

- 1 Effect of biomass burning over the western North Pacific Rim: wintertime maxima of
- 2 anhydrosugars in ambient aerosols from Okinawa
- 3
- 4 Chunmao Zhu, Kimitaka Kawamura, Bhagawati Kunwar
- 5 Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan

Correspondence to: Kimitaka Kawamura ([kawamura@lowtem.hokudai.ac.jp](mailto:kawamura@lowtem.hokudai.ac.jp))

## 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  $\text{nss-K}^+$  ( $r = 0.38$ ,  $p < 0.001$ ); 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. The monthly averaged levoglucosan/mannosan  
19 ratios were lower (2.1-4.8) in May–June and higher (13.3-13.9) in November–December.  
20 The lower values may be associated with softwood burning in north China, Korea and  
21 southwest Japan whereas the higher values are probably caused by agriculture waste  
22 burning of maize straw in the North China Plain. Anhydrosugars comprised 0.22% of  
23 water-soluble organic carbon (WSOC) and 0.13% of organic carbon (OC). The highest  
24 values to WSOC (0.37%) and OC (0.25%) were found in winter, again indicating an  
25 important BB contribution to Okinawa aerosols in winter. This study provides useful  
26 information to better understand the effect of East Asian biomass burning on the air quality  
27 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 (Langenfolds et al., 2002). Moreover,  
42 carbonaceous components and trace gases in the smoke contribute to respiratory diseases  
43 (Laumbach et al., 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 indexes

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

97 East Asia is one of the most active BB regions in the world with high aerosol loadings  
98 (van der Werf et al., 2006). Forest burning resulting from both natural and man-made fires  
99 for land clearing or other purposes comprises 16%, crop residue burning in the agriculture  
100 field comprises 12%, grassland and savanna burning arising from prescribed burning,

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

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

119

## 120 **2 Experimental methods**

### 121 2.1 Site and sampling

122 We collected total suspended particle (TSP) samples from October 2009 to February  
123 2012 at Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS) ( $26.9^{\circ}\text{N}$ ,  
124  $128.2^{\circ}\text{E}$ ) in the northwestern edge of Okinawa Island (Fig. 1). TSPs were collected on pre-

125 combusted (450 °C, 3 h) quartz filters (Pallflex 2500QAT, 20 cm × 25 cm) using a high-  
126 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 =  
127 112). Each of the aerosol-loaded filter was placed in a pre-combusted (450 °C, 6 h) glass jar  
128 with a Teflon-lined screw cap and stored in darkness at -20 °C. Before weighing and  
129 analysis, each filter was placed in a desiccator for 24–72 h at ~20 °C until constant weight  
130 to remove water. Two field blanks following all the collection procedures except for  
131 running sampling pump were collected on November 2009 and March 2011, respectively.  
132 OC levels in field blanks were consistently low (1.16 and 1.54 µg per measured unit of 1.54  
133 cm<sup>2</sup>, < 5% of OC levels in most samples), indicating negligible contamination of the  
134 samples.

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

141

## 142 2.2 Measurement of anhydrosugars

### 143 2.2.1 Extraction and derivatization

144 A small filter section (ca. 10 cm<sup>2</sup>) was sonicated three times for 10 min in a mixture (7  
145 ml) of dichloromethane/methanol (2:1; v/v). The solvent extracts were filtered through  
146 quartz wool packed in a Pasteur pipette to remove particles. The filtrate was concentrated in  
147 a pear-shape flask by a rotary evaporator under vacuum down to 1 ml, and then dried with  
148 pure nitrogen gas in a 1.5 ml glass vial. Compounds in the extracts were then converted to

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

154

### 155 2.2.2 Gas chromatography-mass spectrometry

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

164 Mass spectral data were acquired and processed using the HP-Chemstation software.  
165 Individual anhydrosugars were identified by comparison with the retention times and mass  
166 spectra of authentic standards and the mass spectral library of HP-Chemstation (Medeiros  
167 and Simoneit, 2007). Relative response factor of levoglucosan was obtained by comparing  
168 the peak area differences of the authentic standards to the internal standard (tridecane in n-  
169 hexane, ca. 1 ng  $\mu\text{l}^{-1}$  in the extracts before injection). Concentration of levoglucosan in each  
170 of the ambient samples was determined by comparing its relative response factor with that  
171 of the authentic standard. The relative response factor for levoglucosan was also applied in  
172 mannosan and galactosan. Recoveries for levoglucosan were 83–97% for four replicates as



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

182

### 183 2.3 Water-soluble inorganic ions and carbonaceous components

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

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

204

#### 205 2.4 Backward trajectories and fire counts

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

220

221 **3 Results and discussions**

## 222 3.1 Air mass origins and fire counts

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

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

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

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

257

## 258 3.2 Effect of biomass burning in East Asia on anhydrosugars at Okinawa

### 259 3.2.1 Seasonal variation of anhydrosugars

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

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

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

282

### 283 3.2.2 Effect of continental outflow on high anhydrosugars in winter

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

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

308

### 309 3.2.3 Anhydrosugar levels in summer

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

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

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

337 On the contrary to our expectation, there was little influence of biomass burning in  
338 Southeast Asia to anhydrosugars in Okinawa aerosols (Fig. 2). In August 26% of the air  
339 masses originated from the Philippine islands, however very few fire spots were detected by

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

350

### 351 3.3 Relations between anhydrosugars with inorganic ions and EC

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

358  $\text{nss-K}^+$  is another typical tracer of BB (Sullivan et al., 2011). Positive correlations were  
359 found between  $\text{nss-K}^+$  and levoglucosan ( $r = 0.38$ ,  $p < 0.001$ ) and mannosan ( $r = 0.36$ ,  $p <$   
360  $0.001$ ), supporting that these components are derived from BB. Using levoglucosan as a  
361 representative BB tracer, the correlations between anhydrosugars and  $\text{nss-K}^+$  were further  
362 investigated for seasonal profiles (Table 3). Levoglucosan significantly correlates with  $\text{nss-}$   
363  $\text{K}^+$  in winter ( $r=0.49$ ,  $p < 0.001$ ), spring ( $0.59$ ,  $p < 0.001$ ) and summer ( $0.86$ ,  $p < 0.001$ ). No



364 correlation in autumn may suggest other sources of  $\text{nss-K}^+$ , possibly derived from soil  
365 resuspension during agricultural plowing practices before winter wheat planting in the  
366 North China Plain. Previous studies also indicated that soil dust could be another source of  
367 water-soluble  $\text{nss-K}^+$  in Asian aerosols (Arimoto et al., 2004; Duvall et al., 2008; Shen et al.,  
368 2009).

