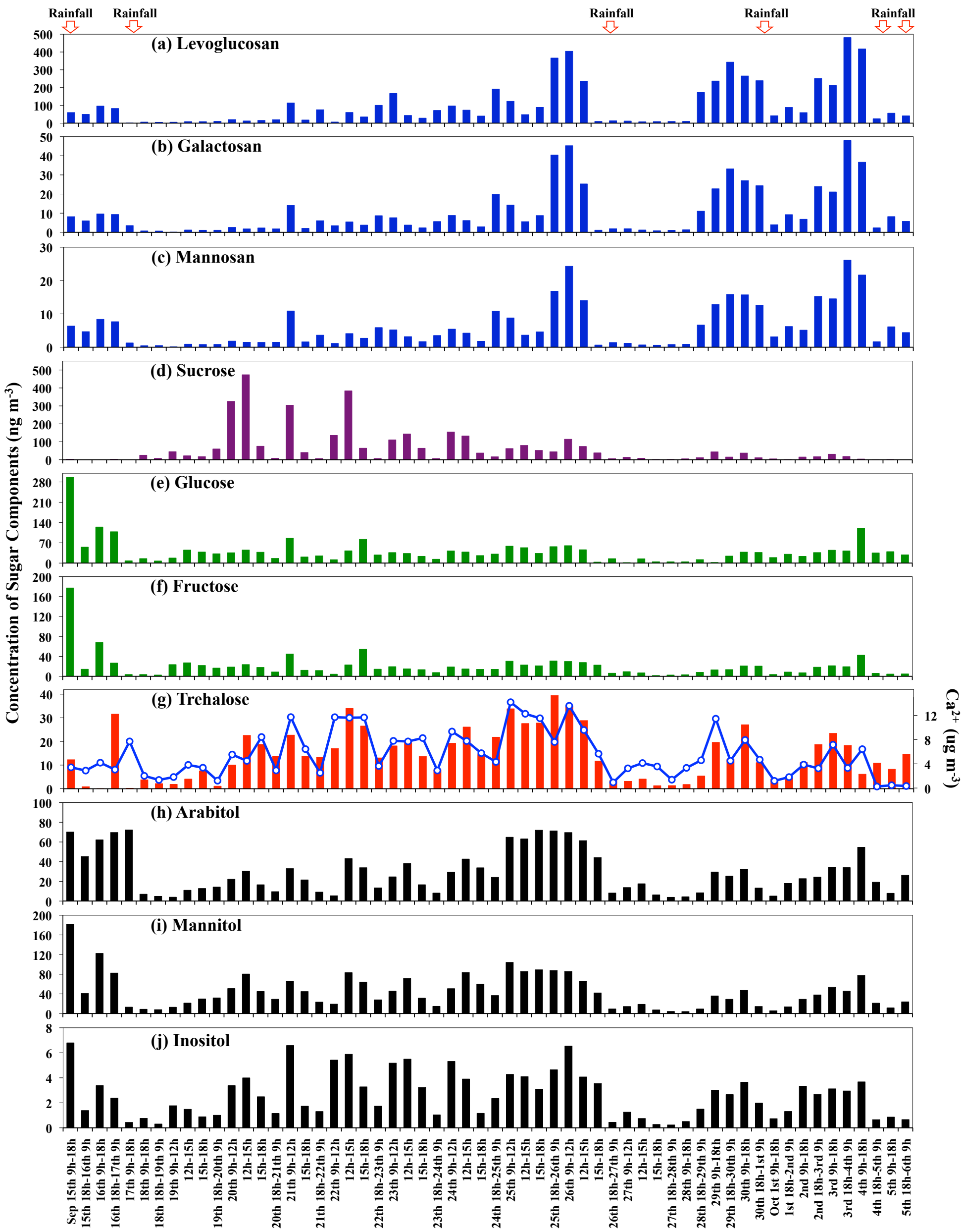

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Fig. 4.

