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Seasonal variations of sugars in atmospheric particulate matter from Gosan, Jeju Island: Significant contributions of airborne pollen and Asian dust in spring

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Abstract

Sugars are important water-soluble organic constituents of atmospheric particulate matter (PM). In order to better understand the sources and seasonal variations of sugars in aerosols, primary saccharides (fructose, glucose, sucrose, and trehalose) and sugar alcohols (arabitol and mannitol), together with levoglucosan, have been studied in ambient aerosols at Gosan, Jeju Island in the western North Pacific, the downwind region of the Asian outflow, using gas chromatography-mass spectrometry. The results showed that the sugar composition varied seasonally with a total concentration range of 6.8-1760 ng m⁻³ (mean 246 ng m⁻³). The total identified sugars had the highest concentration in April, the spring bloom season at Jeju Island, when sucrose contributed up to 80% of the total sugars. The dominance of sucrose was also detected in pollen samples, suggesting that pollen can contribute significantly to sucrose in aerosols during the spring bloom. The seasonal variation of trehalose is consistent with those of non-sea-salt Ca²⁺ and δ¹³C of total carbon with elevated levels during the Asian dust storm events. This study indicates that sugar compounds in atmospheric PM over East Asia can be derived from biomass burning, Asian dust, and primary biological aerosols such as fungal spores and pollen. Furthermore, this study supports the idea that sucrose could be used as a tracer for airborne pollen grains, and trehalose as a tracer for Asian dust outflow.

Keywords: Organic aerosols; Saccharides; Sucrose; Airborne pollen; Asian dust

1. Introduction

Sugars are an important class of water-soluble organic compounds, whose concentrations are substantial in atmospheric aerosols over the continental (Pashynska et al., 2002; Graham et al., 2003; Decesari et al., 2006; Medeiros et al., 2006a; Wan and Yu, 2007; Yttri et al., 2007; Fu et al., 2008; Jia and Fraser, 2011), marine (Simoneit et al., 2004b; Fu et al., 2011), and high Arctic regions (Fu et al., 2009). Levoglucosan, produced in large quantities by the pyrolysis of cellulose, has been recognized as a key tracer of

biomass burning (Simoneit et al., 1999; Fraser and Lakshmanan, 2000). The sources of primary saccharides in the atmosphere are innumerable, including primary biological aerosols such as fungal spores, pollen, vegetative debris, bacteria and viruses (Jaenicke, 2005; Deguillaume et al., 2008). For example, Bauer et al. (2008) reported that arabinol and mannitol are tracers for airborne fungal spores and can be used to estimate the contribution of fungal spores to the organic carbon of atmospheric aerosols. Sugar alcohols, together with glucose, sucrose and trehalose (also called mycose) are generally more abundant in the coarse than in the fine fraction of aerosol particulate matter (PM) (Fuzzi et al., 2007; Yttri et al., 2007; Pio et al., 2008), indicating that they are likely derived from primary biological particles (Graham et al., 2003; Simoneit et al., 2004a; Bauer et al., 2008). Womiloju et al. (2003) reported that airborne pollen and fungal spores contribute 12-22% to the total organic carbon of some ambient aerosols. Jaenicke (2005) showed that primary bioaerosols (including plant fragments, pollen, etc.) can comprise from 20% to 30% of the total atmospheric PM ($>0.2 \mu\text{m}$) from Lake Baikal (Russia) and Mainz (Germany). However, the importance of bioaerosols in atmospheric PM is still controversial (Hoffmann and Warnke, 2007).

