

- 1 Effect of biomass burning over the western North Pacific Rim: wintertime maxima of
- 2 anhydrosugars in ambient aerosols from Okinawa
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## 6 **Abstract**

7 Biomass burning (BB) largely modifies the chemical composition of atmospheric  
8 aerosols on the globe. We collected aerosol samples (TSP) at Cape Hedo, subtropical  
9 Okinawa Island from October 2009 to February 2012 to study anhydrosugars as BB tracers.  
10 Levoglucosan was detected as the dominant anhydrosugar followed by its isomers,  
11 mannosan and galactosan. We found a clear seasonal trend of levoglucosan and mannosan  
12 with winter maxima and summer minima. Positive correlation was found between  
13 levoglucosan and nss-K<sup>+</sup> ( $r = 0.38, p < 0.001$ ); the latter is another BB tracer. The analyses  
14 of air mass trajectories and fire spots demonstrated that the seasonal variations of  
15 anhydrosugars are caused by long-range transport of BB emissions from the Asian  
16 continent. We found winter maxima of anhydrosugars, which may be associated with open  
17 burning and domestic heating and cooking in north and northeast China, Mongolia and  
18 Russia and with the enhanced westerly winds. The monthly averaged  
19 levoglucosan/mannosan ratios were lower (2.1-4.8) in May–June and higher (13.3-13.9) in  
20 November–December. The lower values may be associated with softwood burning in north  
21 China, Korea and southwest Japan whereas the higher values are probably caused by  
22 agricultural waste burning of maize straw in the North China Plain. Anhydrosugars  
23 comprised 0.22% of water-soluble organic carbon (WSOC) and 0.13% of organic carbon  
24 (OC). The highest values to WSOC (0.37%) and OC (0.25%) were found in winter, again  
25 indicating an important BB contribution to Okinawa aerosols in winter. This study provides  
26 useful information to better understand the effect of East Asian biomass burning on the air  
27 quality in the western North Pacific Rim.

28

29 **Keywords:** biomass burning, levoglucosan, burning substrates, aerosols, East Asia

## 30 1 Introduction

31 Biomass burning (BB) is a large source of atmospheric trace gases and aerosols. During  
32 the burning, numerous organic and inorganic gases and particles are emitted to the  
33 atmosphere (Andreae and Merlet, 2001; Mkoma et al., 2013). Most of the burning-emitted  
34 organic compounds and inorganic ions are water-soluble (Graham et al.; 2002; Mayol-  
35 Bracero et al., 2002; Kundu et al., 2010). They can act as cloud condensation nuclei (CCN)  
36 and ice nuclei (IN) (Penner et al., 1992; Lin et al., 2006; Prenni et al., 2012), affecting  
37 climate by altering the hygroscopic properties of aerosols. Emissions of CO and NO<sub>x</sub> during  
38 BB affect O<sub>3</sub> formation and hence force the oxidation capability of the troposphere  
39 (Galanter et al., 2000; Honrath et al., 2004; Tanimoto et al., 2009). Along with direct  
40 emission of CO<sub>2</sub> (Goode et al., 2000; Konovalov et al., 2014), other greenhouse gases and  
41 particles emitted from BB affect radiative forcing (Langenfelts et al., 2002). Moreover,  
42 carbonaceous components and trace gases in the smoke contribute to respiratory diseases  
43 (Laumbach and Kipen, 2012).

44 There are different types of BB including open field fires in forest, savannas, peat lands,  
45 burning and land cultivation practices, burning of agricultural wastes in the fields and  
46 residential heating and cooking, as well as industrial biofuel burning (Akagi et al., 2011,  
47 2014; Engling et al., 2014). The burning materials range from litters of forest trees and  
48 grasses to biofuels such as crop residues, dung and charcoal (Yevich and Logan, 2003; Hays  
49 et al., 2005; Yan et al., 2006). Emission parameters of burning materials are frequently  
50 represented by emission ratios of a particular species to that of a reference species such as  
51 CO<sub>2</sub> or CO, or to the amount of fuel burned (emission factor) (Andreae and Merlet, 2001;  
52 Akagi et al., 2011). It is difficult, however, to obtain either of these two emission indices

53 because extensive measurements are needed with respect to different burning materials and  
54 emitted trace components.

55 Lots of tracers have been used for BB such as water-soluble non-sea salt potassium (nss-  
56  $K^+$ ) (Sullivan et al., 2011; Urban et al., 2012; Zhang et al., 2013), resin acids (Kawamura et  
57 al., 2012; Zhang et al., 2013) and anhydrosugars (Engling et al., 2006, 2009; Fu et al., 2012;  
58 Mochida et al., 2010). Levoglucosan (1, 6-anhydro- $\beta$ -D-glucopyranose), one of the  
59 anhydrosugars, is exclusively generated by the thermal depolymerization of cellulose  
60 (Simoneit, 2002; Simoneit et al., 1999). This compound is stable in the atmosphere with no  
61 decay over 10 days in acidic conditions (Schkolnik and Rudich, 2006). It was proposed as  
62 the most reliable tracer for BB (Simoneit et al., 1999, 2004). The isomers of levoglucosan,  
63 mannosan and galactosan are generated from pyrolysis of cellulose and hemicelluloses and  
64 also used as BB tracers (Engling et al., 2009; Fabbri et al., 2009).

65 Recent studies, however, demonstrated that degradation of levoglucosan occurred on the  
66 exposure to high levels of hydroxyl radicals (OH). Kinetic studies on the reactivity of  
67 levoglucosan with OH,  $NO_3$ , and  $SO_4^-$  radicals in aqueous phase and model simulations  
68 indicated that levoglucosan can be oxidized by OH radicals in daytime by rates of 7.2 ng  
69  $m^{-3} h^{-1}$  in summer and 4.7 ng  $m^{-3} h^{-1}$  in winter for a polluted continental plume (Hoffmann  
70 et al., 2010). Based on the chamber experiment on levoglucosan oxidation by OH,  
71 Hennigan et al. (2010) reported that levoglucosan has an atmospheric lifetime of 0.7–2.2  
72 days when BB particles are exposed to  $1.0 \times 10^6$  molecules  $cm^{-3}$  of OH. A recent study by  
73 flow reactor indicated that pure levoglucosan is degrading by OH with a rate of  
74  $(9.17 \pm 1.16) \times 10^{-12}$   $cm^3$  molecules $^{-1}$  s $^{-1}$  at 25 °C and 40% relative humidity (RH), and the  
75 average atmospheric lifetime is 1.2–3.9 days (Lai et al., 2014). The effect of temperature on  
76 levoglucosan degradation had been reported consistently positive (Bai et al., 2013; Lai et al.,

77 2014), while the effect of RH is divergent (Hennigan et al., 2010; Lai et al., 2014; Slade and  
78 Knopf, 2014). Nevertheless, the study by Bai et al. (2013) indicated that levoglucosan reacts  
79 with OH at a rate of  $2.21 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 25 °C, resulting in an atmospheric  
80 lifetime of 26 days under the OH level of  $2.0 \times 10^6 \text{ molecule cm}^{-3}$ . Although these results  
81 are divergent, levoglucosan is subjected to degradation in BB aerosols during atmospheric  
82 transport.

83 The relative abundance of anhydrosugar isomers is used as diagnostic parameter for  
84 different BB substrates (Fu et al., 2012; Mkoma et al., 2013). The levoglucosan to  
85 mannosan (L/M) ratio is different for smoke generated by burning of hardwood and  
86 softwood (Engling et al., 2009; Iimuma et al., 2007; Schmidl et al., 2008a, b). L/M ratios  
87 derived from softwood combustion are frequently low, e.g., 3.4 for ponderosa pine, 3.9 for  
88 white spruce, 4.4 for Douglas fir and 6.7 for pinyon pine (Fine et al., 2004), or 2.6–5.0 for  
89 ponderosa pine (Engling et al., 2006), or 3.6–3.9 for spruce and larch (Křůmal et al., 2010).  
90 On the other hand, L/M ratios for hardwood combustion are much higher, e.g., 12.9 for  
91 white oak, 19.8 for sugar maple, 23.4 for black oak, 16.9 for American beech, 19.6 for black  
92 cherry and 14.5 for quaking aspen (Fine et al., 2004), or 14.4–14.8 for oak and beech  
93 (Křůmal et al., 2010). L/M ratios from agricultural waste burning are even higher (25–40)  
94 (Engling et al., 2006, 2009; Fu et al., 2012; Sheesley et al., 2003). However, as the observed  
95 tracers in the ambient air often comprise a mixture of emissions from different burning  
96 substrates, it is still challenging to accurately qualify the burning substrate based on aerosol  
97 observations.

