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# Thirteen-years of observations on primary sugars and sugar alcohols over remote Chichijima Island in the western North Pacific

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**Abstract**. In order to understand the atmospheric transport of bioaerosols, we conducted long-term observations of primary sugars and sugar alcohols over remote Chichijima Island in the western North Pacific from 2001 to 2013. Our results showed that concentrations of total sugar compounds for 13 years ranged from 1.2 to 310 ng $m^{-3}$ (average, 46±49 ng $m^{-3}$). We found that atmospheric circulations significantly affect the seasonal variations of bioaerosol distributions over the western North Pacific. The primary sugars (glucose and fructose) maximized in summer, possibly due to a decreased transport of Asian aerosols and increased local emission of vegetation products from the vascular plants in Chichijima. We also found higher concentrations of sugar components (arabitol, mannitol and trehalose) in more recent years during summer/autumn, suggesting an enhanced emission of fungal and microbial species over the island. Sucrose peaked in late winter to early spring, indicating a springtime pollen contribution by long-range atmospheric transport, while elevated concentrations of sucrose in early summer could be assumed to be long-range transport of soil dust from Southeast Asia to Chichijima. Positive matrix factorization analyses suggested the locally emitted sugar compounds as well as long-range transported air borne pollen grains, microbes and fungal spores are the major contributors to total sugar compounds in the Chichijima aerosols. Backward air mass trajectories support the atmospheric transport of continental aerosols from the Asian continent during winter/spring over Chichijima.

**Keywords:** Sugar compounds, fungal and microbial tracer, pollen tracer, bioaerosols, the western North Pacific.

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## 1 Introduction

East Asia has experienced rapid economic developments and population growth since last several decades (Elliot et al., 1997; Jaffe et al., 1999, 2003), whose activities emit organic and bioaerosols into the atmosphere (Xu et al., 2011). The atmospheric particles are transported to downwind region in the Pacific, associated with Asian desert dust from the Taklamakan and Gobi Deserts, and Loess plateau (Duce et al., 1980; Iwasaka et al., 1983; Jaffe et al., 1997; Prospero and Savoie, 1989; Talbot et al., 1997). The transported dust contains bacterial cells, fungal spores, and microbial cells, which fall out over the Pacific and remote islands in the Pacific Ocean (Lacey and West, 2006; Mims and Mims, 2003). The microbes associated with bioaerosols significantly affect the natural environment of marine and land ecosystem in downwind regions (Graffin et al., 2003, 2007; Prospero et al., 2005). Long-range atmospheric transport plays a key role for the global distribution of microbes from source regions to receptor site (Graffin et al., 2001). Fungi and bacteria are often attached to dust particles, which can propagate diseases to human and plants (Brown and Hovmoller, 2002). Therefore, the transported organic and bioaerosols have been the focus of extensive studies for the past years (Yamaguchi et al., 2012).

Organic aerosols are composed of a complex mixture of different types of molecules, in which water-soluble organic compounds (WSOCs) are enriched (Graham et al., 2002). WSOCs play an important role in climate change and global radiative forcing by scattering or absorbing light directly or indirectly (Fuzzi et al., 2007). They can act as cloud condensation nuclei (CCN) (Kanakidou et al., 2005; Martin et al., 2010). Sugar compounds (SCs) contribute 13–26% and 63% of total WSOCs identified in continental and marine aerosols, respectively (Simoneit et al., 2004a). SCs are directly emitted from biological sources such as fungi, algae, pollen, spores and bacteria (Carvalho et al., 2003; Wang et al., 2009) and transported long distances in the atmosphere (Wang et al., 2011). They are also derived from suspended soil



69 particles and associated biota (Rogge et al., 2006; Simoneit et al., 2004b; Wang et al., 2009),
70 and biomass burning (Schmidl et al., 2008; Simoneit et al., 2002).

71 Primary sugars are emitted from biological sources (Medeiros et al., 2006). Glucose and
72 fructose are emitted from terrestrial plant fruits, pollen, and detritus of vascular plants (Cowie
73 and Hedges, 1984; Speranza et al., 1997). Previous studies reported that sucrose is dominant
74 sugar component in airborne pollen grains and plays a significant role in plant blossoming
75 activity (Bieleski, 1995; Fu et al., 2012; Pacini, 2000). Trehalose is emitted from fungal
76 metabolic activities and resuspension of soil particles and unpaved road dust (Rogge et al.,
77 2007; Simoneit et al., 2004). Sugar alcohols are also emitted form biological sources like fungi
78 and microbes via metabolic activities (Bauer et al., 2008). Sugar alcohols, i.e., arabitol and
79 mannitol, are tracers for fungal spores (Jia and Fraser; 2011; Yang et al., 2012). Di Filippo et
80 al. (2013) reported that arabitol and mannitol are key sugar components in fungal spores.

81 Chichijima Island is located in the western North Pacific: an outflow region of Asian
82 dust (Mochida et al., 2003a). Thus, particular attention has been paid to atmospheric chemical
83 studies over Chichijima Island. It is one of the best remote islands to study a long-range
84 transport of Asian aerosols, because local pollutants in Chichijima are insignificant due to low
85 population density and no major industrial or anthropogenic activities (Chen et al., 2013).
86 Kawamura et al. (2003) reported that lower molecular weight fatty acids derived from marine
87 organisms showed higher concentrations in summer, while higher molecular weight fatty acids
88 ($C_{21}$-$C_{34}$), n-alkanes ($C_{25}$-$C_{35}$), n-alcohols ($C_{20}$-$C_{34}$) and dicarboxylic acids ($C_{20}$-$C_{28}$) derived
89 from terrestrial higher plants and soil organic matter maximized in winter to spring. Seasonal
90 variations of low molecular weight dicarboxylic acids and levoglucosan (biomass burning
91 tracer) have been discussed in Chichijima aerosols by Mochida et al. (2003a) and Mochida et
92 al. (2010), respectively. Although seasonal variation of saccharides was reported in Chen et al.
93 (2013), the observation period is rather short. Therefore, long-term observations are needed to



obtain a data set of SCs to better discuss the characteristics, potential sources, and possible effects of atmospheric transport over the western North Pacific.

Here, we report thirteen-year data set of SCs in remote Chichijima Island. The goal of this study is to characterize seasonal and annual variations of SCs and specify their possible source regions. We will also discuss a potential role of Asian dust to control the distributions of bioaerosols over the western North Pacific. The outcomes of this study will improve our understanding about a possible influence of long-range transport of bioaerosols from the continent to the clean oceanic environment. We will compare the data set of SCs for the periods 1990-1993, 2001-2003 and 2010-2013, which may provide imperative information about decadal changes in the atmospheric conditions over Chichijima. Seasonal source identifications by positive matrix factorization (PMF) analysis will also be discussed for the measured SCs.

## 2 Materials and methods

### 2.1 Sampling site and meteorological conditions

The detailed information on the sampling site was reported in Kawamura et al. (2003) and Chen et al. (2013). Briefly, Chichijima Island is located in the western North Pacific (27°04'N; 142°13'E), 1000 km south of Tokyo, Japan, and 2000 km east of the Asian continent (Figure 1). Total area of the island is 24 $km^2$ with a population of 2000 (Verma et al., 2015). The climate of Chichijima is classified as subtropical; it is warm to hot (temperature, 7.8-34.1 °C) and humid (relative humidity, 66-88%) all year round.

Figure 2 shows monthly averaged variations in the meteorological parameters of Chichijima during 2001-2013. It receives more precipitation in between April and July, September and October during the thirteen-year periods. The sampling site is less influenced by the East Asian monsoon to receive heavy rainfall compared to Northeast Asia. The climate over Chichijima is strongly influenced by the seasonal changes in wind system. In



winter/spring, the westerly winds are dominant with the air masses being enriched with Asian dust, industrial pollutants, biomass burning products, organic compounds and black carbon as well as bioaerosols emitted from East Asia and Eurasia (Figure 3) (Seinfeld et al., 2004; Simoneit et al., 2004b; Wang et al., 2009). Trade winds are dominant in summer/autumn, which transport clean and pristine marine air masses from the central Pacific to Chichijima (Kawamura et al., 2003, Mochida et al., 2010).

### 2.2 Aerosol sampling and chemical analysis

The details on aerosol sampling and chemical analysis are reported elsewhere (Chen et al., 2013; Mochida et al., 2010). Briefly, total suspended particle (TSP) samples were collected at the Ogasawara Downrange Station of the Japan Aerospace Exploration Agency (JAXA) in Chichijima Island (254 m, above sea level, asl). The samples were collected on weekly basis (January 2001 to November 2013) using a high volume air sampler (Kimoto AS-810A) at a flow rate of 1.0 $m^3$ $min^{-1}$ and pre-combusted (450°C for 6 h) quartz fiber filters (20 x 25 cm, Pallflex). Filter sample was placed in a pre-combusted glass jar with a Teflon-lined screw cap and stored in a dark freezer room at -20 °C prior to analysis in order to inhibit fungal growth. Due to the maintenance of the JAXA facility at sampling site, TSP samples were not collected for November–December 2004 and March–August 2005.

Total 590 aerosol samples were analyzed to determine the primary sugars (xylose, fructose, glucose, sucrose and trehalose) and sugar alcohols (erythritol, arabitol, mannitol and inositol) during 2001 to 2013. An aliquot (21 $cm^2$) of the filters were extracted three times with dichloromethane/methanol (2:1, v/v) mixture using ultrasonic agitation for 10 minutes. A Pasture pipette packed with quartz wool was used to remove particles and filter debris in the extracts. Filtrates were then concentrated using a rotary evaporator under vacuum and blown down with a stream of pure nitrogen gas. The total extracts were derivatized using 60 µl of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride in the presence of 10 µl of pyridine in a sealed vial at 70 °C for 3 hours to convert hydroxyl groups to

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146 corresponding trimethylsilyl (TMS) ethers. The derivatized fractions were diluted with n-
147 hexane containing internal standard of $C_{13}$ n-alkane (1.43 ng $\mu l^{-1}$), prior to injection to gas
148 chromatography-mass spectrometer (GC-MS).

