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Long-term observations of saccharides in remote marine aerosols from the western North Pacific: A comparison between 1990-1993 and 2006-2009 periods

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Abstract

Anhydrosugars (galactosan, mannosan and levoglucosan), sugars (xylose, fructose, glucose, sucrose and trehalose) and sugar alcohols (erythritol, arabitol, mannitol and inositol) were measured in the aerosol samples collected in a remote island (Chichi-Jima, Japan) in the western North Pacific from 1990 to 1993 and from 2006 to 2009. Total concentrations of anhydrosugars, the biomass burning tracers, were 0.01-5.57 ng m^{-3} (average 0.76 ng m^{-3}) during 1990-1993 versus 0.01-7.19 ng m^{-3} (0.64 ng m^{-3}) during 2006-2009. Their seasonal variations were characterized by winter/spring maxima and summer/fall minima. Such a seasonal pattern should be caused by the enhanced long-range atmospheric transport of biomass burning products and terrestrial organic matter (such as higher plant detritus and soil dust) from the Asian continent in winter/spring seasons, when the westerly or winter monsoon system prevails over the western North Pacific. Sugars and sugar alcohols showed different seasonal patterns. The monthly mean concentrations of erythritol, arabitol, mannitol, inositol, fructose, glucose and trehalose were found to be higher in spring/summer and lower in fall/winter during both 1990-1993 and 2006-2009 periods, indicating an enhanced biogenic emission of aerosols in warm seasons. Interestingly, saccharides showed a gradual decrease in their concentrations from 1991 to 1993 and an increase from 2006 to 2009. In addition, the monthly averaged concentrations of sugars and sugar alcohols showed maxima in early summer during 1990-1993, which occurred about 1-2 months earlier than those during 2006-2009. Such a clear seasonal shift may be attributable to the changes in the strength of westerly and trade wind systems during two periods.

Keywords: marine aerosols; long-term trends; levoglucosan; mannitol; Chichi-Jima Island.

1. Introduction

Organic aerosols have been recognized to account for a significant portion of atmospheric particulate matter and to play an important role in regulating regional and global climate (Jacobson et al., 2000; Kanakidou et al., 2005; Pöschl, 2005). Aerosol particles that are enriched with organic compounds can make the aerosol surfaces more hydrophilic or hydrophobic depending on the chemical composition and mixing state, leading to alter the cloud condensation nuclei (CCN) activities of particles. The long-range atmospheric transport of aerosol particles from continental regions to remote oceans is a key process to control the global distributions of organic aerosols. However, there are very few studies reported on the long-term observations of organic aerosols in the remote marine atmosphere (Kawamura et al., 2003; Mochida et al., 2003).

Saccharides are one of the major classes of water-soluble organic constituents in atmospheric aerosols, which are ubiquitous in urban (Pashynska et al., 2002; Wang et al., 2006; Jia et al., 2010), forest and mountain (Graham et al., 2003; Yttri et al., 2007; Fu et al., 2008; Wang et al., 2009b), marine (Simoneit et al., 2004b; Burshtain et al., 2011; Fu et al., 2011), and the polar regions (Fu et al., 2009). One of the most studied sugar compounds is levoglucosan, which is produced by thermal decomposition of cellulose and hemicellulose. Levoglucosan is emitted during the combustion of biomass such as residential heating and wild/agriculture fires, and has been used as a useful molecular marker of biomass burning (Simoneit et al., 1999; Simoneit et al., 2004a). Recent studies (Hennigan et al., 2010; Hoffmann et al., 2010) have suggested that levoglucosan is prone to degradation by OH radicals in the atmosphere. Thus, its concentration during long-range transport may be underestimated, especially in summer (Mochida et al., 2010).

The sources of primary sugars in the atmosphere include natural biogenic detritus (such as microorganisms, plants) (Simoneit et al., 2004a; Jaenicke, 2005) and resuspended dusts

(Simoneit et al., 2004b). Primary bioaerosols (including plant fragments, airborne pollen, bacteria, etc.) can contribute 20-30% to the total atmospheric particulate matter (PM) (>0.2 μm) from Lake Baikal (Russia) and Mainz (Germany) (Jaenicke, 2005). Sugar alcohols, together with glucose, sucrose and trehalose, are more abundant in the coarse than in the fine size of PM (Fuzzi et al., 2007; Pio et al., 2008), attesting to their primary biological sources (Graham et al., 2003; Simoneit et al., 2004a; Bauer et al., 2008). Fungi are important microorganisms in nature, and most of them are known to emit spores whose sizes range between 1.5 and 12 μm in diameter (Elbert et al., 2007). These spores, which account for a major portion of natural bioaerosols, have long residence time in the atmosphere and can travel long distances (Burshtain et al., 2011). Atmospheric levels of mannitol and arabitol are well correlated with the counts of fungal spores in atmospheric PM_{10}, and thus they have been proposed as specific tracers of fungal activities (Bauer et al., 2008).

In East Asia, the outflows of industrial pollutants, biomass burning products, and mineral dusts form a complex mixture of inorganic species, organic compounds, black carbon, minerals, and water (Seinfeld et al., 2004). During the ACE-Asia campaign, a lot of studies have been conducted on the physical and chemical properties of the Asian dusts and polluted aerosols with a function of altitude above the East Asian surface (Huebert et al., 2003). The Chichi-Jima Island, a small island in the western North Pacific, is located on the outflow pathway of the Asian desert dusts and polluted air masses from China (Simoneit et al., 2004b; Wang et al., 2009a). This island is also in the boundary of westerly and trade wind regimes. Previous studies have reported terrestrial lipid compound classes (Kawamura et al., 2003), dicarboxylic acids (Mochida et al., 2003), and levoglucosan (Mochida et al., 2010) in aerosol samples collected at the Chichi-Jima Island, but little is known about the molecular distribution and seasonal variations of saccharides. Such datasets of long-term measurements of organic aerosols in the marine atmosphere are of great importance in evaluating the

changes in air quality caused by regional meteorology and the changes in the long-range atmospheric transport of terrestrial organic matter to the ocean.

The objectives of the present study are: (i) to investigate the abundances and annual variations of saccharides in marine aerosols collected at Chichi-Jima using a gas chromatography (GC)/mass spectrometry (MS) technique, and (ii) to compare the seasonal and annual changes between 1990-1993 and 2006-2009 periods. In the data interpretation, we performed positive matrix factorization (PMF) analysis to obtain a better understanding on the source of saccharides in the marine aerosols in the western North Pacific.

2. Experimental

The sampling site (142°13'E, 27°04'N; 254 m, a.s.l.) is located at the Ogasawara Downrange Station of the Japan Aerospace Exploration Agency (JAXA) in the Chichi-Jima Island for observing long-range-transported aerosols in the western North Pacific (Figure 1) (Kawamura et al., 2003). The Chichi-Jima Island is an oceanic island, which is located about 2000 km away from the Asian continent and about 1000 km south of Tokyo, Japan. It has never been connected to the land with any continent since its birth. Therefore, a large number of endemic plants are found only in this region. The endemic ratio of vascular plants is 36%. Sclerophyllous scrub woodlands cover large areas of the Chichi-Jima Island (Kawakami, 2010). The island is characterized by a subtropical climate; it is warm (ambient temperature: 7.8-34.1 °C) and humid all year round owing to the warm currents from the North Pacific gyre around the island. Because the population (about 2000) and area (24 km^2) of island are small, the perturbation caused by local biomass-burning emission is insignificant.