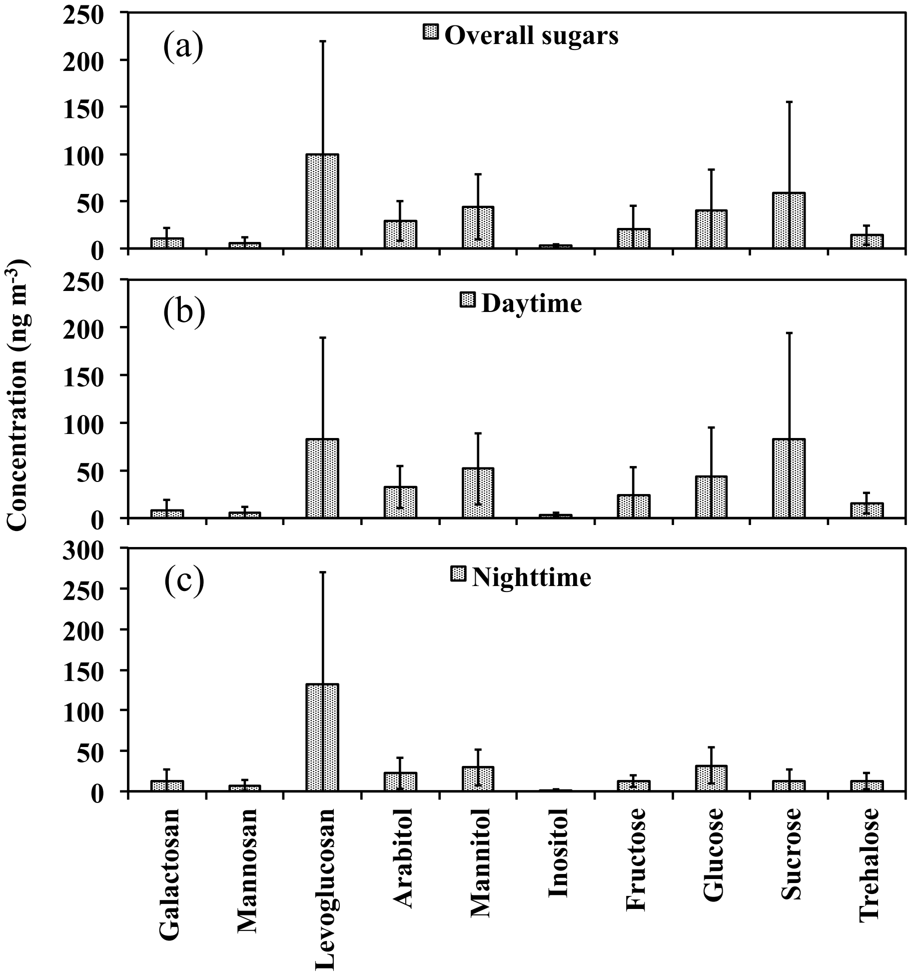

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Fig. 5.