149 Identification of SCs have been confirmed by the comparison of GC retention times and
150 mass spectra with those of authentic standards as well as literature and library data. SCs were
151 characterized by their common base peak at m/z 217 and 204 with specific fragment ions for
152 individual sugars, i.e., m/z = 307 (arabitol), 205 and 319 (mannitol), 205 (erythritol), 305 and
153 318 (inositol), 361 (sucrose and trehalose), 191 (glucose), and 437 (fructose). The selected ion
154 peak area and relative response factors determined by injection of authentic standards have
155 been used for the quantification of sugar compounds. Field blank filters were analyzed as a real
156 sample, but no target compounds were detected in the field blanks. The recoveries of the target
157 compounds were better than 90%. Therefore, the data reported here were not corrected for
158 recoveries. Analytical errors of SCs were generally <15% based on duplicate analysis. The
159 detection limits of primary sugars and sugar alcohols were 105-557 pg $\mu l^{-1}$, which corresponds
160 to ambient concentrations of 0.0015-0.0081 ng $m^{-3}$ under a typical sampling volume of 9000
161 $m^3$ (Zhu et al., 2015).

162 The derivatized fractions were introduced into GC-MS using an Agilent model 7890 GC
163 coupled to an Agilent model 5975 mass selective detector (MSD) operated in an electron
164 impact mode at 70 eV and scanned from 40 to 650 Dalton. The GC separation was carried out
165 on a DB-5MS fused silica capillary column (30 m long, 0.25 mm i.d., 0.25 µm film thickness),
166 with a temperature program of 50 °C for 2 min at a rate of 15 °C $min^{-1}$ from 50 to 120 °C, then
167 from 120 to 305 °C at a rate of 5 °C $min^{-1}$ with a final isotherm hold at 305 °C for 15 min. The
168 sample was injected on a splitless mode at an injector temperature of 280 °C. GC-MS data
169 were acquired and processed with the Agilent GC/MSD ChemStation software.

170 **2.3 Backward air mass trajectory analysis**



In order to identify the source regions of sugar compounds in Chichijima aerosols, ten-day backward trajectories were calculated at 00:00 UTC of each sampling period for thirteen-years using the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (http://ready.arl.noaa.gov/HYSPLIT.php) (Figure 3). The starting height of the trajectories presented in this study is 500 m asl. We plotted thirteen-year trajectories for each sampling day but there are no significant year-to-year changes in the atmospheric circulations. Therefore, we presented seasonal trajectories for recent year (December, 2011 to November, 2012) in Figure 3 to understand the seasonal aerosol mass transport from the source regions to Chichijima Island. Backward trajectories significantly supported a long-range transport of air mass under the influence of existing meteorological parameters (Figure 3). The trajectories clearly show the influences of continental air masses during mid-autumn to mid-spring and of marine air masses during mid-spring to mid-autumn.

### 2.4 Positive matrix factorization (PMF) analysis

Positive matrix factorization (PMF 3.0, Environmental Protection Agency, USA) has been used as a powerful statistical tool that may resolve potential sources contributing to atmospheric levels of particle (as presented by %) when appropriate source profiles are not available (Paatero and Tapper, 1994). At the beginning PMF has been used in precipitation study (Juntto and Paatero, 1994) as well as air pollution and source apportionment studies (Polissar et al., 1999). Recently, it is widely using for the air quality and source apportionment (Xie and Berkowitz, 2006). In addition, PMF has been applied to the wastewater (Soonthornnonda and Christensen, 2008), lakes sediments (Bzdusek et al., 2006) and soils (Lu et al., 2008). One of the main features of PMF results is their quantitative nature; it is possible to obtain the composition of the sources determined by the model.

PMF uses uncertainties for each of the measured concentration ($x_{ij}$). PMF minimize the residual sum of squares (Q) defined by equation:

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$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{e_{ij}}{s_{ij}}\right)^2$$

Where the $j$ is species in the $i^{th}$ sample, $e_{ij}$ is portion of the measurements. In PMF, only measured concentrations ($x_{ij}$) are known and the goal is to estimate the contributions and the fractions. The uncertainties were computed from the measurement errors by equation:

$$s_{ij} = \sigma_{ij} + C_3 \max(|x_{ij}|, |y_{ij}|)$$

Where $y_{ij}$ is the calculated value for $x_{ij}$, $\sigma_{ij}$ is the measurement or estimated error, and $C_3$ is a dimensionless constant value. The estimation of the measurement errors of size distribution data were based on the combination of size bins (Zhou et al., 2004). $C_3$ is used as the estimation of the relative uncertainties of large values (Norris et al., 2008). Using too few factors will combine sources of different nature together and using too many factors will make a real factor further dissociate into two or more non-existing factors. $F_{peak}$ is a parameter in PMF for controlling rotations (Paatero et al., 2002). When the $F_{peak}$ value is positive, the following additional term is included in the object function Q:

$$Q^P = \beta^2 \left(\sum_{K=1}^{P}\sum_{J=1}^{N} f_{kj}\right)^2$$

where, $\beta^2$ corresponds to the $F_{peak}$ value.

PMF analysis was performed for quantitative estimation of sources for the collected samples using tracer compounds for primary sugars, sugar alcohols, and anhydrosugars. Based on given understanding of sugar sources, 4-7 factors were examined and total five interpretable factors were characterized by the enrichment of each tracer compound, which reproduced more than 94% of SCs. Minimal robust and true Q values of the base run were 3001 and 3413, respectively. Concentrations and percentage of tracers in each factor of bootstrap run were close of those of base run results. The Q values and factor profiles of $F_{peak}$ rotation runs showed no significant changes compared with base run, indicating stable PMF results.

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In winter/spring, Chichijima Island receives air masses enriched with anthropogenic aerosols from the Asian continent by strong westerly winds, whereas during summer/autumn it receives clean air masses from the Pacific Ocean under the influences of trade winds. The seasonal changes in the atmospheric circulation over Chichijima may have a significant influence on the seasonal distributions of SCs. Therefore, we performed the seasonal PMF analysis on the thirteen-year sugar data set to better understand the seasonal source profile of individual sugar component. For seasonal PMF analysis, 3-5 factors were examined and 4 factors were determined for each season. We included the data set of anhydrosugars from Verma et al. (2015) for PMF analysis.

## 3. Results and discussion

### 3.1 Ambient concentrations of sugar compounds

Temporal variations of primary sugars and sugar alcohols are shown in Figure 4. Nine sugar compounds (SCs) including five primary sugars and four sugar alcohols were detected in the aerosol samples collected from Chichijima Island. The concentrations of total SCs varied from 1.23 to 339 ng $m^{-3}$ (average, 46.7±49.5 ng $m^{-3}$) during 2001 to 2013 (Table 1). Concentrations of primary sugars and sugar alcohols were in the range of 0.28 to 176 ng $m^{-3}$ (23.3±25.7 ng $m^{-3}$) and 0.37 to 231 ng $m^{-3}$ (23.4±30.8 ng $m^{-3}$), respectively. Average concentration of primary sugars in Chichijima aerosols is several times lower than that of primary sugars (62.0±54.9 ng $m^{-3}$) reported from Cape Hedo, Okinawa, Japan (Zhu et al., 2015) while that of sugar alcohols is equivalent to or little lower than that from Cape Hedo (29.5±35.5 ng $m^{-3}$).

Interestingly, primary sugars (49.9%) and sugar alcohols (50.1%) were found to contribute almost equal to total SCs during the entire study period. Mannitol (26.7%) and arabitol (21.4%) were the main contributors to total SCs followed by glucose (16.7%), sucrose (13.6%), fructose (10.2%), and trehalose (9.2%). Erythritol (1.6%), inositol (0.3%), and xylose (0.3%) were also present in the aerosols at lower concentration levels. Temporal plots of



248 individual sugars clearly indicate a large variation of SCs (Figure 4). This large variation in the
249 concentrations of SCs might be involved with seasonal changes in the atmospheric circulations
250 in the western North Pacific (Kawamura et al., 2003).

251 **3.1.1 Concentrations of primary sugars in total SCs**

252 Glucose is the dominant sugar species among the primary sugars with concentration range of
253 0.05 to 64.3 ng $m^{-3}$ (average, 7.79±8.80 ng $m^{-3}$). Similarly, a wide concentration range of
254 fructose (0.03-115 ng $m^{-3}$; 4.69±8.04 ng $m^{-3}$) was also observed in Chichijima aerosols.
255 Thirteen-year mean concentrations of glucose and fructose were observed to be lower than
256 those (27.2 ng $m^{-3}$ and 16.4 ng $m^{-3}$, respectively) reported for the aerosol samples (TSP) from
257 Cape Hedo, Okinawa, Japan (Zhu et al., 2015). Glucose and fructose significantly contribute to
258 total primary sugars (33.5% and 20.17%, respectively) in Chichijima aerosols. The primary
259 sugars are abundant in the fragments of vascular plants in vegetated and forest areas (Medeiros
260 et al., 2006). Pacini et al. (2000) reported that primary sugars are synthesized in leaves during
261 photosynthesis and stored in root, stem, flower, pollen and fruit of growing plants. The nectars
262 and fruits of tropical and subtropical plants also contain glucose and fructose abundantly
263 (Backer et al., 1998). Graham et al. (2002) reported significant amounts of glucose and
264 fructose in pollen, fern spores, and insects in aerosol samples collected from the Amazon forest.
265 Chichijima Island is covered with endemic and vascular plants, which may emit glucose and
266 fructose. Moreover, different sources such as soil dust (Rogge et al., 2007; Simoneit et al.,
267 2004), lichens (Dahlman et al., 2003) and biomass burning (Medeiros et al., 2006; Nolte et al.,
268 2001) have also been reported as dominate sources for glucose and fructose.