Total suspended particles (TSP) were collected on a biweekly basis from April 1990 to November 1993 (n = 69) and a weekly basis from January 2006 to January 2010 (n = 203) using a high volume air sampler (Shibata HVC-1000 for 1990 to 1993 and Kimoto AS-810A

for 2006-2009) with a flow rate of 1.0 m^3 min^{-1} and quartz fiber filters (QFF, 20 cm × 25 cm, Pallflex). The sampler was placed on the top of the base (5 m, a.g.l.) for the parabola antenna and run without a wind sector control. Before and after sampling, each sample was placed in a pre-combusted (450 °C for 6 h) clean glass jar with a Teflon-lined screw cap. The samples were stored in a dark freezer room at –20 °C prior to analysis.

Filter aliquots (ca. 20 cm^2) were cut off and extracted three times with dichloromethane/methanol (2:1, v/v) under ultrasonication for 10 min. The extracts were concentrated by a rotary evaporator under vacuum, blown down with dry nitrogen gas, and reacted with 50 μl of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride in the presence of 10 μl of pyridine at 70 °C for 3 h. This procedure derivatizes COOH- and OH- groups to the corresponding trimethylsilyl (TMS) esters and ethers, respectively. After reaction, the derivatives were diluted by adding 140 μl of *n*-hexane that contains 1.43 ng μl^{-1} of internal standard (C_{13} *n*-alkane) prior to GC-MS injection.

GC-MS analyses of the samples were performed on a Hewlett-Packard model 6890 GC coupled to Hewlett-Packard model 5973 mass-selective detector (MSD). The GC was equipped with a split/splitless injector and a DB-5MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The mass spectrometer was operated in the electron impact (EI) mode at 70 eV and scanned from 50 to 650 Da. Data were acquired and processed with the Chemstation software. Individual compounds were identified by comparison of mass spectra with those of authentic standards or literature data. Detailed quantification of the organic tracers has been mentioned elsewhere (Fu et al., 2008). Field blank filters were treated as the real samples for quality assurance. No target compounds were found in the blanks. Recoveries for the authentic standards that were spiked into pre-combusted quartz filters were generally better than 90%. Therefore, the data reported here were not corrected for recoveries.

Relative standard deviations of the concentrations of major species based on duplicate analysis were generally <15%.

Ten-day air mass back trajectories were calculated using the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (http://www.arl.noaa.gov/ready/hysplit4.html). The starting height of the trajectories present in this study is 500 m a.s.l. Trajectories at 1000 m a.s.l. were also calculated; the horizontal patterns are in general similar to those at 500 m and thus were not shown here.

3. Results and Discussion

The concentration ranges of saccharides in four seasons are summarized in Table 1 and Table 2 for the period of 1990-1993 and 2006-2009, respectively. The concentrations of total sugars during 1990-1993 (1.34-67.5 ng m^{-3}, mean 14.8 ng m^{-3}) are lower than those (3.64-247 ng m^{-3}, 38.7 ng m^{-3}) during 2006-2009. The concentrations of biomass burning tracers (galactosan, mannosan and levoglucosan), xylose, erythritol, inositol are similar between the 1990-1993 and 2006-2009 periods. However, the mean concentrations of individual species such as arabitol, mannitol, sucrose and trehalose during 1990-1993 are lower than those during 2006-2009 (Table 1 and Figure 2).

Figure 3 presents the temporal variations of the total sugar concentrations in the Chichi-Jima aerosols. Although the concentrations of individual species varied significantly from sample to sample, we found clear seasonal patterns with higher values in warm season and lower values in cold season. The dominant species that contribute to the higher concentrations of saccharides in warmer seasons are mainly arabitol, mannitol, fructose and glucose (Table 1 and Table 2). These primary saccharides can be abundantly emitted as primary biogenic aerosol particles, that is, fungal spores, pollen, bacteria, and plant fragments (Elbert et al., 2007).

Interestingly, a gradual decrease in the saccharide concentrations was found from 1991 to 1993 whereas a gradual increase was detected from 2006 to 2009. The local ambient temperature showed strong seasonal patterns with no clear inter-annual trends, which suggests that the temperature was not the main contributor to such annual variations because there were no significant differences observed during the two sampling periods (Figure 3). However, the monthly averaged temperatures in 1992 were obviously lower than in 1991. The 1991 volcanic eruption of Pinatubo, which is located in the Philippines, has led to a decrease in the average temperatures of 0.5–0.6 °C in the Northern Hemisphere and a global fall of about 0.4 °C in the following years (http://en.wikipedia.org/wiki/Mount_Pinatubo). Lower ambient temperatures may lower the primary biological activities such as the emissions of fungal spores. Thus, the decrease of temperature by such a powerful volcanic eruption may in part contribute to the decreasing concentrations of sugar in the western North Pacific form 1991 to 1993.

3.1 Seasonal variations of anhydrosugars

Levoglucosan and its isomers, galactosan and mannosan, are specific biomass burning tracers in the atmosphere (Simoneit, 2002). These anhydrosugars are derivatives of glucose, galactose, and mannose, respectively (Simoneit et al., 1999; Graham et al., 2003). Their concentration levels and seasonal trends are similar between the 1990-1993 (Figures 4a-c) and 2006-2009 periods (Figures 4m-o), indicating that the impacts of biomass burning on the marine aerosols in the recent years were similar to those in early 1990s. Levoglucosan was detected in all the samples with concentration ranges of 0.004-4.77 ng m^{-3} (0.62 ng m^{-3}) from 1990 to 1993 (Figure 4c) and 0.006-5.20 ng m^{-3} (0.54 ng m^{-3}) from 2006 to 2009 (Figure 4o). These values are similar to those reported in marine aerosols over the western North Pacific (0.01-0.52 ng m^{-3}) (Fu et al., 2011) and Chichi-Jima (0.017-15 ng m^{-3}) from 2001 to 2003

189 (Mochida et al., 2010), representing a background level of levoglucosan in the marine
190 atmosphere.
191 The seasonally averaged concentrations of levoglucosan are higher in winter (mean 1.35
192 ng m^{-3}) than in spring (0.79 ng m^{-3}), summer (0.37 ng m^{-3}) and autumn (0.18 ng m^{-3}) during
193 the 1990-1993 period. Similar atmospheric levels and seasonal trends were found during the
194 2006-2009 period. The seasonal variations of galactosan and mannosan were concurrent to
195 that of levoglucosan. During the 1990-1993 period, the concentration ranges of galactosan
196 and mannosan are 0.001-0.14 ng m^{-3} (mean 0.026 ng m^{-3}) (Figure 4a) and 0.002-0.66 ng m^{-3}
197 (0.11 ng m^{-3}) (Figure 4b), respectively. Similarly, their concentration ranges are 0.001-0.34 ng
198 m^{-3} (0.022 ng m^{-3}) (Figure 4m) and 0.002-1.65 ng m^{-3} (0.085 ng m^{-3}) (Figure 4n) during
199 2006-2009. Being similar to levoglucosan, lower concentrations of galactosan and mannosan
200 were generally observed in the samples collected in summer and autumn.
201 The seasonal variations of anhydrosugars may be controlled by the Asian monsoon
202 system that transports organic aerosols from East Asia to the western North Pacific. In
203 summer, maritime air masses arrived Chichi-Jima under the influence of the Pacific
204 anticyclone. In winter, westerly or monsoon northwesterly winds caused by the Siberian High
205 dominate East Asia and the western North Pacific, transporting air masses from East Asia to
206 Chichi-Jima (Kawamura et al., 2003; Mochida et al., 2010). Ten-day air mass backward
207 trajectories (Figure 5) calculated for the sampling period support the above-mentioned
208 transport pathways. As expected, the concentrations of anhydrosugars are high when air
209 masses are transported from northeast China, east Siberia, Korea and Japan during
210 winter/spring seasons. Lower concentrations were observed more frequently when air parcels
211 were delivered from the Pacific Ocean in summer to autumn.
212 **3.2 Seasonal variations of sugars and sugar alcohols**

