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## RESEARCH ARTICLE

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## Key Points:

- PBAPs in Okinawa aerosols are largely affected by sources from local forest
- PBAP emissions from forest contribute largely to WSOC in aerosols
- Ambient fungal spore and PBAP loadings at Okinawa are estimated

## Supporting Information:

- Figures S1–S3

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## Organic tracers of primary biological aerosol particles at subtropical Okinawa Island in the western North Pacific Rim

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**Abstract** Primary biological aerosol particles (PBAPs) play an important role in affecting atmospheric physical and chemical properties. Aerosol samples were collected at Cape Hedo, Okinawa Island, Japan, from October 2009 to February 2012 and analyzed for five primary saccharides and four sugar alcohols as PBAP tracers. We detected high levels of sucrose in spring when blossoming of plants happens and prolifically emits pollen to the air. Concentrations of glucose, fructose, and trehalose showed levels higher than the other saccharides in spring in 2010. In comparison, primary saccharide levels were mutually comparable in spring, summer, and autumn in 2011, indicating the interannual variability of their local production in subtropical forests, which is driven by local temperature and radiation. High trehalose events were found to be associated with Asian dust outflows, indicating that Asian dust also contributes to PBAPs at Okinawa. Sugar alcohols peaked in summer and correlated with local precipitation and temperature, indicating high microbial activities. Positive matrix factorization analysis confirmed that the PBAPs are mainly derived from local vegetation, pollen, and fungal spores. A higher contribution of PBAP tracers to water-soluble organic carbon (WSOC) was found in summer (14.9%). The annual mean ambient loadings of fungal spores and PBAPs were estimated as  $0.49 \mu\text{g m}^{-3}$  and  $4.12 \mu\text{g m}^{-3}$ , respectively, using the tracer method. We report, for the first time, year-round biomarkers of PBAP and soil dust and their contributions to WSOC in the subtropical outflow region of the Asian continent.

## 1. Introduction

Organic aerosols (OA) affect Earth's climate by directly altering the radiative balance and indirectly modifying cloud properties [Lohmann and Lesins, 2002; Ramanathan et al., 2001]. OA associated with fine particulate matter (PM) also affect human health [Nel, 2005]. Water-soluble organic compounds (WSOC) account for 11–95% of organic carbon (OC) [Mader et al., 2004]. They are highly active in altering the cloud condensation nucleus (CCN) activity of the particles and therefore in affecting radiative forcing and climate [Decesari et al., 2006; Martin et al., 2010]. Recent studies have substantially clarified the sources of WSOC and their contributions to OC in urban [Sullivan et al., 2004; Yttri et al., 2007], forest [Miyazaki et al., 2012b], coastal [Kirillova et al., 2014; Pavuluri et al., 2013], and marine aerosols [Cavalli et al., 2004; Kawamura et al., 2012]. To better understand the role of WSOC in affecting climate change and human health, further studies on WSOC are needed at the molecular level [Kawamura et al., 2010; Wang et al., 2011a].

Primary biological aerosol particles (PBAP), including pollen, bacteria, fungal and fern spores, viruses, algae, and fragments of plants and animals, contribute significantly to primary OA [Despres et al., 2012; O'dowd et al., 2004; Yttri et al., 2007]. Laboratory studies have demonstrated that PBAP can act directly as CCN and ice nuclei (IN) [Haga et al., 2013; Morris et al., 2013; Pummer et al., 2012], whereas atmospheric observations have indicated the presence of PBAPs in clouds and their relation to precipitation [Huffman et al., 2013; Pöschl et al., 2010; Prenni et al., 2009]. In addition, PBAP propagate diseases to humans and crops [Brown and Hovmoller, 2002; Franze et al., 2005; Ho and Duncan, 2005]. Allergies caused by pollen from certain tree species, as well as some grasses, weeds, and molds, have become a major public health issue [Behrendt et al., 2003; D'amato et al., 2007; Emberlin et al., 2002]. Over vegetated regions, simulated surface concentrations of PBAP range from  $0.1\text{--}0.7 \mu\text{g m}^{-3}$  in  $\text{PM}_{2.5}$  to  $0.4\text{--}3.0 \mu\text{g m}^{-3}$  in  $\text{PM}_{10}$ , with the highest concentrations in the tropics where PBAP may be the dominant source of organic aerosols [Heald and Spracklen, 2009]. Elbert et al. [2007] reported that global emissions from fungi ( $\sim 50 \text{ Tg yr}^{-1}$ ) are at similar levels as anthropogenic primary OA ( $\sim 47 \text{ Tg yr}^{-1}$ ) [Volkamer et al., 2006] and secondary OA ( $12\text{--}70 \text{ Tg yr}^{-1}$ )

[Kanakidou *et al.*, 2005]. PBAP in aerosols are often present in the form of WSOC [O'dowd *et al.*, 2004], whereas fungi and bacteria are often attached to dust [Kellogg and Griffin, 2006; Yamaguchi *et al.*, 2012]. Based on the use of ultraviolet aerodynamic particle sizers with fluorescence detection, recent studies have revealed much information on the abundances and size distributions of PBAP [Hairston *et al.*, 1997; Huffman *et al.*, 2010; Tobo *et al.*, 2013]. However, quantitative studies on the relative contributions from different sources are still limited [Di Filippo *et al.*, 2013; Jia *et al.*, 2010].

Primary saccharides are emitted persistently from biological sources and have been used as tracers for PBAP [Medeiros *et al.*, 2006b; Pacini, 2000]. Fructose and glucose have broad biogenic sources from terrestrial plant pollen, fruits, and detritus [Speranza *et al.*, 1997]. Glucose exists as the most abundant carbohydrate in vascular plants [Cowie and Hedges, 1984]. Sucrose plays a key role in plant flowering processes [Bielecki, 1995]. Recent studies have reported that sucrose is the dominant component of airborne pollen grains [Fu *et al.*, 2012a; Pacini, 2000; Yttri *et al.*, 2007]. As a fungal metabolite, the enrichment of trehalose in aerosols is frequently accompanied by the resuspension of soil particles and unpaved road dust [Rogge *et al.*, 2007; Simoneit *et al.*, 2004a]. Among sugar alcohols, arabitol and mannitol are the major species in fungi [Di Filippo *et al.*, 2013; Velez *et al.*, 2007]; they have been used as tracers for fungal spores [Bauer *et al.*, 2008; Carvalho *et al.*, 2003; Jia and Fraser, 2011; Yang *et al.*, 2012]. Erythritol and inositol were recently reported as minor components in remote marine aerosols, having similar sources as other sugar alcohols such as arabitol and mannitol [Chen *et al.*, 2013].

East Asia has been developed rapidly in the past few decades, accompanied by increased emissions of anthropogenic pollutants [Akimoto, 2003; Monks *et al.*, 2009], changes in land use [Rudel *et al.*, 2005], and increased emissions of biogenic particulate matter [Chen *et al.*, 2013]. These emissions are often subjected to long-range atmospheric transport to the North Pacific and even to the American continent [Bendle *et al.*, 2007; Park *et al.*, 2009; Zhu *et al.*, 2012]. Emission studies in East Asia have mainly been focused on anthropogenic species such as sulfur dioxide [Lu *et al.*, 2010; Neely *et al.*, 2014], nitrogen oxides [Itahashi *et al.*, 2014], heavy metals [Hidemori *et al.*, 2014], or carbonaceous components [Kawamura *et al.*, 2010; Mochida *et al.*, 2003; Zhu *et al.*, 2015b]. However, less is known about PBAP emissions and their contributions to WSOC and particulate matter (PM) in subtropical Asia.

In this study, we report a 27 month time series study of primary saccharides and sugar alcohols in ambient aerosols collected at Cape Hedo on Okinawa Island, Japan. We also measured WSOC and inorganic ions in aerosols to better understand the source of the primary saccharides and sugar alcohols. The objectives of our study are to (1) investigate the abundances and seasonal variations of primary saccharides and sugar alcohols, (2) evaluate their contributions to WSOC and ambient PM mass, and (3) understand the contributions of local sources and long-range transport to PBAP in Okinawa. To the best of our knowledge, year-round variations of bioaerosols have never before been reported in the subtropical Asian Pacific region.

## 2. Experimental Section

### 2.1. Site and Sample Collection

Aerosols were collected at the Cape Hedo Atmosphere and Aerosol Measurement Station (CHAAMS) (26.9°N, 128.2°E) in the northwestern edge of Okinawa Island (Figure 1). It has been suggested that the Okinawa aerosols are seasonally affected by emissions from fossil fuel combustion and terrestrial higher plants in East Asia through long-range transport [Takami *et al.*, 2007; Yamamoto and Kawamura, 2011]. Our study could evaluate this idea because there is no major industry on the island and the northern part of the island around Cape Hedo is covered mostly with subtropical evergreen broadleaf forest. Around the sampling site, the dominant species of vegetation are *Castanopsis sieboldii* and *Schima wallichii* [Enoki, 2003]. From October 2009 to February 2012, total suspended particulate (TSP) samples were collected on precombusted (450°C, >3 h) quartz filters (Pallflex 2500QAT-UP, 20 cm × 25 cm) using a high-volume air sampler (Kimoto AS-810B) at a flow rate of 50–60 m<sup>3</sup> h<sup>−1</sup> on a weekly basis (*n* = 112). For most samples, ~9000 m<sup>3</sup> air were pulled through the filter over ~160 h. Filters were changed mostly at noon or in early afternoon (12:00–15:00 local time). Each filter sample was placed in a precombusted (450°C, >3 h) glass jar with a Teflon-lined screw cap and stored in darkness at −20°C. Before weighing and analysis, each filter was placed in a desiccator for 24–72 h until constant weight was obtained. Two field blanks were collected

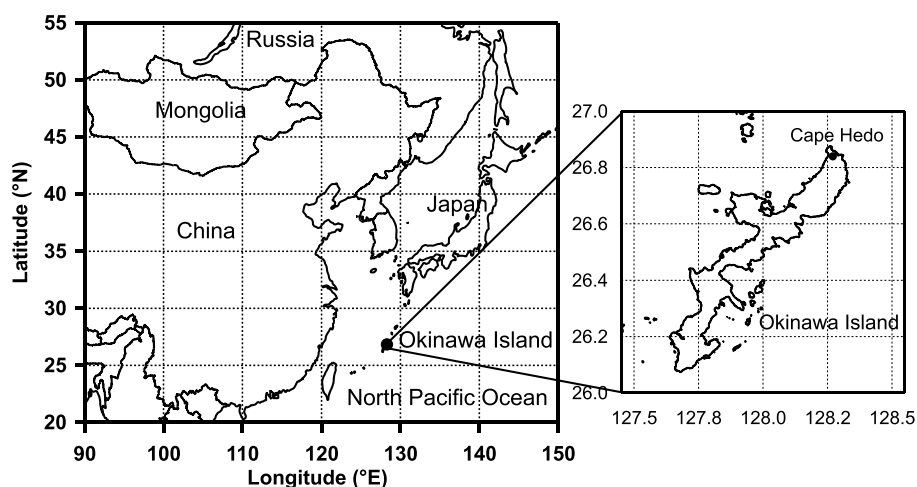


**Figure 1.** Location map of Cape Hedo, Okinawa, in East Asia where total suspended particles (TSP) were collected.

on November 2009 and March 2011, following all the collection procedures except for the operation of the sampling pump.