269 Among all the SCs detected in the Chichijima aerosols, sucrose is the second most
270 abundant sugar species (0.002-100 ng $m^{-3}$ ; 6.43±12.9 ng $m^{-3}$), accounting for 27.3% of total
271 primary sugars. The average sucrose concentration observed in Chichijima is twice lower than
272 that (13.2 ng $m^{-3}$) from Cape Hedo, Okinawa, Japan (Zhu et al., 2015). Sucrose is synthesized
273 in plant leaves and circulated by phloem to different plant sections, which is accumulated in



root cells as well as developing flower buds (Bieleski, 1995; Jia et al., 2010). Sucrose is a dominant component in airborne pollen grains derived from flowering plants (Bieleski, 1995; Pacini, 2000). Simoneit et al. (2004a and 2004b) reported the presence of sucrose in surface soil and paved road dust. Sucrose was also observed in dry plant materials during harvesting period (Ma et al., 2009).

Thirteen-year mean concentration of trehalose ranged from 0.01 to 70.2 ng $m^{-3}$ (4.30±7.28 ng $m^{-3}$), whose average concentration accounts for 18.4% of total primary sugars detected in Chichijima aerosols for 13 years. Microbes (bacterial cell), fungal spores, yeast, algae, invertebrates, suspended soil dust, as well as plant species, contribute significantly to trehalose in the atmosphere (Elbein, 1974; Graham et al., 2003; Medeiros et al., 2006; Rogge et al., 2007; Simoneit et al., 2004; Wiemken, 1990). Xylose is a less abundant primary sugar, accounting for 0.60% of total primary sugars observed in Chichijima aerosols. The concentration range of xylose was 0.001-1.35 ng $m^{-3}$ (0.14±0.18 ng $m^{-3}$) during sampling period of thirteen years. Biomass burning activities emit xylose to the atmosphere. Cowie and Hedges (1984) reported that xylose produced by angiosperm and gymnosperm plants, phytoplankton, as well as groups of microorganisms. Simoneit et al. (2004a) have reported xylose in soil dust from various locations in the United States and Japan. Wan and Yu (2007) also observed xylose in soils and associated micro biota.

### 3.1.2 Concentrations of sugar alcohols in total SCs

Thirteen-year mean concentrations of arabitol and mannitol were found to be 9.99±13.6 ng $m^{-3}$ and 12.5±17.5 ng $m^{-3}$, which contribute to 42.7% and 53.3% of total sugar alcohols, respectively. The concentration ranges of arabitol (0.04–106 ng $m^{-3}$) and mannitol (0.10–118 ng $m^{-3}$) are comparable to those from the Mediterranean region, Israel (arabitol, 1.85–58.3 ng $m^{-3}$ and mannitol, 5.57–138 ng $m^{-3}$) (Burshtein et al., 2011). Yttri et al. (2007) also reported that arabitol and mannitol were main contributors of sugar alcohols in aerosol samples collected from the different background sites in Norway. Sugar alcohols (arabitol, mannitol)



can be used as tracers for various fungal and algal species (Bauer et al., 2008a,b; Pashanska et al., 2002; Zhang et al., 2010). Loos et al. (1994) discussed arabitol and mannitol as potential sources of bacteria and other microbes. High levels of detritus from the spring bloom and autumn decomposition have been reported as significant sources for arabitol and mannitol in the vegetated region (Burshtein et al., 2011; Pashynska et al., 2002). Good positive correlations of arabitol ($r = 0.63$) and mannitol ($r = 0.72$) with glucose indicate a vegetation contribution of both sugar alcohols in Chichijima aerosols. Erythritol and inositol are less abundant sugar species, accounting for 3.29% and 0.66% of total sugar alcohols. Their concentration ranges are 0.01-8.32 ng $m^{-3}$ and 0.01-1.81 ng $m^{-3}$, respectively. Significant positive correlations of both sugar species with arabitol and mannitol indicate similar sources for these SCs in Chichijima aerosols (Table 2).

### 3.2 Seasonal variations of total sugar compounds

Seasonal concentration range, mean and median values of individual sugars during the study periods of thirteen-years are presented in Table 1. The concentrations of individual sugars were extensively fluctuated from season to season in aerosol samples collected at Chichijima (Figures 4 and 5a). The seasonally averaged concentrations of total SCs are higher in summer (71.5±70.9 ng $m^{-3}$) and autumn (57.0±64.2 ng $m^{-3}$) than spring (39.8±67.6 ng $m^{-3}$) and winter (18.2±34.0 ng $m^{-3}$) over Chichijima Island. Zhu et al. (2015) measured sugar components in aerosol samples collected from Cape Hedo, Okinawa, Japan and reported 2 to 3 times higher concentrations in summer (136 ng $m^{-3}$) and spring (133 ng $m^{-3}$) than autumn (86 ng $m^{-3}$) and winter (40 ng $m^{-3}$), whose seasonal trends are similar to Chichijima. Wan and Wu (2007) reported different seasonal variations with the highest concentration in autumn (375 ng $m^{-3}$), followed by winter (292 ng $m^{-3}$) and spring (84 ng $m^{-3}$) for the continental urban aerosols collected from Hong Kong. These concentrations in Hong Kong are 16 and 6 times higher than those of the remote Chichijima samples for winter and autumn, respectively. Interestingly, the different seasonal trends between the continental urban sites and two islands in the western



North Pacific may be associated with different sources and transport pathways between the urban and marine environments.

### 3.2.1 Seasonal variations of primary sugars

Glucose maximized in summer (11.0±9.02 ng $m^{-3}$) followed by autumn (9.25±8.63 ng $m^{-3}$), spring (7.68±10.3 ng $m^{-3}$) and winter (3.11±3.53 ng $m^{-3}$) (Table 1 and Figure 5h). Glucose is the most abundant primary sugar in Chichijima aerosols. In winter/spring, Chichijima is influenced by strong westerly winds that deliver the air masses the Asian continent including Mongolia, Russian Far East and north China, where vegetation is active. Consequently, declined concentration of glucose in winter means the depressed emission of continental bioaerosols from Asia in spite of a long-range transport of Asian dusts due to strong westerly. The local vegetation (vascular plants) in Chichijima Island might be responsible to enhanced glucose during growing season (spring and summer) and decaying periods of plant leaves (autumn). Seasonal PMF analysis also supports dominant sources of vegetation for glucose among four factors, which contributed >75% for mixed factor in summer (Figure 6c), >80% for fungal and vegetation factor in autumn (Figure 6d), and >75% for vegetation factor in spring (Figure 6b).

Fructose shows the highest concentrations in summer (7.25±7.63 ng $m^{-3}$) followed by spring (4.51±9.21 ng $m^{-3}$), autumn (3.70±2.68 ng $m^{-3}$) and winter (3.36±10.2 ng $m^{-3}$). As shown in Table 2, a significant correlation (r=0.57) was obtained between glucose and fructose. Burshtein et al. (2011) reported similar correlations for both sugar species, suggesting an identical input of glucose and fructose from the local vegetation in summer (Baker et al., 1998; Pacini, 2000). Monthly mean concentrations of fructose show two prominent peaks in February-March and June-July, the latter peak may be due to the local vegetation in Chichijima (Figure 5g). The fructose peak in February-March may be influenced by air borne pollen grains in the spring bloom of flowering plants. High concentration of fructose was observed in spring followed by summer, indicating an input of this sugar compound from pollen grains (Fu et al.,



352 2012). The positive correlation of fructose with sucrose (pollen tracer) supports the similar
353 sources. Seasonal PMF analysis further supports the identical source for fructose and sucrose;
354 that is, among four factors, fructose contributes >70% and >60% for pollen factor in spring
355 (Figure 6b) and winter (Figure 6a), respectively.

356 Seasonal mean concentrations of trehalose showed a maximum in summer (7.06±8.49 ng
357 $m^{-3}$) followed by autumn (6.09±8.81 ng $m^{-3}$), spring (2.93±6.08 ng $m^{-3}$) and winter (1.03±1.26
358 ng $m^{-3}$) (Table 1). Monthly mean concentrations of SCs for 13 years show that concentrations
359 of trehalose are higher during June to October (Figure 5j). Ma et al. (2009) reported higher
360 concentrations of trehalose at the urban site of Guangzhou, China during summer and autumn.
361 Similarly, Wan and Wu (2007) reported a similar autumn maximum in Hong Kong. On the
362 other hand, different seasonal trends of trehalose were reported for the aerosol samples (TSP)
363 collected in USA (Medeiros et al., 2006), China (Wang et al., 2011), Australia (Hackl et al.,
364 2000), and Gosan, Jeju Island in the western North Pacific Rim (Fu et al., 2012). In the above
365 studies, highest concentrations of trehalose were reported in early spring due to the re-
366 suspension of soil particles during agricultural practice. Hackl et al. (2000) also obtained
367 abundant trehalose in spring, and proposed that trehalose can be used as a tracer of soil dust
368 emission to the atmosphere. However, we did not detect a spring peak of trehalose in
369 Chichijima aerosols, suggesting that soil dust contribution of trehalose over Chichijima is
370 insignificant via long-range atmospheric transport. Seasonal PMF analysis for autumn showed
371 that more than 85% of trehalose was contributed by microbial factor among four factors
372 (Figure 6d). An indirect contribution of trehalose from soil dust will be discussed later.

373 The seasonal mean concentrations of sucrose are almost equal during spring (8.80±18.0
374 ng $m^{-3}$), summer (7.31±11.5 ng $m^{-3}$) and winter (6.60±13.1 ng $m^{-3}$), except for autumn
375 (2.76±4.35 ng $m^{-3}$) (Table 1). The homogeneous seasonal distribution suggests multiple
376 sources of sucrose in Chichijima aerosols. Monthly mean concentrations of sucrose show two
377 peaks during February-March and June-July (Figure 5i). The March peak of sucrose was



reported in the forest area of Sapporo, Japan to be 3 to 7 times more abundant than other months due to springtime pollen emissions (Miyazaki et al., 2012). Fu et al. (2012) analyzed pollen samples from different plant species (white birch, Chinese willow, Peking willow) for SCs and found the highest concentrations of sucrose followed by fructose and glucose in pollen. The pollen emissions from developing buds of plants may be the reason for the increased concentration of sucrose and fructose in February and March over Chichijima Island in the western North Pacific. Seasonal PMF analysis shows that sucrose contributed 100% in spring and >80% in winter, suggesting a significant pollen contribution for sucrose in those seasons (Figures 6b and 6a).