213 Saccharides have been thought as unique molecular tracers for primary biological aerosol
214 particles (PBAPs) such as pollens and fungal spores (Medeiros et al., 2006). In general,
215 glucose, inositol, sucrose, and trehalose were determined in various representative soils as the
216 common tracers for source evaluation of soil resuspension into the atmosphere (Simoneit et
217 al., 2004a), whereas arabitol and mannitol are linked to vegetation, mature leaves, fungi and
218 algae (Pashynska et al., 2002). Figure 2 shows the 4-year averaged concentrations of
219 saccharides in the Chichi-Jima aerosols during the 1990-1993 and 2006-2009 periods. Sugars
220 (fructose, glucose, sucrose and trehalose) and sugar alcohols (erythritol, arabitol and mannitol)
221 were found to be more abundant than anhydrosugars in both periods. During the 1990-1993
222 period, glucose was found to be the dominant species, followed by mannitol, arabitol, and
223 fructose. During the 2006-2009 period, however, mannitol was the most abundant species,
224 followed by arabitol, sucrose, glucose, trehalose and fructose. A general lack of correlation
225 between the concentrations of sugars/sugar alcohols and anhydrosugars (Table 3) suggests
226 that sugars and sugar alcohols should be emitted from other sources rather than biomass
227 burning.
228 The monthly averaged concentrations of sugar alcohols (erythritol, arabitol, mannitol,
229 and inositol) and sugars (fructose, glucose and trehalose) were found to be highest in
230 spring/summer, and lowest in winter/autumn during both the periods of 1990-1993 and
231 2006-2009, whereas sucrose maximized in winter during the 1990-1993 period but did in
232 spring during the 2006-2009 period, and became lowest in autumn (Table 1 and Table 2).
233 Arabitol and mannitol are the most abundant sugar alcohols detected in the Chichi-Jima
234 samples, ranging from 0.066-11.9 ng m^{-3} (mean 2.34 ng m^{-3}) and 0.12-15.2 ng m^{-3} (2.70 ng
235 m^{-3}) during 1990-1993 versus 0.12-83.3 ng m^{-3} (7.90 ng m^{-3}) and 0.16-88.0 ng m^{-3} (11.0 ng
236 m^{-3}) during 2006-2009, respectively. The summertime mean concentrations of arabitol (11.4
237 ng m^{-3}) and mannitol (19.4 ng m^{-3}) during 2006-2009 are comparable to those (mean 8.43 ng

238 m^{-3} and 21.9 ng m^{-3}) reported in the Mediterranean aerosols (Burshtain et al., 2011), but
239 slightly lower than those (24 ng m^{-3} and 30 ng m^{-3}) at Hyytiälä, Finland in summer (Yttri et al.,
240 2011).

241 Fructose and glucose are also abundant with concentration ranges of 0.04-12.7 ng m^{-3}
242 (2.04 ng m^{-3}) and 0.15-17.6 ng m^{-3} (4.03 ng m^{-3}) during 1990-1993 versus 0.17-14.8 ng m^{-3}
243 (2.54 ng m^{-3}) and 0.27-35.3 ng m^{-3} (5.46 ng m^{-3}) during 2006-2009, respectively. A positive
244 correlation was found between fructose and glucose ($R > 0.70$) (Table 3). Similar relations
245 between sugars and sugar alcohols have been reported in other studies (Burshtain et al., 2011).
246 Pashynska et al. (2002) found that the concentrations of fructose, glucose and sucrose were
247 highest in June, while both arabitol and mannitol peaked in late summer. In a forest site in
248 suburban Sapporo, Japan, sucrose concentrations peaked in spring/early summer (May-June,
249 mean 176 ng m^{-3}) due to pollen emission, whereas trehalose levels (128.5-188.3 ng m^{-3})
250 remained high during summer and autumn (Miyazaki et al., 2012); both sucrose and trehalose
251 in the Sapporo forest aerosols were about 2-7 times more abundant than those in the
252 Chichi-Jima aerosols.

253 Xylose (wood sugar) is a monosaccharide first isolated from wood
254 (http://en.wikipedia.org/wiki/Xylose). It is the main building block of hemicellulose, one of
255 the main constitutes of biomass. In this study, its concentrations were found to be lowest in
256 autumn (mean 0.06 ng m^{-3} in 1990-1993 and 0.11 ng m^{-3} in 2006-2009) compared to other
257 seasons (Tables 1 and 2 and Figure 6f). Sullivian et al. (2011) reported higher concentrations
258 of xylose in winter (mean 2.1 ng m^{-3}) than in summer (mean 0.5 ng m^{-3}) in Detroit, Michigan,
259 USA, and interpreted due to a biomass burning in winter. Interestingly, the positive
260 correlations between xylose and anhydrosugars during 1990-1993 were found to be stronger
261 ($R=0.61$-0.68) than those ($R=0.36$-0.43) during the 2006-2009 period (Table 3). This may

suggest that xylose was more significantly derived from wood burning smokes in the early 1990s than in more recent years.

The seasonal pattern of sucrose is characterized by two sharp increases in February-March and June-July (Figures 4k, 4w, and 6k), which is different from the patterns of other saccharides. Such an enhancement should be influenced by the local emission of airborne pollen grains that contain a large amount of sucrose (Fu et al., 2012). However, long-range atmospheric transport of pollen from Asian continent to the remote island Chichi-Jima under the influence of westerlies cannot be excluded. Previous studies reported that airborne pollen can be transported from North America to Greenland in spring (Rousseau et al., 2008).

The temporal variations of sugar alcohols (erythritol, arabitol, mannitol, and inositol) are similar each other, which are characterized by concentration peaks during warmer seasons (see Figures 4d-g, 4p-s, 6d-e, and 6g-h). Positive correlations ($R>0.47$) were found among these sugar alcohols (Table 3), indicating that they are mainly derived from fungal spores during warm and humid seasons. Fructose and glucose also showed concentration peaks in warm seasons during both 1990-1993 and 2006-2009 periods (Figures 4i-j and 4u-v). As seen in Figure 6, the monthly averaged concentrations of fructose and glucose from January to May in 1990-1993 are higher than those in 2006-2009. However, opposite trend were found in July to November; that is, their concentrations are much higher in 2006-2009 than in 1990-1993.