Particular attention has been paid to atmospheric chemical studies in East Asia because anthropogenic emissions of gas and aerosols in this region are significant due to the rapid increase of industrialization (Huebert et al., 2003). The Gosan site is located on the western edge of Jeju Island in the western north Pacific, and is under the outflow path of Asian desert dusts and polluted air masses from China (Simoneit et al., 2004b; Wang et al., 2009). This locale was used as a supersite during the ACE-Asia campaign (Huebert et al., 2003; Seinfeld et al., 2004). Although many studies have been carried out at Jeju Island focusing on both inorganic and organic components of aerosols (e.g., Kawamura et al., 2004; Simoneit et al., 2004b; Wang et al., 2009), little is known about molecular and seasonal distributions of atmospheric sugars. Such information may help to elucidate the sources of organic aerosols and their atmospheric transport pathways over the western North Pacific.

The objectives of the present study are: (i) to investigate the abundances and temporal variations of sugars and sugar alcohols in atmospheric PM collected at Gosan, Jeju Island, and (ii) to compare the molecular distributions of sugars in the Gosan aerosols with those obtained from pollen and a simulated dust sample. Here we report a significant enhancement of sucrose in April, the spring bloom season. We also discuss how much pollen contributes to the increased sucrose event and evaluate sucrose as a potential tracer for airborne pollen in atmospheric PM. In addition, the contribution of Asian dust events to trehalose is discussed.

2. Experimental section

Aerosol sampling was conducted at the Gosan site (33°29'N, 126°16'E) on Jeju Island during the ACE-Asia campaign from April 2001 to March 2002 (Kawamura et al., 2004). Jeju Island (1847 km²) is located in the western North Pacific, surrounded by mainland China, Korea Peninsula, and Kyushu Island, Japan (Figure 1). The Gosan site is located on a cliff and is isolated from any residential areas. Total suspended particle (TSP) samples were collected on pre-combusted (450 °C, 3h) quartz filters (Pallflex 2500QAT-UP, 20 cm × 25 cm) using a high-volume air sampler (Kimoto AS-810) on a daily or a few days basis (n=47) at a flow rate of 1.0 m³ min⁻¹. Before the sampling, each filter was placed in a pre-combusted (450 °C for 6 h) glass jar with a Teflon-lined cap during transport and storage. After sampling, the filter was recovered into the glass jar, transported to the laboratory and stored at -20 °C prior to analysis.

Three types of pollen from Japanese white birch (*Betula platyphylla*), Chinese willow (*Salix matsudana*), and Peking willow (*Salix babylonica*) were collected in Sapporo during the spring of 2010 and were analyzed for sugar compounds. These species grow widely in China, Japan, and Korea including Jeju Island. The pollen grains were collected into pre-combusted glass bottles. After collection, the bottles that contain pollen grains were kept in a drier under darkness for 24 h to remove water. Pollen standards of Sugi (Japanese cedar, *Cryptomeria japonica*) and Hinoki (Japanese cypress, *Chamaecyparis obtusa*) were

purchased from the Wako Chemical Company (Japan).

One simulated Asian dust sample (CJ-2) was analyzed for sugar compounds to compare with the pollen and aerosol samples. The surface (0-6 cm depth) loess deposit was collected at the southeast of the Tengger Desert (40°N; 116°E) in the Ningxia Hui autonomous region of China. A dust fraction was separated by filtering (<100 µm) and named CJ-2 (Nishikawa et al., 2000).

Filter aliquots (10-20 cm²) of the aerosol samples, and a certain amount (10-100 mg) of pollen and loess samples were extracted three times with dichloromethane/methanol (2:1; v/v) under ultrasonication for 10 min. The solvent extracts were filtered through quartz wool packed in a Pasteur pipette, concentrated using a rotary evaporator under vacuum, and then blown down to nearly dryness with pure nitrogen gas. The extracts were reacted with 50 µl of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA, purchased from Sigma-Aldrich) containing 1 % trimethylsilyl chloride and 10 µl of pyridine at 70 °C for 3 hours. After the reaction, derivatives were diluted by the addition of 140 µl of *n*-hexane containing 1.43 ng µl⁻¹ of the internal standard (C₁₃ *n*-alkane) prior to analysis by gas chromatography-mass spectrometry (GC-MS).