However, the possibilities of pollen transport from East Asia to Chichijima cannot be excluded because pollens can travel long distances with springtime high-speed winds by westerlies (Rousseau et al., 2006). The pollen grains emitted from flowering boreal forest in China, Mongolia, Siberia and Russian Far East, could significantly be delivered to the western North Pacific during spring, which may contribute sucrose and fructose in Chichijima aerosols. Recent studies have discussed a long-range transport of airborne pollen from North America to Greenland in spring (Rousseau et al., 2008). Lorenzo et al. (2006) reported the long distance transport of airborne allergenic pollen to central Italy. Makra et al. (2010) reported a long-range transport of airborne pollen in three European cities by applying three-dimensional clustering of backward trajectories. Several studies also discussed a long-range transport of pollen to the remote arctic region (Andrews et al., 1980; Bourgeois et al., 2001; Campbell et al., 1999; Hicks et al., 2001; Hjelmroos and Franzen, 1994; Rousseau et al., 2004).

These observations may support that westerly winds have delivered pollen grains from the Asian continent including Mongolia, Siberia, and Russian Far East to Chichijima Island in spring. Using a box model and typical settling velocity of pollens (3 cm/sec) with the grain size of 30 μm in diameter (Sosnoskie et al., 2009), we estimated lifetime of pollen grains to be 9.3 hours in the atmospheric marine boundary layer (height of 1 km above the ocean surface). The



settling velocity of the pollens is ca. 20 times larger than that of typical marine aerosols (Slinn and Slinn, 1980). Because pollen grain sizes range from 10 µm to 100 µm in diameter, the lifetime of pollens may have a large uncertainty. If pollens could be largely transported in the free troposphere (e.g., 5 km high) to the North Pacific from the Asian continent, then lifetime of typical pollen grains would increase upto 2 days. These calculations for the lifetime of pollen grains further support their long-range atmospheric transport from the Asian continent over the western North Pacific. Based on backward air mass trajectories (Figure 3), we can roughly estimate the transport time from East Asia to Chichijima site to be 2-4 days in winter and spring. It is also of interest to note that pollens can rapture under condition of high relative humidity (RH) (Hader et al., 2014; Miguel et al., 2006; Wright et al., 2014), which leads to smaller particles with longer residence time in the atmosphere.

In addition, tilling process after wheat crop harvesting in farmland causes an enhanced exposure of wheat root associated with soil particles into the atmosphere. China, India, and USA are three largest countries for wheat production in the world. In China and India there are two seasons (spring and winter) for wheat crops; winter wheat is harvested from mid-May to mid-July. During those periods (early summer), Chichijima Island is highly influenced by trade winds (Figure 3). However, trajectories clearly show the occasional air mass transport during summer from the Southeast Asia to Chichijima (Pavuluri et al., 2010). PMF results of sucrose for summer (Figure 6c) and autumn (Figure 6d) account for >85% and >90%, respectively, for soil dust factor among four source factors, suggesting an additional source of soil dust for sucrose in Chichijima (Simoneit et al., 2004). The elevated sucrose concentrations in June and July (summer; non flowering seasons) suggest the transport of sucrose associated with soil particles under the influence of occasional air mass transport in summer from Southeast Asia (Figure 3).

Xylose was found as the least abundant sugar compound in the aerosol samples. The maximum concentration of xylose (1.35 ng $m^{-3}$) was found in summer whereas minimum



(0.001 ng $m^{-3}$) in spring (Table 1). Summer mean concentration (0.18±0.26 ng $m^{-3}$) was highest (Table 1). The PMF analyses showed that xylose contributed >75% for BB factor in winter (Figure 6a) and >70% in autumn (Figure 6d) for microbial factor. These results suggest different sources and seasons for xylose; i.e., biomass burning in winter (Sullivian et al., 2011) and groups of microorganisms in summer (Cowie and Hedges, 1984).

### 3.2.2 Seasonal variations of sugar alcohols

The seasonal mean concentrations of arabitol and mannitol are higher in summer/autumn than spring/winter (Table 1). The concentrations of arabitol are equally distributed between summer (15.1±12.9 ng $m^{-3}$) and autumn (15.8±18.3 ng $m^{-3}$) with lower levels in spring (7.13±9.50 ng $m^{-3}$) and winter (1.73±2.60 ng $m^{-3}$). Mannitol maximized in summer (21.7±19.7 ng $m^{-3}$) followed by autumn (18.2±19.9 ng $m^{-3}$), spring (7.95±13.8 ng $m^{-3}$) and winter (1.89±2.81 ng $m^{-3}$). Arabitol and mannitol strongly co-varied throughout the study period. As depicted in thirteen-year monthly mean concentrations of total SCs (Figure 5b,c), we found elevated concentrations of sugar alcohols from May to October. Similar seasonal trends were reported for the aerosol samples collected from Gosan, Jeju Island in the western North Pacific Rim (Fu et al. 2012) and urban aerosol samples from Ghent, Belgium (Pashynska et al., 2002). In above studies, higher relative abundances of arabitol and mannitol in total sugar alcohols were reported during late summer to autumn. The higher concentration of arabitol in autumn was also reported for aerosol samples from the Mediterranean region in Israel (Burshtein et al., 2011). Erythritol and inositol showed the similar seasonal trend, but their concentrations are lower than the former two sugar species.

Sugar alcohols are emitted to the atmosphere from a variety of bacteria, few green algal lichens and fungi (Dahlman et al., 2003; Filippo et al., 2013). Arabitol and mannitol are abundant in fungal spores (Lewis and Smith, 1967; Yttri et al., 2007). Arabitol (r = 0.73) and mannitol (r = 0.80) showed a strong co-variance with trehalose, suggesting identical sources of sugar species in Chichijima. The PMF analysis showed that fungal factor and mixed factor



(fungal, vegetation, and microbial) accounted for 25% and 54.2% of total SCs observed in summer, respectively (Figure 6c). In autumn fungal and vegetation factor contributed 71% of total SCs detected in Chichijima aerosols (Figure 6c). In winter (Figure 6a) and spring (Figure 6b) fungal and vegetation factor and mixed factor account for 31.2% and 37.2% of total SCs, respectively. This is reasonable because fungal and microbial activities are lower during winter/spring as compared to summer/autumn. The meteorological factors such as RH and temperature significantly affect fungal and bacterial activity (Kim and Xiao, 2005; Malik and Singh, 2004). Higher RH and temperature are crucial in increasing fungal and bacterial growth (Sharma and Razak, 2003). Their maximum growth was observed under the condition of 92-100% RH (Ibrahim et al., 2011). Higher concentrations of arabitol and mannitol in summer and autumn may be due to the increased fungal and bacterial activities in Chichijima Island in the western North Pacific.

Several studies have described the occurrence of fungi in marine environment (Jones, 1976; Kohlmeyer and Kohlmeyer, 1991; Moss, 1986). The fungal species eject spores from hard materials like coral and sand grains. Some fungi also eject spores from woods associated with sand in summer/autumn when higher ambient temperature and RH are available (Jones and Mitchell, 1996). Marine fungal growths are observed on several mediums of substrates such as wood, sediments, muds, soil, sand, algae, corals, decaying leaves of mangroves and living animals in marine environment (Bremer, 1995; Kohlmeyer and Kohlmeyer, 1979; Nagakiri et al., 1996). However, the above studies have claimed to the occurrence and growth of marine fungi on several mediums of substrates but still the knowledge of the role of marine fungi in sediments and decaying dead animals are insufficient due to the lack of appropriate data set. It is still unclear if these fungi are active in sediments or if inactive spores are isolated (Hyde et al., 1998). Therefore, due to the inadequate data set, we doubt the marine contribution of sugar alcohols (arabitol, mannitol) in Chichijima aerosols.



Thirteen-year monthly mean concentrations of SCs clearly show slightly decreased concentrations of arabitol, mannitol, and erythritol in July and August; a similar trend was observed for trehalose (Figure 5b,c,e,j). These sugar compounds are derived from the microbial activities in source regions. The thirteen-year precipitation record over Chichijima Island shows that precipitations were lowered in July and August (Figure 2). The lower precipitation amount decreases the RH (Figure 2) and thus depresses the fungal and microbial activities. The lower precipitation also suppresses the moisture contents in the surface soil of Chichijima, which should cause a significant decline of local fungal and other microbial activities on the ground of Chichijima Island. Decreased precipitation might be a possible reason for the lower concentrations of arabitol, mannitol, and trehalose in July and August.

### 3.3 Annual variations and decadal comparisons of SCs

The annual variations in the concentrations of primary sugars and sugar alcohols are shown in Figure 7a. The annual mean concentrations of total SCs varied randomly during 2001 to 2013. As shown in Figure 7 (i, j, f and d), concentrations of sucrose, trehalose, xylose, and inositol increase from 2001 to 2013 in Chichijima aerosols. Similarly, arabitol (Figure 7b), glucose (Figure 7h), and fructose (Figure 7g) show clear increasing trends from 2006 to 2013 whereas mannitol (Figure 7c) and erythritol (Figure 7e) show a random trend. Thirteen-year data set provides significant information regarding the decadal variation in the atmospheric conditions over Chichijima Island in the western North Pacific. Here, we compare the data set of SCs for the periods of 1990-1993 (Period, P-I) with the current observations from 2001 to 2003 (P-II) and 2010 to 2013 (P-III) (Table 3) (Figures 8a, b, c).