98 East Asia is one of the most active BB regions in the world with high aerosol loadings  
99 (van der Werf et al., 2006). Forest burning resulting from both natural and man-made fires  
100 for land clearing or other purposes comprises 16%, crop residue burning in the agriculture

101 field comprises 12%, grassland and savanna burning arising from prescribed burning,  
102 natural fires, and grassland conversion comprises 7%, and biofuel consumption of fuelwood,  
103 agricultural residues, and dried animal waste for cooking and heating comprises 64% of the  
104 total burnt biomass across the Asian continent (Streets et al., 2003). Regionally, the largest  
105 contributions to BB emissions are from Southeast Asian countries (Philippines, Thailand,  
106 Laos, Malaysia, Myanmar, Vietnam and Indonesia), China and Mongolia, and boreal Asia  
107 (Russia) (Streets et al., 2003; van der Werf et al., 2006, 2010). On the other hand, open  
108 burning (mostly of forest) is a dominant source in Southeast Asia and boreal Asia, while  
109 burning of crop residues is dominant in China and of grassland in Mongolia (Streets et al.,  
110 2003). A recent estimate of  $2.33 \text{ Tg y}^{-1}$  for nonmethane volatile organic compounds  
111 (NMVOCs) is obtained from the burning of crop residues in China (Kudo et al., 2014).  
112 Emissions from such burning may be submitted to long distance transport affecting regional  
113 air quality and climate (Mochida et al., 2010; Kawamura et al., 2012; Chen et al., 2013).

114 In this work, we use anhydrosugars in aerosols as tracers to investigate the influence of  
115 BB on regional air quality in East Asia. We collected aerosol samples at Okinawa from  
116 October 2009 to February 2012 and analyzed for anhydrosugars as well as water-soluble  
117 inorganic ions, water-soluble organic carbon (WSOC), organic carbon (OC) and elemental  
118 carbon (EC). We are aiming to clarify the seasonality of burning in East Asia and its effects  
119 on aerosol properties in the Asian outflow region in the western North Pacific.

120

## 121 **2 Experimental methods**

### 122 2.1 Site and sampling

123 We collected total suspended particle (TSP) samples from October 2009 to February  
124 2012 at Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS) ( $26.9^{\circ}\text{N}$ ,

125 128.2°E) in the northwestern edge of Okinawa Island (Fig. 1). TSP samples were collected  
126 on pre-combusted (450 °C, 3 h) quartz filters (Pallflex 2500QAT, 20 cm × 25 cm) using a  
127 high-volume air sampler (Kimoto AS-810B) at a flow rate of 60 m<sup>3</sup> h<sup>-1</sup> on a weekly basis (n  
128 = 112). Each aerosol-loaded filter was placed in a pre-combusted (450 °C, 6 h) glass jar  
129 with a Teflon-lined screw cap and stored in darkness at -20 °C. Before weighing and  
130 analysis, each filter was placed in a desiccator for 24–72 h at ~20 °C until constant weight  
131 to remove water. Two field blanks following the entire collection procedure except for  
132 running the sampling pump were collected on November 2009 and March 2011,  
133 respectively. The OC levels in the field blanks were consistently low (1.16 and 1.54 µg per  
134 measured unit of 1.54 cm<sup>2</sup>, < 5% of OC levels in most samples), indicating negligible  
135 contamination of the samples.

136 The region near CHAAMS is covered by subtropical evergreen broadleaf forest. There  
137 are industrial practices of biomass recycling to make biofuel pellets for application in power  
138 plants in the southern part of the island, which is 70–80 km from CHAAMS. However, as  
139 the mass of burning is quite limited (biomass production amounted to 3.05 Mt y<sup>-1</sup> in the  
140 whole prefecture over 2000–2003) (Okinawa prefecture, 2005), the influence of local  
141 biomass burning on anhydrosugars in aerosols at Cape Hedo is negligible.

142

## 143 2.2 Measurement of anhydrosugars

### 144 2.2.1 Extraction and derivatization

145 A small filter section (ca. 10 cm<sup>2</sup>) was sonicated three times for 10 min in a mixture (7  
146 ml) of dichloromethane/methanol (2:1; v/v). The solvent extracts were filtered through  
147 quartz wool packed in a Pasteur pipette to remove particles. The filtrate was concentrated in  
148 a pear-shape flask by a rotary evaporator under vacuum down to 1 ml, and then dried with

149 pure nitrogen gas in a 1.5 ml glass vial. Compounds in the extracts were then converted to  
150 their trimethylsilyl (TMS) derivatives by reacting with 50  $\mu\text{l}$  of N, O-bis-  
151 (trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethyl chloride and 10  $\mu\text{l}$  of  
152 pyridine for 3 h at 70  $^{\circ}\text{C}$ . OH groups of anhydrosugars in the extracts were derivatized to  
153 trimethylsilyl (TMS) ethers before GC/MS quantification (Medeiros and Simoneit, 2007; Fu  
154 et al., 2008).

155

### 156 2.2.2 Gas chromatography-mass spectrometry

157 A small fraction (2  $\mu\text{l}$ ) of derivatized extracts was analyzed using gas chromatography-  
158 mass spectrometry (GC/MS): Agilent 7890A GC interfaced with Agilent 5975C mass-  
159 selective detector (MSD). An HP-5ms Ultra Inert capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  
160  $\mu\text{m}$ ) was used with helium as a carrier gas at a flow rate of 1.0 ml  $\text{min}^{-1}$ . The sample was  
161 injected in a splitless mode at 280  $^{\circ}\text{C}$ . The column temperature was programmed from 50  $^{\circ}\text{C}$   
162 (2 min) to 120  $^{\circ}\text{C}$  at 15  $^{\circ}\text{C min}^{-1}$  and then to 305  $^{\circ}\text{C}$  at 5  $^{\circ}\text{C min}^{-1}$ , followed by a final  
163 isothermal hold at 305  $^{\circ}\text{C}$  for 15 min. The mass spectrometer was operated in electron  
164 ionization (EI) mode at 70 eV and scanned over the m/z range of 50–650 Da.

165 Mass spectral data were acquired and processed using the HP-Chemstation software.  
166 Individual anhydrosugars were identified by comparison with the retention times and mass  
167 spectra of authentic standards and the mass spectral library of HP-Chemstation (Medeiros  
168 and Simoneit, 2007). Relative response factor of levoglucosan was obtained by comparing  
169 the peak area differences of the authentic standards to the internal standard (tridecane in n-  
170 hexane, ca. 1 ng  $\mu\text{l}^{-1}$  in the extracts before injection). Concentration of levoglucosan in each  
171 of the ambient samples was determined by comparing its relative response factor with that  
172 of the authentic standard. The relative response factor for levoglucosan was also applied in



173 mannosan and galactosan. Recoveries for levoglucosan were 83–97% for four replicates as  
174 obtained by spiking standards to pre-combusted quartz filters following the extraction and  
175 derivatization described above. No peaks were found for anhydrosugars in the laboratory  
176 and field blank filters. The analytical errors by duplicate sample analyses were less than  
177 15%. The limit of detection (LOD) of levoglucosan was  $520 \text{ pg } \mu\text{l}^{-1}$ , under a mean signal to  
178 noise ratio (S/N) of 84 in three replicate injections (279 pg per injection), which  
179 corresponds to  $0.005 \text{ ng m}^{-3}$  for ambient aerosols under a typical sampling volume of 9000  
180  $\text{m}^3$ , and an aliquot of  $10 \text{ cm}^2$  of the used filter. LODs of mannosan and galactosan are  
181 considered the same as for levoglucosan, because levoglucosan was used as surrogate  
182 standard for mannosan and galactosan.

183

### 184 2.3 Water-soluble inorganic ions and carbonaceous components

185 Major water-soluble inorganic ions were determined using an ion chromatograph (IC)  
186 (761 Compact IC, Metrohm, Switzerland) following Kunwar and Kawamura (2014). The  
187 detection limits for anions and cations were ca.  $0.1 \text{ ng m}^{-3}$ . Based on IC-determined  $\text{K}^+$ ,  
188  $\text{SO}_4^{2-}$  and  $\text{Na}^+$ , we estimated the fractions of  $\text{K}^+$  ion derived from sea salt (ss) and none-sea-  
189 salt (nss-) sources following the method of George et al. (2008). The results of nss- $\text{K}^+$ ,  
190  $\text{NH}_4^+$  and nss- $\text{SO}_4^{2-}$  are discussed in this study. We also investigated  $\text{K}^+$  components using  
191 a tracer-based method (Pio et al., 2008) and positive matrix factorization (PMF) model  
192 (Paatero and Tapper, 1994) (Supplementary materials). Water-soluble organic carbon  
193 (WSOC) was measured using a Shimadzu carbon/nitrogen analyzer (TOC-V<sub>CSH</sub>). following  
194 Miyazaki et al. (2011). The analytical errors for water-soluble inorganic ions and WSOC in  
195 duplicate analyses of laboratory standards were both within 5%. The concentrations of ions  
196 and WSOC in the samples were corrected for field blanks.

197           Organic carbon (OC) and elemental carbon (EC) were determined using a  
198 thermal/optical carbon analyzer (Sunset Laboratory Inc., USA) (Birch and Cary, 1996),  
199 following the Interagency Monitoring Protected Visual Environments (IMPROVE) thermal  
200 evolution protocol. Details on the determination were described elsewhere (Wang et al.,  
201 2005). The analytical errors in replicate analyses were within 8% for OC and 5% for EC.  
202 The OC and EC concentrations in the samples were corrected for field blanks. The data of  
203 inorganic ions, WSOC and OC/EC for the first year are from Kunwar and Kawamura  
204 (2014).