Such a contrast is more significant for arabitol, mannitol, inositol and trehalose (Figure 6). For example, the monthly averaged concentrations of arabitol and mannitol peaked in early summer (May-June) during 1990-1993, whereas they remained at high levels from June to September during 2006-2009. Such a difference in the seasonal variation may be attributable to the potential shift in westerly and trade wind regimes although we could not specify the changes in climate systems. In addition to the changes in climatological conditions during the

287 past two decades, another possible reason is that the local vegetation coverage may have been
288 changed at Chichi-Jima Island, a point that warrants further support. Leck and Bigg (2005)
289 have reported that the marine bubble bursting can create aerosols containing micro-organisms
290 and lead to primary biological particles in the atmosphere above the central Arctic Ocean.
291 Such a creation of primary bioaerosols may also contribute to the marine aerosols collected at
292 the remote Chichi-Jima Island in the North Pacific Ocean.

293 **3.3 Positive matrix factorization (PMF) analysis**

294 To better understand the possible sources of the observed saccharides, positive matrix
295 factorization (PMF3.0, USEPA) analysis was used in this study. PMF is a useful approach to
296 verify underlying covariance among chemical parameters (Paatero and Tapper, 1994). The
297 analytical errors estimated for the measured values of saccharides in PMF analysis are 15%
298 uncertainty. Based on Q values (the objective function to be minimized), four interpretable
299 factors appeared to be the optimal solution as the probable origin of sugars in the atmosphere.
300 Figure 7 shows composition profiles for the four factors resolved by PMF. Factor 1 is
301 dominated by sucrose (100% during 1990-1993 and 100% during 2006-2009), which should
302 be associated with airborne pollen grains (Pacini, 2000; Graham et al., 2003; Fu et al., 2012).
303 Factor 2 is characterized by galactosan (83.5%, 93.2%), mannosan (84.0%, 96.8%),
304 levoglucosan (80.0%, 94.7%), and xylose (37.9%, 23.6%) during 1990-1993 and 2006-2009,
305 respectively, which should be associated with biomass burning sources. As mentioned earlier,
306 smoke plumes from biomass burning are often transported over the Chichi-Jima site from the
307 Asian continent during the colder winter period rather than in summer under the control of the
308 Asian monsoon system by long-range atmospheric transport (Kawamura et al., 2003;
309 Mochida et al., 2010). However, factor 2 shows different percent values with the same
310 resource between 1990-1993 and 2006-2009.

311 As shown in Figure 4, sharp increases in the concentrations of levoglucosan and its
312 isomers are clearly found in mid-May 1991 (Figure 4c) and mid-January 2006 (Figure 4o). To
313 further explain the source regions of the observed biomass burning tracers, 10-day backward
314 air mass trajectory analyses were conducted for the two samples with the highest
315 concentration of levoglucosan during 1990-1993 (sample ID of QFF212) and during
316 2006-2009 (QFF2871) (Figure 9). The sample QFF212 was collected on 13-16 May 1991
317 when the air masses were mainly transported from the Central Pacific to the sampling site
318 (Figure 9). In the QFF212 sample, the concentrations of other sugars and sugar alcohols were
319 also high, but such an enhancement of other sugars and sugar alcohols cannot be detected in
320 the QFF2871 sample (Figure 4). A possible explanation is that the QFF212 sample might be
321 involved with a local fire event in Chichi-Jima in early summer; primary saccharides that are
322 generally present in coarse modes can co-transport to the sampling site with smoke aerosols.
323 A recent study also reported that the atmospheric levels of sugar alcohols (arabitol and
324 mannitol) were enhanced by biomass burning events in an urban site in China (Yang et al.,
325 2012). The back trajectory analysis of QFF2871 showed that most of the air masses originated
326 from the arid regions in China, Mongolia and Siberia and then transported to the sampling site
327 through long-range atmospheric transport (Figure 9), leading to the highest concentration of
328 levoglucosan during 2006 to 2009 (Figure 4o).
329 Factor 3 is dominated by trehalose (100% during 1990-1993 and 100% during
330 2006-2009), which is proposed as a tracer for biologically suspended soil dust (Simoneit et al.,
331 2004a; Rogge et al., 2007), and should be associated with fungal metabolism. During
332 1990-1993, factor 4 is associated with arabitol (98.2%), mannitol (82.6%), inositol (48.6%),
333 and xylose (37.2%), indicating an influence of fungal spores. During 2006-2009, factor 4 is
334 characterized by erythritol (73.5%), arabitol (70.1%), fructose (27.1%), glucose (52.8%),

mannitol (54.1%), and inositol (34.5%), suggesting the mixing source emissions from fungal spores and growing plant and so on.

During 1990-1993, factor 5 includes erythritol (91.2%), fructose (71.3%), glucose (61.6%) and inositol (28.7%) (Figure 7a). During 2006-2009, however, factor 5 includes xylose (76.4%), fructose (48.8%), glucose (38.8%), inositol (20.9%), and erythritol (18.1%) (Figure 7b). Therefore, factor 5 was mainly associated with other sources, for example, the emission of primary saccharides such as fructose and glucose during the growing seasons in both early 1990s and late 2000s.

As resolved by the PMF analysis, the average contributions of each factor to the measured saccharides in 1990-1993 and 2006-2009 are shown in Figure 8. The emission of fungal spore (factor 4) was found to be the dominant contributor to the sugar compounds in both periods, although the average contribution was higher in 2006-2009 (40.4%) than 1990-1993 (33.2%). Similarly, the contribution of airborne pollen was 17.2% in 2006-2009, being higher than that (13.9%) in 1990-1993. The contribution of biomass burning to total sugars was only 5.3% in 1990-1993; even lower value (2.5%) was found in 2006-2009. These results suggest that the emission of primary biological aerosols is the dominant source of water-soluble saccharides, while the contribution of biomass burning was minor in the remote marine atmosphere.

Pearson correlation coefficients (Table 3) are relatively high among the concentrations of sugars/sugar alcohols with a maximum (R=0.90) for the combination of fructose and glucose during 1990 to 1993. Such a good covariance suggests that terrestrial organic materials are transported over the island from the similar source regions, but the source regions should have been changed according to seasons and meteorological conditions (Kawamura et al., 2003). The years of 1991 and 1992 were also characterized by a strong E1 Niño event, during which the air over the western equatorial Pacific turned dry and hot, leading to frequent forest fires

in Southeast Asia (Kita et al., 2000). These situations may partly interpret the different distribution patterns of the five factors resolved by PMF between the two sampling periods.

Significantly high concentrations of arabitol and mannitol were detected in the aerosol samples collected on 24-25 September 2009 (QFF3267) (Figure 4q-r), which contributed to the maximum concentration of total sugars during 2006-2009 (Figure 3b). Relatively high levels of total saccharides in summer-autumn seem to be connected with the diversity of wind directions and source regions. During 2006-2009, high correlation coefficients were found among the concentrations of arabitol, mannitol, glucose and trehalose (Table 3). The aerosol samples collected in autumn are heavily influenced by trade winds, whose pathways cover most of the Central North Pacific and a few other source regions such as Southeast Asia and Asian continents (Figure 5d). Correlation coefficients of glucose and fructose also showed higher values in warmer seasons annually (Table 3). When sucrose is rich in spring aerosols, the atmospheric levels of glucose and fructose are also enhanced, indicating their similar pollen sources (Fu et al., 2012). As a result, it would be difficult to explain factors 4 and 5 as a specific source (Figure 7), given that these saccharides were possibly originated from either PBAPs or other sources such as resuspended soil/dust and associated biota (Graham et al., 2003; Simoneit et al., 2004a; Medeiros et al., 2006).