GC-MS analyses were performed on a Hewlett-Packard model 6890 GC coupled to Hewlett-Packard model 5973 MSD. The GC separation was achieved on a DB-5 fused silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) with the same GC oven temperature program as used in a previous work (Simoneit et al., 2004b). Helium was used as the carrier gas at a constant flow rate of 1.0 ml min⁻¹. The GC injector and MS ion source temperatures were maintained at 280 °C and 230 °C, respectively. The mass spectrometer was operated in the electron impact (EI) mode at 70 eV and scanned over the range of 50-650 Dalton. GC-MS response factors were determined using authentic standards. Fragment ions of sugar compounds at *m/z*=217 and 204 were monitored and used for quantification. Field blank filters were analyzed by the procedure used for the real samples. The results showed no contamination for any target compound. The limits of detection (LOD) for target sugar compounds in the injected extracts ranged from 0.6 to 3

pg μl^{-1} (S/N=3). Recoveries for sugars that were spiked onto pre-combusted quartz filters were better than 80 %.

3. Results and discussion

Table 1 presents the concentrations of sugar compounds detected in this study. Total concentrations of sugars were higher in spring (22-1760 ng m^{-3} , mean 374 ng m^{-3}) than other seasons owing to the significant contribution of sucrose. Sucrose was the dominant sugar in spring (1.4-1390 ng m^{-3} , mean 245 ng m^{-3}), which is about one order of magnitude more abundant than other species (Table 1). In summer, mannitol, arabitol and glucose were the major species, while sucrose (mean 1.0 ng m^{-3}) was relatively minor. In fall and winter, levoglucosan was by far the dominant sugar.

Figure 2a-g presents the seasonal variations of sugar compounds detected in the Gosan aerosol samples. During the study period, the concentrations of levoglucosan ranged from 0.7 to 222 ng m^{-3} , with an annual average of 37 ng m^{-3} . Levoglucosan is a specific tracer for biomass burning (Simoneit et al., 1999), which is considered as the largest source of primary, fine organic aerosols in the atmosphere (Bond et al., 2004). It is water-soluble and thus contributes to water-soluble organic carbon (WSOC) in aerosols. Higher levels of levoglucosan were found in winter (20-168 ng m^{-3} , mean 62 ng m^{-3}), followed by spring (3.4-222 ng m^{-3} , mean 38 ng m^{-3}), fall (11-71 ng m^{-3} , mean 35 ng m^{-3}), and summer (0.7-29 ng m^{-3} , mean 8.0 ng m^{-3}) (Table 1), indicating an influence of biomass burning from the Asian continent under the conditions of strong westerlies and/or from local burning activities during winter/spring.

Primary saccharides consisting of glucose, fructose, sucrose, and trehalose, as well as some saccharide polyols including arabitol and mannitol, were detected in the Gosan samples (Figure 2b-g). The temporal patterns of arabitol and mannitol are similar, being consistent with the idea that these polyols are tracers for airborne fungal spores (Lewis and Smith, 1967; Bauer et al., 2008; Zhang et al., 2010). The maximum concentrations of arabitol and mannitol were observed in early summer (June) and late summer-early

fall (August-September). In addition to the contribution of airborne fungal spores, Burshtein et al. (2011) proposed that arabitol and mannitol may also be attributed to high levels of vegetation detritus from the spring bloom and autumn decomposition. The temporal variation of fructose is similar to that of glucose. A strong positive correlation ($R^2=0.76$, $p<0.01$) was observed between them. Fructose and glucose originate from plant materials such as pollen, fruits, and their fragments (Speranza et al., 1997; Baker et al., 1998; Pacini, 2000). It should be emphasized that biomass burning does not emit sucrose, trehalose, glucose, nor fructose, but does emit mainly inositol and of course levoglucosan (Medeiros and Simoneit, 2008).