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

386 On the other hand, positive relations were found between  $\text{NH}_4^+$  and levoglucosan ( $r =$   
387  $0.39, p < 0.001$ ) and mannosan ( $r = 0.20, p < 0.05$ ). These results imply that BB in MNA

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

398 Biomass burning is frequently accompanied by elevated emission of EC (Akagi et al.,  
399 2011). Positive relations of EC with levoglucosan ( $r = 0.31, p < 0.05$ ) and mannosan ( $r =$   
400  $0.52, p < 0.001$ ) were obtained (Table 2). These results indicate that EC in Okinawa  
401 aerosols are partly derived from BB. Meanwhile, air masses with mixed sources from  
402 emissions of BB and fossil fuel would also result in such relations. Observation of black  
403 carbon (BC) by aethalometer at Rishiri Island, northern Japan indicated outflow of high  
404 level BC from fossil fuel combustion from the Asian continent (Zhu et al., 2015). Fossil fuel  
405 combustion in the Asian continent is probably a more significant source of EC in Okinawa  
406 aerosols compared to BB sources. Seasonally, levoglucosan correlates significantly with EC  
407 in summer, autumn and winter. No correlation in spring may be associated with higher EC  
408 source from fossil fuel combustion in the upwind Asian continent.

409

410 3.4 Implication for burning substrates based on L/M ratios

411 Levoglucosan/Mannosan (L/M) ratio has been used to differentiate the burning substrates  
412 (Table 1, Fig. 6). Monthly L/M ratios ranged from 2.1 to 4.8 in May–June and from 12.3 to  
413 13.9 in November–January. Higher ratios were found in late autumn to winter whereas  
414 lower ratios in late spring to early summer (Fig 6b). Previous biomass burning studies  
415 showed that L/M ratios from crop residues are often  $> 40$ , whereas those from hard wood  
416 are in a range of 15–25, and those of soft wood to be 3–10 (Schmidl et al., 2008a, b;  
417 Engling et al., 2009; Fu et al., 2012; Mkoma et al., 2013; Engling et al., 2014). Higher  
418 monthly means of L/M ratios in November–January suggest that the burning substrates  
419 were hardwood, mixture of softwood and hardwood, or mixture of softwood and plant  
420 straws in NMA. The lower L/M ratios in May–June suggest that Okinawa aerosols are  
421 influenced by the burning of softwood, possibly from north China, Korea or southwest  
422 Japan, as supported by backward trajectories (Fig 2 f–g). It is worthy noting that the  
423 possible different degradation rates between levoglucosan and mannosan would contribute  
424 to L/M variations. With respect to this point, the low L/M ratios in May–June may imply  
425 that levoglucosan is degrading faster than mannosan during atmospheric transport.

426 Sporadically high L/M ratio events were observed. The highest ratio of 38.9 was  
427 observed in the sample collect on October 27–November 3, 2009. Elevated concentrations  
428 of OC, EC and water-soluble ions were also observed for this sample. On these days, 44%  
429 of air masses originated from the North China Plain, while another 28% originated from  
430 west Siberia, en route Mongolia and north China to Okinawa (Fig. 7). October–November  
431 are the harvest season of maize in the North China Plain where fire spots were observed.  
432 This event indicates that emissions of particulate matter from burning of maize straw  
433 residues were transported to the western North Pacific. High L/M ratios had been reported  
434 for smoke from chamber burning of rice straw (40–42) and ambient aerosols affected by

435 burning of wheat straw (40–46) (Engling et al., 2009; Fu et al., 2008). A higher average  
436 L/M ratio of 55 was obtained for the burning of rice straw, wheat straw and maize straw by  
437 chamber experiment (Zhang et al., 2009). These results implied that maize straw smoke  
438 may have higher L/M ratio. Our results gave a relatively high L/M ratio of 38.9 even after  
439 long-range transport to Okinawa, supporting the above proposition.

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

448

449 3.5 L/OC and L/EC ratios

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

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

475 EC is emitted primarily via coal combustion, motor vehicle exhaust and BB (Cao et al.,  
476 2005; Waked et al., 2014, Yttri et al., 2014). The ratio between levoglucosan to EC (L/EC)  
477 was also investigated (Fig. 5 e–f, Table 1). Being similar to L/OC, L/EC ratios indicate a  
478 clear seasonal trend with winter maximum ( $14.5 \times 10^{-3}$ ) and summer minimum ( $3.3 \times 10^{-3}$ ).  
479 Moreover, L/EC ratios in Okinawa and Chichijima are one order of magnitude lower than  
480 that of Changdao in winter, spring and autumn (Feng et al., 2007; Mochida et al., 2010). As  
481 there was little source of EC in the ocean, this result may imply a degradation of

482 levoglucosan during atmospheric transport. In summer, L/EC ratios in Okinawa ( $3.3 \times 10^{-3}$ )  
483 and Chichijima ( $6.5 \times 10^{-3}$ ) were in the same order with that of Changdao ( $4.0 \times 10^{-3}$ ). This  
484 is likely related to the different EC sources at these sites. As long as the majorities of air  
485 masses are from the ocean for all these three sites, there is higher emission of EC from local  
486 fossil fuel combustion at Changdao, whereas EC at Okinawa and Chichijima might  
487 represent a regional background level in summer.