4. Conclusions

Long-term variations of anhydrosugars (galactosan, mannosan and levoglucosan), sugars (xylose, fructose, glucose, sucrose and trehalose), and sugar alcohols (erythritol, arabitol, mannitol and inositol) in marine aerosols were obtained at Chichi-Jima Island in the western North Pacific with distinct seasonality and variability. Although the atmospheric concentrations of anhydrosugars in 2006-2009 were similar to those in 1990-1993, the tracers of fungal spores, arabitol and mannitol, as well as other primary saccharides were much

higher in late 2000s than those in early 1990s. The seasonal variations of anhydrosugars were characterized by the concentration peaks in winter/spring due to heavy biomass-burning activities in up-wind Asian continent followed by a long-range atmospheric transport and/or potential local fires in Chichi-Jima. Backward air mass trajectory analysis demonstrated that the air masses in winter/spring were influenced by westerlies and transported from East Asia to the western North Pacific, whereas the air masses in summer/autumn are delivered from the directions of the Central Pacific. The concentration maxima of sugar alcohols (erythritol, arabitol, mannitol, and inositol) were observed in May-June during 1990-1993, while the maxima were recorded in few months later (June-September) during the 2006-2009 periods. PMF analysis demonstrates that primary biological emissions such as pollen grains and fungal spores, trehalose-doninant emission, and biomass burning emission are the major sources of saccharides in the Chichi-Jima aerosols, although the contribution of biomass burning to the measured saccharides was rather minor in the remote marine atmosphere.

Acknowledgements

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534 **Table 1.** Concentrations (ng m^{-3}) of saccharides measured in the marine aerosols collected at
535 Chichi-Jima Island in the western North Pacific during 1990-1993.

Compounds	Winter (Dec-Feb, n=12)		Spring (Mar-May, n=20)		Summer (Jun-Aug, n=21)		Autumn (Sept-Nov, n=16)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Anhydrosugars								
Galactosan	0.054	0.008-0.13	0.036	0.002-0.14	0.012	0.001-0.043	0.010	0.001-0.06
Mannosan	0.18	0.023-0.41	0.18	0.009-0.65	0.054	0.002-0.22	0.055	0.002-0.23
Levoglucosan	1.35	0.41-2.78	0.79	0.023-4.77	0.37	0.04-1.94	0.18	0.004-1.44
Sugar Alcohols								
Erythritol	0.21	0.07-0.32	0.62	0.14-3.04	1.22	0.11-3.35	0.51	0.02-1.52
Arabitol	0.70	0.07-1.80	3.06	0.20-11.9	3.08	0.57-9.36	1.68	0.28-6.69
Mannitol	0.92	0.12-2.66	2.90	0.16-11.9	4.00	0.21-15.2	2.07	0.32-8.36
Inositol	0.03	0.01-0.06	0.06	0.01-0.16	0.06	0.01-0.20	0.03	0.01-0.08
Sugars								
Xylose	0.19	0.05-0.39	0.19	0.05-0.48	0.14	0.01-0.35	0.06	0.01-0.19
Fructose	1.44	0.32-3.77	2.81	0.18-12.7	2.73	0.06-9.16	0.62	0.04-3.01
Glucose	1.99	0.44-3.99	5.47	0.83-17.6	5.60	0.23-16.5	1.69	0.15-8.69
Sucrose	2.67	0.02-14.2	1.66	0.01-13.2	0.89	0.001-5.68	0.24	0.002-1.54
Trehalose	0.47	0.05-1.11	0.99	0.01-2.91	1.20	0.001-7.43	0.27	0.001-1.36
Total	10.2	3.65-19.6	18.8	3.60-53.6	19.3	2.63-67.5	7.42	1.34-28.6

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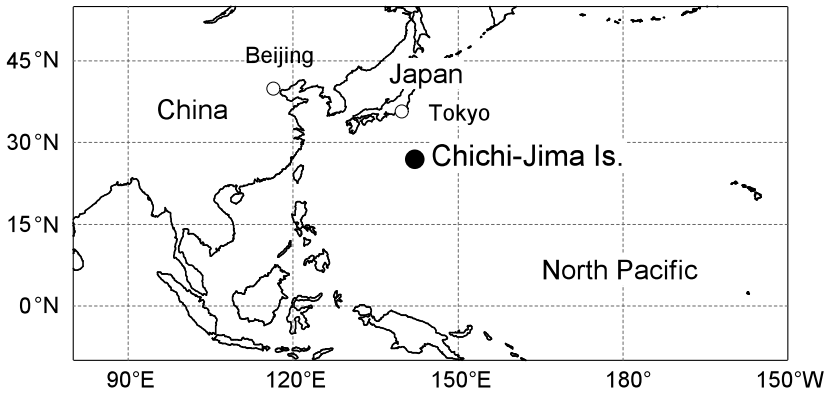
Table 2. Concentrations (ng m^{-3}) of saccharides measured in the marine aerosols collected at Chichi-Jima Island in the western North Pacific during 2006-2009.

Compounds	Winter (Dec-Feb, n=47)		Spring (Mar-May, n=52)		Summer (Jun-Aug, n=52)		Autumn (Sept-Nov, n=52)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Anhydrosugars								
Galactosan	0.055	0.001-0.33	0.019	0.002-0.08	0.009	0.001-0.13	0.007	0.001-0.07
Mannosan	0.21	0.006-1.65	0.089	0.003-0.40	0.03	0.002-0.41	0.026	0.003-0.21
Levoglucosan	1.25	0.04-5.20	0.50	0.012-2.53	0.22	0.019-1.43	0.24	0.006-1.14
Sugar Alcohols								
Erythritol	0.31	0.07-0.83	0.33	0.09-0.96	1.65	0.18-4.50	1.15	0.06-5.97
Arabitol	2.11	0.12-21.2	4.67	0.24-21.6	11.4	1.98-45.9	12.9	0.69-83.3
Mannitol	2.52	0.18-24.0	5.23	0.16-31.0	19.4	1.72-88.0	16.2	1.31-84.3
Inositol	0.03	0.01-0.19	0.06	0.01-0.32	0.17	0.03-0.47	0.12	0.02-0.42
Sugars								
Xylose	0.15	0.01-0.76	0.11	0.01-0.31	0.18	0.02-1.02	0.11	0.01-0.55
Fructose	1.20	0.17-5.85	2.07	0.27-12.2	4.14	0.89-14.8	2.63	0.22-7.70
Glucose	2.03	0.27-6.97	4.67	0.79-13.7	8.47	1.94-26.9	6.34	0.75-35.3
Sucrose	3.50	0.02-58.8	10.2	0.01-87.4	6.97	0.02-41.1	3.36	0.002-31.1
Trehalose	1.09	0.13-10.5	2.51	0.29-21.9	5.93	0.34-28.0	5.72	0.04-33.9
Total	14.5	4.12-86.9	30.5	5.18-117	58.5	12.7-196	48.8	3.64-247

Table 3. Pearson correlation coefficients (R) for the dataset of sugars in aerosols collected during 1990-1993 (n=69) and during 2006-2009 (n=203). The R-values > 0.5 are displayed in bold character with those of R>0.8 being underlined.