205

#### 206 2.4 Backward trajectories and fire counts

207           In order to investigate the influence of biomass burning in different part of East Asia on  
208 anhydrosugars in aerosols at Cape Hedo, Okinawa, 5-day backward trajectories starting at  
209 500 m above ground level at 0900 local time were calculated every day from December  
210 2009 to November 2011 using HYSPLIT4 (Draxler and Rolph, 2013). Six-hourly archived  
211 Global Data Assimilation System (GDAS) ( $1^{\circ}\times 1^{\circ}$ ) from the National Centers for  
212 Environmental Prediction (NCEP) (<http://ready.arl.noaa.gov/gdas1.php>, accessed July 8,  
213 2014) were used as meteorological data. Cluster analyses were then applied to better  
214 illustrate the characteristic air mass origins, in which three seed clusters (centroids) were  
215 generated in each month. Cluster trajectories were also generated for typical anhydrosugar  
216 events (three seed clusters in each event), where hourly trajectories were obtained for each  
217 event period. Burning activities in East Asia were illustrated by fire spots, whose data were  
218 obtained from Fire Information for Resource Management System (FIRMS) operated by  
219 National Aeronautics and Space Administration (NASA) of the United States (available at  
220 <https://earthdata.nasa.gov/data/near-real-time-data/firms>, accessed July 8, 2014).

221

222 **3 Results and discussions**

## 223 3.1 Air mass origins and fire counts

224 Monthly backward trajectories and fire spots in 2010–2011 (December 2009 to  
225 November 2011) are plotted in Figure 2. In December and January, air masses are  
226 exclusively originating from the Asian continent (Fig. 2a–b). These are the months of the  
227 strongest influence of Asian outflow dominated by the winter Asian monsoon. Specifically,  
228 65–70% of air masses originated from west to middle Russia, passed through Mongolia,  
229 north and northeast China, en route the East China Sea to Okinawa, while another 30–35%  
230 of air masses originating from north and northeast China had shorter transport distances.  
231 These areas are generally located in 30–60 °N, 80–130 °E, and will be termed as Middle to  
232 North Asia (MNA) in this study. In December and January, fire spots were observed in  
233 north and northeast China. However, few fire spots were observed in the winter months in  
234 Mongolia and Russia.

235 As season changed from winter to summer, the influence of continental outflow from  
236 MNA was weakened, whereas the influence of maritime air masses was strengthened. In  
237 June–August, 75–85% of the air masses were originating from the western Northern Pacific,  
238 while the remaining 15–25% were originating from the East China Sea, South China Sea  
239 and Philippine islands (Fig. 2g–i). Interestingly, there are very few air mass trajectories  
240 passing through Southern China throughout the year, where dense fire spots were observed.  
241 From summer to winter, air masses shifted reversely to those of continental origin, until the  
242 highest influence of continental outflow from MNA in December–January.

243 Based on satellite observation and model simulation, Van der Werf et al. (2006) reported  
244 that BB emissions in boreal East Asia (most of Russia) maximized in summer, whereas in

245 central Asia (Mongolia, China and Japan) they showed a bimodal pattern with two maxima  
246 in spring and autumn. Monthly total fire counts in MNA indicated a consistent pattern with  
247 a major peak in May (total counts 45020) and a secondary peak in October (total counts  
248 17838) (Fig. S1). In Southeast Asia, they maximized in spring. Furthermore, Van der Werf  
249 et al. (2010) reported that the dominant type was forest fire in Russia and part of northeast  
250 China, savanna in Mongolia and Inner Mongolia of China, agricultural wastes in north and  
251 northeast China, and deforestation in south China and Southeast Asia. With considerations  
252 of such seasonality and fire types, the biomass burning types that affect Okinawa aerosols  
253 could be summarized as follows: both indoor and open field burning of woods and  
254 agricultural wastes in MNA in winter, open burning of wheat straw in north China in spring,  
255 and open burning of maize straw in north and northeast China in autumn. There is little  
256 influence of BB on Okinawa aerosols from South China and Southeast Asia where  
257 deforestation is the main BB source.

258

## 259 3.2 Effect of biomass burning in East Asia on anhydrosugars at Okinawa

### 260 3.2.1 Seasonal variation of anhydrosugars

261 Temporal and monthly means of anhydrosugars are plotted in Figure 3, and the annual  
262 and seasonal means and ranges are shown in Table 1. Of the three isomers, levoglucosan is  
263 most abundant with a mean concentration of  $3.09 \pm 3.70 \text{ ng m}^{-3}$  (mean  $\pm 1 \sigma$ ). Mannosan  
264 and galactosan are 1 order of magnitude less abundant than levoglucosan. Seasonally,  
265 levoglucosan clearly shows a winter maximum ( $5.30 \pm 4.88 \text{ ng m}^{-3}$ ) and summer minimum  
266 ( $0.57 \pm 0.84 \text{ ng m}^{-3}$ ). Specifically, the monthly mean of levoglucosan in December ( $7.21 \pm$   
267  $7.14 \text{ ng m}^{-3}$ ) is  $> 20$  times higher than that in July ( $0.34 \pm 0.20 \text{ ng m}^{-3}$ ) (Fig. 2). A similar  
268 seasonal trend was observed for mannosan ( $0.47 \pm 0.38 \text{ ng m}^{-3}$  in winter and  $0.08 \pm 0.12 \text{ ng}$

269  $\text{m}^{-3}$  in summer). However, galactosan did not show such a clear seasonal trend. This is  
270 likely associated with changes in the relative content of cellulose and hemicellulose in  
271 varying BB fuel types along with changes in seasons and source regions. A second possible  
272 reason may be the different degradation rate of galactosan than those of levoglucosan and  
273 mannosan. Following the trend of levoglucosan, total anhydrosugars maximized in  
274 December ( $7.91 \pm 7.63 \text{ ng m}^{-3}$ ) and minimized in August ( $0.71 \pm 0.52 \text{ ng m}^{-3}$ ), with a mean  
275 of  $3.53 \pm 3.91 \text{ ng m}^{-3}$  over the sampling period.

276 The primary cause of the seasonality of the three anhydrosugars in Okinawa aerosols is  
277 the shift of air mass source regions. The highest levels of levoglucosan and mannosan in  
278 winter months are associated with the most strengthened continental outflow from MNA  
279 (Fig. 2a–c, 3). The decreases of these anhydrosugars in summer months co-occur with the  
280 weakening of continental outflow. As a result, the lowest levels in summer were caused by  
281 the transport of air masses from the ocean, where there was no source of biomass burning.  
282 The winter and the summer cases are discussed separately as follows.

283

### 284 3.2.2 Effect of continental outflow on high anhydrosugar concentrations in winter

285 Under the enhanced continental outflow in winter, higher abundances of anhydrosugars  
286 in Okinawa aerosols are likely caused by two sources of biomass burning in MNA as  
287 follows: open field burning and domestic burning for space heating and cooking. Fire spots  
288 in north and northeast China indicate large scale burning in the open fields (Fig. 2 a–e, l).  
289 Most of the air masses arriving at Okinawa passed through such regions. One example is the  
290 high anhydrosugar event observed in November 2–9, 2010 (see Fig. 3, Event I). During this  
291 period, air masses originated from or passed through north to northeast China, where high  
292 loadings of fire spots were observed (Fig. 4a).

293 Domestic burning for heating and cooking in winter is another source of anhydrosugars,  
294 as such practice is common in MNA. Yan et al. (2006) reported that satellite observation  
295 detected less than 1% of the burning of total crop residues recorded by ground observation  
296 survey, due to a large portion of indoor burning or small sizes of field burning that could not  
297 be detected by satellite. Therefore, domestic burning for heating and cooking in MNA may  
298 have largely contributed to anhydrosugars in aerosols at Okinawa although relatively small  
299 amount of fire spots were observed in winter. Another example is the highest anhydrosugar  
300 level of the sample collected in December 28, 2010–January 4, 2011, (Fig. 3, Event II).  
301 Backward trajectory clusters indicate that 63% of the air masses were originated from the  
302 southeastern edge of Russia, and transported over northeast China, whereas the remaining  
303 37% were transported longer distances from western Russia (Fig. 4b). However, only few  
304 fire spots were detected in such region, implying that major burning activities leading to the  
305 elevated emissions of anhydrosugars are not in the open field, but may have been associated  
306 with indoor biofuel burning. Zhang et al. (2008) also reported that, of  $9.6 \times 10^7$  kg crop  
307 residues in northeast China (Heilongjiang, Liaoning, Jilin provinces and Inner Mongolia  
308 district) in 2004, about half was burned in the open field (22%) and indoor (26%).

309

### 310 3.2.3 Anhydrosugar levels in summer

311 There is little air mass delivery from the Asian continent that directly affects  
312 anhydrosugars in Okinawa aerosols during summer (Fig. 2g–i, 3). Air masses from the  
313 western North Pacific in summer are expected to bring “clean” air without the contribution  
314 of anhydrosugars. Moreover, the summer minimum of levoglucosan at Okinawa ( $0.32 \text{ ng m}^{-3}$ )  
315 was 78% higher than that at Chichijima, a remote oceanic site in the western North  
316 Pacific, ca. 1400 km east of Okinawa (Mochida et al., 2010). Other than the dilution and

317 deposition during long-range transport, the gradient of anhydrosugars from Okinawa to  
318 Chichijima suggests that levoglucosan may undergo photochemical degradation in the  
319 troposphere. A higher level of OH in the troposphere is expected in summer as a result of  
320 higher temperature and stronger ultraviolet light (Stone et al., 2012), which would lead to  
321 the degradation of levoglucosan (Hennigan et al., 2010; Hoffmann et al., 2010; Mochida et  
322 al., 2010).