## 2.2. Extraction and Derivatization

A small filter section ( $\sim 10 \text{ cm}^2$ ) was extracted three times with dichloromethane/methanol (2:1, vol/vol) under ultrasonication for 10 min ( $\sim 7 \text{ mL}$  each time,  $\sim 21 \text{ mL}$  in total). The solvent extracts were passed through quartz wool packed in a Pasteur pipette, concentrated by a rotary evaporator under vacuum, and blown down to dryness with pure nitrogen gas. The extracts were then reacted with  $50 \mu\text{L}$  of N, O-bis-(trimethylsilyl)trifluoroacetamide containing 1% trimethyl chloride and  $10 \mu\text{L}$  of pyridine for 3 h at  $70^\circ\text{C}$ . During this step, the OH groups of sugars were converted to trimethylsilyl (TMS) ethers [Fu et al., 2008; Simoneit et al., 2004b].

## 2.3. Gas Chromatography/Mass Spectrometry

Gas chromatography/mass spectrometry (GC/MS) analyses were performed for the derivatized total extracts using an Agilent 7890A GC coupled to Agilent 5975C mass-selective detector. An HP-5ms capillary column ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ ) was used for compound isolation. Two microliters of each extract were injected into the GC in splitless mode with the injector temperature at  $280^\circ\text{C}$ . The GC oven temperature was programmed to hold at  $50^\circ\text{C}$  for 2 min, increase from 50 to  $120^\circ\text{C}$  at  $15^\circ\text{C min}^{-1}$  and then to  $305^\circ\text{C}$  at  $5^\circ\text{C min}^{-1}$  with a final isothermal hold at  $305^\circ\text{C}$  for 15 min. Helium was used as a carrier gas at a flow rate of  $1.0 \text{ mL min}^{-1}$ . The mass spectrometer was operated in the electron ionization mode at 70 eV and scanned over the  $m/z$  range of 50–650 Da. Mass spectra were acquired and processed using the software Chemstation. GC/MS response factors of individual compounds were determined using authentic standards. Primary saccharides and sugar alcohols showed fragment ions at  $m/z$  207 and 204. By comparing the mass spectra with authentic standards, individual compounds were identified.

Recoveries for primary saccharides and sugar alcohols were better than 80% as obtained by spiking standards to precombusted quartz filters followed by extraction and derivatization. No peak for primary saccharides and sugar alcohols was found in the field and laboratory blanks. The analytical errors by duplicate analyses were less than 15%. The detection limits of primary saccharides and sugar alcohols were  $105\text{--}557 \text{ pg } \mu\text{L}^{-1}$ , which corresponds to ambient concentrations of  $0.0015\text{--}0.0081 \text{ ng m}^{-3}$  under a typical sampling volume of  $9000 \text{ m}^3$  and an extraction using a filter section of  $10 \text{ cm}^2$ .

## 2.4. Ion Chromatography and Water-Soluble Organic Compounds

Major cations and anions including methanesulfonic acid (MSA) were measured using an ion chromatograph (IC) (761 Compact IC, Metrohm, Switzerland). Data for  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ , and MSA were

used in this study. Details on the measurements were described elsewhere [Kunwar and Kawamura, 2014]. Briefly, a small filter section ( $\sim 3.14 \text{ cm}^2$ ) was extracted with organic-free pure water (10 mL) under ultrasonication for 30 min. The extracts were filtered through a syringe filter (Millipore Millex-GV, polyvinylidene difluoride (PVDF)  $0.22 \mu\text{m}$ ) and analyzed for ions using IC. The detection limits for anions and cations were  $\sim 0.1 \text{ ng m}^{-3}$ . The analytical error in replicate analyses of laboratory standards was within 5%. The concentrations of ions in the samples were corrected for field blanks. Non-sea-salt (nss-)  $\text{Ca}^{2+}$ , indicating  $\text{Ca}^{2+}$  of terrestrial origin differing from that of maritime origin, was calculated following the method of George *et al.* [2008].

WSOC was measured using a Shimadzu carbon/nitrogen analyzer (total organic carbon (TOC)- $V_{\text{CSH}}$ ). Details on the measurements are described elsewhere [Miyazaki *et al.*, 2011]. Briefly, a small filter section ( $\sim 3.14 \text{ cm}^2$ ) was extracted with organic-free pure water (20 mL) under ultrasonication for 30 min. The extracts were passed through a syringe filter (Millipore Millex-GV, PVDF  $0.22 \mu\text{m}$ ) and measured for WSOC using TOC- $V_{\text{CSH}}$ . The analytical error in replicate analyses of laboratory standards was within 5%. The WSOC concentrations were corrected for field blanks. The ion and WSOC data for the first year are from Kunwar and Kawamura [2014].

### 2.5. Air Mass Trajectory Analysis

To investigate the source regions of air masses arriving in Cape Hedo, backward trajectories were calculated using Hybrid Single-Particle Lagrangian Integrated Trajectory version 4 for both seasonal means and typical PBAP tracer events [Draxler and Rolph, 2014]. For seasonal mean trajectories, 120 h backward trajectories starting at 500 m aboveground level at 09:00 local time were calculated every day during the sampling period. Six-hourly archived Global Data Assimilation System data ( $1^\circ \times 1^\circ$ ) from the National Centers for Environmental Prediction (<http://ready.arl.noaa.gov/gdas1.php>, accessed 20 June 2014) were used as meteorology data. The obtained daily trajectories were subjected to cluster analyses to generate three seed clusters (centroids) in each season. For typical PBAP event analyses, hourly trajectories were obtained for each event period. Three seed clusters (centroids) were calculated for these hourly trajectories in each event. Meteorological data were recorded at the Oku meteorological station ( $26.8^\circ\text{N}$ ,  $128.3^\circ\text{E}$ ) operated by the Japan Meteorological Agency (JMA). The days of occurrence of aeolian dust events were observed at JMA's Naha meteorological station ( $26.2^\circ\text{N}$ ,  $127.7^\circ\text{E}$ ).

### 2.6. Positive Matrix Factorization Analysis

The detected primary saccharides and sugar alcohols were subjected to positive matrix factorization (PMF) analysis to constrain their source classifications using PMF 3.0 from Environmental Protection Agency of the United States [Environmental Protection Agency of the United States, 2008; Paatero and Tapper, 1994]. Five primary saccharides, four sugar alcohols, WSOC, and MSA were used for calculations. As our parallel study proved that Okinawa is seasonally affected by long-range transport of biomass burning aerosols [Zhu *et al.*, 2015a], we also included levoglucosan in PMF analysis to investigate the possible sources of PBAPs from biomass burning. During model convergence, WSOC was used as the sum of total variables. However, we do not aim to estimate the contributions from each component to WSOC using PMF here because there may be many sources other than PBAP tracers.

Based on the replicate analyses, 15% and 5% of the uncertainties for the measurement of organic compounds and ions/WSOC were applied, respectively, to PMF analysis. The method detection limits (MDLs) of primary saccharides and sugar alcohols were assigned using the analytical values of  $0.0015\text{--}0.0081 \text{ ng m}^{-3}$ . Similarly, MDLs of WSOC and MSA were assigned as  $0.1 \text{ ng m}^{-3}$ . When measured concentrations were below MDLs, 1/3 of MDL was assigned to the data points and the corresponding uncertainties were 5/6 of MDL. The signal-to-noise values of different input components ranged from 5.7 to 19.0. Based on given understanding of PBAP sources, 3–7 factors were examined and 5 factors were determined. The minimal robust and true  $Q$  values of the base run were 3001 and 3413, respectively. The concentrations and percentages of tracers in each factor of bootstrap run were close to those of the base run results. The  $Q$  values and factor profiles of  $F_{\text{peak}}$  rotation runs showed no significant changes comparing with base run, indicating stable PMF results.

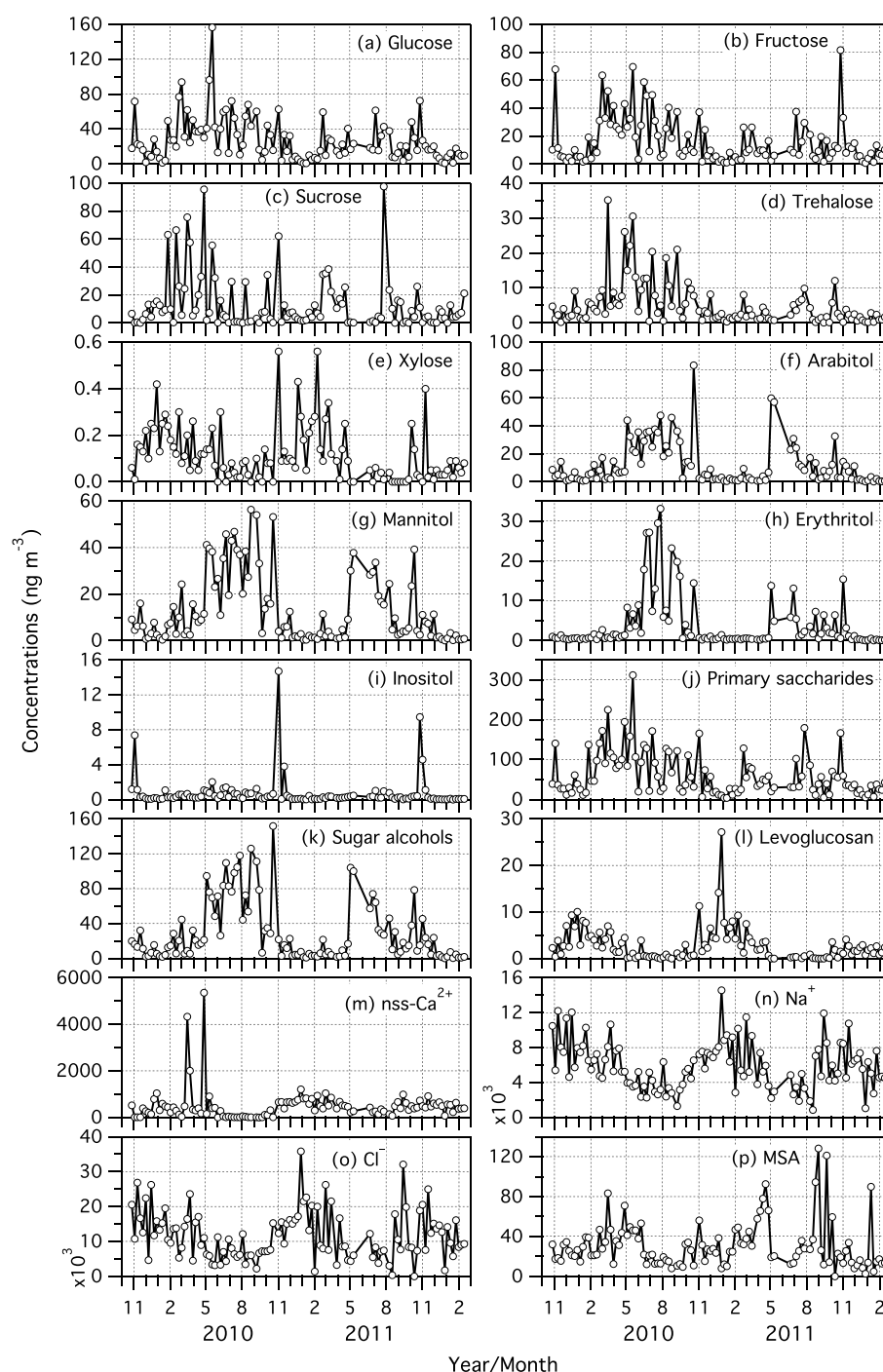


**Figure 2.** Temporal variation of primary saccharides, sugar alcohols, levoglucosan, and selected ions in aerosols at Cape Hedo, Okinawa, from October 2009 to February 2012. Levoglucosan data are from Zhu *et al.* [2015a], while ion data for October 2009 to September 2010 are from Kunwar and Kawamura [2014].