90-93 / 06-09	galactosan	mannosan	levoglucosan	erythritol	arabitol	mannitol	inositol	xylose	fructose	glucose	sucrose	trehalose
galactosan	1	**0.85**	**0.86**	-0.01	0.14	0.11	0.20	**0.68**	0.17	0.18	0.17	0.32
mannosan	**0.81**	1	**0.83**	-0.03	0.17	0.15	0.24	**0.63**	0.16	0.20	0.19	0.38
levoglucosan	**0.82**	**0.87**	1	0.03	0.19	0.19	0.28	**0.61**	0.24	0.22	0.20	0.35
erythritol	-0.24	-0.22	-0.29	1	**0.63**	**0.53**	0.48	0.01	0.20	0.29	-0.12	0.33
arabitol	-0.25	-0.24	-0.30	**0.54**	1	**0.88**	**0.70**	0.17	0.33	**0.55**	-0.08	0.43
mannitol	-0.27	-0.25	-0.31	**0.51**	**0.85**	1	**0.78**	0.25	0.46	**0.66**	-0.01	**0.63**
inositol	-0.26	-0.24	-0.27	0.47	**0.54**	**0.72**	1	0.42	**0.77**	**0.86**	0.23	**0.57**
xylose	0.36	0.44	0.43	-0.11	-0.12	0.10	0.22	1	0.51	0.49	0.38	0.49
fructose	-0.20	-0.17	-0.20	0.40	0.38	**0.57**	**0.71**	0.30	1	**0.90**	0.27	0.41
glucose	-0.24	-0.21	-0.26	0.44	**0.73**	**0.84**	**0.71**	0.18	**0.74**	1	0.19	**0.55**
sucrose	-0.05	-0.04	-0.01	-0.03	-0.07	0.05	0.37	0.20	0.43	0.21	1	0.21
trehalose	-0.22	-0.21	-0.24	0.33	**0.79**	**0.87**	**0.63**	0.12	0.47	**0.77**	0.07	1



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547 **Figure 1.** Map of sampling site (Chichi-Jima Island) in the western North Pacific.

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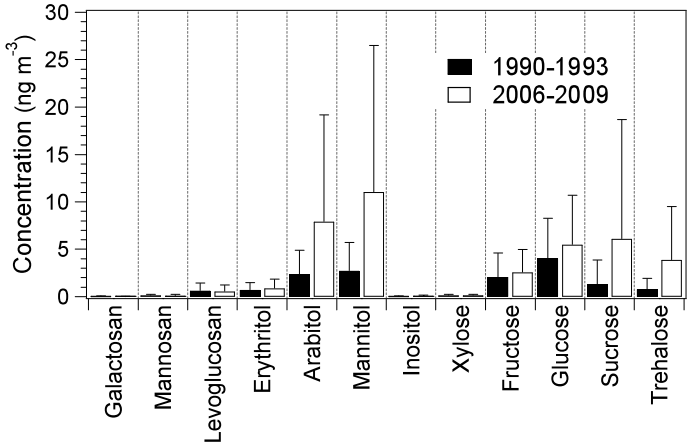

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550 **Figure 2.** Averaged concentrations of saccharides in atmospheric aerosols collected at
551 Chichi-Jima Island in the western North Pacific during the 1990-1993 and 2006-2009 periods.
552 Error bars represent the standard deviation.

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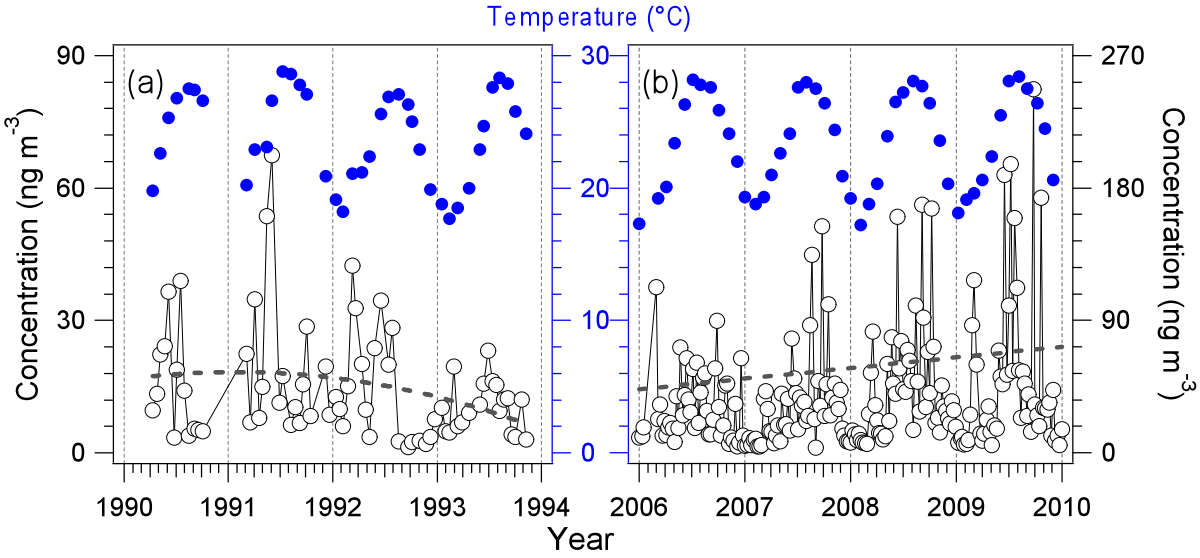
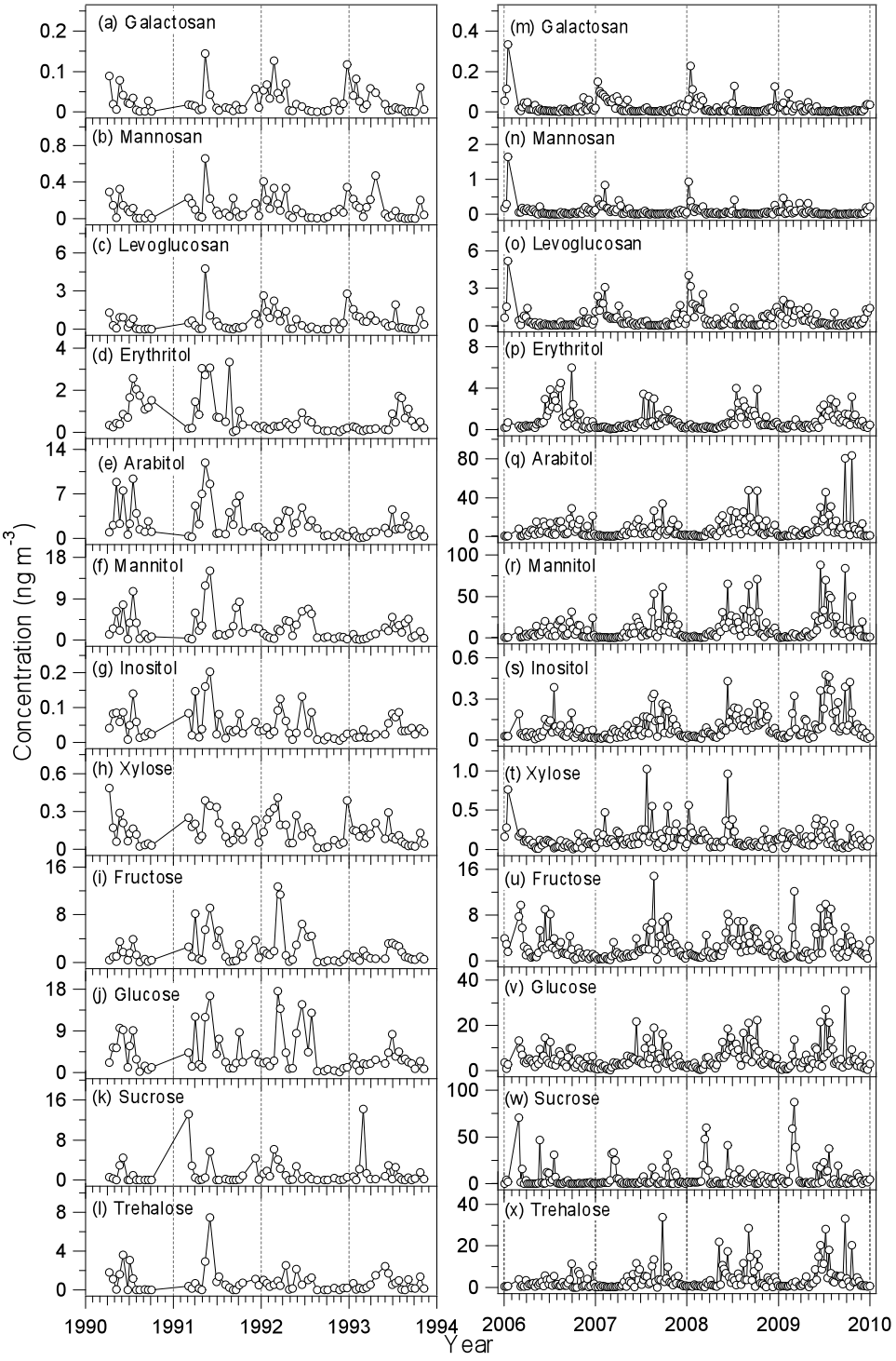