323 A clear diurnal cycle of OH was observed at Okinawa showing a daytime maximum of  
324 around  $4 \times 10^6$  radicals  $\text{cm}^{-3}$  in summer (Kanaya et al., 2001). In light of literature reports  
325 on levoglucosan degradation by OH (Hennigan et al., 2010; Lai et al., 2014), the average  
326 atmospheric lifetime of levoglucosan could be roughly estimated as 1 day in summer and 3  
327 days in winter. The corresponding transport distances of levoglucosan in summer and  
328 winter are estimated by weighted arithmetic means of trajectory clusters as represented in  
329 July and January, respectively. In July, air masses traveled 564 km for 1 day before arriving  
330 at Cape Hedo, where the regions passed over were mostly ocean with no BB sources.  
331 Therefore, the observed low levels of anhydrosugars in summer represent a regional  
332 background level, incorporating atmospheric deposition and degradation. Similarly, Hu et al.  
333 (2013) reported that levoglucosan was detected in marine aerosols from the Arctic in boreal  
334 summer to the Antarctic in austral summer at  $\text{ng m}^{-3}$  levels. In comparison, air masses  
335 traveled 2480 km for 3 days before arriving at Cape Hedo in January, a distance in which  
336 MNA was broadly passed through. It can be inferred that degradation plays a minor role in  
337 winter during strengthened continental outflow under low temperature and high wind speed  
338 conditions.

339 On the contrary to our expectation, there was little influence of biomass burning in  
340 Southeast Asia to anhydrosugars in Okinawa aerosols (Fig. 2). In August 26% of the air

341 masses originated from the Philippine islands, however very few fire spots were detected by  
342 satellite (84 and 9 counts in the whole Philippines and close to the trajectory centroid,  
343 respectively). Previous studies indicated that biomass burning in the Philippine islands  
344 control the levels of anhydrosugars in the northwest aerosols at Hok Tsui, Hong Kong and  
345 Hainan in coastal southeast China in spring (Zhang et al., 2012). However, the biomass  
346 burning in the Philippines did not seriously affect the aerosols in the northeast region where  
347 Okinawa is located. Anhydrosugars emitted from the Philippine region are likely  
348 decomposed and/or scavenged from the atmosphere by dry/wet deposition in summer  
349 before arriving at Okinawa, given the long travel distance of ~2000 km, more frequency of  
350 precipitation and short lifetime of levoglucosan (roughly 1 day, corresponding to 663 km in  
351 the trajectory cluster).

352

### 353 3.3 Relations between anhydrosugars and inorganic ions and EC

354 Linear correlations among anhydrosugars and major ions that are possibly related to BB  
355 were investigated (Table 2). Positive relations were found between levoglucosan and  
356 mannosan over the whole observation period ( $r = 0.34$ ,  $p < 0.001$ ) as well as in each season  
357 (Table 3), indicating that they were derived from similar emission sources. Galactosan did  
358 not co-vary with other anhydrosugars, probably due to different BB types that vary with  
359 time and source region and/or different degradation rate.

360 Nss-K<sup>+</sup> is another typical tracer of BB (Sullivan et al., 2011). Positive correlations were  
361 found between nss-K<sup>+</sup> and levoglucosan ( $r = 0.38$ ,  $p < 0.001$ ) and mannosan ( $r = 0.36$ ,  $p <$   
362  $0.001$ ), supporting that these components are derived from BB. Using levoglucosan as a  
363 representative BB tracer, the correlations between anhydrosugars and nss-K<sup>+</sup> were further  
364 investigated for seasonal profiles (Table 3). Levoglucosan significantly correlates with nss-



365  $K^+$  in winter ( $r=0.49$ ,  $p < 0.001$ ), spring ( $0.59$ ,  $p < 0.001$ ) and summer ( $0.86$ ,  $p < 0.001$ ). No  
366 correlation in autumn may suggest other sources of nss- $K^+$ , possibly derived from soil  
367 resuspension during agricultural plowing practices before winter wheat planting in the  
368 North China Plain. Previous studies also indicated that soil dust could be another source of  
369 water-soluble nss- $K^+$  in Asian aerosols (Arimoto et al., 2004; Duvall et al., 2008; Shen et al.,  
370 2009).

371 To further account for the fraction of BB-derived  $K^+$  (bb- $K^+$ ), the  $K^+$  balance was  
372 investigated using a tracer-based method and PMF model (Supplementary materials). Pio et  
373 al. (2008) reported that bb- $K^+$  could be calculated by subtracting ss- $K^+$  and dust-related  $K^+$   
374 (dust- $K^+$ ) from total  $K^+$ , using a typical  $K^+/Ca^{2+}$  ratio of 0.12 for soil dust in Europe. In East  
375 Asia,  $K^+/Ca^{2+}$  ratios during dust storm periods are reported as 0.012 in Zhenbeitai, northern  
376 China (Arimoto et al., 2004), 0.07 in Xi'an, northwestern China (Shen et al., 2009), and  
377 0.12 in Tongliao, northeastern China (Shen et al., 2007). We estimated the  $K^+$  component  
378 using an average  $K^+/Ca^{2+}$  ratio of 0.07 for Asian dust, following the method of Pio et al.  
379 (2007, 2008). We found that bb- $K^+$  accounted for 23% of total  $K^+$ . This result is similar to  
380 that (24%) obtained by PMF model (Fig. 5). Interestingly, the relation between  
381 levoglucosan and tracer-based bb- $K^+$  was not strong, although a positive relation was found  
382 between levoglucosan and nss- $K^+$ . This phenomenon, as well as the seasonal difference of  
383 the relations between levoglucosan and nss- $K^+$ , might be caused by the following reasons:  
384 (1) during open field burning, a large amount of dust- $K^+$  is mixed with bb- $K^+$ ; (2) dust- $K^+$   
385 and bb- $K^+$  are mixed during atmospheric transport. Being consistent with previous studies,  
386 these results suggest that a combined analysis of  $K^+$  and other tracers is recommended to  
387 characterize BB activities (Zhang et al., 2010).

388 On the other hand, positive relations were found between  $\text{NH}_4^+$  and levoglucosan ( $r =$   
389  $0.39, p < 0.001$ ) and mannosan ( $r = 0.20, p < 0.05$ ). These results imply that BB in MNA  
390 could be an important direct source of  $\text{NH}_4^+$  (Andreae and Merlet et al., 2001; Akagi et al.,  
391 2011).  $\text{NH}_4^+$  could also be formed in the atmosphere by the protonation of  $\text{NH}_3$ , which is  
392 abundantly emitted from livestock excreta, fertilizer application, agricultural soil and plants,  
393 biomass burning, and so on (Asman et al., 1998; Huang et al., 2012; Paulot et al., 2014;  
394 Sutton et al., 2008; Zhang et al., 2010). The seasonal relations between levoglucosan and  
395  $\text{NH}_4^+$  showed no correlation in summer and autumn although there is a weak positive  
396 correlation in winter and spring. This may be caused by the enrichment of  $\text{NH}_3$ -derived  
397  $\text{NH}_4^+$  from agricultural activities, and transformation and wet scavenging during  
398 atmospheric transport. Levoglucosan did not correlate with  $\text{nss-SO}_4^{2-}$  ( $r=0.12$ ), indicating  
399 that sulfur emission from BB may not be significant.

400 Biomass burning is frequently accompanied by elevated emission of EC (Akagi et al.,  
401 2011). Positive relations of EC with levoglucosan ( $r = 0.31, p < 0.05$ ) and mannosan ( $r =$   
402  $0.52, p < 0.001$ ) were obtained (Table 2). These results indicate that EC in Okinawa  
403 aerosols is partly derived from BB. Meanwhile, air masses with mixed sources from  
404 emissions of BB and fossil fuel would also result in such relations. Observation of black  
405 carbon (BC) by aethalometer at Rishiri Island, northern Japan indicated outflow of a high  
406 BC level from fossil fuel combustion from the Asian continent (Zhu et al., 2015b). Fossil  
407 fuel combustion in the Asian continent is probably a more significant source of EC in  
408 Okinawa aerosols compared to BB sources. Seasonally, levoglucosan correlates  
409 significantly with EC in summer, autumn and winter. No correlation in spring may be  
410 associated with a higher EC source from fossil fuel combustion in the upwind Asian  
411 continent.