### 3. Results and Discussion

#### 3.1. Abundances and Seasonal Variations of Primary Saccharides and Sugar Alcohols

##### 3.1.1. Primary Saccharides

The temporal variations of primary saccharides and sugar alcohols are shown in Figure 2. Their annual and seasonal means and ranges are given in Table 1. Primary saccharides have an annual mean concentration

**Table 1.** Abundances ( $\text{ng m}^{-3}$ ) and Seasonal Variations of Primary Saccharides, Sugar Alcohols, Levoglucosan, Selected Ions, and WSOC in Aerosols Collected at Cape Hedo, Okinawa, Japan, from October 2009 to February 2012

| Compounds                                      | Annual ( $n = 112$ )       |                      | Winter ( $n = 36$ ) <sup>a</sup> |            | Spring ( $n = 23$ ) |            | Summer ( $n = 23$ ) |            | Autumn ( $n = 30$ ) |            |
|------------------------------------------------|----------------------------|----------------------|----------------------------------|------------|---------------------|------------|---------------------|------------|---------------------|------------|
|                                                | Mean $\pm$ SD <sup>b</sup> | Range                | Mean $\pm$ SD                    | Range      | Mean $\pm$ SD       | Range      | Mean $\pm$ SD       | Range      | Mean $\pm$ SD       | Range      |
| <i>Primary saccharides</i>                     |                            |                      |                                  |            |                     |            |                     |            |                     |            |
| Glucose                                        | 27.2 $\pm$ 24.8            | 0.81–157             | 13.7 $\pm$ 16.8                  | 0.81–77.0  | 41.3 $\pm$ 33.9     | 10.1–157   | 34.7 $\pm$ 21.5     | 7.60–72.3  | 26.9 $\pm$ 19.1     | 3.48–72.6  |
| Fructose                                       | 16.4 $\pm$ 16.7            | 0.63–81.6            | 6.62 $\pm$ 6.85                  | 0.63–31.0  | 25.5 $\pm$ 18.5     | 2.51–69.6  | 21.4 $\pm$ 16.5     | 3.44–58.8  | 17.2 $\pm$ 18.3     | 1.67–81.6  |
| Sucrose                                        | 13.2 $\pm$ 19.3            | 0.03–97.8            | 11.6 $\pm$ 15.0                  | 0.03–66.5  | 25.6 $\pm$ 25.3     | 0.13–95.7  | 10.8 $\pm$ 21.2     | 0.06–97.8  | 7.63 $\pm$ 13.0     | 0.03–62.2  |
| Trehalose                                      | 5.08 $\pm$ 6.30            | 0.04–35.2            | 2.35 $\pm$ 2.22                  | 0.21–9.07  | 8.99 $\pm$ 10.1     | 0.76–35.2  | 6.51 $\pm$ 5.61     | 0.19–20.4  | 4.24 $\pm$ 4.56     | 0.04–21.1  |
| Xylose                                         | 0.12 $\pm$ 0.12            | nd–0.56 <sup>c</sup> | 0.17 $\pm$ 0.13                  | 0.02–0.56  | 0.14 $\pm$ 0.09     | nd–0.34    | 0.05 $\pm$ 0.07     | nd–0.30    | 0.10 $\pm$ 0.13     | nd–0.56    |
| Subtotal                                       | 62.0 $\pm$ 54.9            | 4.29–313             | 34.4 $\pm$ 36.1                  | 4.29–142   | 101.4 $\pm$ 70.3    | 20.8–313   | 73.5 $\pm$ 51.5     | 11.6–180   | 56.0 $\pm$ 43.4     | 5.28–167   |
| <i>Sugar alcohols</i>                          |                            |                      |                                  |            |                     |            |                     |            |                     |            |
| Arabitol                                       | 12.0 $\pm$ 15.0            | 0.14–83.6            | 2.55 $\pm$ 2.78                  | 0.14–12.2  | 14.2 $\pm$ 17.9     | 0.68–59.8  | 24.0 $\pm$ 12.9     | 1.54–47.6  | 12.3 $\pm$ 16.1     | 1.63–83.6  |
| Mannitol                                       | 12.9 $\pm$ 14.6            | 0.11–56.3            | 2.84 $\pm$ 3.43                  | 0.11–14.6  | 14.1 $\pm$ 14.2     | 0.90–41.3  | 27.5 $\pm$ 14.2     | 2.49–56.3  | 13.0 $\pm$ 14.2     | 1.20–54.1  |
| Inositol                                       | 0.72 $\pm$ 1.82            | 0.01–14.7            | 0.15 $\pm$ 0.20                  | 0.01–1.07  | 0.49 $\pm$ 0.42     | 0.16–2.02  | 0.58 $\pm$ 0.39     | 0.09–1.42  | 1.68 $\pm$ 3.32     | 0.04–14.7  |
| Erythritol                                     | 3.88 $\pm$ 6.70            | 0.05–33.1            | 0.49 $\pm$ 0.37                  | 0.05–1.67  | 2.42 $\pm$ 3.29     | 0.22–13.8  | 10.9 $\pm$ 10.2     | 0.57–33.1  | 3.69 $\pm$ 5.38     | 0.25–19.8  |
| Subtotal                                       | 29.5 $\pm$ 34.4            | 0.32–152             | 6.03 $\pm$ 6.55                  | 0.32–28.7  | 31.2 $\pm$ 34.2     | 2.06–104.1 | 62.9 $\pm$ 34.4     | 4.84–126   | 30.7 $\pm$ 33.3     | 3.14–152   |
| Total PBAP tracers                             | 91.4 $\pm$ 71.9            | 5.5–382              | 40.4 $\pm$ 40.9                  | 5.5–162    | 133 $\pm$ 81.5      | 36.1–382   | 136 $\pm$ 65.3      | 35.7–249   | 86.7 $\pm$ 57.2     | 10.1–233   |
| Levoglucosan <sup>d</sup>                      | 3.09 $\pm$ 3.70            | nd–27.18             | 5.30 $\pm$ 4.88                  | 0.78–27.18 | 2.87 $\pm$ 2.15     | nd–7.43    | 0.57 $\pm$ 0.84     | nd–3.89    | 2.12 $\pm$ 2.34     | nd–11.28   |
| WSOC                                           | 663 $\pm$ 373              | 81.4–1899            | 721 $\pm$ 364                    | 81.4–1693  | 901 $\pm$ 372       | 254–1882   | 452 $\pm$ 347       | 105–1899   | 571 $\pm$ 291       | 99.0–1511  |
| nss- $\text{Ca}^{2+}$ ( $\mu\text{g m}^{-3}$ ) | 0.49 $\pm$ 0.68            | 0.002–5.36           | 0.52 $\pm$ 0.27                  | 0.07–1.21  | 0.9 $\pm$ 1.32      | 0.03–5.36  | 0.16 $\pm$ 0.18     | 0.002–0.67 | 0.39 $\pm$ 0.29     | 0.002–0.99 |
| $\text{Na}^+$ ( $\mu\text{g m}^{-3}$ )         | 5.95 $\pm$ 2.71            | 0.86–14.6            | 6.92 $\pm$ 2.72                  | 1.05–14.6  | 5.82 $\pm$ 2.47     | 2.23–11.5  | 3.71 $\pm$ 1.75     | 0.86–7.82  | 6.62 $\pm$ 2.55     | 1.31–12.2  |
| $\text{Cl}^-$ ( $\mu\text{g m}^{-3}$ )         | 11.7 $\pm$ 6.85            | 0.35–35.8            | 13.8 $\pm$ 6.98                  | 1.38–35.8  | 10.7 $\pm$ 6.88     | 3.23–26.2  | 7.24 $\pm$ 3.85     | 0.35–17.8  | 13.3 $\pm$ 6.98     | 2.22–32.1  |
| MSA ( $\mu\text{g m}^{-3}$ )                   | 0.03 $\pm$ 0.02            | 0.003–0.13           | 0.02 $\pm$ 0.02                  | 0.003–0.09 | 0.05 $\pm$ 0.02     | 0.01–0.09  | 0.03 $\pm$ 0.03     | 0.008–0.13 | 0.03 $\pm$ 0.02     | 0.008–0.12 |
| TSP ( $\mu\text{g m}^{-3}$ )                   | 57.2 $\pm$ 39.8            | 7.8–286              | 54.8 $\pm$ 29.7                  | 7.8–151    | 84.6 $\pm$ 59.8     | 28.4–286   | 35.9 $\pm$ 22.9     | 11.4–114   | 55.6 $\pm$ 30.6     | 18.8–165   |

<sup>a</sup>Seasons are divided as December–February in winter, March–May in spring, June–August in summer, and September–November in autumn.<sup>b</sup>SD denotes standard deviation ( $1\sigma$ ).<sup>c</sup>nd denotes not detected.<sup>d</sup>Levoglucosan data are from Zhu *et al.* [2015a].

of  $62.0 \pm 54.9 \text{ ng m}^{-3}$  (mean  $\pm 1\sigma$ ); glucose is the most abundant ( $27.2 \pm 24.8 \text{ ng m}^{-3}$ ), followed by fructose ( $16.4 \pm 16.7 \text{ ng m}^{-3}$ ), sucrose ( $13.2 \pm 19.3 \text{ ng m}^{-3}$ ), trehalose ( $5.08 \pm 6.30 \text{ ng m}^{-3}$ ), and xylose ( $0.12 \pm 0.12 \text{ ng m}^{-3}$ ) (Table 1). In 2010, all these compounds showed spring maxima and winter minima. However, the seasonality was weakened in the 2011 samples, where primary saccharides had equivalent (sucrose and trehalose) or higher levels (glucose and fructose) in summer and autumn (Figure S1 in the supporting information). The latter phenomenon can be related to changing local productivity of the subtropical forest, which will be discussed in section 3.2.1.

Temporal variations of glucose and fructose in aerosols are linearly well correlated ( $r = 0.86$ ,  $p < 0.001$ ) (Figures 2a and 2b and Table 2). Glucose was the most abundant primary saccharide throughout the year. Glucose maximized in spring ( $41.3 \pm 33.9 \text{ ng m}^{-3}$ ), followed by summer ( $34.7 \pm 21.5 \text{ ng m}^{-3}$ ), autumn ( $26.9 \pm 19.1 \text{ ng m}^{-3}$ ), and winter ( $13.7 \pm 16.8 \text{ ng m}^{-3}$ ) (Table 1 and Figure 2a). This sugar compound comprised 25–34% of the total identified PBAP tracers. Similar seasonality was observed for fructose, indicating common sources for these two compounds, although the abundances of fructose were 36–52% lower than those of glucose (Table 1 and Figure 2b). In winter, the air mass source regions were north China, Mongolia, and middle to western Russia (Figure 3a), where the vegetation was inactive. On the other hand, air mass origins in summer were dominantly from the ocean (Figure 3c), where few sources of glucose and fructose are known to be present. Meanwhile, Okinawa Island is characterized by subtropical vegetation that is active throughout the year. These results suggest that the dominant sources of glucose and fructose are from Okinawa Island. Interestingly, in 2011, glucose and fructose levels were slightly higher in summer than in spring and hence different from those in 2010 (Figure S1 in the supporting information). These differences imply that local productivity changed interannually. The relations between these primary saccharides with meteorological parameters are discussed in section 3.2.1.