488

### 489 3.6 Contributions of biomass burning to WSOC, OC and TSP

490 Positive linear relations were found between total and each anhydrosugar component and  
491 WSOC (Table 2), as well as between levoglucosan and WSOC in each season (Table 3).  
492 Although the relations between levoglucosan and OC in most of the seasons are not  
493 significant (Tables 2, 3), clear seasonal trend of L/OC ratios indicates that the contribution  
494 of anhydrosugars to OC varied depending on seasons (Fig. 6 c–d). We further investigated  
495 the contributions of anhydrosugars to WSOC and OC, and total anhydrosugars mass to TSP  
496 (Table 4). Anhydrosugars account for 0.22% of WSOC and 0.13% of OC annually. The  
497 highest contributions of anhydrosugars to WSOC (0.37%) and OC (0.25%) were obtained in  
498 winter, indicating a strong influence of BB on winter aerosols. The contribution of  
499 anhydrosugars to WSOC in Okinawa is lower than those of the Amazon rainforest sites  
500 (levoglucosan-C/WSOC of 2–7%) where the burning happened in situ (Graham et al., 2002).  
501 These values are also lower than those of the Pearl River Delta sites in China  
502 (levoglucosan-C/WSOC of 0.59–3.12%) that are directly affected by biomass burning in  
503 South China (Ho et al., 2014). Anhydrosugars accounted for 0.006% of TSP on annual basis  
504 in Okinawa aerosols with maximum (0.01%) in winter.

505 L/OC ratio has been used to estimate the contributions of BB to OC in aerosols as stated  
506 above. L/OC ratios ranged from 8.0 to 8.2% in the burning of savanna and grassland,  
507 tropical and extratropical forest, biofuel and agricultural residues (Andreae and Merlet,  
508 2001). Moreover, the mean emission factor of L/OC during the burning of wheat, corn and  
509 rice straws in China was derived as 8.27% (Zhang et al., 2007). Although L/OC ratios in the  
510 BB source emissions vary among different types of biomass fuels and burning conditions  
511 (e.g., Mochida et al., 2010), the value of ~8.2% have been widely used to estimate BB  
512 contributions to OC (Fu et al., 2014; Graham et al., 2002; Ho et al., 2014; Mkoma et al.,  
513 2013; Sang et al., 2011). Using the L/OC of 8.2% from the source of biomass burning, we  
514 estimated that biomass burning in East Asia contributes 2.9% of OC in Okinawa aerosols on  
515 annual basis (Table 4). This is lower than the contribution of BB to OC in the Pearl River  
516 Delta in China (13.1%) (Ho et al., 2014). However, in winter, the mean contribution from  
517 biomass burning was 5.6%, although the highest contribution became as large as 30%. A  
518 further estimation on the OC components by PMF analysis may provide more information,  
519 which would be our future work. These results indicate that BB, especially from MNA in  
520 winter, may significantly affects the regional air quality in Okinawa in winter, especially  
521 during Asian outflow episodes.

522

#### 523 **4 Conclusions**

524 Anhydrosugars were studied in aerosols from Okinawa, Japan for their abundances,  
525 seasonal variations and relations to biomass burning in East Asia. We found that the  
526 dominant anhydrosugar is levoglucosan, which showed a clear seasonal cycle with winter  
527 maximum and summer minimum. The degradation of anhydrosugars during atmospheric  
528 transport may contribute to the summer low levels, while in winter the observed levels of

529 anhydrosugars are less influenced by degradation. In winter, biomass-burning emissions  
530 either from open field or domestic heating and cooking in north and northeast China,  
531 Mongolia, and Russia affect the abundances of anhydrosugars in Okinawa aerosols via  
532 long-range atmospheric transport. On the contrary, there is little influence of biomass  
533 burning from Southeast Asia to Okinawa in summer. Moreover, there is little influence of  
534 biomass burning in South China throughout the year. High L/M ratios of 11.5–13.5 were  
535 obtained in autumn to spring when continental outflow dominated over Okinawa, indicating  
536 that the burning substances in north China, Mongolia and middle to eastern Russia are  
537 hardwood, mixture of softwood and hardwood, or mixture of softwood and plant straws.  
538 Clear seasonal trends of the contributions of anhydrosugars to WSOC and OC were  
539 obtained with winter maxima and summer minima. This study demonstrates that biomass  
540 burning plays an important role in regulating chemical and physical properties of aerosols in  
541 the western North Pacific Rim in winter.

542

### 543 **Acknowledgement**

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

552



553 **References**

- 554 Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T.,  
555 Crouse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass  
556 burning for use in atmospheric models, *Atmos. Chem. Phys.*, 11, 4039–4072,  
557 doi:10.5194/acp-11-4039-2011, 2011.
- 558 Akagi, S. K., Burling, I. R., Mendoza, A., Johnson, T. J., Cameron, M., Griffith, D. W. T.,  
559 Paton-Walsh, C., Weise, D. R., Reardon, J., and Yokelson, R. J.: Field measurements of  
560 trace gases emitted by prescribed fires in southeastern US pine forests using an open-  
561 path FTIR system, *Atmos. Chem. Phys.*, 14, 199–215, doi:10.5194/acp-14-199-2014,  
562 2014.
- 563 Andreae, M. O., and Merlet, P.: Emission of trace gases and aerosols from biomass burning,  
564 *Global Biogeochem. Cycles*, 15, 955–966, doi:10.1029/2000gb001382, 2001.
- 565 Arimoto, R., Zhang, X. Y., Huebert, B. J., Kang, C. H., Savoie, D. L., Prospero, J. M., Sage,  
566 S. K., Schloesslin, C. A., Khaing, H. M., and Oh, S. N.: Chemical composition of  
567 atmospheric aerosols from Zhenbeitai, China, and Gosan, South Korea, during ACE-Asia,  
568 *J. Geophys. Res.*, 109, D19S04, 10.1029/2003JD004323, 2004.
- 569 Asman, W. A. H., Sutton, M. A., and Schjørring, J. K.: Ammonia: emission, atmospheric  
570 transport and deposition, *New Phytol.*, 139, 27–48, 10.1046/j.1469-8137.1998.00180.x,  
571 1998.
- 572 Birch, M. E., and Cary, R. A.: Elemental carbon-based method for occupational monitoring  
573 of particulate diesel exhaust: methodology and exposure issues, *Analyst*, 121, 1183–1190,  
574 doi:10.1039/an9962101183, 1996.
- 575 Cao, J. J., Wu, F., Chow, J. C., Lee, S. C., Li, Y., Chen, S. W., An, Z. S., Fung, K. K.,  
576 Watson, J. G., Zhu, C. S., and Liu, S. X.: Characterization and source apportionment of  
577 atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China,  
578 *Atmos. Chem. Phys.*, 5, 3127–3137, 10.5194/acp-5-3127-2005, 2005.
- 579 Chen, J., Kawamura, K., Liu, C. Q., and Fu, P.: Long-term observations of saccharides in  
580 remote marine aerosols from the western North Pacific: A comparison between 1990–  
581 1993 and 2006–2009 periods, *Atmos. Environ.*, 67, 448–458,  
582 doi:10.1016/j.atmosenv.2012.11.014, 2013.

