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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 Ca^{2+} and $\delta^{13}C$ 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.

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 arabitol 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 μm) 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

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(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 km^2) is located in the western North Pacific, surrounded by mainland China, Korea Peninsula, and Kyushu Island, Japan (Fig. 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, 3 h) 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 m^3 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 desiccator jar 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 cm^2) 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 h. 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 (C_{13} *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 Da. 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%.

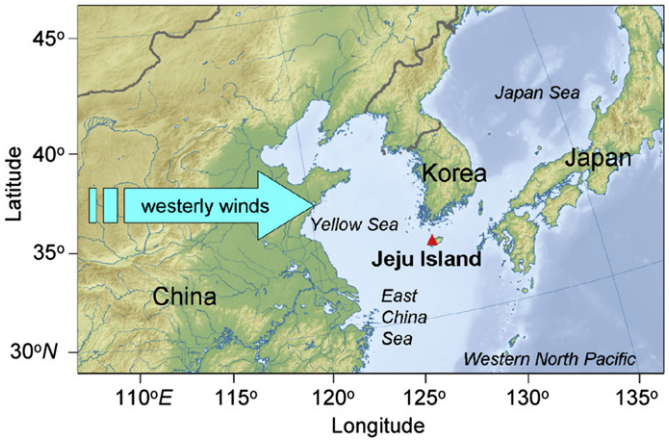

Fig. 1. A map showing the Gosan site (the red triangle) at Jeju Island in the western North Pacific. The westerly winds prevail during winter/spring. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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.

Fig. 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},