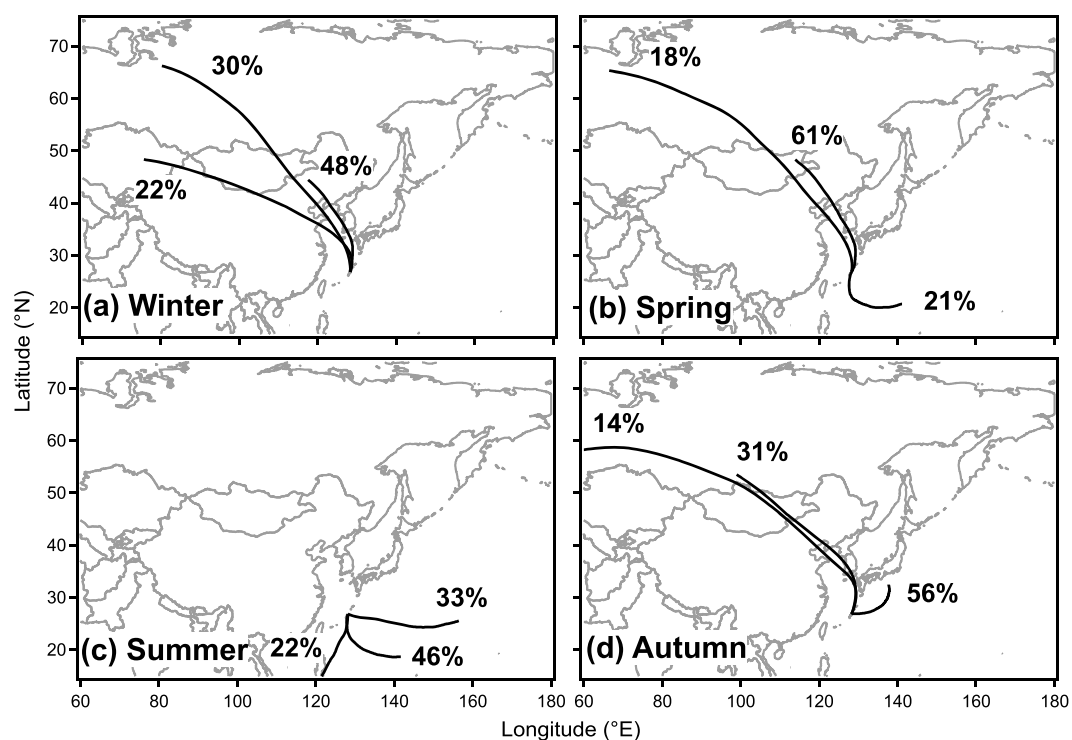
The covariation of glucose and fructose has also been reported in other continental outflow sites in East Asia [Chen *et al.*, 2013; Fu *et al.*, 2012a], the Amazon forest [Graham *et al.*, 2002], and urban Europe [Pashynska *et al.*, 2002]. These two primary saccharides were found in plant fragments [Medeiros *et al.*, 2006b], pollen grains [Fu *et al.*, 2012a; Vesprini *et al.*, 2002], lichens [Dahlman *et al.*, 2003], and in soil dust [Rogge *et al.*, 2007;

**Table 2.** Linear Correlation Coefficients ( $r$ ) Among Primary Saccharides and Sugar Alcohols, and With Levoglucosan and Selected Ions in Aerosols Collected at Cape Hedo, Okinawa, from October 2009 to February 2012

|                      | Glucose            | Fructose | Sucrose | Trehalose | Xylose | Arabitol | Mannitol | Inositol | Erythritol | Levoglucosan | nss-Ca <sup>2+</sup> | Na <sup>+</sup> | Cl <sup>-</sup> | MSA |
|----------------------|--------------------|----------|---------|-----------|--------|----------|----------|----------|------------|--------------|----------------------|-----------------|-----------------|-----|
| Glucose              | 1                  |          |         |           |        |          |          |          |            |              |                      |                 |                 |     |
| Fructose             | 0.86**             | 1        |         |           |        |          |          |          |            |              |                      |                 |                 |     |
| Sucrose              | 0.31*              | 0.33*    | 1       |           |        |          |          |          |            |              |                      |                 |                 |     |
| Trehalose            | 0.69**             | 0.59**   | 0.48**  | 1         |        |          |          |          |            |              |                      |                 |                 |     |
| Xylose               | -0.05 <sup>a</sup> | -0.11    | 0.17    | 0.05      | 1      |          |          |          |            |              |                      |                 |                 |     |
| Arabitol             | 0.27*              | 0.15     | -0.23   | 0.29*     | -0.28* | 1        |          |          |            |              |                      |                 |                 |     |
| Mannitol             | 0.49**             | 0.34**   | -0.14   | 0.49**    | -0.29* | 0.90**   | 1        |          |            |              |                      |                 |                 |     |
| Inositol             | 0.37**             | 0.52**   | 0.19    | 0.03      | -0.13  | -0.03    | -0.01    | 1        |            |              |                      |                 |                 |     |
| Erythritol           | 0.16               | 0.16     | -0.23   | 0.16      | -0.29* | 0.75**   | 0.73**   | 0.02     | 1          |              |                      |                 |                 |     |
| Levoglucosan         | -0.24              | -0.21    | 0.03    | -0.11     | 0.39** | -0.38**  | -0.41**  | -0.08    | -0.33**    | 1            |                      |                 |                 |     |
| nss-Ca <sup>2+</sup> | -0.03              | 0.14     | 0.52**  | 0.39**    | 0.11   | -0.27*   | -0.28*   | 0.01     | -0.25      | 0.25         | 1                    |                 |                 |     |
| Na <sup>+</sup>      | -0.32**            | -0.21    | 0.002   | -0.28*    | 0.21   | -0.44**  | -0.52**  | 0.03     | -0.37**    | 0.37**       | 0.32**               | 1               |                 |     |
| Cl <sup>-</sup>      | -0.36**            | -0.20    | -0.06   | -0.30*    | 0.14   | -0.34**  | -0.44**  | 0.02     | -0.26*     | 0.35**       | 0.32**               | 0.96**          | 1               |     |
| MSA                  | 0.08               | 0.05     | 0.31**  | 0.17      | -0.04  | -0.20    | -0.19    | 0.01     | -0.23      | -0.02        | 0.34**               | 0.10            | -0.01           | 1   |

<sup>a</sup>Negative values indicate negative correlations.\* $p < 0.01$ .\*\* $p < 0.001$ .

Simoneit *et al.*, 2004a]. Graham *et al.* [2002] found that high levels of glucose and fructose in daytime coincided with high counts of pollen, fern spores, and insects (fragmented and whole) in the Amazon forest. Baker *et al.* [1998] reported that the nectars and fruits of tropical and subtropical plants had more glucose than fructose. In vegetated regions with high primary biological emissions, glucose and fructose are the major saccharides in aerosols.

**Figure 3.** Seasonal variations of air mass origins to Cape Hedo, Okinawa, shown by clusters of 5 day backward trajectories arriving at 500 m aboveground level in (a) winter, (b) spring, (c) summer, and (d) autumn during October 2009 to February 2012. The numbers in each panel indicate the percentages of daily trajectories in the season with such origins. Winter includes December to February, and each of the following seasons includes three successive months.

Sucrose was more abundant in the spring samples ( $25.6 \pm 25.3 \text{ ng m}^{-3}$ ) than in the summer ( $10.8 \pm 21.2 \text{ ng m}^{-3}$ ) and winter ( $11.6 \pm 15.0 \text{ ng m}^{-3}$ ) samples (Table 1 and Figure 2c). Because pollen could be the largest type of PBAP [Despres *et al.*, 2012], sucrose was more abundant in coarse ( $>7.0 \mu\text{m}$ ) than in fine aerosol particles [Agarwal *et al.*, 2010]. Therefore, the densely vegetated broadleaf forest in Okinawa Island is likely the major source of sucrose. We suggest that emissions of pollen during flowering of local vegetation largely contribute to sucrose in aerosols. Such a phenomenon was also observed in a deciduous forest [Miyazaki *et al.*, 2012b]. Nevertheless, pollen could be uplifted to high altitudes and transported long distances [Skjoth *et al.*, 2007; Smith *et al.*, 2008; Sofiev *et al.*, 2006]. Long-range transport of air masses from north China, Mongolia, and middle to western Russia occurs in spring when flowering in boreal forests and agricultural plants peaked (Figure 3b), providing additional source of sucrose.

Trehalose has been reported at high abundance in association with an abundance of fungal spores [Medeiros *et al.*, 2006a]. Trehalose maximized in spring ( $8.99 \pm 10.1 \text{ ng m}^{-3}$ ), with a value 38% higher than that in summer ( $6.51 \pm 5.61 \text{ ng m}^{-3}$ ), followed by autumn ( $4.24 \pm 4.56 \text{ ng m}^{-3}$ ) and winter ( $2.35 \pm 2.22 \text{ ng m}^{-3}$ ) (Table 1 and Figure 2d). Positive linear correlations were obtained between trehalose and glucose ( $r = 0.69$ ,  $p < 0.001$ ), fructose ( $r = 0.59$ ,  $p < 0.001$ ), and sucrose ( $r = 0.48$ ,  $p < 0.001$ ) (Table 2). These correlations indicate that trehalose is abundant during the high plant productivity period, suggesting a main contribution from local forests in Okinawa. Sea spray containing algae may also contribute to the trehalose in maritime aerosols [Nagashima and Fukuda, 1981]. However, this is likely a minor source to Okinawa aerosols because only  $0.21\text{--}0.37 \text{ ng m}^{-3}$  of trehalose was detected in the western North Pacific [Fu *et al.*, 2011]. Our PMF classifications also indicated that a minor portion of trehalose was attributable to maritime source (section 3.4).

Primary saccharides such as trehalose, sucrose, glucose, and fructose are also present in soil dusts, where trehalose is the most abundant [Rogge *et al.*, 2007; Simoneit *et al.*, 2004a]. Correlations between trehalose and other primary saccharides also imply effects of soil dusts on Okinawa aerosols. Spring is the season when Asian dust is common [e.g., Xuan *et al.*, 2000; Zhou and Zhang, 2003]. Spring is also an intensive tilling season in rural regions of northeast China [e.g., He *et al.*, 2010]. Cluster analyses of backward trajectories in spring indicate that 79% of the air masses originate from areas in East Mongolia to north China, of which 18% traveled longer distances from middle to western Russia (Figure 3b). These areas cover regions of both natural and agricultural dust sources [Dong *et al.*, 2000; Prospero *et al.*, 2002]. In winter, although the air masses exclusively originate from the continent (Figure 3a), the source strength of soil dust is comparatively weak [Xuan *et al.*, 2000; Zhou and Zhang, 2003].  $\text{Ca}^{2+}$  has been used as a characteristic tracer for soil dust [e.g., Athanasopoulou *et al.*, 2010; Brahney *et al.*, 2013]. A positive correlation was obtained between trehalose and  $\text{nss-Ca}^{2+}$  ( $r = 0.39$ ,  $p < 0.001$ ) (Table 2). The seasonal trends of trehalose and  $\text{nss-Ca}^{2+}$ , along with the occurrence of dusts and air mass origins, imply that dusts from natural sources and agricultural practices in the Eurasia continent affected the Okinawa aerosols. Because  $\text{Ca}^{2+}$  is also a key component of plant [McLaughlin and Wimmer, 1999], local forests could also contribute to the observed  $\text{nss-Ca}^{2+}$ . Therefore, trehalose in Okinawa aerosols is likely coinfluenced by both local and regional sources.