- 583 Draxler, R.R., and G. D. Rolph: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated  
584 Trajectory) Model, access via NOAA ARL READY Website,  
585 <http://www.arl.noaa.gov/HYSPLIT.php> (accessed July 8, 2014), NOAA Air Resources  
586 Laboratory, College Park, MD, 2013.
- 587 Duvall, R. M., Majestic, B. J., Shafer, M. M., Chuang, P. Y., Simoneit, B. R. T., and  
588 Schauer, J. J.: The water-soluble fraction of carbon, sulfur, and crustal elements in Asian  
589 aerosols and Asian soils, *Atmos. Environ.*, 42, 5872–5884,  
590 doi:10.1016/j.atmosenv.2008.03.028, 2008.
- 591 Engling, G., Carrico, C. M., Kreidenweis, S. M., Collett Jr, J. L., Day, D. E., Malm, W. C.,  
592 Lincoln, E., Min Hao, W., Iinuma, Y., and Herrmann, H.: Determination of levoglucosan  
593 in biomass combustion aerosol by high-performance anion-exchange chromatography  
594 with pulsed amperometric detection, *Atmos. Environ.*, 40, 299–311,  
595 doi:10.1016/j.atmosenv.2005.12.069, 2006.
- 596 Engling, G., Lee, J. J., Tsai, Y. W., Lung, S. C. C., Chou, C. C. K., and Chan, C. Y.: Size-  
597 resolved anhydrosugar composition in smoke aerosol from controlled field burning of  
598 rice straw, *Aerosol Sci. Technol.*, 43, 662–672, doi:10.1080/02786820902825113, 2009.
- 599 Engling, G., He, J., Betha, R., and Balasubramanian, R.: Assessing the regional impact of  
600 Indonesian biomass burning emissions based on organic molecular tracers and chemical  
601 mass balance modeling, *Atmos. Chem. Phys.*, 14, 8043–8054, doi:10.5194/acp-14-8043-  
602 2014, 2014.
- 603 Fabbri, D., Torri, C., Simoneit, B. R. T., Marynowski, L., Rushdi, A. I., and Fabiańska, M.  
604 J.: Levoglucosan and other cellulose and lignin markers in emissions from burning of  
605 Miocene lignites, *Atmos. Environ.*, 43, 2286–2295, doi:10.1016/j.atmosenv.2009.01.030,  
606 2009.
- 607 Feng, J., Guo, Z., Chan, C. K., and Fang, M.: Properties of organic matter in PM<sub>2.5</sub> at  
608 Changdao Island, China-A rural site in the transport path of the Asian continental  
609 outflow, *Atmos. Environ.*, 41, 1924–1935, doi:10.1016/j.atmosenv.2006.10.064, 2007.
- 610 Fine, P. M., Cass, G. R., and Simoneit, B. R.: Chemical characterization of fine particle  
611 emissions from the fireplace combustion of wood types grown in the Midwestern and  
612 Western United States, *Environ. Eng. Sci.*, 21, 387–409, 2004.

- 613 Fu, P., Kawamura, K., Chen, J., and Miyazaki, Y.: Secondary Production of Organic  
614 Aerosols from Biogenic VOCs over Mt. Fuji, Japan, *Environ. Sci. Technol.*, 48, 8491–  
615 8497, 10.1021/es500794d, 2014.
- 616 Fu, P., Kawamura, K., Okuzawa, K., Aggarwal, S. G., Wang, G., Kanaya, Y., and Wang,  
617 Z.: Organic molecular compositions and temporal variations of summertime mountain  
618 aerosols over Mt. Tai, North China Plain, *J. Geophys. Res.*, 113, D19107,  
619 doi:10.1029/2008jd009900, 2008.
- 620 Fu, P. Q., Kawamura, K., Chen, J., Li, J., Sun, Y. L., Liu, Y., Tachibana, E., Aggarwal, S.  
621 G., Okuzawa, K., Tanimoto, H., Kanaya, Y., and Wang, Z. F.: Diurnal variations of  
622 organic molecular tracers and stable carbon isotopic composition in atmospheric aerosols  
623 over Mt. Tai in the North China Plain: an influence of biomass burning, *Atmos. Chem.*  
624 *Phys.*, 12, 8359–8375, 10.5194/acp-12-8359-2012, 2012.
- 625 Galanter, M., Levy, H., and Carmichael, G. R.: Impacts of biomass burning on tropospheric  
626 CO, NO<sub>x</sub>, and O<sub>3</sub>, *J. Geophys. Res.*, 105, 6633–6653, doi:10.1029/1999jd901113, 2000.
- 627 George, S. K., Nair, P. R., Parameswaran, K., Jacob, S., and Abraham, A.: Seasonal trends  
628 in chemical composition of aerosols at a tropical coastal site of India, *J. Geophys. Res.*,  
629 113, D16209, doi:10.1029/2007jd009507, 2008.
- 630 Goode, J. G., Yokelson, R. J., Ward, D. E., Susott, R. A., Babbitt, R. E., Davies, M. A., and  
631 Hao, W. M.: Measurements of excess O<sub>3</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, HCN, NO, NH<sub>3</sub>,  
632 HCOOH, CH<sub>3</sub>COOH, HCHO, and CH<sub>3</sub>OH in 1997 Alaskan biomass burning plumes by  
633 airborne Fourier transform infrared spectroscopy (AFTIR), *J. Geophys. Res.*, 105,  
634 22147–22166, doi:10.1029/2000jd900287, 2000.
- 635 Graham, B., Mayol-Bracero, O. L., Guyon, P., Roberts, G. C., Decesari, S., Facchini, M. C.,  
636 Artaxo, P., Maenhaut, W., Köll, P., and Andreae, M. O.: Water-soluble organic  
637 compounds in biomass burning aerosols over Amazonia 1. Characterization by NMR and  
638 GC-MS, *J. Geophys. Res.*, 107, D20, doi:10.1029/2001jd000336, 2002.
- 639 Hays, M. D., Fine, P. M., Geron, C. D., Kleeman, M. J., and Gullett, B. K.: Open burning of  
640 agricultural biomass: Physical and chemical properties of particle-phase emissions,  
641 *Atmos. Environ.*, 39, 6747–6764, doi:10.1016/j.atmosenv.2005.07.072, 2005.
- 642 Hennigan, C. J., Sullivan, A. P., Collett, J. L., and Robinson, A. L.: Levoglucosan stability  
643 in biomass burning particles exposed to hydroxyl radicals, *Geophys. Res. Lett.*, 37,  
644 L09806, doi:10.1029/2010gl043088, 2010.