The comparison for three periods indicates that concentrations of anhydrosugars are highest in winter followed by autumn. Their concentrations significantly increased from P-I to P-II/P-III (Figure 8a). The detailed discussions on anhydrosugars were reported in Verma et al. (2015). Here, we refer the data set of anhydrosugars for the decadal comparison with SCs. Interestingly, biomass-burning tracers (BB tracers; levoglucosan, mannosan and galactosan)



showed a significant difference in the decadal trends among three periods (i.e., P-I, P-II, and P-III) during winter and autumn. In winter, BB tracers showed an increasing trend from P-I to P-III (Figure 8a). Biomass burning is common in winter for house heating (Simoneit et al., 20004a), thus it is obvious that the lower ambient temperature is the more biomass burning activities are. Westerly winds abundantly transport biomass-burning products over Chichijima Island in the western North Pacific with air masses derived from East Asia, Siberia, Mongolia, and Russian Far East during winter (Bendle et al., 2007; Simoneit and Elias, 2010; Verma et al., 2015). In contrast, BB-tracers in autumn show an opposite trend (i.e., higher concentrations in P-I followed by P-II and P-III) compared to those in winter (Figure 8a).

The difference in the concentrations of anhydrosugars in winter and autumn during P-I is insignificant while the concentrations are 3 and 5 times higher in winter than autumn for P-II and P-III, respectively. This seasonal shifting in the concentrations of anhydrosugars may be attributable to the changes in the strength of both westerly and trade wind systems from mid autumn to early winter among three periods (Chen et al., 2013). In contrast, the concentrations of primary sugars were 2 to 7 times higher during P-II and P-III than P-I period in summer and autumn (Figure 8b). PMF analysis showed that local emissions from vegetation are important contributor for primary sugars (glucose, fructose and sucrose). Therefore, a drastic increase in concentration of primary sugars in summer/autumn for P-II and P-III than P-I may be caused by an increase in the emission of primary sugars by local vegetation under the influence of meteorological conditions in the western North Pacific. However, a possible soil dust contribution of primary sugar (sucrose) associated with an occasional air mass transport from Southeast Asia cannot be excluded.

Similarly to primary sugars, a drastic increase in the concentrations of sugar alcohols was observed for P-II and P-III compared to P-I period (Figure 8c). The concentrations of sugar alcohols in P-II and P-III are 6 to 19 times higher than those of P-I in summer/autumn (Table 3; Figure 8c). Arabitol and mannitol are key sugar alcohols and reported as fungal and



533 microbial tracers, which contribute significantly to total SCs (Bauer et al., 2008b; Lewis and
534 Smith, 1967; Zhang et al., 2010). Microbes such as fungi and bacteria are significantly
535 increasing in the Asian and European countries (Yamaguchi et al., 2012). They are largely
536 transported towards downwind regions in the Pacific Ocean from the Asian Continent in
537 winter/spring under the influence of strong westerlies (Griffin et al., 2001, 2003, 2007; Hua et
538 al., 2007; Uno et al., 2009) and settled down by wet and dry deposition in the western North
539 Pacific according to air mass trajectories (Figure 3). Hirst and Stedman (1967) reported the life
540 time of the fungal spores, they studied long-range spores transport and discussed that the
541 fungus spores are between 2 and 200 µm in diameter (mostly 5 to 30 µ m); they have settling
542 velocity between 0.005 and 3.0 cm/sec with a mode of less than 1 cm/sec, and different fungal
543 spores vary significantly in shape and ornamentation. Most fungus spores are usually nearly
544 spherical and larger, have a specific gravity close to 1.0. Because of their larger mass, settle
545 velocity is at 1 to 40 cm/sec, with a mode of 3 cm/sec. This study suggested the possibilities of
546 the fungal spores long-range fungal spores. Jeon et al. (2011) and Yamaguchi et al. (2012)
547 have analyzed aerosol samples collected during the Asian dust event over the Sea of Japan, and
548 identified similar groups of microbes (bacterial cells) transported from the source regions of
549 Asian dust. Consequently, bacteria and fungi grow extensively during summer/autumn, when
550 the climate conditions (i.e., higher RH and temperature) are favorable for their metabolic
551 activities (Morris et al., 2004). Accordingly, an increased transport of bioaerosols since the last
552 decade may have caused a drastic increase in the concentrations of sugar alcohols during P-II
553 and P-III compared to P-I period over the western North Pacific.

554 **3.4 Source apportionment of SCs**

555 To investigate the source apportionment of sugar components, the data sets of Chichijima
556 aerosols were subjected to positive matrix factorization (PMF) analysis. Based on the PMF
557 analysis, total five factors were determined to be significant to classify the sources of sugar



558 compounds (SCs). Five factors successfully explored the source profile for the individual sugar
559 component. Factor profiles resolved by PMF analysis are shown in Figures 6 and 9-11, where
560 percentages of each component summed for factors 1 to 5 are calculated to be 100%.

561 Vegetation factor (Figure 9) was dominated by xylose (75%), glucose (48%), and
562 fructose (36%). Xylose is significantly produced by gymnosperm and angiosperm (Cowie and
563 Hegdes, 1984; Sjostrom, 1981). Fructose and glucose are highly water-soluble sugar species,
564 and present in the bark and leaves of plants (Fu et al., 2012). Glucose is the second most
565 abundant sugar that contributed to this factor. Cowie and Hegdes (1984) reported higher
566 concentration of glucose in vascular plants and phytoplankton in the marine environment. The
567 SCs emitted by the vegetation during growing season significantly contribute to vegetation
568 factor. In Chichijima aerosols, glucose and fructose are significantly contributed in spring
569 (Figure 6b), summer (Figure 6c) and autumn (Figure 6d), Therefore, the respective factors in
570 Figure 6 are termed as a vegetation source for the both sugar species. This is reasonable
571 because plants started growing in spring and summer seasons. In autumn, leaf senescence and
572 decay result in the emission of glucose and fructose to the atmosphere.

573 Fungal and microbial factor (Figure 9) was characterized by trehalose (88%), mannitol
574 (64%), and arabitol (54%). These sugars that contribute to fungal and microbial factor are
575 associated with fungal spores, bacteria and yeast (Bauer et al., 2008a; Medeiros et al., 2006;
576 Wiemken, 1990). The three sugars are good tracers of fungal spores and microbes (Loos et al.,
577 1994; Rogge et al., 2007). Arabitol and mannitol are produced by a large variety of fungal
578 species (Ion et al., 2005; Medeiros et al., 2006), and considered as a suitable tracer for fungal
579 and bacterial metabolic activities (Bauer et al., 2008b; Elbein et al., 1974; Rogge et al., 2007).
580 Arabitol is strongly correlated with mannitol (r=0.88), suggesting similar sources for both
581 species (Table 2) (Elbert et al., 2007). Fungi, bacteria, and other microbes in soils are the main
582 sources for trehalose (Graham et al., 2003; Rogge et al., 2007; Simoneit et al., 2004). An



excellent correlation of trehalose with arabitol and mannitol suggested similar sources in the marine environment (Table 2) (Lewis and Smith, 1967).

Sugar alcohols have been proposed as tracers for microbes and fungal spores (Bauer et al., 2008b; Ion et al., 2005; Medeiros et al., 2006; Rogge et al., 2007). The fungal and microbial activities are considered higher during summer and autumn due to higher temperature and RH. The above discussions for the sources of arabitol, mannitol and trehalose are well supported by the seasonal PMF analysis. Arabitol and mannitol are well contributed in summer (Figure 6c, fungal factor and mixed factor) and autumn (Figure 6d, fungal and vegetation factor). Correspondingly, trehalose also contributed in summer (Figure 6c, mixed factor) and autumn (Figure 6d, microbial factor). Therefore, significant contributions of arabitol, mannitol and trehalose are observed during the respective seasons in Chichijima aerosols.

Mixed factor (Figure 9) is associated with erythritol (94%), arabitol (44%), mannitol (34%), inositol (32%), glucose (24%), and fructose (31%). Due to the highly miscellany characteristics of fungi, other microbes, and plant debris, it is quite difficult to specify the particular source for individual sugar species (Percival, 1970). Arabitol and mannitol are also attributed to the vegetation (photosynthesized by mature leaves) (Burshtein et al., 2011; Pashynska et al., 2002). The contributions of arabitol and mannitol in winter (Figure 6a, mixed factor) and spring (Figure 6b, mixed factor) indicate other sources than fungal spores in the Chichijima aerosols. Because the fungal and microbial growth is less important in winter and spring compared to summer/autumn. Therefore, this factor (Figure 9) should be associated with mixed sources from microbial and vegetational activities. Contemplating of mixed sources is very likely because sugar species that are highly apportioned to vegetation factor contribute, to some extent, to the same sources that are responsible to fungal and microbial factor (Figure 9).

BB (biomass burning) factor (Figure 9) is loaded significantly with levoglucosan (94%), mannosan (91%), and galactosan (90%), and moderately with xylose (20%). These species are



associated with biomass burning (Fraser and Lakshmanan, 2000; Graham et al., 2002; Simoneit, 2002). Nolte et al. (2001) and Medeiros et al. (2006) also reported that biomass burning-influenced aerosols are enriched with levoglucosan, mannosan, and galactosan. Kawamura et al. (2003) and Mochida et al. (2010) reported that biomass-burning products are abundantly transported to Chichijima under the influence of westerly winds during winter/spring (Figure 3). These results are well supported by the fact that BB factor is associated with SCs, which are derived from biomass burning in East Asia. The seasonal PMF analysis (Figure 6) also supports the above explanation; BB products are contributed highest in winter/spring (18.8% and 6.3%) under the influence of westerly winds, followed by summer/autumn (3.8% and 4.1%) for total sugars in the aerosol samples collected from Chichijima Island.