Xylose is a less abundant primary saccharide in the Okinawa aerosols, accounting for 0.2% of the total primary saccharides on an annual basis. However, its pattern of a winter maximum ( $0.17 \pm 0.13 \text{ ng m}^{-3}$ ) and a summer minimum ( $0.05 \pm 0.07 \text{ ng m}^{-3}$ ) is different from those of other primary saccharides (Table 1 and Figure 2e). The long-range transport of biomass burning products may contribute largely to the elevated levels of xylose in Okinawa winter aerosols because of a positive correlation between xylose and biomass burning tracer levoglucosan ( $r = 0.39$ ,  $p < 0.001$ ) and dominant air masses from the Asian continent (Table 2 and Figure 3a). A similar seasonal trend has been reported for xylose in the midwestern United States, with relatively higher abundances of  $2.1 \text{ ng m}^{-3}$  in winter and  $0.5 \text{ ng m}^{-3}$  in summer and has been attributed to biomass burning based on a good correlation with levoglucosan [Sullivan *et al.*, 2011]. Further details regarding the contribution from biomass burning in the Eurasia continent to Okinawa are discussed in a parallel study [Zhu *et al.*, 2015a]. Moreover, xylose is produced at higher levels by angiosperm plants than by gymnosperm plants, plankton, and bacteria [Cowie and Hedges, 1984]. The dominant vegetation close to the sampling site, *Castanopsis sieboldii* and *Schima wallichii*, are evergreen angiosperms. Xylose in Okinawa aerosols may be contributed in part by these evergreen trees. However, xylose was also found in

soils of Rondônia, Brazil, and various locations in the United States [Simoneit *et al.*, 2004a], and Wan and Yu [2007] reported that soil and associated microbiota are the source of xylose.

### 3.1.2. Sugar Alcohols

The concentrations of total sugar alcohols ( $29.5 \pm 34.4 \text{ ng m}^{-3}$ ) were half as great as those of primary saccharides (Table 1). Among the sugar alcohols, mannitol ( $12.9 \pm 14.6 \text{ ng m}^{-3}$ ) and arabitol ( $12.0 \pm 15.0 \text{ ng m}^{-3}$ ) were the most abundant, followed by erythritol ( $3.88 \pm 6.70 \text{ ng m}^{-3}$ ). Inositol ( $0.72 \pm 1.82 \text{ ng m}^{-3}$ ) contributed only 1–5% of the total sugar alcohols. Mannitol and arabitol showed clear seasonal trends with summer maxima ( $27.5 \pm 14.2 \text{ ng m}^{-3}$  and  $24.0 \pm 12.9 \text{ ng m}^{-3}$ , respectively) and winter minima ( $2.84 \pm 3.43 \text{ ng m}^{-3}$  and  $2.55 \pm 2.78 \text{ ng m}^{-3}$ , respectively) (Table 1 and Figures 2f and 2g). Meanwhile, their abundances were comparable throughout the year with strong positive linear correlation ( $r = 0.90$ ,  $p < 0.001$ ) (Table 2). Such a relation implies common sources, as reported previously [Fu *et al.*, 2012a; Medeiros *et al.*, 2006b]. The dominant sources of mannitol and arabitol were airborne fungal spores [Bauer *et al.*, 2008], along with detritus from mature leaves [Pashynska *et al.*, 2002]. Heald and Spracklen [2009] found that mannitol concentrations are highly correlated with the leaf area index and atmospheric water vapor. These results and considerations indicate that mannitol and arabitol are largely associated with the activity of the terrestrial biosphere.

In summer, the air masses to Okinawa were dominantly from the western North Pacific (78%) with the rest were from South Asia (Figure 3c). Bubble bursting related to sea spray could contribute bacteria, viruses, and dissolved organic species, along with sea salts, to aerosols [Guasco *et al.*, 2013; Prather *et al.*, 2013]. However, we found that mannitol and arabitol were negatively related to  $\text{Cl}^-$  ( $r = -0.44$ ,  $p < 0.001$  and  $r = -0.34$ ,  $p < 0.001$ , respectively) and  $\text{Na}^+$  ( $r = -0.52$ ,  $p < 0.001$  and  $r = -0.44$ ,  $p < 0.001$ ) (Table 2), which are two typical inorganic tracers of maritime sources. These results indicate that there were minimal contributions from marine sources to sugar alcohols in Okinawa. In comparison, higher loadings of mannitol ( $21.0 \pm 20.4 \text{ ng m}^{-3}$ ) and arabitol ( $31.9 \pm 26.9 \text{ ng m}^{-3}$ ) in  $\text{PM}_{10}$  were reported in Beijing, China, as a result of mixed sources from soil disturbance, transported dust, and vegetation depending on the season [Liang *et al.*, 2013]. We suggest that the main sources of mannitol and arabitol are simply from microbes in the local subtropical forest, whose activities are highest in summer. Moreover, mannitol and arabitol were sometimes detected in aerosols sampled from air masses influenced by smoke from biomass burning, especially on synoptic scales [Fu *et al.*, 2012b; Medeiros and Simoneit, 2008; Yang *et al.*, 2012]. However, there were no positive relations between any sugar alcohols and the biomass burning tracer levoglucosan in aerosols at Okinawa (Table 2). It therefore seems unlikely that the sources of sugar alcohols from biomass burning were significant at this site.

Erythritol was recently reported as another sugar alcohol [Chen *et al.*, 2013; Pietrogrande *et al.*, 2014]. Erythritol shows a summer maximum ( $10.9 \pm 10.2 \text{ ng m}^{-3}$ ) and winter minimum ( $0.49 \pm 0.37 \text{ ng m}^{-3}$ ) (Table 1 and Figure 2h). Temporally, erythritol covaried with mannitol ( $r = 0.73$ ,  $p < 0.001$ ) and arabitol ( $r = 0.75$ ,  $p < 0.001$ ) (Table 2 and Figures 2f–2h), suggesting that erythritol is of local origin. Nevertheless, it should be noticed that erythritol is subject to degradation in the atmosphere with a lifetime of  $\sim 12.7$  days [Kessler *et al.*, 2010], whereas there has been no report to date on such an aging process for other sugar alcohols.

Very few studies have reported inositol in aerosols [Chen *et al.*, 2013; Pashynska *et al.*, 2002]. In Okinawa aerosols, low levels of inositol were observed, except for some sporadic high events (Figure 1i). Except for those events, inositol showed summer maximum ( $0.58 \pm 0.39 \text{ ng m}^{-3}$ ) and winter minimum ( $0.15 \pm 0.20 \text{ ng m}^{-3}$ ) (Table 1), whose seasonal behaviors are similar with those of other sugar alcohols, responding probably to microbial activities in local forests. Recent biological studies have indicated that inositol acts as a functional component in regulating plant salt tolerance [Golani *et al.*, 2013]. In those high inositol event weeks (e.g., samples collected in 3–10 November 2009,  $7.39 \text{ ng m}^{-3}$ ; 2–9 November 2010,  $14.7 \text{ ng m}^{-3}$ ; and 25 October to 1 November 2011,  $9.46 \text{ ng m}^{-3}$ ), local weather was controlled by stagnant patterns with daily mean temperatures of 19–23°C and little precipitation. Such conditions may favor the production of inositol from plants.

## 3.2. Interannual Variations and Elevated Local Emission Events

### 3.2.1. Interannual Variations and Relations With Meteorological Parameters

Although there were notable seasonal variations and occasional large sample by sample variations, the abundances of primary saccharides and sugar alcohols significantly decreased from 2010 to 2011 by 46%

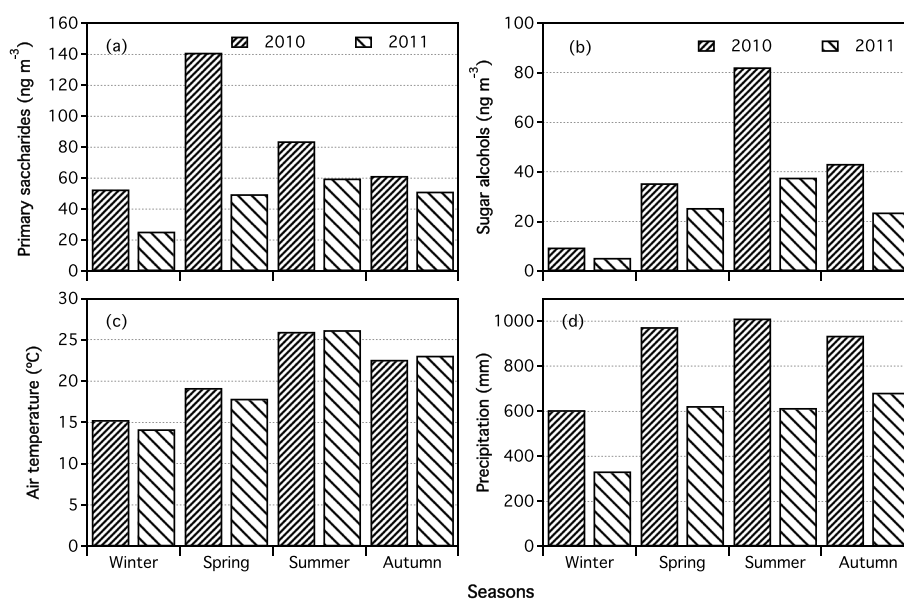


**Figure 4.** Interannual comparisons of (a) primary saccharides and (b) sugar alcohols in aerosols, and (c) temperature, and (d) precipitation between 2010 and 2011 at Cape Hedo, Okinawa.

and 48% ( $t$  test, primary saccharides,  $p < 0.001$  and sugar alcohols,  $p < 0.01$ ), respectively. This decrease was maximized in spring (64%) for primary saccharides ( $p < 0.001$ ), followed by winter (52%,  $p = 0.10$ ), summer (29%,  $p = 0.28$ ), and autumn (17%,  $p = 0.57$ ) (Figure 4a). Meanwhile, the seasonality of primary saccharides in 2011 was weakened or changed compared to 2010 (Figure S1 in the supporting information). For example, glucose maximized in spring in 2010, whereas it maximized in summer in 2011. The maximum interannual decrease of sugar alcohols was found in summer (54%,  $p < 0.001$ ), followed by autumn (45%,  $p = 0.18$ ), winter (44%,  $p = 0.15$ ), and spring (28%,  $p = 0.50$ ) (Figure 4b). Backward trajectories indicated that there were no obvious changes in composites of continental versus maritime air mass origins in any season between 2010 and 2011 (Figure S2 in the supporting information). These interannual variations were further examined in terms of changes of meteorological parameters as follows.