- 645 Ho, K. F., Engling, G., Ho, S. S. H., Huang, R., Lai, S., Cao, J., and Lee, S. C.: Seasonal  
646 variations of anhydrosugars in PM<sub>2.5</sub> in the Pearl River Delta Region, China, *Tellus*, 66B,  
647 22577, doi:10.3402/tellusb.v66.22577, 2014.
- 648 Hoffmann, D., Tilgner, A., Iinuma, Y., and Herrmann, H.: Atmospheric stability of  
649 levoglucosan: a detailed laboratory and modeling study, *Environ. Sci. Technol.*, 44, 694–  
650 699, doi:10.1021/es902476f, 2010.
- 651 Honrath, R. E., Owen, R. C., Val Martín, M., Reid, J. S., Lapina, K., Fialho, P., Dziobak, M.  
652 P., Kleissl, J., and Westphal, D. L.: Regional and hemispheric impacts of anthropogenic  
653 and biomass burning emissions on summertime CO and O<sub>3</sub> in the North Atlantic lower  
654 free troposphere, *J. Geophys. Res.*, 109, D24310, doi:10.1029/2004jd005147, 2004.
- 655 Hu, Q. H., Xie, Z. Q., Wang, X. M., Kang, H., and Zhang, P.: Levoglucosan indicates high  
656 levels of biomass burning aerosols over oceans from the Arctic to Antarctic, *Sci. Rep.*, 3,  
657 doi:10.1038/srep03119, 2013
- 658 Huang, X., Song, Y., Li, M., Li, J., Huo, Q., Cai, X., Zhu, T., Hu, M., and Zhang, H.: A  
659 high-resolution ammonia emission inventory in China, *Global Biogeochem. Cycles*, 26,  
660 GB1030, 10.1029/2011GB004161, 2012.
- 661 Iinuma, Y., Brüggemann, E., Gnauk, T., Müller, K., Andreae, M. O., Helas, G., Parmar, R.,  
662 and Herrmann, H.: Source characterization of biomass burning particles: The combustion  
663 of selected European conifers, African hardwood, savanna grass, and German and  
664 Indonesian peat, *J. Geophys. Res.*, 112, D08209, doi:10.1029/2006jd007120, 2007.
- 665 Itahashi, S., Uno, I., Irie, H., Kurokawa, J. I., and Ohara, T.: Regional modeling of  
666 tropospheric NO<sub>2</sub> vertical column density over East Asia during the period 2000–2010:  
667 comparison with multisatellite observations, *Atmos. Chem. Phys.*, 14, 3623–3635,  
668 10.5194/acp-14-3623-2014, 2014.
- 669 Kanaya, Y., Sadanaga, Y., Nakamura, K., and Akimoto, H.: Behavior of OH and HO<sub>2</sub>  
670 radicals during the Observations at a Remote Island of Okinawa (ORION99) field  
671 campaign: 1. Observation using a laser-induced fluorescence instrument, *J. Geophys.*  
672 *Res.*, 106, 24197–24208, doi:10.1029/2000jd000178, 2001.
- 673 Kawamura, K., Izawa, Y., Mochida, M., and Shiraiwa, T.: Ice core records of biomass  
674 burning tracers (levoglucosan and dehydroabietic, vanillic and p-hydroxybenzoic acids)  
675 and total organic carbon for past 300 years in the Kamchatka Peninsula, Northeast Asia,  
676 *Geochim. Cosmochim. Ac.*, 99, 317–329, doi:10.1016/j.gca.2012.08.006, 2012.