The atmospheric concentrations of trehalose were relatively low throughout the year (Table 1), except several high loading events that occurred in March-April (Figure 2g). Trehalose is present in a variety of microorganisms (fungi, bacteria and yeast), and a few higher plants and invertebrates (Medeiros et al., 2006a). Previous studies (Simoneit et al., 2004a; 2004b; Medeiros et al., 2006b; Rogge et al., 2007) have reported that trehalose is the most abundant saccharide in soils from different locations, and can be used as a tracer for the resuspension of surface soil and unpaved road dust. A recent study also reported that trehalose was the most abundant sugar in soil, with an enrichment in the fine mode ($PM_{2.5}$) over the coarse mode ($PM_{2.5-10}$) of soils (Jia and Fraser, 2011). In the present study, high levels of trehalose are in accordance with the Asian dust events observed at the Gosan site (April 11-13 and 24-25, 2001 and March 21-23, 2002 with average aerosol mass concentrations of $288 \mu\text{g m}^{-3}$, $241 \mu\text{g m}^{-3}$ and $883 \mu\text{g m}^{-3}$, respectively), indicating soil resuspension as an important source. This is supported by the positive correlation ($R^2=0.55$, $p<0.01$) between trehalose (Figure 2g) and non-sea-salt calcium (nss-Ca^{2+}) (Figure 2h) during the sample collection period. nss-Ca is representative of natural sources, normally associated with soil dust resuspension (Virkkula et al., 2006), although nss-Ca can also be of a biological origin such as skeletal material from coccolithophore phytoplankton (Artaxo et al., 1992). At Gosan, nss-Ca is an indicator of Asian dust storms because high loadings of nss-Ca were observed only during the dust storm events

in winter/spring, and Ca is abundantly present (5.3 weight %) in the simulated loess sample (CJ-2) (Nishikawa et al., 2000).

Interestingly, the temporal variations of trehalose and nss-Ca are also comparable to those of the stable carbon isotopic ratios ($\delta^{13}\text{C}$) of total carbon (TC) in the aerosols (Figure 2h) (Kawamura et al., 2004). The $\delta^{13}\text{C}$ values of TC range from -15.5 to -26.6 ‰ with higher isotopic ratios (> -20 ‰) in spring. Such high values in spring have not been reported for both continental and marine aerosols (Cachier, 1989; Narukawa et al., 2008). The high isotope ratios in spring are proposed to be associated with the presence of carbonate carbon derived from desert dusts (Kawamura et al., 2004), which generally contain calcium carbonate whose $\delta^{13}\text{C}$ values are close to zero (Craig, 1953). In fact, the $\delta^{13}\text{C}$ value of TC in the dust sample (CJ-2) from the loess layer in China is -9.8 ‰, with $\delta^{13}\text{C}$ values of -1.3 ‰ for inorganic carbon (IC) and -23.4 ‰ for organic carbon (OC) (Kawamura et al., 2004). In addition, the molecular composition of the sugar compounds in CJ-2 is characterized by a predominance of trehalose; it constitutes 94.3 % of the total sugars ($14.2 \mu\text{g g}^{-1}$, Table 2). Thus, the co-variation among trehalose, nss-Ca, and $\delta^{13}\text{C}$ value of TC for the Gosan aerosols indicates that trehalose may be used as a specific tracer for Asian dust storms, which mainly occur in winter/spring. Asian dusts are transported over Jeju Island under the influence of the westerlies.

Among the detected saccharides, sucrose is the dominant species at the Gosan site with a maximum concentration up to 1390 ng m^{-3} in April (Table 1 and Figure 2f), the spring bloom season on Jeju Island and its upwind Asian continent. Bielecki (1995) reported that sucrose is the dominant sugar in the phloem of plants and is important in developing flower buds. Pashynska et al. (2002) showed that the atmospheric levels of inositol and sucrose and their contributions to organic carbon (OC) were highest at the beginning of summer (June) owing to the developing leaves. Graham et al. (2003) discussed the potential sources of both sugars and sugar alcohols in fine and coarse aerosols in the Amazon region. They found that sugars peak during daytime, whereas sugar alcohols peak during nighttime. These diurnal variations have been interpreted by the increased activities of