Pollen factor (Figure 9) is characterized by high loading of sucrose (91%), fructose (35%), and inositol (33%); these sugar species are associated with airborne pollen sources. Previous studies have also reported that sucrose is an excellent tracer for airborne pollen grains of flowering plants (Pacini, 2000; Graham et al., 2003; Wang et al., 2008; Medeiros et al., 2006). Fructose is well correlated with inositol (r=0.57), indicating a similar origin for both sugar species (Table 2). Two prominent peaks of sucrose, fructose, and inositol, which appeared in late winter to early spring or summer, also indicate a similar source of those sugars. Contributions of sucrose (pollen factor) in winter (39.5%; Figure 6a) and spring (36%; Figure 6b) are supported the sources of airborne pollen for sucrose in Chichijima Island. The sucrose contribution (soil dust factor) in non-flowering seasons, i.e., summer (17.1%; Figure 6c) and autumn (8.4%; Figure 6d) indicates different sources for sucrose in Chichijima aerosols. According to the seasonal PMF analysis (Figure 6), we termed additional sources of sucrose in Chichijima Island as soil dust factor as well as pollen factor.

In Figure 6a, b, c and d, PMF analysis for seasonal source identification indicated variable contributions of individual SCs in different seasons according to their seasonal source



635 origin. In winter (Figure 6a), airborne pollen (39.5%) contributed highest followed by
636 vegetation, microbial, fungal (mixed) (31.2%), biomass burning (18.8%) and microbial
637 (10.5%) sources. However, in spring, vegetation, microbial, and fungal (mixed) sources
638 (37.2%) contributed almost equal to the airborne pollen (36.0%) followed by vegetation
639 (21.2%) and biomass burning (6.3%) sources. The vegetation, microbial, fungal (mixed)
640 (54.2%), fungal (25.2%), soil particles (17.1%) and biomass burning (3.8%) sources are
641 characterized to maximize in summer season. Similar to summer, vegetation and fungal
642 (mixed) sources (71.2%) are also leading to the contribution of total SCs followed by microbial
643 (16.4%), soil particles (8.4%) and biomass burning (4.1%) in total SCs observed in autumn
644 season for Chichijima aerosols.

645 Overall, average contributions of each factor to measured SCs as resolved by the PMF
646 analyses are shown in Figure 10. Fungal and microbial factor accounts for 41% of total SCs
647 measured. The emission from microbes including fungal spores was found as a dominant
648 contributor to total SCs. Mixed factor (27%) indicates a common involvement of fungal,
649 microbial and vegetation sources. Figure 11 shows annual trends in % contributions of five
650 source factors to SCs in Chichijima aerosols. Fungal and microbial factor, and mixed factor
651 contributed higher than other sources for SCs during 2001 to 2013. However, no clear trends in
652 annual % contributions were observed for both source factors during thirteen-years study
653 period. The sugar species assigned as pollen tracers were found to contribute 18% in pollen
654 factor. Vegetation accounts for 11% of total SCs, indicating less emission from vegetation as
655 compared to fungi and microbes. As indicated by BB factor, biomass-burning source
656 contributes only 3% of total SCs.

657 Interestingly, we found an increasing trend in % contribution of vegetation, pollen, and
658 BB factors to SCs in 2006 to 2013 (see Figure 11). Sugar components, which are contributed
659 from pollen (sucrose, fructose, and inositol), vegetation (glucose and fructose), and biomass
660 burning sources (levoglucosan, galactosan, and mannosan), also show a similar increasing



trend for the period of 2006 to 2013 (Figure 7). The increased annual trends of BB and pollen factors might be due to an enhanced long-range transport of airborne pollens and biomass burning products from the Asian continent to the western North Pacific under the influence of strong westerly winds. The increasing annual trends in % contribution of vegetation factor to SCs may denote a significantly increased activity of local vegetation in Chichijima Island from 2006 to 2013, which could be involved with a recent global warming especially in the western North Pacific region (http://climate.nasa.gov/vital-signs/global-temperature/).

## 4 Summary and conclusions

In this study we reported thirteen-years of temporal, seasonal and decadal observations on sugar compounds (SCs) in the aerosol samples collected at Chichijima Island in the western North Pacific, an outflow region of Asian aerosols. We observed the highest abundances of total SCs and primary sugars in summer, while sugar alcohols are almost equally distributed during summer and autumn. Thus, seasonal variations are well regulated by the atmospheric circulation and meteorological parameters of Chichijima Island. The seasonal distributions of arabitol, mannitol and trehalose are strongly influenced by long-range transport of microbe-, fungi- and bacteria-associated bioaerosols and their metabolic activities under the influences of westerly winds and other meteorological parameters (high RH and temperature) in summer/autumn.

Seasonal variation of sucrose is controlled by locally emitted and long-range transported pollen from East Asia to Chichijima during spring bloom periods. On the other hand, the increased concentrations of sucrose and fructose in summer may be caused by the local activity of vegetation and possibly by the atmospheric transport of plant root-associated soil dust particles potentially delivered from East and Southeast Asia with the occasional transport of air mass from the respective regions.



PMF analysis of long-term observations clearly indicated specific sources for individual SCs during different seasons. The results separate biogenic emissions into two parts, i.e., vegetation and microbes including fungal species. The emissions from vegetation, pollen as well as microbial activities contributed almost 97% of total SCs determined, with the remaining fraction being derived from biomass burning activities. In the present decadal study, we found a drastic increase in the concentrations of sugar alcohols and primary sugars during 2001-2003 and 2010-2013, which may be explained by a significant transport of bioaerosols in last decades from East Asia to Chichijima Island in the western North Pacific.

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1008
1009 **Figure Captions**

1010 **Figure 1.** Geographical location of Chichijima Island (27°04'N; 142°13'E; 254 m, asl) in the
1011 western North Pacific.

1012 **Figure 2.** The monthly variation of the meteorological parameters over Chichijima Island
1013 during 2001-2013 (The error bars denote the standard deviations).

1014 **Figure 3.** The seasonal ten-day air mass backward trajectories over Chichijima for 2012
1015 (winter: Dec-Feb, spring: Mar-May, summer: Jun-Aug, autumn: Sep-Nov). The trajectory
1016 calculations were performed everyday starting at Chichijima Island.

1017 **Figure 4.** Temporal plots for the concentrations (ng $m^{-3}$) of sugar compounds in Chichijima
1018 aerosol samples collected for 2001-2013 in the western North Pacific.

1019 **Figure 5.** Monthly mean concentrations (ng $m^{-3}$) of sugar compounds in aerosol samples from
1020 Chichijima Island in the western North Pacific during 2001-2013.

1021 **Figure 6.** Seasonal source contributions to sugar compounds from various sources based on
1022 PMF analyses. (BB – biomass-burning; Mixed – vegetation, fungal and microbial sources).

1023 **Figure 7**. Annual mean concentrations (ng $m^{-3}$) of sugar compounds in aerosol samples
1024 collected from Chichijima Island in the western North Pacific during 2001-2013.

1025 **Figure 8.** The seasonal concentrations of anhydrosugars (biomass burning tracers), primary
1026 sugars and sugar alcohols measured in Chichijima aerosols during three periods, i.e., P-I
1027 (1990-1993), P-II (2001-2003) and P-III (2010-2013).

1028 **Figure 9.** PMF analyses of sugar compounds in Chichijima aerosols based on the 2001-2013
1029 data set. (BB – biomass-burning; Mixed – vegetation, fungal and microbial sources).

1030 **Figure 10.** Source contributions to sugar compounds from various sources based on PMF
1031 analyses. (BB – biomass-burning; Mixed – vegetation, fungal and microbial sources).

1032 **Figure 11.** Annual trends in % contributions of five source factors: (a) vegetation, (b) fungal
1033 and microbial, (c) mixed, (d) biomass burning (BB), and (e) pollen factors to SCs in
1034 Chichijima aerosols. The data of 2005 are not plotted due to limited data points.