- 677 Konovalov, I. B., Berezin, E. V., Ciais, P., Broquet, G., Beekmann, M., Hadji-Lazaro, J.,  
678 Clerbaux, C., Andreae, M. O., Kaiser, J. W., and Schulze, E. D.: Constraining CO<sub>2</sub>  
679 emissions from open biomass burning by satellite observations of co-emitted species: a  
680 method and its application to wildfires in Siberia, *Atmos. Chem. Phys. Discuss.*, 14,  
681 3099–3168, doi:10.5194/acpd-14-3099-2014, 2014.
- 682 Kudo, S., Tanimoto, H., Inomata, S., Saito, S., Pan, X., Kanaya, Y., Taketani, F., Wang, Z.,  
683 Chen, H., Dong, H., Zhang, M., and Yamaji, K.: Emissions of nonmethane volatile  
684 organic compounds from open crop residue burning in the Yangtze River Delta region,  
685 China, *J. Geophys. Res.*, 119, 7684–7698, doi:10.1002/2013jd021044, 2014.
- 686 Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Diurnal  
687 variation in the water-soluble inorganic ions, organic carbon and isotopic compositions  
688 of total carbon and nitrogen in biomass burning aerosols from the LBA-SMOCC  
689 campaign in Rondônia, Brazil, *J Aerosol Sci.*, 41, 118–133,  
690 doi:10.1016/j.jaerosci.2009.08.006, 2010.
- 691 Kunwar, B., and Kawamura, K.: One-year observations of carbonaceous and nitrogenous  
692 components and major ions in the aerosols from subtropical Okinawa Island, an outflow  
693 region of Asian dusts, *Atmos. Chem. Phys.*, 14, 1819–1836, doi:10.5194/acp-14-1819-  
694 2014, 2014.
- 695 Křůmal, K., Mikuška, P., Vojtěšek, M., and Večeřa, Z.: Seasonal variations of  
696 monosaccharide anhydrides in PM<sub>1</sub> and PM<sub>2.5</sub> aerosol in urban areas, *Atmos. Environ.*,  
697 44, 5148–5155, doi:10.1016/j.atmosenv.2010.08.057, 2010.
- 698 Langenfelds, R. L., Francey, R. J., Pak, B. C., Steele, L. P., Lloyd, J., Trudinger, C. M., and  
699 Allison, C. E.: Interannual growth rate variations of atmospheric CO<sub>2</sub> and its δ<sup>13</sup>C, H<sub>2</sub>,  
700 CH<sub>4</sub>, and CO between 1992 and 1999 linked to biomass burning, *Global Biogeochem.*  
701 *Cycles*, 16, 1048, doi:10.1029/2001gb001466, 2002.
- 702 Laumbach, R. J., and Kipen, H. M.: Respiratory health effects of air pollution: Update on  
703 biomass smoke and traffic pollution, *J. Allergy Clin. Immunol.*, 129, 3–11,  
704 doi:10.1016/j.jaci.2011.11.021, 2012.
- 705 Lin, J. C., Matsui, T., Pielke, R. A., and Kummerow, C.: Effects of biomass-burning-  
706 derived aerosols on precipitation and clouds in the Amazon Basin: a satellite-based  
707 empirical study, *J. Geophys. Res.*, 111, D19204, doi:10.1029/2005jd006884, 2006.

- 708 Mayol-Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari, S.,  
709 Facchini, M. C., Fuzzi, S., and Artaxo, P.: Water-soluble organic compounds in biomass  
710 burning aerosols over Amazonia 2. Apportionment of the chemical composition and  
711 importance of the polyacidic fraction, *J. Geophys. Res.*, 107, 8091,  
712 doi:10.1029/2001jd000522, 2002.
- 713 Medeiros, P. M., and Simoneit, B. R. T.: Analysis of sugars in environmental samples by  
714 gas chromatography-mass spectrometry, *J. Chromatogr. A*, 1141, 271–278,  
715 doi:10.1016/j.chroma.2006.12.017, 2007.
- 716 Miyazaki, Y., Kawamura, K., Jung, J., Furutani, H., and Uematsu, M.: Latitudinal  
717 distributions of organic nitrogen and organic carbon in marine aerosols over the western  
718 North Pacific, *Atmos. Chem. Phys.*, 11, 3037–3049, doi:10.5194/acp-11-3037-2011,  
719 2011.
- 720 Mkoma, S. L., Kawamura, K., and Fu, P. Q.: Contributions of biomass/biofuel burning to  
721 organic aerosols and particulate matter in Tanzania, East Africa, based on analyses of  
722 ionic species, organic and elemental carbon, levoglucosan and mannosan, *Atmos. Chem.*  
723 *Phys.*, 13, 10325–10338, doi:10.5194/acp-13-10325-2013, 2013.
- 724 Mochida, M., Kawamura, K., Fu, P., and Takemura, T.: Seasonal variation of levoglucosan  
725 in aerosols over the western North Pacific and its assessment as a biomass-burning tracer,  
726 *Atmos. Environ.*, 44, 3511–3518, doi:10.1016/j.atmosenv.2010.06.017, 2010.
- 727 Okinawa prefecture: Integrative usage plan of biomass in Okinawa (in Japanese), Okinawa  
728 prefecture website,  
729 <http://www.pref.okinawa.jp/site/norin/norinkikaku/kikaku/documents/biomass.pdf>  
730 (accessed July 8, 2014), 2005.
- 731 Paatero, P., and Tapper, U.: Positive Matrix Factorization – a nonnegative factor model with  
732 optimal utilization of error–estimates of data values, *Environmetrics*, 5(2), 111–126,  
733 1994.
- 734 Paulot, F., Jacob, D. J., Pinder, R. W., Bash, J. O., Travis, K., and Henze, D. K.: Ammonia  
735 emissions in the United States, European Union, and China derived by high-resolution  
736 inversion of ammonium wet deposition data: Interpretation with a new agricultural  
737 emissions inventory (MASAGE\_NH3), *J. Geophys. Res.*, 119, 4343–4364,  
738 doi:10.1002/2013JD021130, 2014.