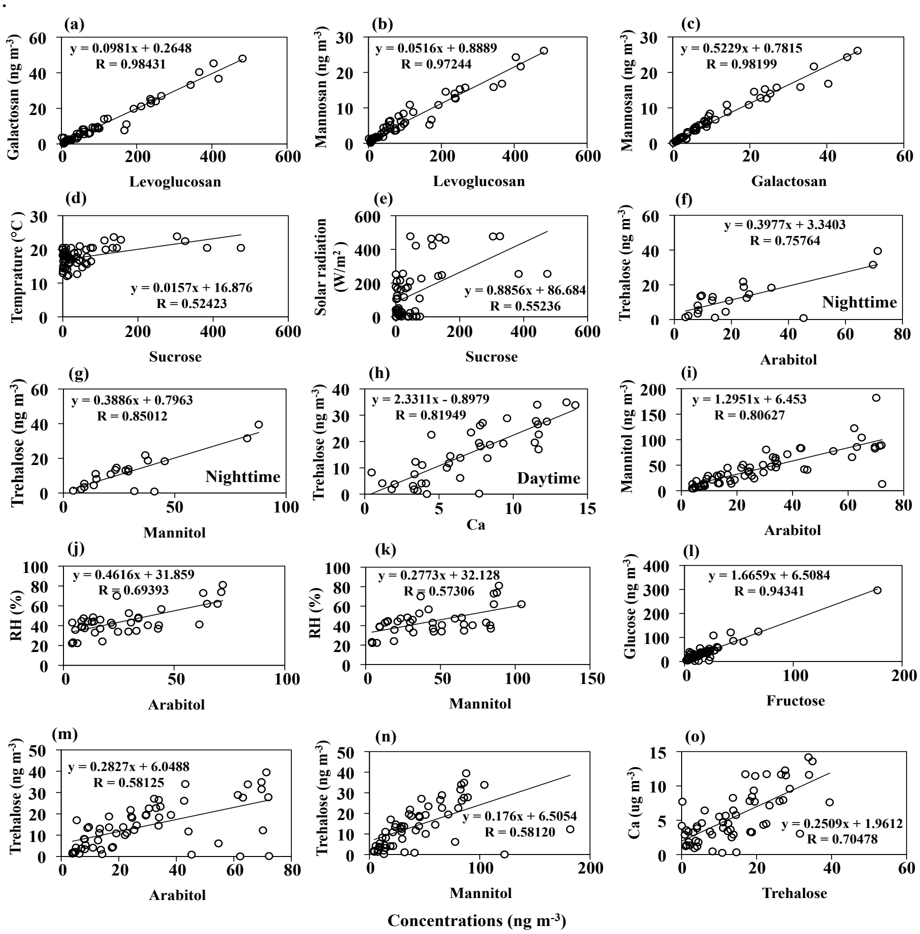

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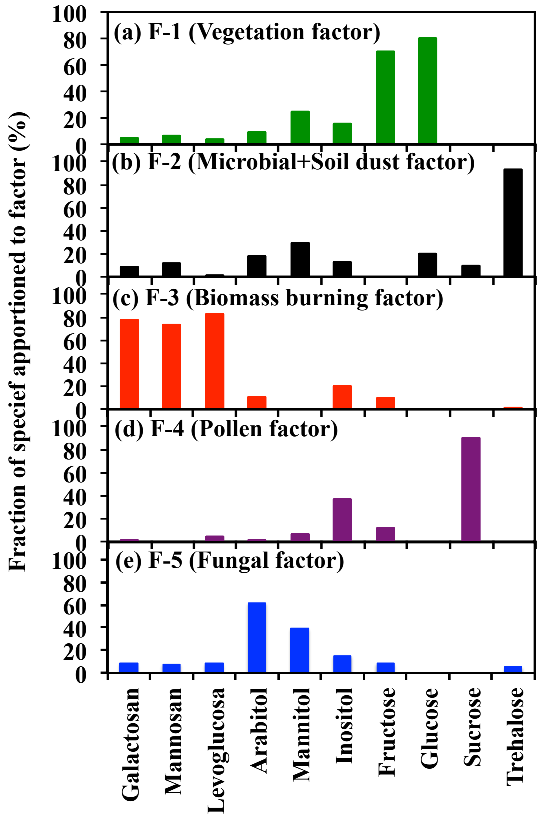
Fig. 6.



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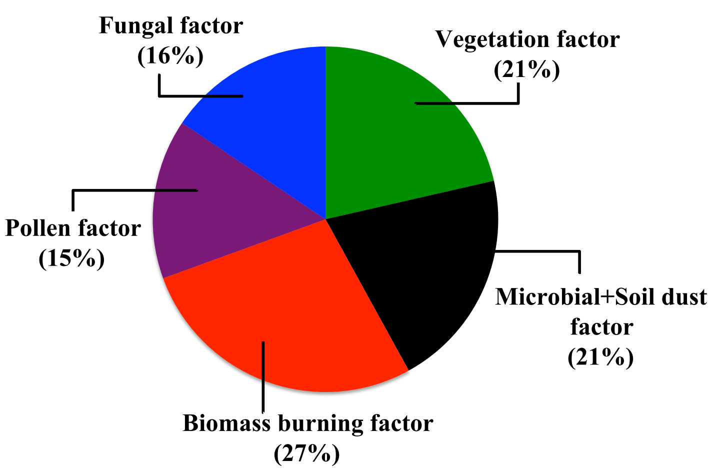

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Fig. 8.

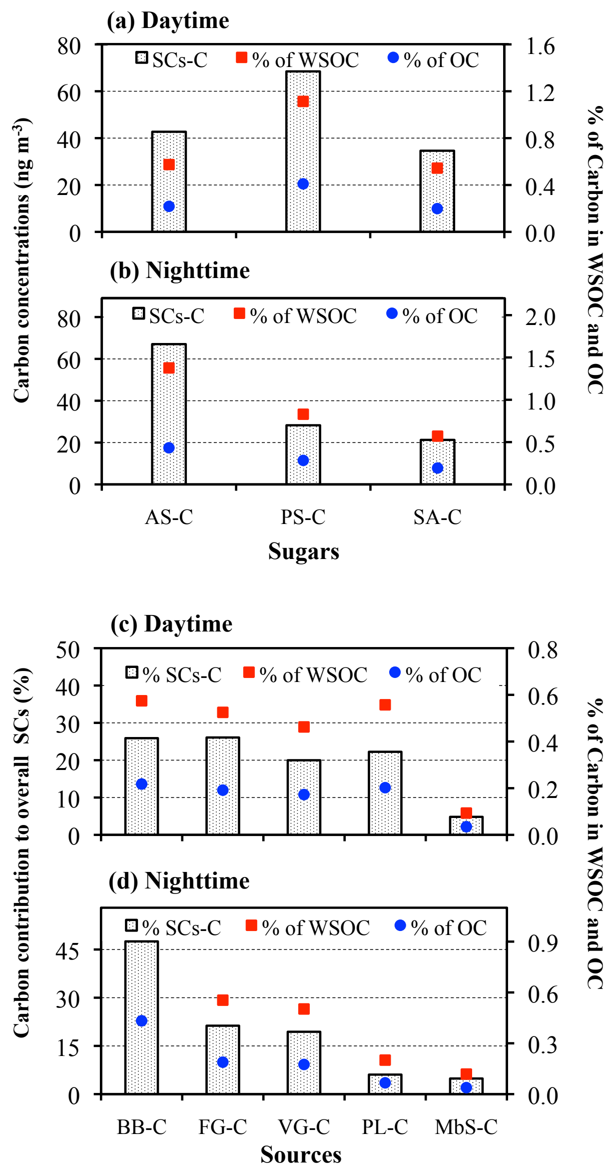

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Fig. 9.