yeasts and fungi during nighttime, and the release of pollen, fern spores and other “giant” bioaerosols during daytime (Graham et al., 2003). The springtime enhancement of sucrose, together with fructose and glucose, was observed in PM₁₀ at Birkenes, a rural site in Norway (Yttri et al., 2007), which coincides with the onset of the birch pollen season. Jia et al. (2010a; 2010b) also reported that the atmospheric concentrations of sucrose in both fine (PM_{2.5}) and coarse (PM₁₀) particles were significant only in spring (March-April) in Texas, with higher levels at the rural site than at the urban site (Jia et al., 2010a). In the present study, the elevated concentrations of sucrose during the spring bloom season also support the idea that airborne pollen grains should be the main source of sucrose in these atmospheric TSP samples.

In order to confirm this idea, we analyzed five pollen samples from different plant species for their sugar composition (Table 2). Among these, *Betula platyphylla* (white birch), *Salix matsudana* (Chinese willow) and *Salix babylonica* (Peking willow) are the most common pollen emitters in the mid-latitudinal region in East Asia, including the Jeju Island, during the spring bloom season. *Cryptomeria japonica* (Sugi) and *Chamaecyparis obtusa* (Hinoki) trees (during February-April) are widely planted in Japan, and their pollen emissions are the major cause of hay fever in Japan. As shown in Table 2, all the pollen samples contain arabinol, fructose, glucose and sucrose. Pollens from broad-leaved species are clearly characterized by the predominance of sucrose. For example, pollen grains of Chinese willow and Peking willow contain 37.3 $\mu\text{g mg}^{-1}$ and 33.8 $\mu\text{g mg}^{-1}$ of sucrose, respectively (Table 2). These high contents of sucrose are similar to those reported for pollen from maize (*Zea mays*) (43.2 $\mu\text{g mg}^{-1}$), but still lower than those from other species of gymnosperms and angiosperms (Speranza et al., 1997). For example, sucrose contents in pollen from *Pinus halepensis* (66.4 $\mu\text{g mg}^{-1}$), *Malus domestica* (100.5 $\mu\text{g mg}^{-1}$), *Prunus avium* (109.4 $\mu\text{g mg}^{-1}$), *Ricinus communis* (120.8 $\mu\text{g mg}^{-1}$), and *Typha latifolia* (143.7 $\mu\text{g mg}^{-1}$) (Speranza et al., 1997) are much higher than those found in this study. Figure 3 shows the seasonal variation of the total concentrations of sugars detected in the Gosan aerosols. The concentration peaks observed in April are attributed mainly to the elevated

levels of sucrose as shown in Pie D (Fig. 3), which is similar to the patterns of the pollen samples shown in Pies A, B and C. During the rest of the year, levoglucosan was generally found as the dominant sugar species (Pie E), suggesting that biomass-burning activities such as crop residue burning, natural forest fires, as well as anthropogenic burning (e.g., heating) are one of the major sources of atmospheric sugars.

To further investigate the sources of the sugars, the datasets for the Gosan aerosols were subjected to positive matrix factorization (PMF) analysis. PMF is a useful approach for verifying sources of atmospheric aerosols (Paatero and Tapper, 1994; Kim et al., 2003; Miyazaki et al., 2012). The measurement uncertainties (15%) were used for the error estimates of the measured values of sugar compounds. Half of the LOD was used for the values below the detection limit and 5/6 of the LOD was used for the corresponding error estimate. PMF runs were performed with 3-7 factors. Based on Q values (the objective function to be minimized) and physical interpretation of the solution, five factors appeared to be the optimal solution.