Average spring temperature was  $1.3^{\circ}\text{C}$  lower in 2011 than in 2010 in northeastern Okinawa (Figures 4c). Meanwhile, average summer temperature was  $0.3^{\circ}\text{C}$  higher in 2011 than in 2010. Further investigations indicated that glucose ( $r = 0.37$ ,  $p < 0.001$ ), fructose ( $r = 0.34$ ,  $p < 0.001$ ), and trehalose ( $r = 0.27$ ,  $p < 0.001$ ) in weekly samples were positively related to weekly mean air temperature (Table 3). These compounds were also positively related to weekly mean radiation (glucose,  $r = 0.24$ ,  $p < 0.01$ ; fructose,  $r = 0.25$ ,  $p < 0.01$ ; and trehalose,  $r = 0.24$ ,  $p < 0.01$ ). These results imply that primary saccharides in aerosols are closely related to local productivity, which is partially regulated by temperature and radiation. Interestingly, one of the main vegetation species in Okinawa Island, the mangrove *Bruguiera gymnorhiza*, showed obvious interannual variation of litter falls, with higher litter fall masses of  $1232\text{ g m}^{-2}\text{ yr}^{-1}$  in 2010 (April 2010 to March 2011) than those of  $971\text{ g m}^{-2}\text{ yr}^{-1}$  in 2011 (April 2011 to March 2012) [Kamruzzaman *et al.*, 2013], implying lower productivity in 2011.

**Table 3.** Linear Correlation Coefficients ( $r$ ) Between Primary Saccharides/Sugar Alcohols in Aerosols With Meteorological Parameters

|                   | Glucose | Fructose | Sucrose            | Trehalose | Xylose  | Arabitol | Mannitol | Inositol | Erythritol | Sugars | Sugar Alcohols |
|-------------------|---------|----------|--------------------|-----------|---------|----------|----------|----------|------------|--------|----------------|
| Temperature       | 0.37**  | 0.34**   | −0.08 <sup>a</sup> | 0.27*     | −0.40** | 0.54**   | 0.65**   | 0.13     | 0.57**     | 0.27*  | 0.63**         |
| Precipitation     | 0.15    | −0.05    | −0.21              | 0.20      | −0.14   | 0.50**   | 0.43**   | −0.10    | 0.25*      | 0.00   | 0.45**         |
| Radiation         | 0.24*   | 0.25*    | 0.24               | 0.24*     | −0.09   | 0.09     | 0.25*    | 0.02     | 0.27*      | 0.30   | 0.20           |
| Relative humidity | 0.15    | 0.14     | 0.01               | 0.05      | −0.18   | 0.15     | 0.14     | 0.06     | 0.11       | 0.12   | 0.15           |

<sup>a</sup>Negative values indicate negative correlations.

\* $p < 0.01$ .

\*\* $p < 0.001$ .

On the other hand, precipitation in Okinawa declined by 27–45% from 2010 to 2011, depending on the season, with an annual mean of 36% (Figures 4d). Further investigations indicated that arabinol ( $r=0.66$ ,  $p<0.001$ ) and mannitol ( $r=0.54$ ,  $p<0.001$ ) were positively related with precipitation. Relations were also found between arabinol ( $r=0.19$ ,  $p<0.05$ ) and mannitol ( $r=0.17$ ,  $p<0.1$ ) with relative humidity, although the weekly means of this parameter are comparatively less indicative than precipitation. Less humid conditions in 2011 depressed propagation of fungal spores, resulting in decreased levels of sugar alcohols. It is worth noting that the precipitation process would scavenge aerosols, a process recorded as wet deposition. At Okinawa, we postulate that the source effect of microbial growth stimulated by precipitation is larger than the wet scavenging. Moreover, sugar alcohols were also positively correlated with air temperature (arabinol,  $r=0.54$ ,  $p<0.001$ ; mannitol,  $r=0.65$ ,  $p<0.001$ ; and erythritol,  $r=0.57$ ,  $p<0.001$ ), indicating that the activities of fungal spores were coregulated by humid conditions and temperature.

Another factor possibly contributing to interannual PBAP tracer variations is the occurrences of typhoons. In 2010, 2 typhoons impacted Okinawa on 31 August and 4 September, respectively. Other than direct scavenging, such extreme weather with heavy rain may damage local vegetation, causing reduced PBAP emissions in late summer and early autumn. On the other hand, five typhoons impacted Okinawa in 2011 on 11 May, 28 May, 5 July, 9 September, and 20 September. The two consecutive typhoons that passed through Okinawa in May of 2011 likely caused severe disturbances to local forests. As a result, PBAP emissions in spring and following seasons of 2011 were likely much lower than those of 2010, causing decreased primary saccharides and sugar alcohols in atmospheric particles. These results indicated that interannual variations of PBAP tracers in aerosols respond to the activities of vegetation and microbes in subtropical evergreen forests in Okinawa, which are regulated by local meteorological parameters and extreme weather processes.

### 3.2.2. Elevated Local Emission Events

Over the 2 year observation period, PBAP tracers showed characteristic seasonal trends. These trends were generally driven by variations of meteorological parameters in Okinawa as discussed in the previous section. Nevertheless, we detected some events with extraordinarily high levels of specific compounds that deviated from the general trends. Under stable or relatively stable meteorological conditions, the local emissions of PBAP from the subtropical evergreen forests were evidently magnified. One example is the filter sample collected from 26 July to 2 August 2011, during which high concentrations of primary saccharides were recorded (Figure 2j). Over this period, the wind speed was relatively low (mean value  $3.2 \text{ m s}^{-1}$ ). Backward trajectories indicated that the air masses traveled over short distances, originating from the western North Pacific (Figure 5a). Relatively, static atmospheric conditions were formed, which enhanced the influence of PBAP emitted from the local forest on the aerosol composition in Okinawa.

Similarly, from 19 to 26 October 2010, the highest concentrations of sugar alcohols were observed (Figure 2k). On these sampling days, the weather at Okinawa was characterized by the passage of a front followed by sunny days. Higher relative humidity (91% for weekly mean) that resulted from heavy rain (308 mm in the week) favored the thriving of fungal spores. Backward trajectories indicated that 95% of the air masses had a maritime origin followed by short-range transport (Figure 5b). Such information indicated that the enhanced concentrations of sugar alcohols in aerosols were mainly derived from local sources. It is noteworthy that sugar alcohols have been reported to be more prevalent during the period of leaf senescence [Medeiros *et al.*, 2006b], whereas the largest leaf litter fall season in Okinawa is summer [Kamruzzaman *et al.*, 2013]. These factors indicate that local emissions from fungi are important sources of total PBAP.

## 3.3. Intersite Variations and Long-Range Transport Events

### 3.3.1. Intersite Variations

Seasonal variations of primary saccharides and sugar alcohols in aerosols at Okinawa were compared with those from different sites including Mount Tai [Fu *et al.*, 2008] and Nanjing [Wang *et al.*, 2011b] in China, coastal Jeju Island [Fu *et al.*, 2012a], and remote Chichijima Island [Chen *et al.*, 2013] in the western North Pacific (Figure 6). We found that the abundances of total primary saccharides and sugar alcohols in Okinawa aerosols are  $\sim 1/2$ – $1/3$  those of the inland aerosols but are 1.2–15 times higher than the remote marine aerosols depending on the year and season. Although the interannual variations of PBAP tracers at Okinawa are of the same orders of magnitude as the gradients between the inland sites and Okinawa,

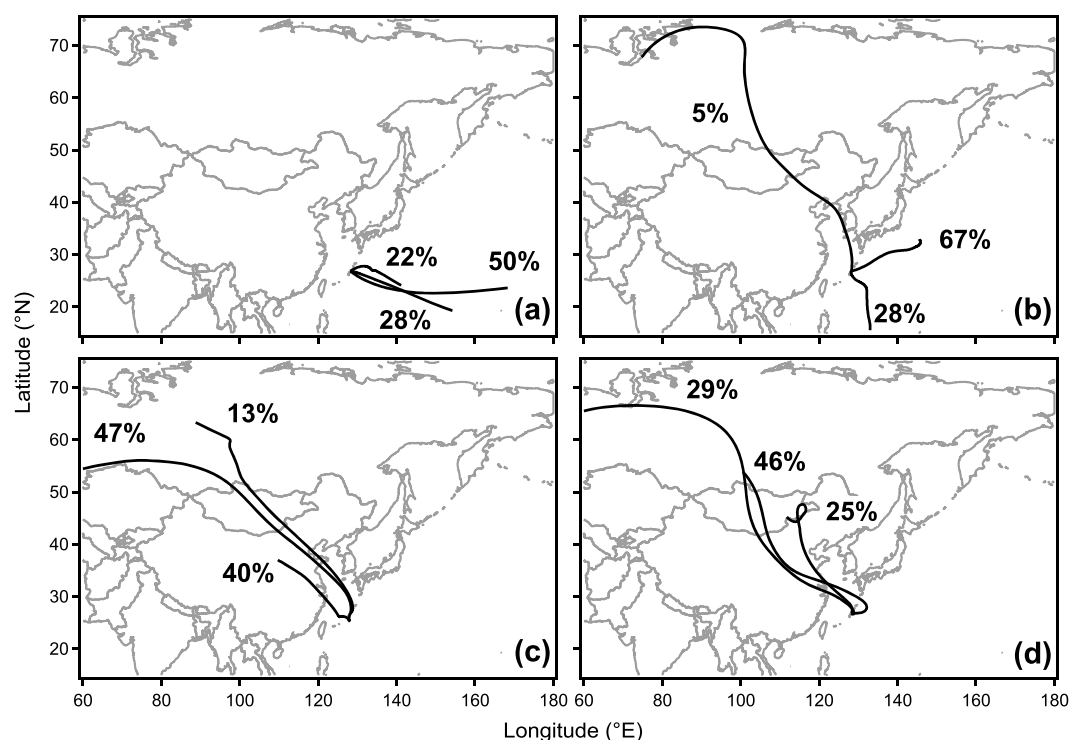


**Figure 5.** Air mass origins for the events of primary saccharides and sugar alcohols, showing the days of exaggerated local emissions in (a) 26 July to 2 August 2011, (b) 19–26 October 2010, and of long-range transport of dust in (c) 16–23 March 2010 and (d) 27 April to 4 May 2010. Clusters of 5 day backward trajectories arriving at 500 m aboveground level at Cape Hedo, Okinawa, are given. The numbers in each panel indicate the percentages of hourly trajectories in the events with such origins.

these results imply that long-range transport of PBAP from the Asian continent to the remote North Pacific could not be excluded as possible sources contributing to aerosols at Okinawa, possibly along with deposition [Zhao *et al.*, 2003], dilution, and secondary reactions in the atmosphere [Feng *et al.*, 2012; Mochida *et al.*, 2003].

### 3.3.2. Long-Range Transport of Soil Dust

Over the sample collection period, several high trehalose events were observed. In addition to local sources from forest, long-range transport of soil dust may have contributed to some of these events. During the week of 16–23 March 2010, elevated concentrations of primary saccharides were observed, among which trehalose showed the highest level ( $35.2 \text{ ng m}^{-3}$ ) for the whole period (mean  $5.08 \text{ ng m}^{-3}$ ) (Table 1 and Figure 2d). The aerosol mass in this sample ( $286.1 \text{ } \mu\text{g m}^{-3}$ ) also had the highest level (mean  $57.2 \text{ } \mu\text{g m}^{-3}$ ). Moreover,  $\text{nss-Ca}^{2+}$  in aerosols at Okinawa was  $\sim 35$  times higher than the baseline level (defined by mean values in June–August,  $0.15 \text{ ng m}^{-3}$ ) (Figure 2m). Backward trajectory clusters indicated that 40% of the air masses originated from the Loess Plateau in China, whereas the other 60% passed over the Gobi Desert via north China to Okinawa (Figure 5c). In 21–23 March 2010, aeolian dust events were observed in Naha, Okinawa by JMA. The elevated levels of primary saccharides, aerosol mass, and  $\text{nss-Ca}^{2+}$  correspond well with these Asian dust events.