412

## 413 3.4 Implication for burning substrates based on L/M ratios

414 The levoglucosan/mannosan (L/M) ratio was used to differentiate the burning substrates  
415 (Table 1, Fig. 6). Monthly L/M ratios ranged from 2.1 to 4.8 in May–June and from 12.3 to  
416 13.9 in November–January. Higher ratios were found in late autumn to winter whereas  
417 lower ratios in late spring to early summer (Fig 6b). Previous biomass burning studies  
418 showed that L/M ratios from crop residues are often  $> 40$ , whereas those from hard wood  
419 are in a range of 15–25, and those of soft wood to be 3–10 (Schmidl et al., 2008a, b;  
420 Engling et al., 2009; Fu et al., 2012; Mkoma et al., 2013; Engling et al., 2014). Higher  
421 monthly means of L/M ratios in November–January suggest that the burning substrates  
422 were hardwood, a mixture of softwood and hardwood, or a mixture of softwood and plant  
423 straws in NMA. The lower L/M ratios in May–June suggest that Okinawa aerosols are  
424 influenced by the burning of softwood, possibly from north China, Korea or southwest  
425 Japan, as supported by backward trajectories (Fig 2 f–g). It is worth noting that the possible  
426 different degradation rates between levoglucosan and mannosan would contribute to L/M  
427 variations. With respect to this point, the low L/M ratios in May–June may imply that  
428 levoglucosan is degrading faster than mannosan during atmospheric transport.

429 Sporadically high L/M ratio events were observed. The highest ratio of 38.9 was  
430 observed in the sample collected on October 27–November 3, 2009. Elevated  
431 concentrations of OC, EC and water-soluble ions were also observed for this sample. On  
432 these days, 44% of the air masses originated from the North China Plain, while another 28%  
433 originated from west Siberia, en route Mongolia and north China to Okinawa (Fig. 7).  
434 October–November are the harvest season of maize in the North China Plain where fire  
435 spots were observed. This event indicates that emissions of particulate matter from burning

436 of maize straw residues were transported to the western North Pacific. High L/M ratios had  
437 been reported for smoke from chamber burning of rice straw (40–42) and ambient aerosols  
438 affected by burning of wheat straw (40–46) (Engling et al., 2009; Fu et al., 2008). A higher  
439 average L/M ratio of 55 was obtained for the burning of rice straw, wheat straw and maize  
440 straw by chamber experiment (Zhang et al., 2007). These results implied that maize straw  
441 smoke may have a higher L/M ratio. Our results gave a relatively high L/M ratio of 38.9  
442 even after long-range transport to Okinawa, supporting the above proposition.

443 Nevertheless, two high L/M ratios (24.7 and 22.4) were observed on July 15–27, 2010  
444 and June 30–July 12, 2011, respectively. During July 15–27, 2010, the air masses traveled  
445 short distances originating from the western North Pacific where little source of  
446 anhydrosugars is present. The high L/M ratios might be related to local burning events from  
447 industrial biofuel production/consumption or open field cooking for barbeque. On the other  
448 hand, on June 30–July 12, 2011, 44% of air masses originated from east Indonesia, en route  
449 Philippines to Okinawa. Burning of agricultural residues, as well as burning of wood and  
450 peat might contribute to high L/M ratios (Sheesley et al., 2003; Engling et al., 2014).

451

#### 452 3.5 L/OC and L/EC ratios

453 The levoglucosan to OC (L/OC) ratio has been used to evaluate the contribution of  
454 different BB sources (Sullivan et al., 2008; Mkoma et al., 2013; Ho et al., 2014), and  
455 possible aging of levoglucosan (Mochida et al., 2010). Clear seasonal trends were found for  
456 L/OC, with a maximum in winter ( $4.6 \times 10^{-3}$ ) and minimum in May ( $0.3 \times 10^{-3}$ ) (Fig. 6 c–d,  
457 Table 1). This seasonal trend is consistent with those reported for a coastal Asian  
458 continental site in Changdao, China (Feng et al., 2007), four cities in the Pearl River Delta

459 Region in South China (Ho et al., 2014), and a remote maritime site (Chichijima) in the  
460 western North Pacific (Mochida et al., 2010).

461 Here, we discuss the longitudinal gradient of L/OC in Changdao, Okinawa and  
462 Chichijima in the context of the Asian outflow. It is worth noting that, in comparison to the  
463 other two sites (2001–03), the data of Okinawa aerosols were obtained in different years  
464 (2009–12) when the tropospheric oxidizing capability was likely enhanced (Itahashi et al.,  
465 2014). However, such comparison is still helpful for understanding atmospheric processes  
466 in terms of deposition and degradation of levoglucosan. Interestingly, L/OC ratios at  
467 Okinawa are in between those of Changdao and Chichijima in winter ( $10.0 \times 10^{-3}$ ,  $4.6 \times 10^{-3}$   
468  $^3$  and  $3.8 \times 10^{-3}$  for Changdao, Okinawa and Chichijima, respectively), spring ( $9.3 \times 10^{-3}$ ,  
469  $1.6 \times 10^{-3}$  and  $1.3 \times 10^{-3}$ ) and autumn ( $5.4 \times 10^{-3}$ ,  $1.5 \times 10^{-3}$  and  $1.1 \times 10^{-3}$ ). This  
470 longitudinal gradient suggests that levoglucosan may be degraded during the atmospheric  
471 transport. Alternative interpretations for this difference include the formation of OC during  
472 transport and/or the enrichment of OC from the local terrestrial/maritime biosphere of  
473 Okinawa and Chichijima. In summer when the L/OC ratio at Changdao ( $1.2 \times 10^{-3}$ ) is the  
474 highest among the three sites, the L/OC ratio at Okinawa ( $0.3 \times 10^{-3}$ ) is lower than that of  
475 Chichijima ( $0.6 \times 10^{-3}$ ). This may be caused by elevated local biogenic sources of OC in  
476 summer at Okinawa Island, where subtropical forests emit a large amount of primary  
477 organic aerosols (Zhu et al., 2015a).

478 EC is emitted primarily via coal combustion, motor vehicle exhaust and BB (Cao et al.,  
479 2005; Waked et al., 2014, Yttri et al., 2014). The ratio between levoglucosan and EC  
480 (L/EC) was also investigated (Fig. 5 e–f, Table 1). Showing a similar behavior as the L/OC  
481 ratios, the L/EC ratios indicate a clear seasonal trend with winter maximum ( $14.5 \times 10^{-3}$ )  
482 and summer minimum ( $3.3 \times 10^{-3}$ ). Moreover, the L/EC ratios in Okinawa and Chichijima

483 are one order of magnitude lower than those of Changdao in winter, spring and autumn  
484 (Feng et al., 2007; Mochida et al., 2010). As there was little source of EC in the ocean, this  
485 result may imply a degradation of levoglucosan during atmospheric transport. In summer,  
486 the L/EC ratios in Okinawa ( $3.3 \times 10^{-3}$ ) and Chichijima ( $6.5 \times 10^{-3}$ ) were of the same order  
487 as those of Changdao ( $4.0 \times 10^{-3}$ ). Other than levoglucosan degradation, this is also likely  
488 related to the relatively high level of EC in summer at Changdao. Although a clear seasonal  
489 variation was found for the longitudinal gradient of levoglucosan between Changdao and  
490 Okinawa (the ratios for these two sites are 27.9, 25.3, 7.5 and 18.3 for winter, spring,  
491 summer and autumn, respectively) with winter maximum and summer minimum, the  
492 longitudinal gradient of EC (6.9, 2.6, 6.5, 5.0) was similar between winter and summer. As  
493 long as the majorities of the air masses are from the ocean for all these three sites in summer,  
494 there is a higher emission of EC from local fossil fuel combustion at Changdao, whereas EC  
495 at Okinawa and Chichijima might represent a regional background level. Compared to other  
496 seasons, the elevated EC at Changdao in summer lowered the L/EC ratio to a comparative  
497 level as those of the maritime sites.

498

### 499 3.6 Contributions of biomass burning to WSOC, OC and TSP

500 Positive linear relations were found between the sum of the three anhydrosugars or each  
501 anhydrosugar component separately and WSOC (Table 2), as well as between levoglucosan  
502 and WSOC in each season (Table 3). Although the relations between levoglucosan and OC  
503 in most of the seasons are not significant (Tables 2, 3), a clear seasonal trend of L/OC ratios  
504 indicates that the contribution of anhydrosugars to OC varied depending on season (Fig. 6  
505 c–d). We further investigated the contributions of the anhydrosugar carbon to the WSOC  
506 and OC, and of the total anhydrosugar mass to the TSP (Table 4). The anhydrosugars

507 account for 0.22% of the WSOC and 0.13% of the OC annually. The highest contributions  
508 of the anhydrosugars to the WSOC (0.37%) and OC (0.25%) were obtained in winter,  
509 indicating a strong influence of BB on winter aerosols. The contribution of the  
510 anhydrosugars to the WSOC in Okinawa is lower than that of the Amazon rainforest sites  
511 (levoglucosan-C/WSOC of 2–7%) where the burning happened in situ (Graham et al., 2002).  
512 These values are also lower than those of the Pearl River Delta sites in China  
513 (levoglucosan-C/WSOC of 0.59–3.12%) that are directly affected by biomass burning in  
514 South China (Ho et al., 2014). The anhydrosugars accounted for 0.006% of the TSP on an  
515 annual basis in Okinawa aerosols with maximum (0.01%) in winter.