Figure 3. Temporal variations in the concentrations of total saccharides measured in the marine aerosols collected from Chichi-Jima Island, the western North Pacific during (a) 1990-1993, and (b) 2006-2009. The monthly-averaged ambient temperatures are present in the figure.



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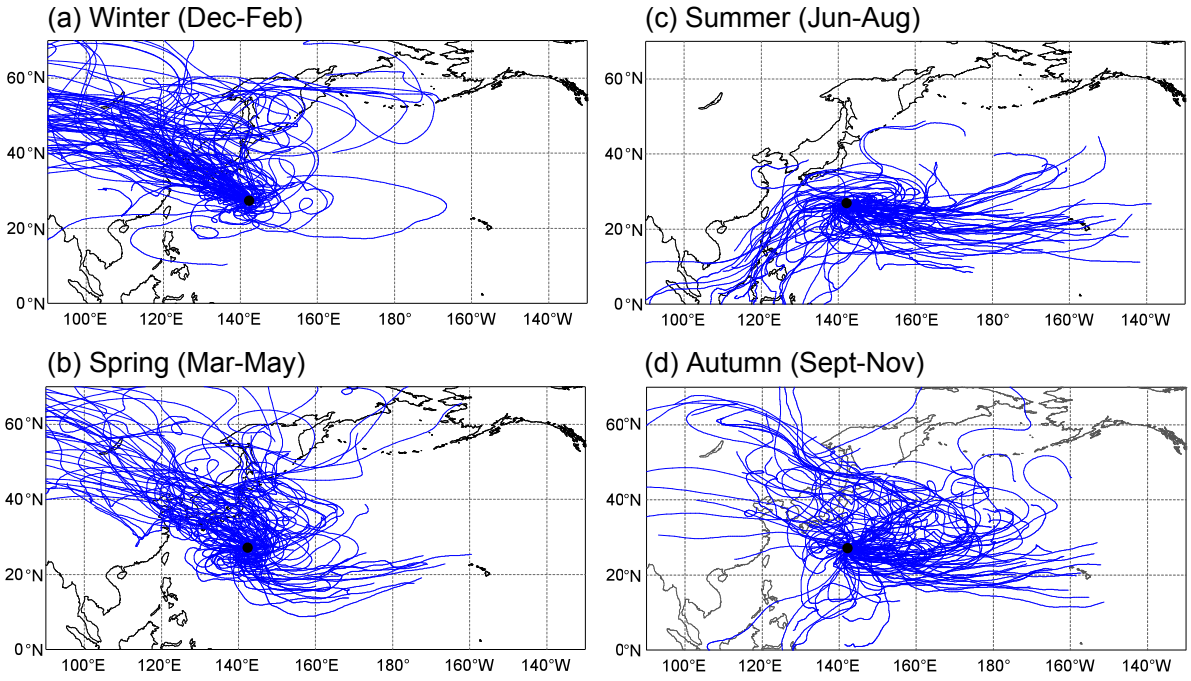
561 **Figure 4.** Temporal variations of anhydrosugars (galactosan, mannosan and levoglucosan),
562 sugar alcohols (erythritol, arabitol, mannitol and inositol), and sugars (xylose, fructose,
563 glucose, sucrose and trehalose) in the marine aerosols from Chichi-Jima Island, the western
564 North Pacific.



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567 **Figure 5.** Ten-day back trajectories of air masses that arrived over the Chichi-Jima Island in
568 (a) winter (December 2008-February 2009), (b) spring (March-May, 2009), (c) summer
569 (June-August, 2009), and (d) autumn (September-November, 2009). The trajectories were
570 calculated every 24 h at 12:00 (Local Time).