As shown in Figure 4, factor 1 is characterized by high level of levoglucosan (92%), confirming the influence of biomass burning. Smoke plumes from biomass burning are more often transported over the Gosan site during the colder fall-winter-spring period rather than in summer by long-range atmospheric transport from the Asian continent, especially in the northern regions. Factor 2 is characterized by arabitol (34%) and mannitol (35%), suggesting a common biological origin. These sugar-polyols are produced in large amounts by many fungi. Factor 3 is dominated by fructose and glucose; these monosaccharides are major soluble carbohydrates in the bark of trees, branches and leaves. Factor 4 is characterized by the dominance of sucrose (98%), which is mainly associated with airborne pollen grains. Factor 5 is dominated by trehalose (74%), which is known to be a fungal metabolite, and could be used as a marker compound for suspended soil dust (Simoneit et al., 2004a; Rogge et al., 2007) and/or Asian dust storms over the downwind regions in East Asia.

4. Conclusions

Atmospheric concentrations and seasonal variations of sugar compounds were studied for aerosol samples collected at Gosan, Jeju Island in the western North Pacific. The total identified sugars (6.8-1760 ng m⁻³, mean 246 ng m⁻³) showed the highest concentration in April, the spring bloom season at Jeju Island and the Asian mainland. The dominance of sucrose was also detected in pollen samples, suggesting that pollen can contribute significantly to sucrose in aerosols during the spring bloom in this region. The seasonal variation of trehalose is consistent with those of non-sea-salt Ca and $\delta^{13}\text{C}$ of total carbon, supporting the idea that trehalose could be used as a tracer for the Asian dust outflow. The results of positive matrix factorization analysis suggest that sugar compounds in the marine aerosol PM collected at the Gosan site originate mainly from biomass burning, fungal spores, and suspended soil/Asian dust, as well as direct release of airborne pollen.

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Table 1. Concentrations of sugar compounds in aerosol samples (TSP) collected at Gosan, Jeju Island in the western North Pacific (ng m^{-3})

Sugars	Spring (<i>n</i> =26)		Summer (<i>n</i> =5)		Autumn (<i>n</i> =9)		Winter (<i>n</i> =7)	
	mean	range	mean	range	mean	range	mean	range
Levogluconan	38	3.4-222	8.0	0.7-29	35	11-71	62	20-168
Arabitol	6.7	2.8-18	9.6	1.1-26	12	5.3-23	4.7	2.4-8.8
Fructose	11	1.9-61	3.8	0.8-7.4	9.7	1.3-33	4.0	1.0-19
Glucose	18	2.8-69	9.6	2.3-22	16	2.7-42	7.3	2.0-24
Mannitol	5.5	1.8-19	11	1.3-29	12	3.1-25	3.4	1.6-5.2
Sucrose	245	1.4-1390	1.0	0.04-2.3	11	1.4-45	6.9	nd-31
Trehalose	15	0.3-147	3.3	0.06-9.5	6.0	0.3-16	3.9	0.1-10
Total	374	22-1760	47	6.8-127	103	55-192	98	37-277

nd = not detected.

Table 2. Concentrations ($\mu\text{g g}^{-1}$) of sugars measured in airborne pollen and simulated dust samples

Sugars	Pollen					Dust
	White birch	Chinese willow	Peking willow	Sugi	Hinoki	CJ2
Levogluconan	nd	nd	nd	nd	nd	0.05
Arabitol	8.5	129	27	10	8.8	nd
Fructose	505	678	1,090	162	1,813	0.03
Glucose	751	1,170	1,610	378	3,601	0.08
Mannitol	nd	nd	nd	nd	nd	0.03
Sucrose	6,570	37,300	33,800	182	1,016	0.64
Trehalose	nd	nd	nd	4.5	nd	13.4
Total	7,830	39,300	36,500	737	6,438	14.2