516 The L/OC ratio has been used to estimate the contributions of BB to the OC in aerosols  
517 as stated above. The L/OC ratios ranged from 8.0 to 8.2% in the burning of savanna and  
518 grassland, tropical and extratropical forest, biofuel and agricultural residues (Andreae and  
519 Merlet, 2001). Moreover, the mean emission factor of L/OC during the burning of wheat,  
520 corn and rice straws in China was derived as 8.27% (Zhang et al., 2007). Although the  
521 L/OC ratios in the BB source emissions vary among different types of biomass fuels and  
522 burning conditions (e.g., Mochida et al., 2010), the value of ~8.2% has been widely used to  
523 estimate BB contributions to the OC (Fu et al., 2014; Graham et al., 2002; Ho et al., 2014;  
524 Mkoma et al., 2013; Sang et al., 2011). Using the L/OC ratio of 8.2% from the source of  
525 biomass burning, we estimated that biomass burning in East Asia contributes 2.9% of the  
526 OC in Okinawa aerosols on an annual basis (Table 4). This is lower than the contribution of  
527 BB to the OC in the Pearl River Delta in China (13.1%) (Ho et al., 2014). However, in  
528 winter, the mean contribution from biomass burning was 5.6%, although the highest  
529 contribution became as large as 30%. A further estimation on the OC components by PMF  
530 analysis may provide more information, which would be our future work. These results

531 indicate that BB, especially from MNA in winter, may significantly affect the regional air  
532 quality in Okinawa in winter, especially during Asian outflow episodes.

533

#### 534 **4 Conclusions**

535 Anhydrosugars were studied in aerosols from Okinawa, Japan for their abundances,  
536 seasonal variations and relations to biomass burning in East Asia. We found that the  
537 dominant anhydrosugar is levoglucosan, which showed a clear seasonal cycle with winter  
538 maximum and summer minimum. The degradation of anhydrosugars during atmospheric  
539 transport may contribute to the summer low levels, while in winter the observed levels of  
540 anhydrosugars are less influenced by degradation. In winter, biomass-burning emissions  
541 either from open field or domestic heating and cooking in north and northeast China,  
542 Mongolia, and Russia affect the abundances of the anhydrosugars in Okinawa aerosols via  
543 long-range atmospheric transport. On the contrary, there is little influence of biomass  
544 burning from Southeast Asia to Okinawa in summer. Moreover, there is little influence of  
545 biomass burning in South China throughout the year. High L/M ratios of 11.5–13.5 were  
546 obtained in autumn to spring when continental outflow dominated over Okinawa, indicating  
547 that the burning substances in north China, Mongolia and middle to eastern Russia are  
548 hardwood, a mixture of softwood and hardwood, or a mixture of softwood and plant straws.  
549 Clear seasonal trends of the contributions of anhydrosugars to the WSOC and OC were  
550 obtained with winter maxima and summer minima. This study demonstrates that biomass  
551 burning plays an important role in regulating chemical and physical properties of aerosols in  
552 the western North Pacific Rim in winter.

553

#### 554 **Acknowledgement**



555 This study was in part supported by the Japan Society for the Promotion of Science  
556 (Grant-in-Aid No. 24221001). We thank S. Yamamoto and T. Arakaki for their help in  
557 aerosol sampling and A. Takami of the National Institute of Environmental Studies, Japan  
558 for the courtesy to use the CHAARM site at Cape Hedo. We acknowledge the use of  
559 meteorological data at Oku station, Okinawa from Japan Meteorological Agency. We also  
560 acknowledge the use of FIRMS data and imagery from the Land Atmosphere Near-real time  
561 Capability for EOS (LANCE) system operated by the NASA/GSFC/Earth Science Data and  
562 Information System (ESDIS) with funding provided by NASA/HQ.  
563

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888 Table 1. Annual and seasonal means of anhydrosugars and ratios of levoglucosan to mannosan (L/M), OC (L/OC) and EC (L/EC)

Compounds	annual (n = 112)		winter (n = 36) <sup>a</sup>		spring (n = 23)		summer (n = 23)		autumn (n = 30)	
	Mean ± sd. <sup>b</sup>	Range	Mean ± sd.	Range	Mean ± sd.	Range	Mean ± sd.	Range	Mean ± sd.	Range
Levoglucosan	3.09±3.70	nd–27.18 <sup>c</sup>	5.30±4.88	0.78–27.18	2.87±2.15	nd–7.43	0.57±0.84	nd–3.89	2.12±2.34	nd–11.28
Mannosan	0.30±0.31	nd–1.76	0.47±0.38	0.06–1.76	0.31±0.24	nd–0.97	0.08±0.12	nd–0.57	0.23±0.23	nd–0.83
Galactosan	0.39±0.25	nd–1.27	0.27±0.23	0.03–1.27	0.54±0.25	nd–1.17	0.43±0.24	nd–1.16	0.40±0.20	nd–0.92
Anhydrosugars	3.53±3.91	nd–29.20	6.04±5.22	0.87–29.20	3.44±2.32	nd–8.22	0.93±1.09	nd–5.62	2.58±2.55	nd–12.72
L/M	10.7±6.1	0.3–38.9	11.9±3.9	3.7–18.4	9.9±6.7	0.3–24.3	7.9±4.8	2.1–20.0	11.5±8.1	0.8–38.9
L/OC, ×10 <sup>-3</sup>	2.4±3.0	0.04–24.6	4.6±4.0	1.0–24.6	1.6±1.2	0.04–5.4	0.3±0.3	0.05–1.3	1.5±1.4	0.1–5.8
L/EC, ×10 <sup>-3</sup>	8.6±7.4	0.2–31.3	14.5±8.1	3.5–31.3	6.1±4.8	0.2–16.8	3.3±2.2	0.2–7.2	6.5±5.2	0.7–23.8

889 <sup>a</sup> Seasons are divided as December–February in winter, March–May in spring, June–August in summer, and September–November in autumn.890 <sup>b</sup> sd. denotes standard deviation (1σ).891 <sup>c</sup> nd denotes not detected.

892 Table 2. Linear correlation coefficients ( $r$ ) among anhydrosugars, major ions and carbonaceous components in Okinawa aerosols from  
 893 October 2009 to February 2012

	Levoglucosan	Mannosan	Galactosan	Anhydrosugars	nss-K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	WSOC	OC	EC
Levoglucosan	1									
Mannosan	0.34 <sup>***</sup>	1								
Galactosan	-0.19 <sup>a</sup>	0.17	1							
Anhydrosugars	0.42	0.80	-0.06	1						
nss-K <sup>+</sup>	0.38 <sup>***</sup>	0.36 <sup>***</sup>	0.08	0.35 <sup>***</sup>	1					
NH <sub>4</sub> <sup>+</sup>	0.39 <sup>***</sup>	0.20 <sup>*</sup>	-0.10	0.32 <sup>***</sup>	-0.03	1				
nss-SO <sub>4</sub> <sup>2-</sup>	0.12	-0.05	-0.19	0.04	-0.18	0.21 <sup>*</sup>	1			
WSOC	0.21 <sup>*</sup>	0.59 <sup>***</sup>	0.32 <sup>*</sup>	0.50 <sup>***</sup>	0.57 <sup>***</sup>	0.03	-0.18	1		
OC	-0.04	0.12	0.33 <sup>***</sup>	0.09	0.32 <sup>***</sup>	-0.09	-0.17	0.67 <sup>***</sup>	1	
EC	0.31 <sup>*</sup>	0.52 <sup>***</sup>	0.02	0.54 <sup>***</sup>	0.40 <sup>***</sup>	0.16	0.16	0.64 <sup>***</sup>	0.28 <sup>***</sup>	1

894 \* denotes  $p < 0.05$ ; \*\* denotes  $p < 0.01$ ; \*\*\* denotes  $p < 0.001$ .

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

896 Table 3. Linear correlation coefficients ( $r$ ) between levoglucosan and other parameters including the other two anhydrosugars, major  
 897 ions and carbonaceous components in Okinawa aerosols in different seasons.

Components	Winter (n = 36) <sup>a</sup>	Spring (n = 23)	Summer (n = 23)	Autumn (n = 30)
Mannosan	0.82 <sup>***</sup>	0.50 <sup>*</sup>	0.90 <sup>***</sup>	0.61 <sup>***</sup>
Galactosan	0.07	-0.31 <sup>b</sup>	0.73 <sup>***</sup>	0.22
nss-K <sup>+</sup>	0.49 <sup>**</sup>	0.59 <sup>**</sup>	0.86 <sup>***</sup>	-0.03
NH <sub>4</sub> <sup>+</sup>	0.23	0.31	0.02	-0.21
nss-SO <sub>4</sub> <sup>2-</sup>	0.26	0.25	-0.19	-0.04
WSOC	0.47 <sup>**</sup>	0.47 <sup>*</sup>	0.95 <sup>***</sup>	0.48 <sup>*</sup>
OC	0.26	0.43	0.65 <sup>**</sup>	0.16
EC	0.61 <sup>***</sup>	0.17	0.68 <sup>**</sup>	0.65 <sup>***</sup>

898 <sup>\*</sup> denotes  $p < 0.05$ ; <sup>\*\*</sup> denotes  $p < 0.01$ ; <sup>\*\*\*</sup> denotes  $p < 0.001$ .

899 <sup>a</sup> Seasons are divided as December–February in winter, March–May in spring, June–August in summer, and September–November in autumn.

900 <sup>b</sup> Negative values indicate negative correlations.

901 Table 4. Annual and seasonal means of contributions of total carbon in the anhydrosugars to the WSOC and OC, of the total  
 902 anhydrosugar mass to the TSP, and of biomass burning (BB) to the OC.