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**Figure 1.**

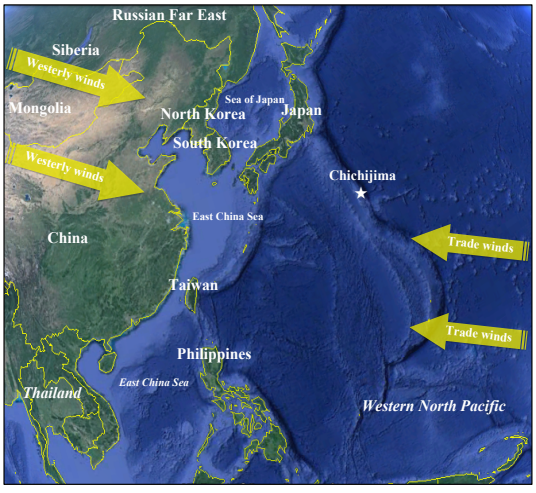

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**Figure 2.**

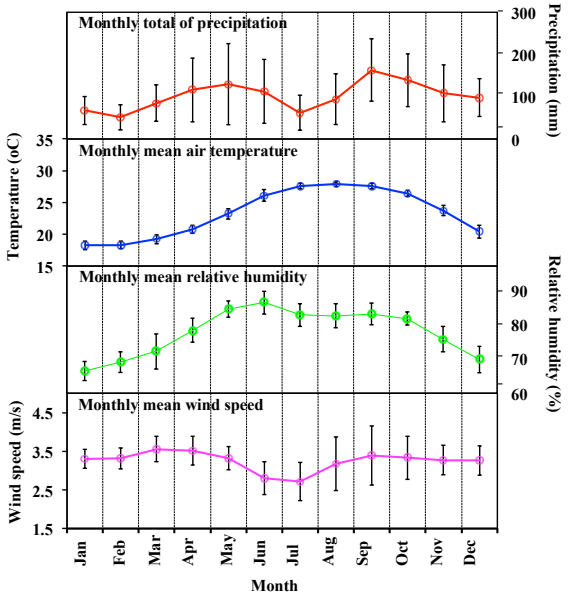

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**Figure 3.**

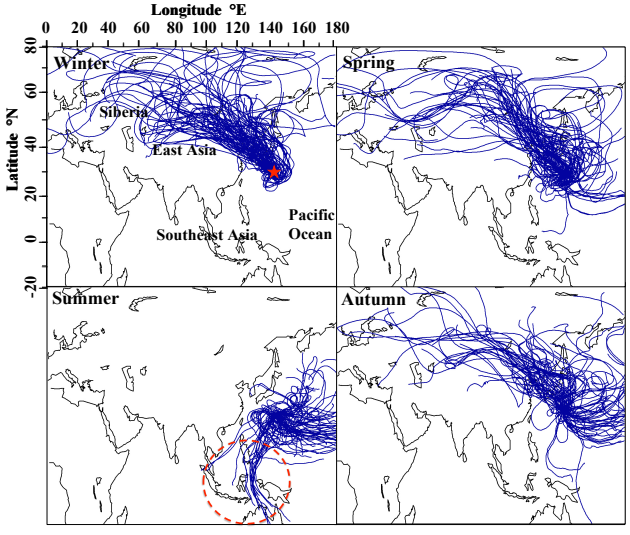

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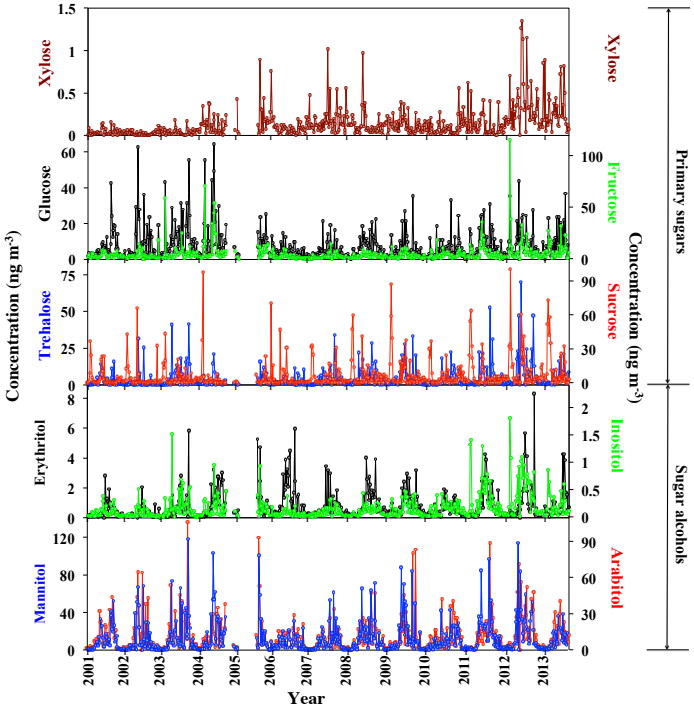
**Figure 4.**



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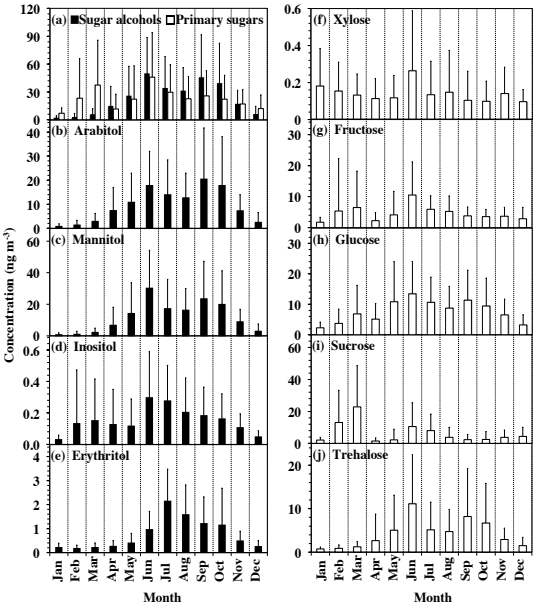


**Figure 5.**

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**Figure 6.**

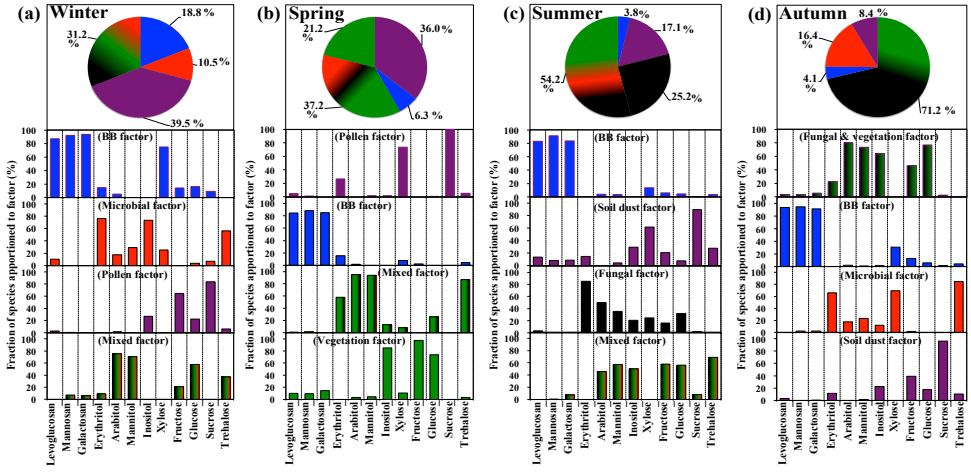

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**Figure 7.**

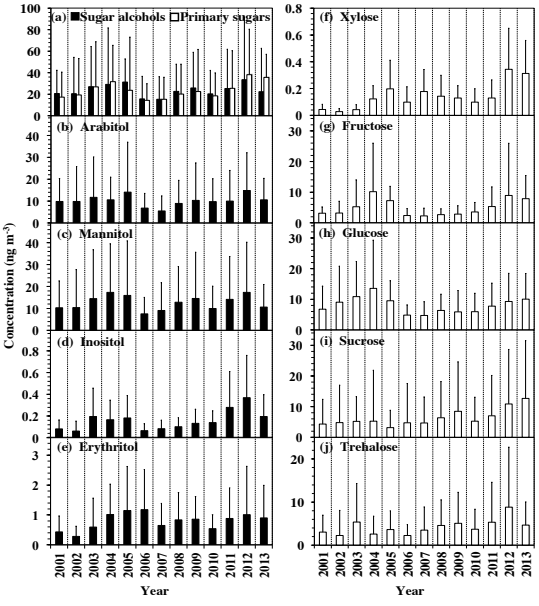

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**Figure 8.**

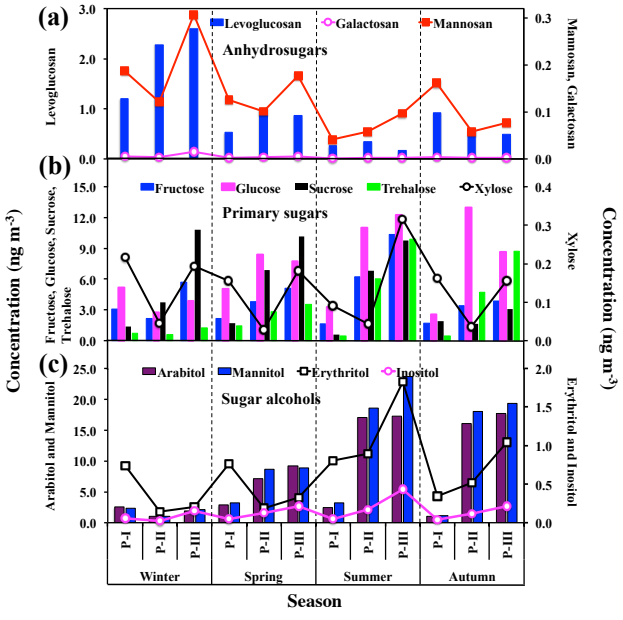

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**Figure 9.**

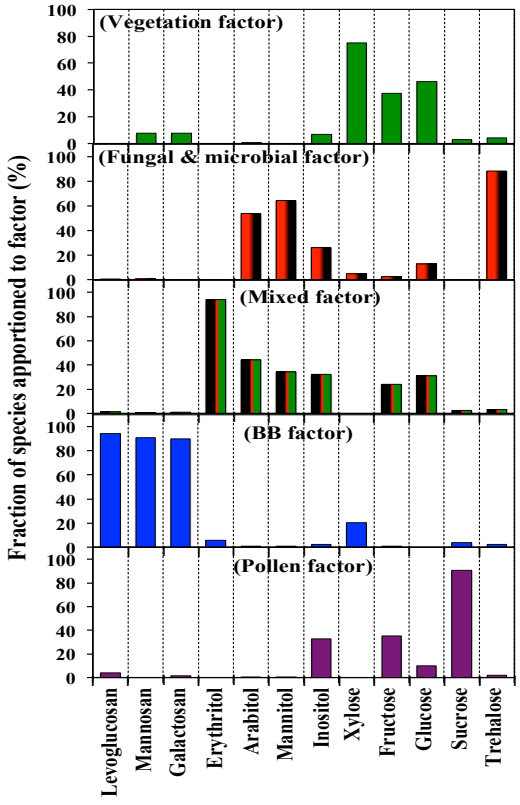
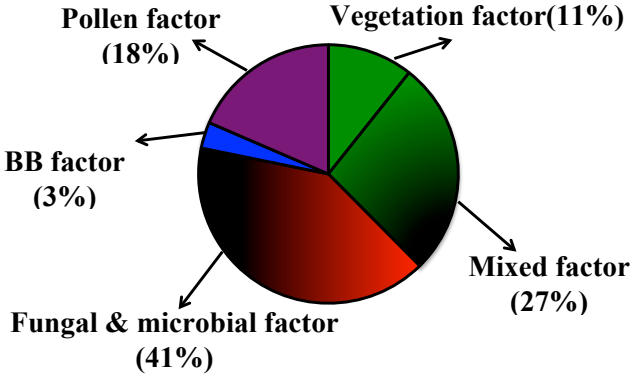