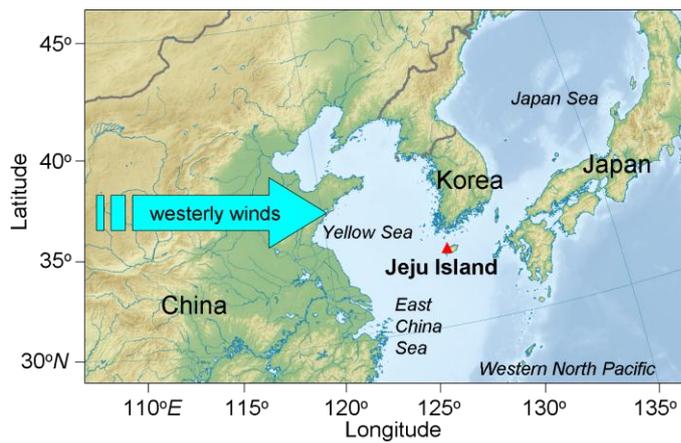


Fig. 1. A map showing the Gosan site (the red triangle) at Jeju Island in the western North Pacific. The westerly winds prevail during winter/spring.

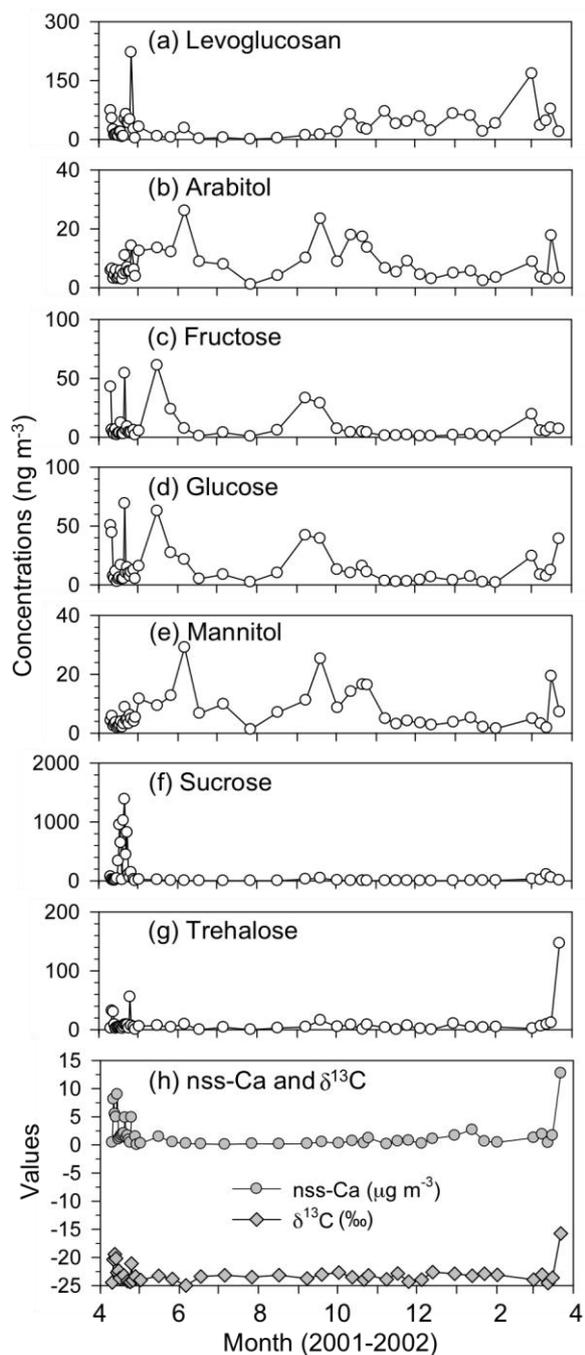


Fig. 2. Temporal variations of individual sugar compounds, non-sea-salt Calcium (nss-Ca), and $\delta^{13}\text{C}$ values of total carbon (TC) (Kawamura et al., 2004) in the aerosol samples collected at Gosan, Jeju Island in the western North Pacific.