- 739 Penner, J. E., Dickinson, R. E., and O'Neill, C. A.: Effects of Aerosol from Biomass  
740 Burning on the Global Radiation Budget, *Science*, 256, 1432–1434,  
741 doi:10.1126/science.256.5062.1432, 1992.
- 742 Pio, C. A., Legrand, M., Alves, C. A., Oliveira, T., Afonso, J., Caseiro, A., Puxbaum, H.,  
743 Sanchez-Ochoa, A., and Gelencsér, A.: Chemical composition of atmospheric aerosols  
744 during the 2003 summer intense forest fire period, *Atmos. Environ.*, 42, 7530–7543,  
745 doi:10.1016/j.atmosenv.2008.05.032, 2008.
- 746 Pio, C. A., Legrand, M., Oliveira, T., Afonso, J., Santos, C., Caseiro, A., Fialho, P., Barata,  
747 F., Puxbaum, H., Sanchez-Ochoa, A., Kasper-Giebl, A., Gelencsér, A., Preunkert, S., and  
748 Schock, M.: Climatology of aerosol composition (organic versus inorganic) at nonurban  
749 sites on a west-east transect across Europe, *J. Geophys. Res.*, 112, D23S02,  
750 10.1029/2006JD008038, 2007.
- 751 Prenni, A. J., DeMott, P. J., Sullivan, A. P., Sullivan, R. C., Kreidenweis, S. M., and Rogers,  
752 D. C.: Biomass burning as a potential source for atmospheric ice nuclei: Western  
753 wildfires and prescribed burns, *Geophys. Res. Lett.*, 39, L11805,  
754 doi:10.1029/2012gl051915, 2012.
- 755 Sang, X. F., Chan, C. Y., Engling, G., Chan, L. Y., Wang, X. M., Zhang, Y. N., Shi, S.,  
756 Zhang, Z. S., Zhang, T., and Hu, M.: Levoglucosan enhancement in ambient aerosol  
757 during springtime transport events of biomass burning smoke to Southeast China, *Tellus*,  
758 63B, 129–139, doi:10.1111/j.1600-0889.2010.00515.x, 2011.
- 759 Schkolnik, G., and Rudich, Y.: Detection and quantification of levoglucosan in atmospheric  
760 aerosols: a review, *Anal. Bioanal. Chem.*, 385, 26–33, doi:10.1007/s00216-005-0168-5,  
761 2006.
- 762 Schmidl, C., Bauer, H., Dattler, A., Hitzenberger, R., Weissenboeck, G., Marr, I. L., and  
763 Puxbaum, H.: Chemical characterisation of particle emissions from burning leaves,  
764 *Atmos. Environ.*, 42, 9070–9079, doi:10.1016/j.atmosenv.2008.09.010, 2008a.
- 765 Schmidl, C., Marr, I. L., Caseiro, A., Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A.,  
766 and Puxbaum, H.: Chemical characterisation of fine particle emissions from wood stove  
767 combustion of common woods growing in mid-European Alpine regions, *Atmos.*  
768 *Environ.*, 42, 126–141, doi:10.1016/j.atmosenv.2007.09.028, 2008b.

- 769 Sheesley, R. J., Schauer, J. J., Chowdhury, Z., Cass, G. R., and Simoneit, B. R. T.:  
770 Characterization of organic aerosols emitted from the combustion of biomass indigenous  
771 to South Asia, *J. Geophys. Res.*, 108, 4285, doi:10.1029/2002jd002981, 2003.
- 772 Shen, Z., Cao, J., Arimoto, R., Han, Z., Zhang, R., Han, Y., Liu, S., Okuda, T., Nakao, S.,  
773 and Tanaka, S.: Ionic composition of TSP and PM<sub>2.5</sub> during dust storms and air pollution  
774 episodes at Xi'an, China, *Atmos. Environ.*, 43, 2911–2918,  
775 doi:10.1016/j.atmosenv.2009.03.005, 2009.
- 776 Shen, Z. X., Cao, J. J., Arimoto, R., Zhang, R. J., Jie, D. M., Liu, S. X., and Zhu, C. S.:  
777 Chemical composition and source characterization of spring aerosol over Horqin sand  
778 land in northeastern China, *J. Geophys. Res.*, 112, D14315, 10.1029/2006JD007991,  
779 2007.
- 780 Simoneit, B. R. T.: Biomass burning - a review of organic tracers for smoke from  
781 incomplete combustion, *Appl. Geochem.*, 17, 129–162, doi:10.1016/S0883-  
782 2927(01)00061-0, 2002.
- 783 Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P.,  
784 Rogge, W. F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning  
785 and atmospheric particles, *Atmos. Environ.*, 33, 173–182, doi:10.1016/S1352-  
786 2310(98)00145-9, 1999. Simoneit, B. R. T., Elias, V. O., Kobayashi, M., Kawamura, K.,  
787 Rushdi, A. I., Medeiros, P. M., Rogge, W. F., and Didyk, B. M.: Sugars Dominant Water-  
788 Soluble Organic Compounds in Soils and Characterization as Tracers in Atmospheric  
789 Particulate Matter, *Environ. Sci. Technol.*, 38, 5939–5949, doi:10.1021/es0403099, 2004.
- 790 Stone, D., Whalley, L. K., and Heard, D. E.: Tropospheric OH and HO<sub>2</sub> radicals: field  
791 measurements and model comparisons, *Chem. Soc. Rev.*, 41, 6348–6404,  
792 doi:10.1039/c2cs35140d, 2012.
- 793 Streets, D. G., Yarber, K. F., Woo, J. H., and Carmichael, G. R.: Biomass burning in Asia:  
794 Annual and seasonal estimates and atmospheric emissions, *Global Biogeochem. Cycles*,  
795 17, 1099, doi:10.1029/2003gb002040, 2003.
- 796 Sullivan, A. P., Holden, A. S., Patterson, L. A., McMeeking, G. R., Kreidenweis, S. M.,  
797 Malm, W. C., Hao, W. M., Wold, C. E., and Collett, J. L.: A method for smoke marker  
798 measurements and its potential application for determining the contribution of biomass  
799 burning from wildfires and prescribed fires to ambient PM<sub>2.5</sub> organic carbon, *J. Geophys*  
800 *Res.*, 113, D22302, doi:10.1029/2008JD010216, 2008.