**Figure 10.**



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1251 **Figure 11.**

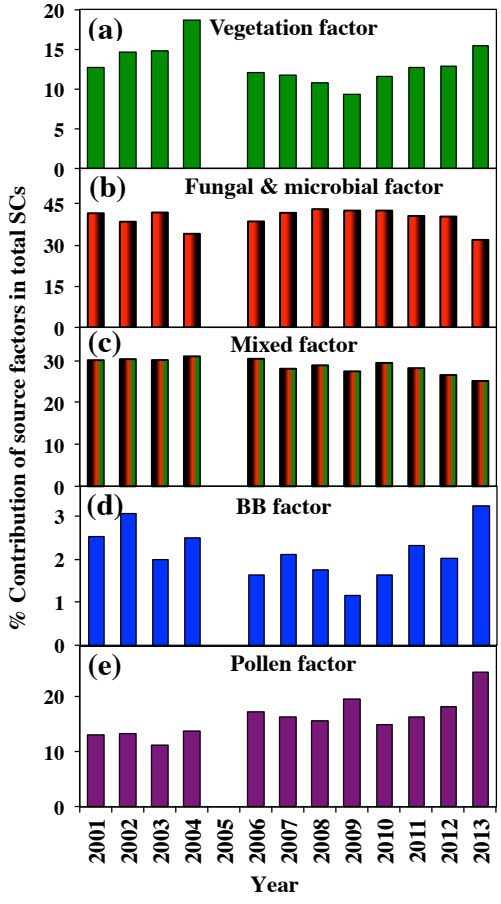


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**Table 1.** Seasonal concentrations (ng $m^{-3}$) of sugar compounds (SCs) in the aerosol samples collected at ChichiJima Island in the western North Pacific during 2001-2013.

| Sugars | Winter[a] (n=139) | | | Spring[b] (n=155) | | | Summer[c] (n=146) | | | Autumn[d] (n=150) | | | 2001-2013 (n=590) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Range | Mean±SD | Med[e] | Range | Mean±SD | Med[e] | Range | Mean±SD | Med[e] | Range | Mean±SD | Med[e] | Range | Mean±SD | Med[e] |
| **Primary sugars** | | | | | | | | | | | | | | | |
| **Xylose** | 0.05-0.89 | 0.14±0.15 | 0.12 | 0.001-0.56 | 0.12±0.11 | 0.08 | 0.002-1.35 | 0.18±0.26 | 0.08 | 0.004-0.89 | 0.11±0.14 | 0.07 | 0.001-1.35 | 0.14±0.18 | 0.08 |
| **Fructose** | 0.17-115 | 3.36±10.2 | 1.38 | 0.03-70.4 | 4.51±9.21 | 1.90 | 0.24-54.0 | 7.25±7.63 | 5.23 | 0.22-13.0 | 3.70±2.68 | 2.82 | 0.03-115 | 4.69±8.04 | 2.53 |
| **Glucose** | 0.27-23.3 | 3.11±3.53 | 2.13 | 0.05-62.6 | 7.68±10.3 | 4.36 | 0.23-64.3 | 11.0±9.02 | 7.99 | 0.72-55.5 | 9.25±8.63 | 5.77 | 0.05-64.3 | 7.79±8.80 | 4.73 |
| **Sucrose** | 0.02-73.4 | 6.60±13.1 | 2.08 | 0.005-100 | 8.80±18.0 | 1.30 | 0.003-66.0 | 7.31±11.5 | 2.58 | 0.002-31.1 | 2.76±4.35 | 1.14 | 0.002-100 | 6.43±12.9 | 1.71 |
| **Trehalose** | 0.03-10.5 | 1.03±1.26 | 0.72 | 0.006-47.2 | 2.93±6.08 | 1.23 | 0.03-70.2 | 7.06±8.49 | 4.46 | 0.04-52.5 | 6.09±8.81 | 2.46 | 0.01-70.2 | 4.30±7.28 | 1.61 |
| **Σ Primary sugars** | **0.49-223** | **14.2±28.2** | | **0.09±281** | **24.2±43.8** | | **0.51-256** | **32.8±36.9** | | **0.99-153** | **22.0±24.6** | | **0.28-176** | **23.3±25.7** | |
| **Sugar alcohols** | | | | | | | | | | | | | | | |
| **Erythritol** | 0.03-1.17 | 0.23±0.18 | 0.18 | 0.008-2.25 | 0.31±0.28 | 0.23 | 0.07-5.70 | 1.55±1.21 | 1.18 | 0.05-8.32 | 0.99±1.16 | 0.56 | 0.01-8.32 | 0.77±1.01 | 0.37 |
| **Arabitol** | 0.12-21.2 | 1.73±2.60 | 0.96 | 0.04-70.8 | 7.13±9.50 | 4.44 | 0.24-64.5 | 15.1±12.9 | 12.0 | 0.57-106 | 15.8±18.3 | 8.83 | 0.04-106 | 9.99±13.6 | 4.97 |
| **Mannitol** | 0.10-23.9 | 1.89±2.81 | 1.11 | 0.16-114 | 7.95±13.8 | 4.07 | 0.25-104 | 21.7±19.7 | 16.9 | 0.59-118 | 18.2±19.9 | 9.15 | 0.10-118 | 12.5±17.5 | 5.54 |
| **Inositol** | 0.01-1.81 | 0.07±0.20 | 0.03 | 0.008-1.51 | 0.13±0.22 | 0.06 | 0.01-1.29 | 0.26±0.25 | 0.17 | 0.01-0.93 | 0.16±0.15 | 0.10 | 0.01-1.81 | 0.16±0.22 | 0.08 |
| **Σ Sugar alcohols** | **0.26-48.2** | **3.93±5.79** | | **0.22-188** | **15.5±23.8** | | **0.56-175** | **38.6±34.1** | | **1.22-234** | **35.1±39.5** | | **0.37-231** | **23.4±30.8** | |
| **Σ SCs** | **0.75-272** | **18.2±34.0** | **10.6** | **0.31-469** | **39.8±67.6** | **18.2** | **1.07-431** | **71.5±70.9** | **50.7** | **2.21-387** | **57.0±64.2** | **31.1** | 1.23-339 | 46.7±49.5 | 30.9 |

[a] Winter (December-February), [b]Spring (March-May), [c]Summer (June-August) and [d]Autumn (September-November); Med.=Median

**Table 2.** Pearson correlation coefficients (r) for the dataset of sugars in Chichijima aerosols during 2001-2013 (n = 590).

| | Levoglucosan[a] | Mannosan[a] | Galactosan[a] | Erythritol | Arabitol | Mannitol | Inositol | Xylose | Fructose | Glucose | Sucrose | Trehalose |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Levoglucosan** | 1.00 | | | | | | | | | | | |
| **Mannosan** | 0.79 | 1.00 | | | | | | | | | | |
| **Galactosan** | 0.55 | 0.58 | 1.00 | | | | | | | | | |
| **Erythritol** | -0.18 | -0.12 | -0.16 | 1.00 | | | | | | | | |
| **Arabitol** | -0.16 | -0.09 | -0.16 | 0.48 | 1.00 | | | | | | | |
| **Mannitol** | -0.18 | -0.12 | -0.17 | 0.49 | 0.88 | 1.00 | | | | | | |
| **Inositol** | -0.06 | -0.02 | 0.10 | 0.35 | 0.49 | 0.58 | 1.00 | | | | | |
| **Xylose** | 0.20 | 0.32 | 0.34 | 0.15 | 0.18 | 0.23 | 0.42 | 1.00 | | | | |
| **Fructose** | 0.02 | 0.08 | 0.26 | 0.17 | 0.16 | 0.28 | 0.57 | 0.31 | 1.00 | | | |
| **Glucose** | -0.11 | 0.00 | -0.06 | 0.32 | 0.63 | 0.72 | 0.53 | 0.19 | 0.57 | 1.00 | | |
| **Sucrose** | 0.05 | 0.07 | 0.18 | -0.02 | -0.06 | 0.01 | 0.40 | 0.26 | 0.30 | 0.14 | 1.00 | |
| **Trehalose** | -0.10 | -0.05 | -0.10 | 0.33 | 0.73 | 0.80 | 0.55 | 0.33 | 0.22 | 0.54 | 0.13 | 1.00 |

[a] data from Verma et al. (2015)

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**Table 3.** Comparisons of seasonal concentrations (ng $m^{-3}$) of primary sugars and relative contributions (%) of sugar compounds (SCs) in total SCs in Chichijima aerosols among 1990-1993[a], 2001-2003 and 2010-2013.

| Season | Anhydrosugars | | | Sugar alcohols | | | Primary sugars | | | Total Sugars | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1990-93 [a] | 2001-03[b] | 2010-13 [b] | 1990-93 [a] | 2001-03 | 2010-13 | 1990-93 [a] | 2001-03 | 2010-13 | 1990-93 [a] | 2001-03 | 2010-13 |
| Winter | 1.44 | 2.44 | 3.05 | 5.64 | 2.27 | 4.37 | 10.6 | 9.34 | 21.8 | 17.7 | 14.0 | 29.2 |
| % | 11.4 | 23.7 | 16.6 | 31.6 | 16.5 | 19.8 | 57.0 | 59.9 | 63.6 | | | |
| Spring | 0.68 | 1.12 | 1.10 | 6.91 | 16.2 | 18.6 | 10.5 | 21.3 | 26.7 | 18.1 | 38.6 | 46.4 |
| % | 5.08 | 5.17 | 4.04 | 39.2 | 39.7 | 42.0 | 55.7 | 55.1 | 53.9 | | | |
| Summer | 0.31 | 0.43 | 0.29 | 6.50 | 36.7 | 43.1 | 6.07 | 30.0 | 42.5 | 12.9 | 67.1 | 86.0 |
| % | 2.92 | 0.91 | 0.43 | 55.6 | 51.3 | 51.1 | 41.4 | 47.8 | 48.5 | | | |
| Autumn | 1.12 | 0.65 | 0.60 | 2.57 | 34.7 | 38.3 | 6.79 | 22.6 | 24.5 | 10.5 | 57.9 | 63.4 |
| % | 12.9 | 3.45 | 1.73 | 29.2 | 50.4 | 57.2 | 57.9 | 46.2 | 41.1 | | | |

[a] data from Chen et al. (2013), [b] data from Verma et al. (2015).