Contributions	Annual (n = 112)		Winter (n = 36) <sup>a</sup>		Spring (n = 23)		Summer (n = 23)		Autumn (n = 30)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
to WSOC (%)	0.22±0.19	0–1.5	0.37±0.24	0.09–1.5	0.17±0.1	0–0.44	0.09±0.05	0–0.17	0.19±0.13	0–0.54
to OC (%)	0.13±0.19	0–0.51	0.25±0.29	0.07–0.51	0.09±0.06	0–0.27	0.03±0.02	0–0.08	0.09±0.07	0–0.3
to TSP (%)	0.006±0.006	0–0.03	0.01±0.006	0.004–0.03	0.005±0.003	0–0.01	0.003±0.002	0–0.007	0.005±0.005	0–0.023
BB to OC (%)	2.9±3.7	0–30	5.6±4.9	1.2–30	2±1.5	0–6.5	0.4±0.4	0–1.6	1.8±1.7	0–7.1

903 <sup>a</sup> Seasons are divided as December–February in winter, March–May in spring, June–August in summer, and September–November in autumn.



904 **Figure captions**

905

906 Fig. 1. Location of Cape Hedo, Okinawa in East Asia where total suspended particles (TSP)  
907 were collected.

908 Fig. 2. Monthly distribution of air mass origins to Cape Hedo, Okinawa shown by clusters of  
909 5-day backward trajectories arriving at 500 m above ground level during December  
910 2009–November 2011. The numbers in each panel indicate the percentages of daily  
911 trajectories in the month with such origins. Fire spots in East Asia in each month of the  
912 same period are also shown.

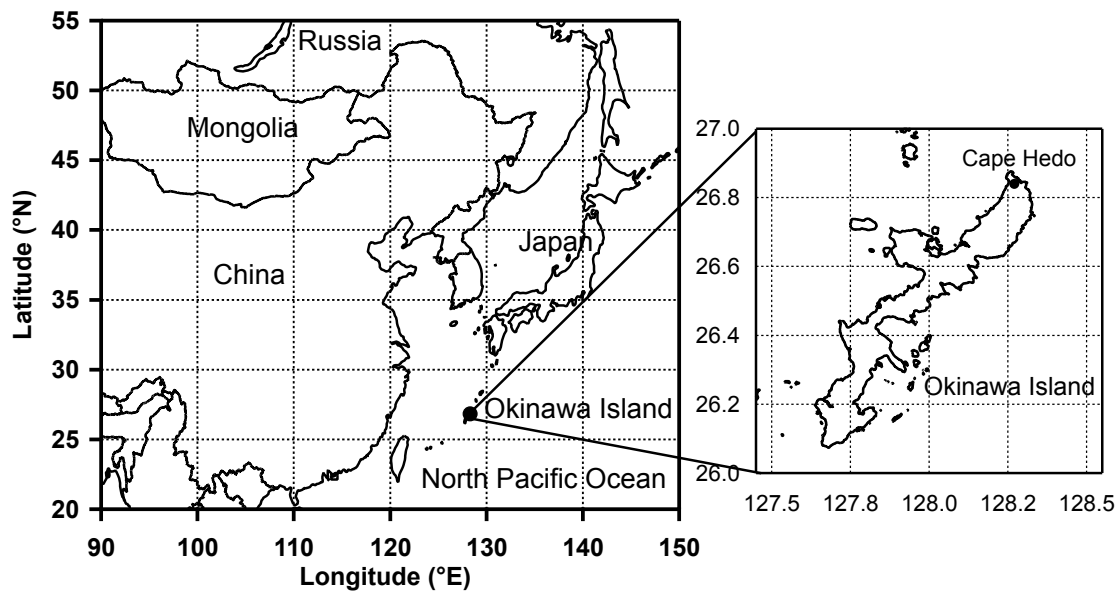
913 Fig. 3. Temporal variation (a, c, e, g) and monthly means (b, d, f, h) of anhydrosugars in  
914 aerosols at Cape Hedo, Okinawa from October 2009 to February 2012. Typical elevation  
915 events of anhydrosugars are marked I and II and analyzed in details.

916 Fig. 4. Air mass origins for the events of elevated anhydrosugars corresponding to I and II in  
917 Figure 3 in (a) November 2–9, 2010 and (b) December 28, 2010–January 4, 2011,  
918 respectively. Clusters of 5-day backward trajectories arriving at 500 m above ground  
919 level at Cape Hedo, Okinawa are given. The numbers in each panel indicate the  
920 percentages of hourly trajectories in the events with such origins. Fire spots in East Asia  
921 during (a) October 28–November 9, 2010 and (b) December 23, 2010–January 4, 2011  
922 are also shown.

923 Fig. 5. Components of water-soluble  $K^+$  derived by (a) tracer-based method (Pio et al., 2008)  
924 and (b) PMF analysis. Details on PMF analysis can be found in the supplementary  
925 material.

926 Fig. 6 Temporal variations (a, c, e) and monthly means (b, d, f) of the ratios of levoglucosan to  
927 mannosan (L/M), OC (L/OC) and EC (L/EC) in aerosols at Cape Hedo, Okinawa from  
928 October 2009 to February 2012.

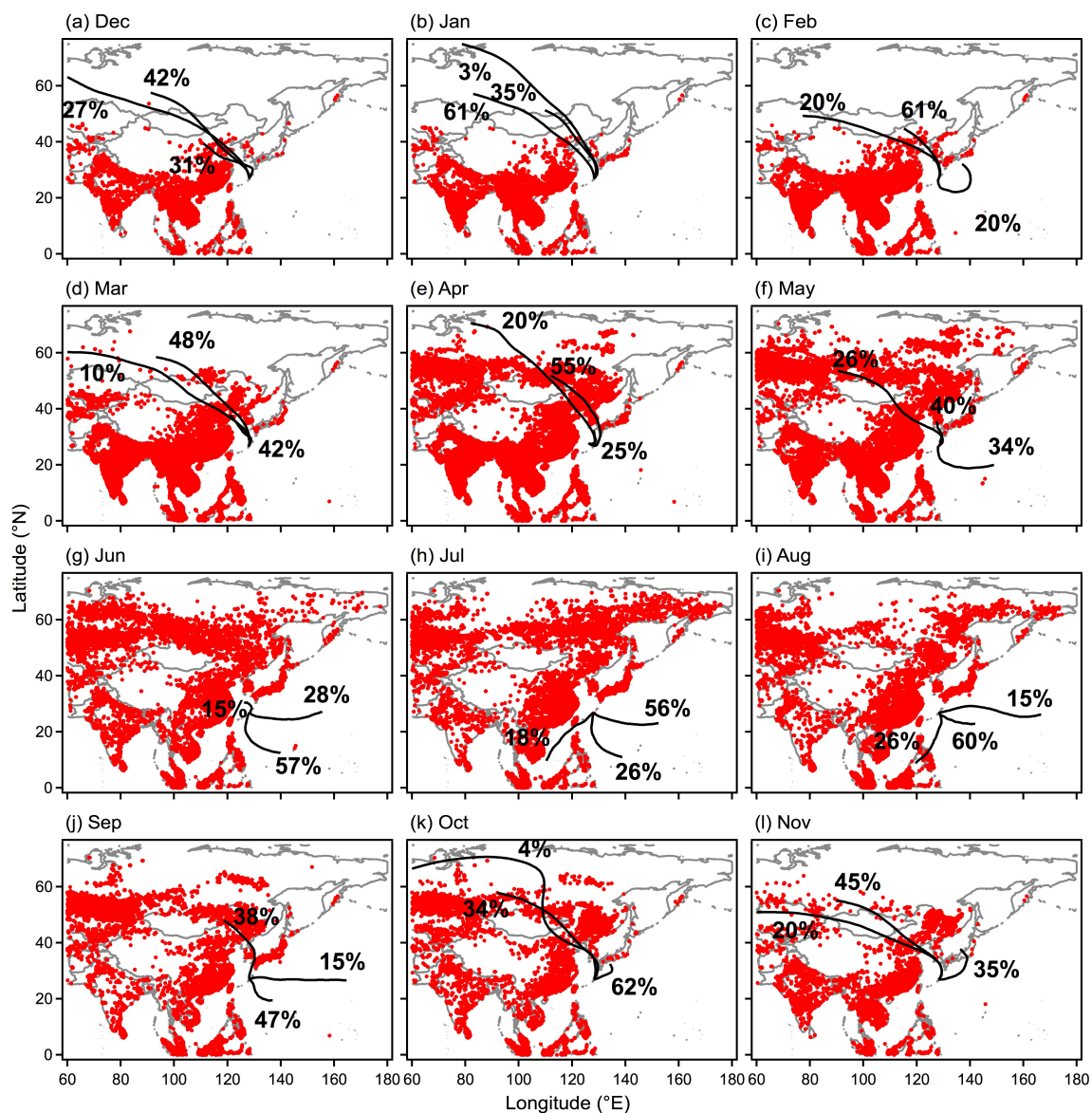
929 Fig. 7 Air mass origins for the event of elevated ratio of levoglucosan to mannosan (L/M) in  
930 October 27–November 3, 2009. Clusters of 5-day backward trajectories arriving at 500  
931 m above ground level at Cape Hedo, Okinawa are given. The numbers in the panel  
932 indicate the percentages of hourly trajectories with such origins. Fire spots in East Asia  
933 over October 22–November 3, 2009 are also shown.