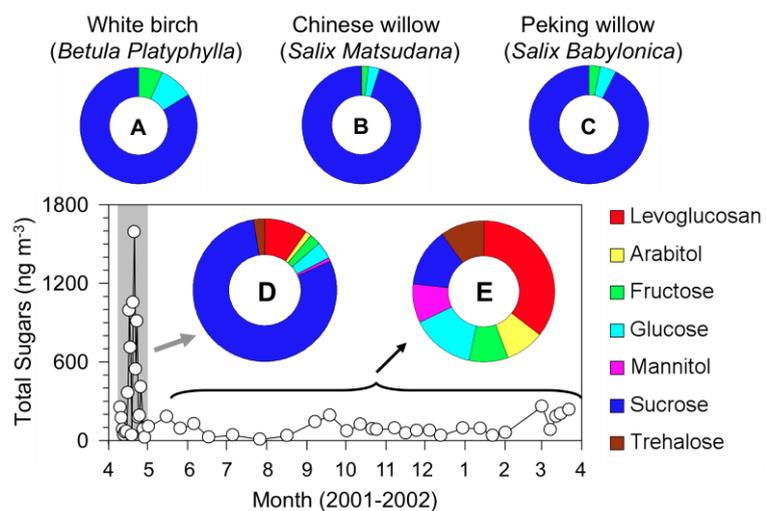


Fig. 3. Temporal variations of total sugars identified in the atmospheric aerosols at Gosan, Jeju Island. Pies A, B and C represent the relative abundances of sugar compounds detected in the pollen samples; Pies D and E show the sugar compositions in the aerosols collected in April (spring bloom season) and the rest of the year, respectively.

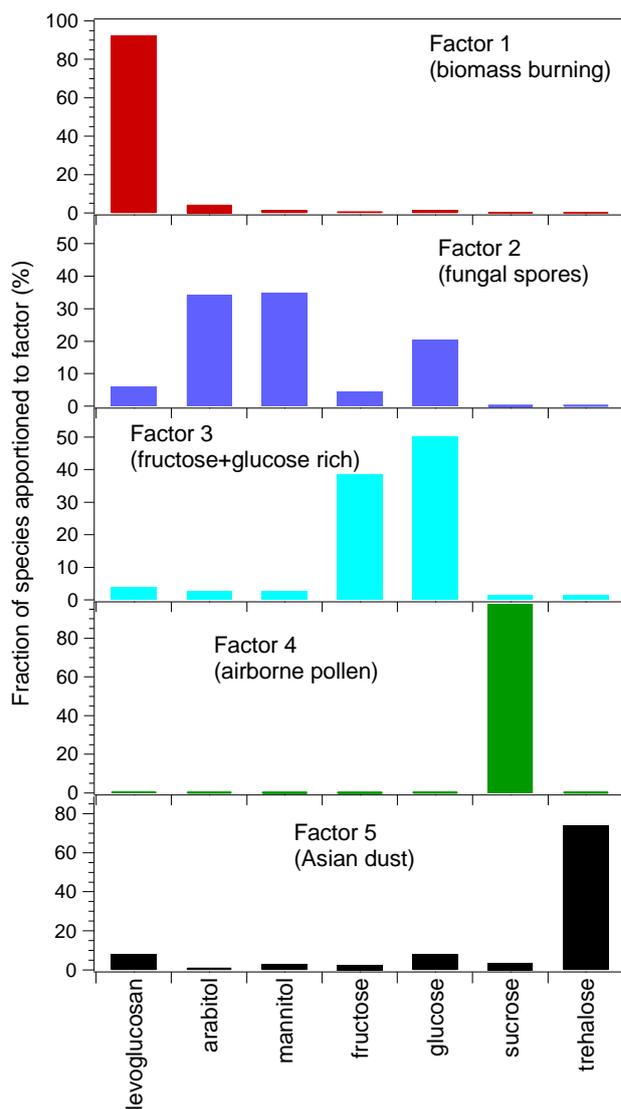


Fig. 4. Composition profiles (% of total of each species) for the five factors resolved by PMF analysis based on the dataset of sugar compounds.