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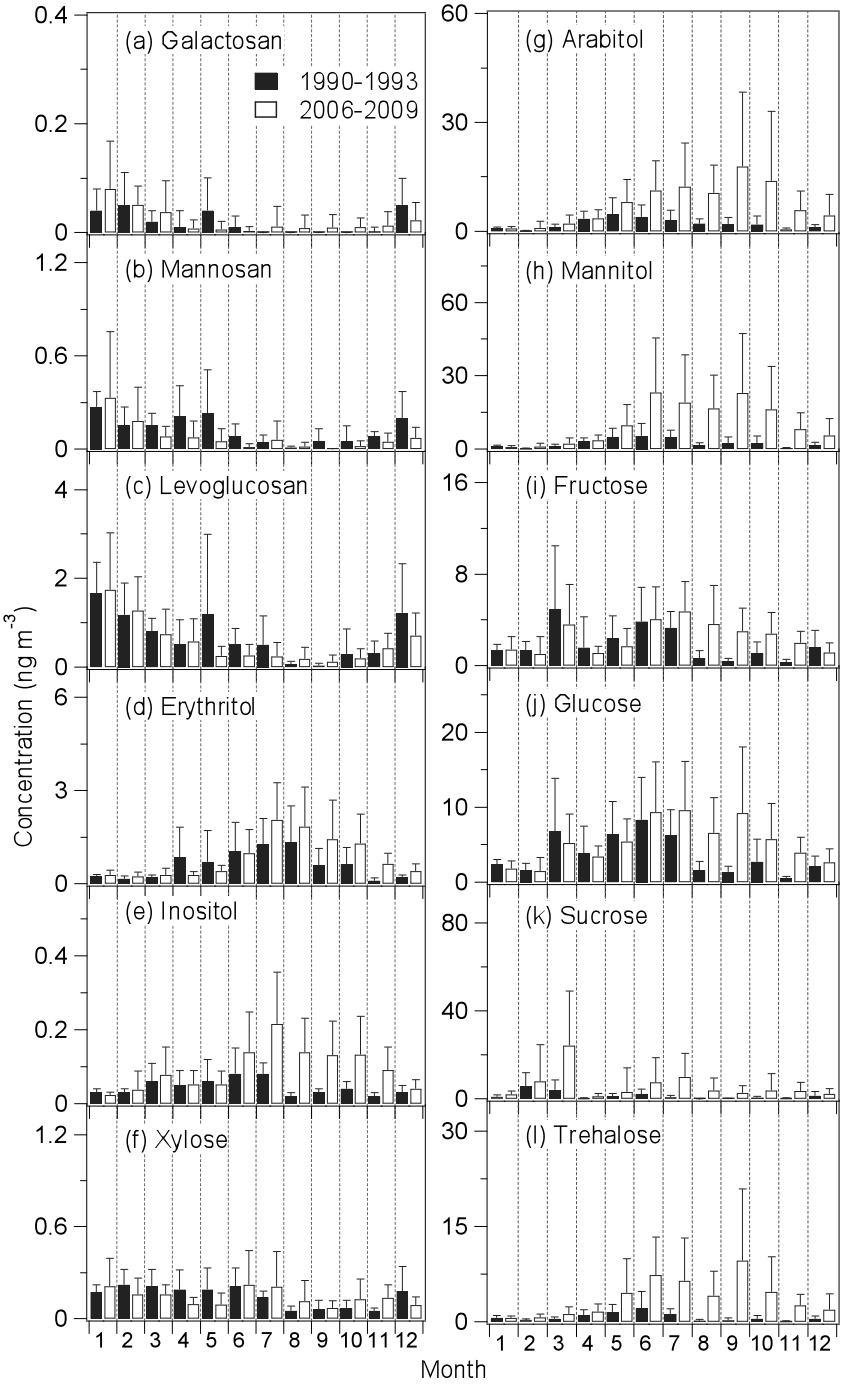

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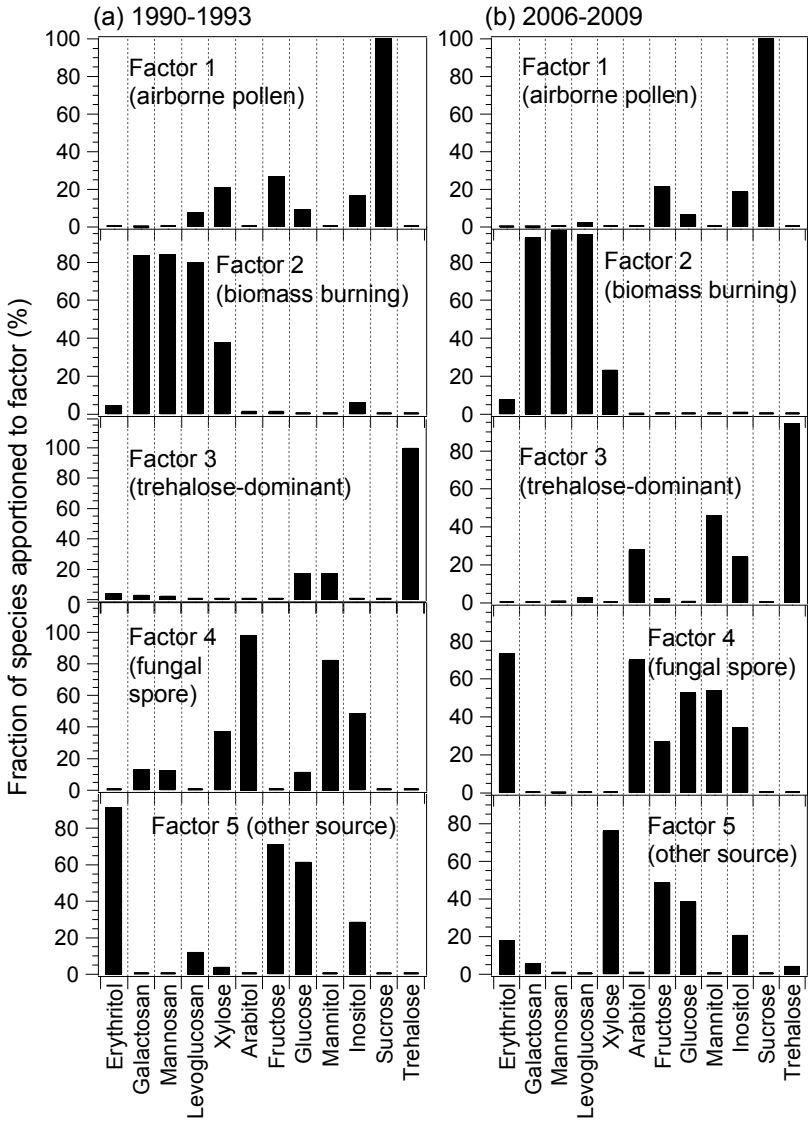
573 **Figure 6.** Monthly averaged concentrations of saccharides in the marine aerosols collected

574 from Chichi-Jima Island. Error bars represent the standard deviation.



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577 **Figure 7.** Composition profiles (% of total of each species) for the five factors resolved by

578 PMF analysis based on the dataset of saccharide compounds.

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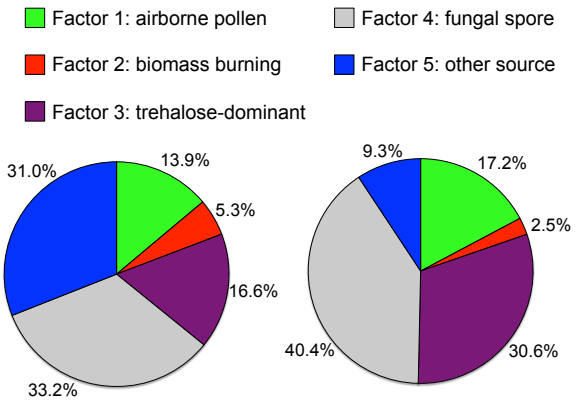

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581 Figure 8. Pie diagrams showing the estimated average contributions of the five factors

582 resolved by PMF to the measured saccharide compounds in the Chichi-Jima aerosol samples.

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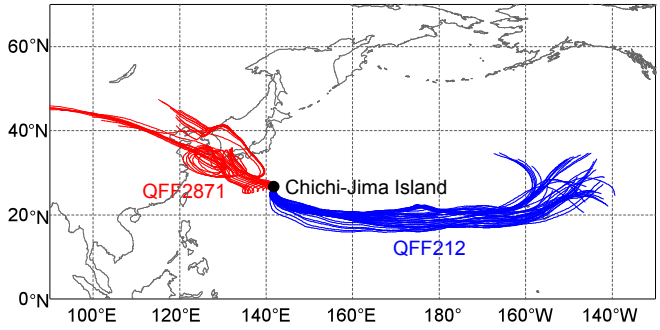

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585 **Figure 9.** Ten-day back trajectories of air masses that arrived over Chichi-Jima Island during
586 13-16 May 1991 (QFF212) and during 16-17 January 2006 (QFF2871). The trajectories were
587 calculated every 3 h. The concentrations of levoglucosan in the QFF212 and QFF2871
588 samples were the highest during 1990-1993 and 2006-2009, respectively.