934

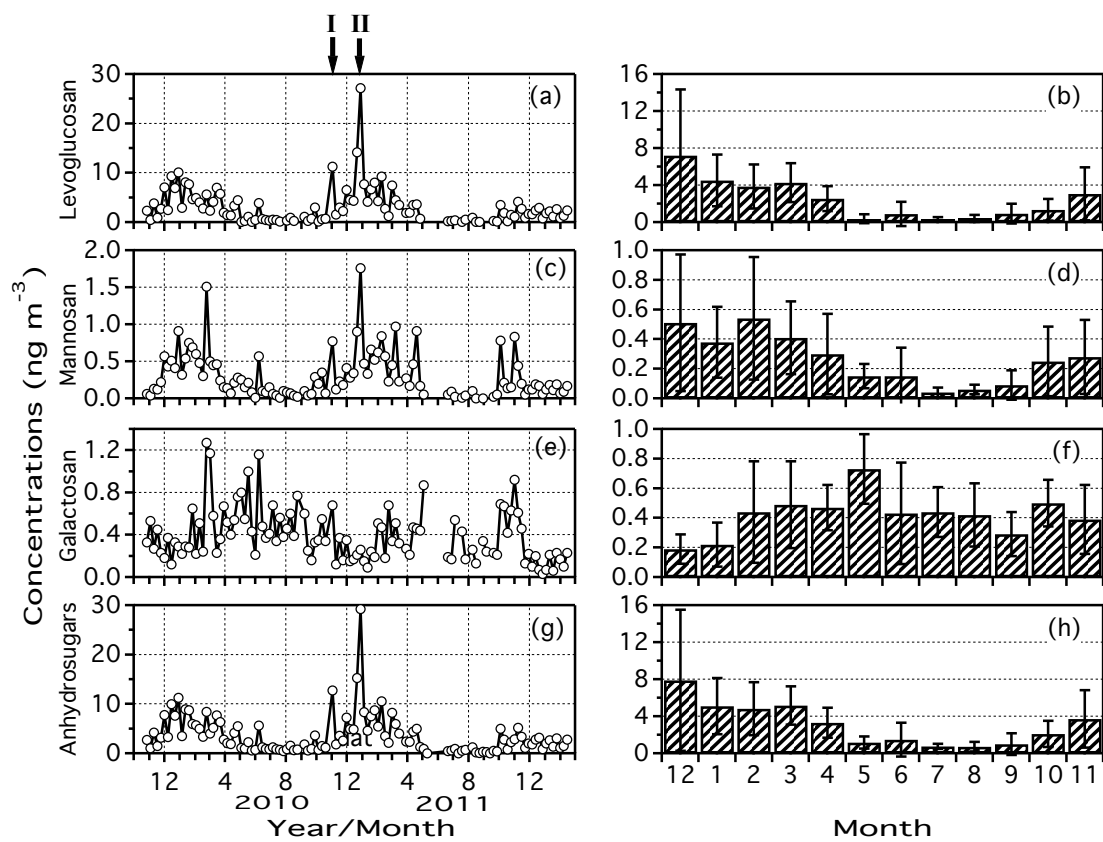
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 940 November 2011. The numbers in each panel indicate the percentages of daily trajectories in  
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 942 shown.

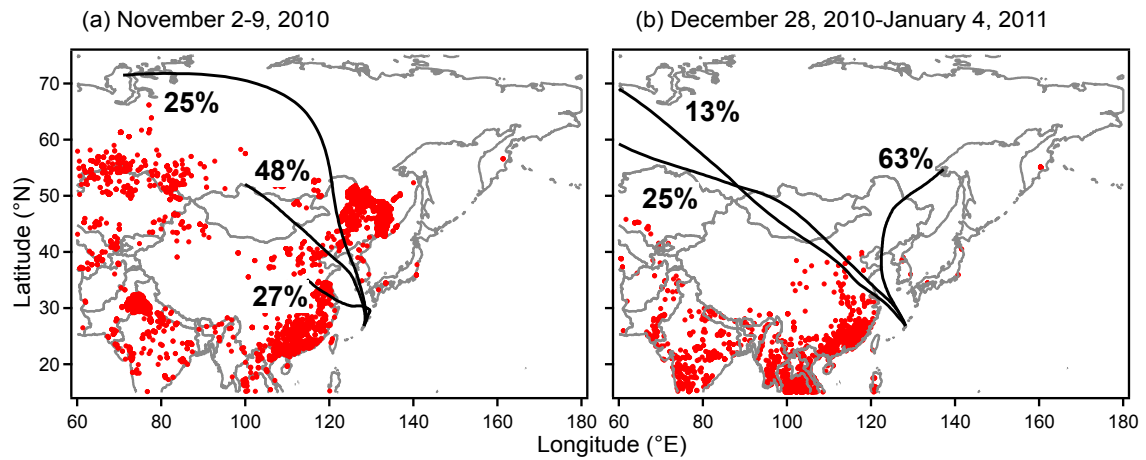


943

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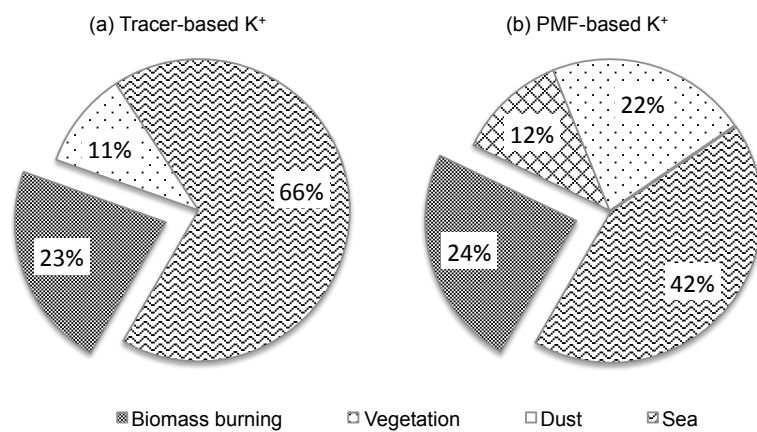
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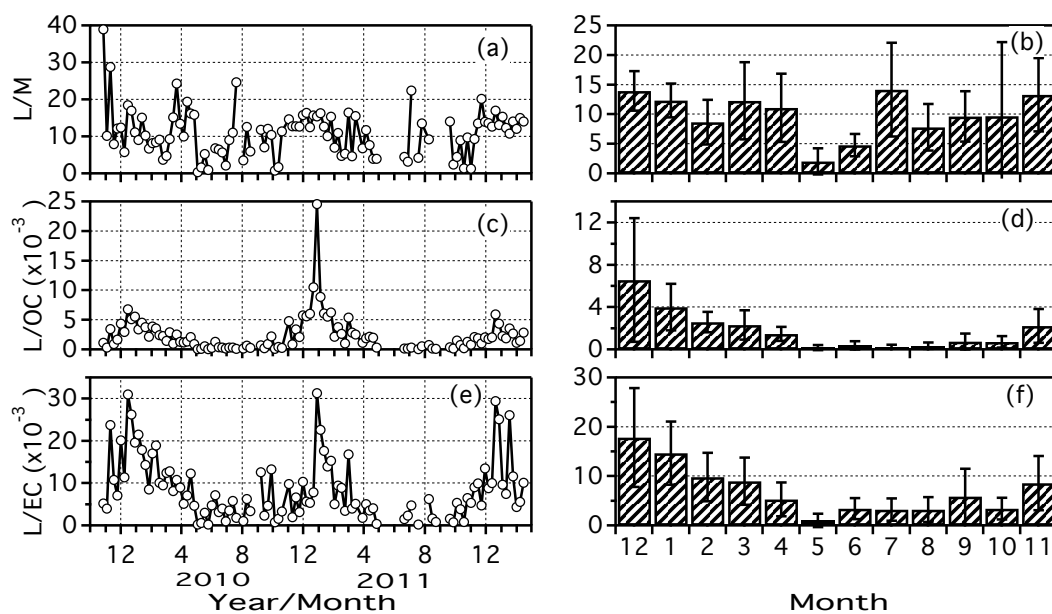
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954

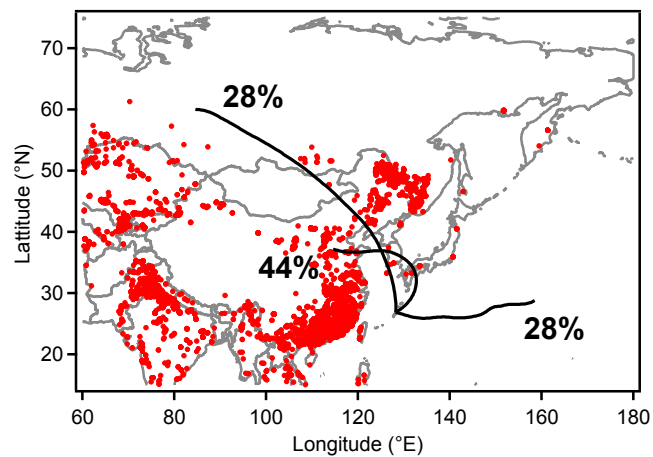
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