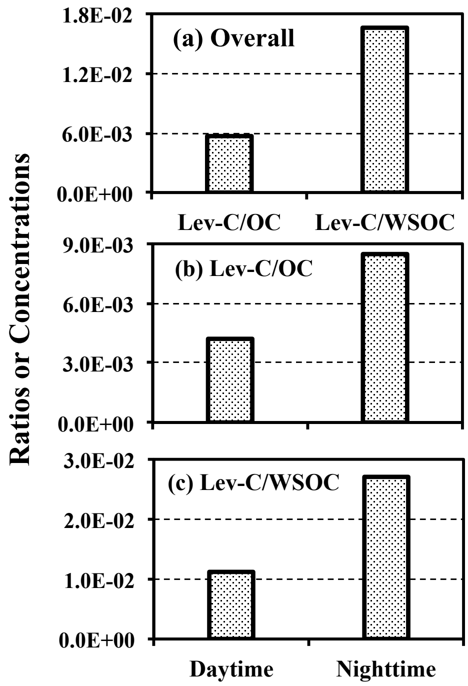

Fig. 10.

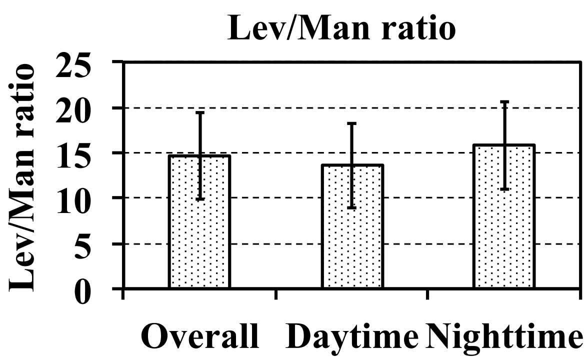

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Table 1. Minimum, maximum, average and standard deviations of concentrations of sugar compounds in aerosol samples (TSP) from Mangshan, China.

	Overall				Daytime (n = 38)				Nighttime (n = 20)			
	Min	Max	Avg.	S.D.	Min	Max	Avg.	S.D.	Min	Max	Avg.	S.D.
Anhydrosugars												
Galactosan	0.14	48.0	10.1	11.9	0.14	45.3	8.53	10.5	0.69	48.0	13.0	14.0
Mannosan	0.13	26.1	6.05	6.33	0.13	24.3	5.37	6.01	0.53	26.1	7.35	6.87
Levoglucosan	1.17	482	100	119	1.17	418	83.2	106	5.66	482	132	138
Sugar alcohols												
Arabitol	3.89	72.2	29.1	21.5	3.99	72.2	32.5	22.0	3.89	71.3	22.5	19.4
Mannitol	4.19	182	44.1	34.5	4.19	182	51.7	37.5	4.40	87.7	29.6	22.3
Inositol	0.23	6.8	2.62	1.81	0.27	6.80	3.14	1.90	0.23	4.65	1.62	1.09
Primary sugars												
Fructose	1.72	177	20.1	24.6	1.72	177	23.9	29.3	2.64	30.9	12.8	7.67
Glucose	1.86	297	40.0	43.4	1.86	297	44.2	50.8	4.52	108	32.0	22.8
Sucrose	0.02	474	58.5	96.5	0.02	474	82.9	112	0.04	60.1	12.3	15.1
Trehalose	0.06	39.5	14.3	10.5	0.06	34.9	15.3	10.6	0.87	39.5	12.3	10.2
Anhydrosugars	6.01	556	116	137	6.01	476	97.1	122	6.88	556	152	159
Primary sugars	9.41	565	133	125	9.41	565	166	141	10.5	172	69.4	43.0
Sugar alcohols	8.53	259	75.8	54.7	9.09	259	87.4	57.5	8.53	164	53.7	41.9
Total Sugars	30.8	875	325	232	34.1	875	351	240	30.8	759	276	212
Anhydrosugars (%)			31.9				24.6				45.7	
Primary sugars (%)			41.8				47.3				31.3	
Sugar alcohols (%)			26.4				28.1				23.0	