During 27 April to 4 May 2010, another event of high trehalose ( $26.1 \text{ ng m}^{-3}$ ) along with high aerosol mass ( $200.9 \text{ } \mu\text{g m}^{-3}$ ) was observed (Figure 2d). Meanwhile, the  $\text{nss-Ca}^{2+}$  in aerosols at Okinawa was  $\sim 28$  times higher than the baseline level (Figure 2m). Backward trajectory clusters indicated that 25% of the air masses originated from southeastern Mongolia were transported over northeastern China, a region undergoing agricultural tillage in spring, whereas the remaining 75% were transported longer distances from southern to western Russia, via the Gobi Desert and Loess Plateau to Okinawa (Figure 5d). Such air mass origins again indicated the long-range transport of Asian dust from natural processes and agricultural activities to the North Pacific. These results were verified by the occurrence of aeolian dusts from 27 April to 2 May 2010, which were observed in Naha ( $\sim 120 \text{ km}$  south from Cape Hedo), Okinawa,

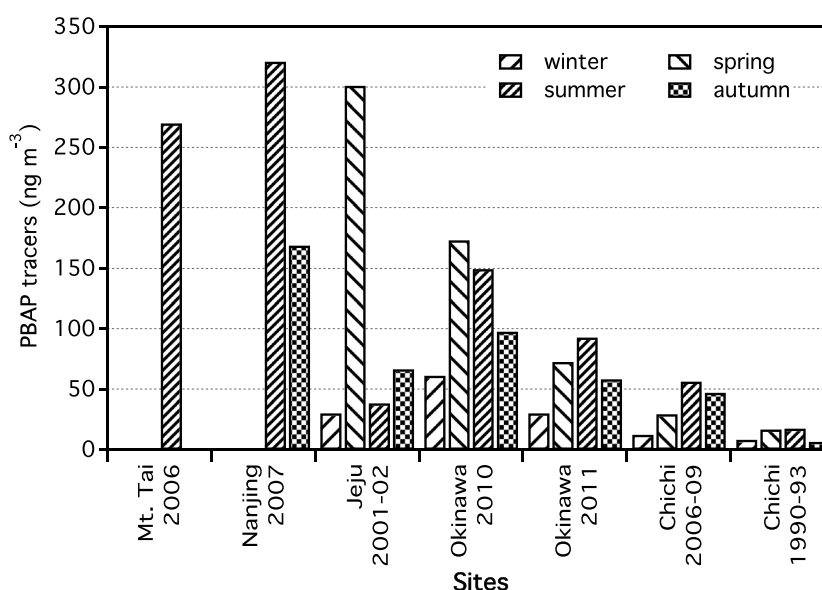


**Figure 6.** Comparisons of total abundances of major PBAP tracers in aerosols from Okinawa Island with inland (Mount Tai, Nanjing), coastal (Jeju, Jeju Island), and remote (Chichi, Chichijima Island) sites. Total abundances of major PBAP tracers mean the sum of fructose, glucose, sucrose, trehalose, arabinol, and mannitol. Concentrations for other sites are from *Fu et al.* [2008] for Mount Tai, *Wang et al.* [2011b] for Nanjing, *Fu et al.* [2012a] for Jeju Island, and *Chen et al.* [2013] for Chichijima Island.

by JMA. Furthermore, there were 14 aeolian dust days in four consecutive periods (21–24 March, 27 April to 2 May, 25–26 May, and 3–4 December) in 2010 in Naha, whereas only four aeolian dust days occurred during three periods (11–12 April, 2 May, and 13 May) in 2011. Similar dust events along with elevated black carbon (BC) and OC had been observed in 2008 in Okinawa under the influences of Asian outflow [*Handa et al.*, 2011]. In short, outflow of Asian dust likely contributes to the elevated PBAP tracers in Okinawa.

### 3.4. PBAP Classifications

Based on PMF analysis, five factors were determined to be significant to classify the sources of PBAP (Figure 7). Factor 1 shows a high allocation for glucose (65% of the total glucose; the following percentages in this section are also presented relative to the total content of each respective compound), fructose (51%), and trehalose (66%), along with a relatively high contribution from sugar alcohols, indicating that the sources may be derived from local forest trees. Time series and seasonal means of the fraction of WSOC attributed to Factor 1 based on the PMF analysis showed higher levels in spring/summer than autumn/winter (Figure S3 in the supporting information). Factor 2 included 86% of the total sucrose mass, indicating that this primary saccharide is derived from plant pollen. This factor was more abundant in spring as a result of the plant flowering. In Factor 3, major allocations were found in erythritol (84%), arabinol (65%), mannitol (57%), and inositol (25%). Factor 3 showed a higher abundance in summer due to elevated fungal spore sources. Factor 4 was abundantly loaded by xylose (90%), accompanied by levoglucosan (99.6%), a tracer for biomass burning. The seasonality of this factor was consistent with the outflow of biomass burning aerosols [*Zhu et al.*, 2015a]. This result indicates that the long-range transport of biomass burning aerosols is the major source of ambient xylose. The dominance of MSA (84%) in Factor 5 indicates a maritime source. Although MSA could also be formed in the forest floor [*Miyazaki et al.*, 2012b], given the location of Cape Hedo in the western North Pacific, the contributions from maritime sources are dominant. The low loading of MSA in other factors supported such arguments. The allocations of compounds in each factor and the time series variations of the fraction of WSOC attributed to each factor generated by the PMF analyses confirm that the dominant sources of trehalose, glucose, and fructose are local vegetation; those of sucrose are plant pollens; and those of sugar alcohols are airborne spores.

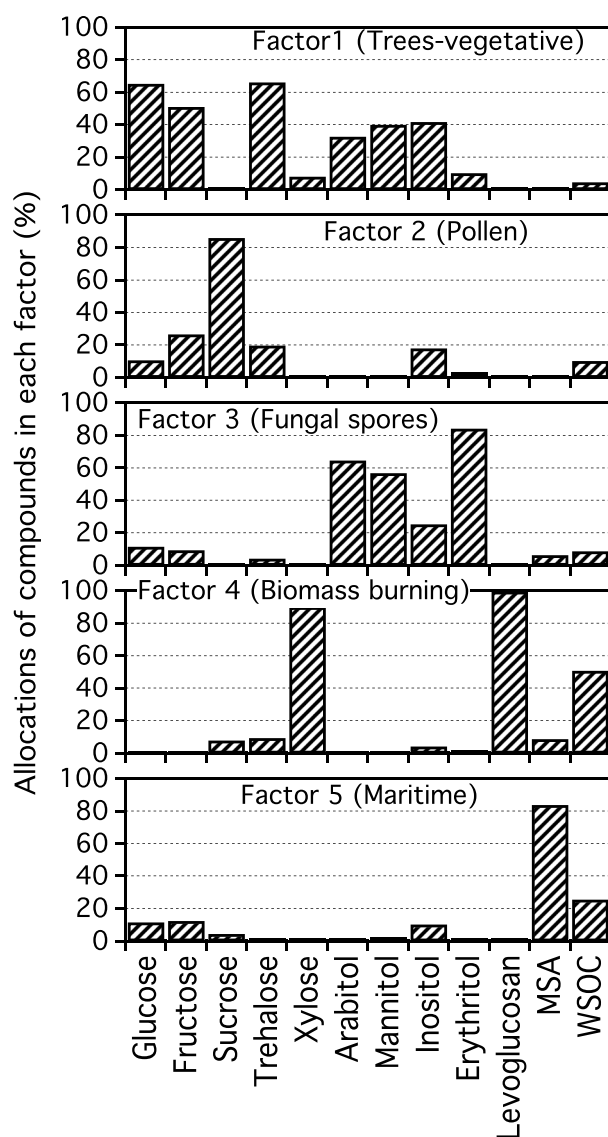


**Figure 7.** Source apportionment of primary saccharides and sugar alcohols in aerosols by positive matrix factorization (PMF) analysis at Cape Hedo, Okinawa.

sugar alcohols were also found in autumn (4.4% and 2.7%, respectively). As a result, the annual mean contribution of primary saccharides to WSOC (4.4%) is higher than that of sugar alcohols (2.7%). Our values are higher than those reported in urban or suburban sites in Norway, where the sum of primary saccharides and sugar alcohols accounts for 0.6–3.6% of WSOC in  $PM_{10}$  [Yttri *et al.*, 2007]. These results indicate that the contributions of primary biological emissions to WSOC are higher in densely vegetated Okinawa than in urban and suburban sites.

Similar seasonal trends were found in the contributions of primary saccharides and sugar alcohols to TSP (Table 4). The contributions of total primary saccharides and sugar alcohols to PM were the highest in summer (0.49%) and the lowest in winter (0.08%), while spring (0.20%) and autumn (0.21%) fell in between. These estimates for Okinawa aerosols are higher than those reported in a suburb of Phoenix, the United States, where total sugar compounds in January–April accounted for 0.11% of  $PM_{10}$  mass [Jia and Fraser, 2011]. One possible reason for such a difference is that we calculated the contributions of PBAP tracers to PM mass in TSP but not  $PM_{10}$ . Some PBAP might be present in coarse particles  $>10\ \mu m$  [Despres *et al.*, 2012]. Our results were also higher than those in urban Nanjing, China, where primary saccharides

### 3.5. Contributions of PBAP Tracers to WSOC and PM

The contributions of primary saccharides and sugar alcohols to WSOC and to TSP are summarized in Table 4. For comparison, the contributions of primary saccharides and sugar alcohols to WSOC are calculated on a carbon basis [e.g., Yttri *et al.*, 2007]. Annually, PBAP tracers contributed 7.1% of WSOC, and the highest contribution (27.6%) was observed on 24 August 2010. Seasonally, contributions of PBAP tracers to WSOC were the highest in summer (14.9%) and lowest in winter (2.5%), indicating that high emission loadings from local vegetation contribute to aerosol WSOC. Based on PMF analysis, Miyazaki *et al.* [2012a] reported that PBAP tracers (sum of sucrose-rich and trehalose-rich factors) contribute ~24% of WSOC in aerosols collected near the deciduous forest floor in early summer, a value which is higher than our estimate in Okinawa. In summer, contributions of primary saccharides and sugar alcohols to WSOC are similar at Cape Hedo, Okinawa (mean values of 7.8% and 7.1%, respectively). In spring, the contribution of primary saccharides to WSOC (4.6%) is higher than that of sugar alcohols (2.2%).

Abundances of sucrose in spring are ~2.5 times higher than in summer, but contributions of sucrose to WSOC in both seasons are almost same (1.0% in spring and 1.1% in summer). This pattern is related to the seasonal changes of WSOC, whose level in spring was ~2 times higher than in summer. Higher contributions of primary saccharides to WSOC than that of

**Table 4.** Contributions of Primary Saccharides and Sugar Alcohols to WSOC (%) and TSP (%) at Cape Hedo, Okinawa, During October 2009 to February 2012<sup>a</sup>

| Compounds                                  | Annual ( <i>n</i> = 112) |            | Winter ( <i>n</i> = 36) |            | Spring ( <i>n</i> = 23) |            | Summer ( <i>n</i> = 23) |            | Autumn ( <i>n</i> = 30) |            |
|--------------------------------------------|--------------------------|------------|-------------------------|------------|-------------------------|------------|-------------------------|------------|-------------------------|------------|
|                                            | Mean ± SD <sup>b</sup>   | Range      | Mean ± SD               | Range      | Mean ± SD               | Range      | Mean ± SD               | Range      | Mean ± SD               | Range      |
| <i>Contribution to WSOC (%)</i>            |                          |            |                         |            |                         |            |                         |            |                         |            |
| Primary saccharides                        | 4.4 ± 4.0                | 0.3–18.9   | 2.1 ± 1.9               | 0.3–10.1   | 4.6 ± 2.4               | 1.2–10.9   | 7.8 ± 5.5               | 1.9–18.9   | 4.4 ± 3.7               | 0.3–15.6   |
| Sugar alcohols                             | 2.7 ± 3.9                | 0.05–17.8  | 0.3 ± 0.4               | 0.05–1.9   | 2.2 ± 3.7               | 0.07–15.6  | 7.1 ± 4.4               | 0.2–17.8   | 2.7 ± 3.1               | 0.2–11.3   |
| Total                                      | 7.1 ± 6.7                | 0.4–27.6   | 2.5 ± 2.2               | 0.4–11.8   | 6.8 ± 4.6               | 1.3–20.4   | 14.9 ± 7.8              | 2.1–27.6   | 7.1 ± 5.2               | 0.5–24.0   |
| <i>Contribution to TSP (%)<sup>c</sup></i> |                          |            |                         |            |                         |            |                         |            |                         |            |
| Primary saccharides                        | 0.14 ± 0.16              | 0.008–0.91 | 0.07 ± 0.08             | 0.008–0.38 | 0.14 ± 0.14             | 0.05–0.73  | 0.27 ± 0.24             | 0.03–0.91  | 0.13 ± 0.13             | 0.008–0.65 |
| Sugar alcohols                             | 0.08 ± 0.12              | 0.001–0.59 | 0.01 ± 0.01             | 0.001–0.06 | 0.06 ± 0.09             | 0.003–0.37 | 0.22 ± 0.13             | 0.009–0.49 | 0.08 ± 0.12             | 0.006–0.59 |
| Total                                      | 0.23 ± 0.25              | 0.009–1.24 | 0.08 ± 0.09             | 0.009–0.45 | 0.20 ± 0.19             | 0.06–0.9   | 0.49 ± 0.31             | 0.08–1.06  | 0.21 ± 0.23             | 0.02–1.24  |

<sup>a</sup>Seasons are divided as December–February in winter, March–May in spring, June–August in summer, and September–November in autumn.<sup>b</sup>SD denotes standard deviation (1σ).<sup>c</sup>The contribution for each sample is first calculated and then the annual/seasonal means are derived.

and sugar alcohols contributed 0.2% and 0.07%, respectively, to TSP during nonhaze days in June and October [Wang *et al.*, 2011b]. This difference could be attributed to difference in vegetation: the subtropical forest in Okinawa has higher emissions of PBAP than a megacity. Throughout the year, primary saccharides (0.07–0.27%) had higher contributions to TSP than sugar alcohols (0.01–0.22%). Annually, primary saccharides and sugar alcohols contributed 0.14% and 0.08% to PM mass, respectively, leading to a total contribution of 0.23% to PM mass.

### 3.6. Abundances of Fungal Spores and PBAP

Fungal spores can directly act as CCN and IN [Haga *et al.*, 2013; Pummer *et al.*, 2012]. Estimates of their abundance may provide information for simulations of their epidemiological effect on human health and radiative effect on climate. In a parallel investigation of spore counts and sugar alcohols, Bauer *et al.* [2008] determined that there were on average 1.7 pg mannitol per spore and 1.2 pg arabitol per spore in urban and suburban Vienna. Di Filippo *et al.* [2013] found a comparative conversion factor of mannitol to fungal spores by considering different abundances of the most representative fungal genera in the atmosphere. Using the conversion factor of 1.7 pg mannitol per spore and average spore mass of 65 pg per spore reported by Elbert *et al.* [2007], we estimated the ambient mass loading of fungal spores for each sample. The annual mean fungal spore loading was calculated as  $0.49 \pm 0.56 \mu\text{g m}^{-3}$ , which contributed  $1.4 \pm 2.1\%$  to TSP mass (Table 5). It is noteworthy that the uncertainties of such calculation and the subsequent estimation of PBAP concentrations cannot be quantified due to the differences in natural environments between Okinawa and other locations previously studied. Nonetheless, the calculation is still meaningful to deepen our understanding on the role of airborne fungal spores in affecting air quality and climate.

The maximum concentration of fungal spores over subtropical Okinawa in summer ( $1.05 \pm 0.54 \mu\text{g m}^{-3}$ ) is comparable to the global mean of  $\sim 1 \mu\text{g m}^{-3}$  [Elbert *et al.*, 2007]. The seasonality is in accordance with the observed fungal abundances in urban and suburban Vienna [Bauer *et al.*, 2008; Winiwarter *et al.*, 2009], urban Hualien, Taiwan [H M Ho *et al.*, 2005], and the simulated results in extratropical regions of the world [Heald and Spracklen, 2009]. The fungal spore abundances in Okinawa (seasonal means of 0.11–1.05  $\mu\text{g m}^{-3}$ ) are lower than those estimated in urban Rome using mannitol as a tracer (0.52–1.87  $\mu\text{g m}^{-3}$ ) [Di Filippo *et al.*, 2013]. However, the fungal contributions to PM mass were higher in Okinawa (0.2–3.8% to TSP in different seasons) than in urban Rome (0.1–0.3% to PM<sub>10</sub>) and nearby suburban/rural sites (0.2–0.8% to PM<sub>10</sub>). These results suggest that the sources of fungal spores in Okinawa are simply from the local forest, in comparison with multiple sources in urban sites.

Using the Goddard Earth Observing System Chemistry model, Heald and Spracklen [2009] estimated that fungal spores make up  $\sim 12\%$  of coarse PBAP. Accordingly, we calculated the annual mean surface PBAP concentrations at Okinawa as  $4.12 \pm 4.65 \mu\text{g m}^{-3}$ , which contributes  $\sim 12\%$  of TSP in Okinawa (Table 5). In summer, when the local biological activity is the highest, the mean PBAP loading was up to  $8.75 \pm 4.51 \mu\text{g m}^{-3}$ , contributing  $\sim 31\%$  of TSP. Nevertheless, it is worth noting that this calculation should be considered as the lower end because the relation between mannitol (and hence force fungal spore) and

**Table 5.** Abundances of Ambient Fungal Spores and Surface PBAP ( $\mu\text{g m}^{-3}$ ) and Their Contribution to TSP (%) at Cape Hedo, Okinawa, During October 2009 to February 2012<sup>a</sup>

| Compounds                                           | Annual ( $n = 112$ )       |            | Winter ( $n = 36$ ) |            | Spring ( $n = 23$ ) |           | Summer ( $n = 23$ ) |           | Autumn ( $n = 30$ ) |           |
|-----------------------------------------------------|----------------------------|------------|---------------------|------------|---------------------|-----------|---------------------|-----------|---------------------|-----------|
|                                                     | Mean $\pm$ SD <sup>b</sup> | Range      | Mean $\pm$ SD       | Range      | Mean $\pm$ SD       | Range     | Mean $\pm$ SD       | Range     | Mean $\pm$ SD       | Range     |
| <i>Abundances (<math>\mu\text{g m}^{-3}</math>)</i> |                            |            |                     |            |                     |           |                     |           |                     |           |
| Fungal spores                                       | $0.49 \pm 0.56$            | 0.004–2.15 | $0.11 \pm 0.13$     | 0.004–0.56 | $0.54 \pm 0.54$     | 0.03–1.58 | $1.05 \pm 0.54$     | 0.1–2.15  | $0.5 \pm 0.54$      | 0.05–2.07 |
| PBAP                                                | $4.12 \pm 4.65$            | 0.04–18.0  | $0.91 \pm 1.09$     | 0.04–4.66  | $4.49 \pm 4.52$     | 0.29–13.2 | $8.75 \pm 4.51$     | 0.79–18.0 | $4.14 \pm 4.52$     | 0.38–17.2 |
| <i>Contributions to TSP (%)<sup>c</sup></i>         |                            |            |                     |            |                     |           |                     |           |                     |           |
| Fungal spores                                       | $1.4 \pm 2.1$              | 0.02–11    | $0.2 \pm 0.2$       | 0.02–1.3   | $1 \pm 1.3$         | 0.06–4    | $3.8 \pm 2.2$       | 0.2–7.8   | $1.3 \pm 2.2$       | 0.09–11   |
| PBAP                                                | $11.6 \pm 17.2$            | 0.15–91.6  | $1.69 \pm 2.02$     | 0.15–10.9  | $8.3 \pm 10.8$      | 0.47–33.7 | $31.3 \pm 18.7$     | 1.46–65.2 | $11 \pm 18.2$       | 0.76–91.6 |

<sup>a</sup>Seasons are divided as December–February in winter, March–May in spring, June–August in summer, and September–November in autumn.<sup>b</sup>SD denotes standard deviation ( $1\sigma$ ).<sup>c</sup>The contribution for each sample is first calculated and then the annual/seasonal means are derived.

PBAP concentration for coarse particles ( $\text{PM}_{10}$ ) was applied to TSP samples. Previous studies showed evidence that Okinawa aerosol is affected by continental outflow of dust [Handa *et al.*, 2011], inorganic ions [Kunwar and Kawamura, 2014; Takami *et al.*, 2007], BC [Kondo *et al.*, 2011; Verma *et al.*, 2011], organic molecular components [Wang *et al.*, 2009; Yamamoto and Kawamura, 2011], along with secondary oxidation products [Kunwar and Kawamura, 2014; Takami *et al.*, 2007]. In the present study, we discovered that primary emissions from local subtropical forest are also important aerosol sources, especially in summer under the trade wind regime when regional sources from anthropogenic pollution and dust are minimal (Figure 3c).

#### 4. Conclusions

We used primary saccharides and sugar alcohols as tracers of PBAPs to investigate their concentrations, seasonal variations, and contributions to WSOC and PM mass in aerosols at Okinawa Island in the western North Pacific Rim, an outflow region of Asian aerosols. We observed the highest abundances of primary saccharides in spring and the highest abundances of sugar alcohols in summer. These seasonal variations were regulated by local meteorological parameters. Local emission from broadleaf forests is the main contributor to the primary saccharides in aerosols in Okinawa. Higher concentrations of mannitol and arabitol in summer imply their main sources to be from microbes and plants in the local subtropical forest. Sporadic high trehalose events along with elevated aerosol masses and  $\text{nss-Ca}^{2+}$  indicate that Okinawa was also influenced by Asian dust outflows that deliver soil organic matter from natural and agricultural source regions, especially in spring. The abundances of PBAP tracers in Okinawa fell between those of Mainland China and remote Chichijima Island, implying that PBAP originating from the Asian continent may be transported long distances to the western North Pacific.

The PBAP tracers showed higher contributions to WSOC in summer (mean: 14.9% and maximum: 27.6%), indicating the importance of PBAP to the climate forcing properties of aerosols. Using mannitol as a tracer, the mean ambient loadings of fungal spore and PBAP were estimated to be  $0.49 \mu\text{g m}^{-3}$  and  $4.12 \mu\text{g m}^{-3}$ , respectively. In summer, PBAP could contribute up to 31% of TSP mass. These results provide information to better understand the impact of PBAP on aerosol chemical and physical properties in the western North Pacific.

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