- 801 Sullivan, A. P., Frank, N., Onstad, G., Simpson, C. D., and Collett, J. L.: Application of  
802 high-performance anion-exchange chromatography-pulsed amperometric detection for  
803 measuring carbohydrates in routine daily filter samples collected by a national network: 1.  
804 Determination of the impact of biomass burning in the upper Midwest, *J. Geophys. Res.*,  
805 116, D08302, doi:10.1029/2010jd014166, 2011.
- 806 Sutton, M. A., Erisman, J. W., Dentener, F., and Möller, D.: Ammonia in the environment:  
807 From ancient times to the present, *Environ. Pollut.*, 156, 583–604,  
808 doi:10.1016/j.envpol.2008.03.013, 2008.
- 809 Tanimoto, H., Sato, K., Butler, T. I. M., Lawrence, M. G., Fisher, J. A., Kopacz, M.,  
810 Yantosca, R. M., Kanaya, Y., Kato, S., Okuda, T., Tanaka, S., and Zeng, J.: Exploring  
811 CO pollution episodes observed at Rishiri Island by chemical weather simulations and  
812 AIRS satellite measurements: long-range transport of burning plumes and implications  
813 for emissions inventories, *Tellus*, 61B, 394–407, doi:10.1111/j.1600-0889.2008.00407.x,  
814 2009.
- 815 Urban, R. C., Lima-Souza, M., Caetano-Silva, L., Queiroz, M. E. C., Nogueira, R. F. P.,  
816 Allen, A. G., Cardoso, A. A., Held, G., and Campos, M. L. A. M.: Use of levoglucosan,  
817 potassium, and water-soluble organic carbon to characterize the origins of biomass-  
818 burning aerosols, *Atmos. Environ.*, 61, 562–569, doi:10.1016/j.atmosenv.2012.07.082,  
819 2012.
- 820 van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Kasibhatla, P. S., and  
821 Arellano Jr, A. F.: Interannual variability in global biomass burning emissions from 1997  
822 to 2004, *Atmos. Chem. Phys.*, 6, 3423–3441, doi:10.5194/acp-6-3423-2006, 2006.
- 823 van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S.,  
824 Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and  
825 the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009),  
826 *Atmos. Chem. Phys.*, 10, 11707–11735, doi:10.5194/acp-10-11707-2010, 2010.
- 827 Waked, A., Favez, O., Alleman, L. Y., Piot, C., Petit, J. E., Delaunay, T., Verlinden, E.,  
828 Golly, B., Besombes, J. L., Jaffrezo, J. L., and Leoz-Garziandia, E.: Source  
829 apportionment of PM<sub>10</sub> in a north-western Europe regional urban background site (Lens,  
830 France) using positive matrix factorization and including primary biogenic emissions,  
831 *Atmos. Chem. Phys.*, 14, 3325–3346, doi:10.5194/acp-14-3325-2014, 2014.

- 832 Wang, H., Kawamura, K., and Shooter, D.: Carbonaceous and ionic components in  
833 wintertime atmospheric aerosols from two New Zealand cities: Implications for solid fuel  
834 combustion, *Atmos. Environ.*, 39, 5865–5875, doi:10.1016/j.atmosenv.2005.06.031,  
835 2005.
- 836 Yan, X., Ohara, T., and Akimoto, H.: Bottom-up estimate of biomass burning in mainland  
837 China, *Atmos. Environ.*, 40, 5262–5273, doi:10.1016/j.atmosenv.2006.04.040, 2006.
- 838 Yevich, R., and Logan, J. A.: An assessment of biofuel use and burning of agricultural  
839 waste in the developing world, *Global Biogeochem. Cycles*, 17, 1095,  
840 doi:10.1029/2002gb001952, 2003.
- 841 Yttri, K. E., Lund Myhre, C., Eckhardt, S., Fiebig, M., Dye, C., Hirdman, D., Ström, J.,  
842 Klimont, Z., and Stohl, A.: Quantifying black carbon from biomass burning by means of  
843 levoglucosan – a one-year time series at the Arctic observatory Zeppelin, *Atmos. Chem.*  
844 *Phys.*, 14, 6427–6442, doi:10.5194/acp-14-6427-2014, 2014.
- 845 Zhang, H., Ye, X., Cheng, T., Chen, J., Yang, X., Wang, L., and Zhang, R.: A laboratory  
846 study of agricultural crop residue combustion in China: Emission factors and emission  
847 inventory, *Atmos. Environ.*, 42, 8432–8441, doi:10.1016/j.atmosenv.2008.08.015, 2008.
- 848 Zhang, Y., Dore, A. J., Ma, L., Liu, X. J., Ma, W. Q., Cape, J. N., and Zhang, F. S.:  
849 Agricultural ammonia emissions inventory and spatial distribution in the North China  
850 Plain, *Environ. Pollut.*, 158, 490–501, doi:10.1016/j.envpol.2009.08.033, 2010.
- 851 Zhang, Y., Obrist, D., Zielinska, B., and Gertler, A.: Particulate emissions from different  
852 types of biomass burning, *Atmos. Environ.*, 72, 27–35,  
853 doi:10.1016/j.atmosenv.2013.02.026, 2013.
- 854 Zhang, Y. N., Zhang, Z. S., Chan, C. Y., Engling, G., Sang, X. F., Shi, S., and Wang, X. M.:  
855 Levoglucosan and carbonaceous species in the background aerosol of coastal southeast  
856 China: case study on transport of biomass burning smoke from the Philippines, *Environ.*  
857 *Sci. Pollut. Res.*, 19, 244–255, doi:10.1007/s11356-011-0548-7, 2012.
- 858 Zhang, Y. X., Shao, M., Zhang, Y. H., Zeng, L. M., He, L. Y., Zhu, B., Wei, Y. J., and Zhu,  
859 X. L.: Source profiles of particulate organic matters emitted from cereal straw burnings, *J.*  
860 *Environ. Sci.*, 19, 167–175, doi:10.1016/S1001-0742(07)60027-8, 2007.
- 861 Zhu, C., and Kawamura K.: Seasonal variations of organic tracers of primary biological  
862 aerosol particles and soil dust at subtropical Okinawa Island in the western North Pacific  
863 rim: Asian outflow and local sources, *J. Geophys. Res.*, under review, 2014.

864 Zhu, C., Yoshikawa-Inoue, H., Tohjima, Y., and Irino, T.: Variations in black carbon on  
865 Rishiri Island, northern Japan, *Geochem. J.*, accepted, 2015.

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

867 (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

868 <sup>a</sup> Seasons are divided as December-February in winter, March-May in spring, June-August in summer, and September-November in autumn.869 <sup>b</sup> sd. denotes standard deviation (1σ).870 <sup>c</sup> nd denotes not detected.

871 Table 2. Linear correlation coefficients ( $r$ ) among anhydrosugars, major ions and carbonaceous components in Okinawa aerosols from  
 872 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***	1								
Galactosan	-0.19 <sup>a</sup>	0.17	1							
Anhydrosugars	0.42	0.80	-0.06	1						
nss-K <sup>+</sup>	0.38***	0.36***	0.08	0.35***	1					
NH <sub>4</sub> <sup>+</sup>	0.39***	0.20*	-0.10	0.32***	1	1				
nss-SO <sub>4</sub> <sup>2-</sup>	0.12	-0.05	-0.19	0.04	-0.03	0.21*	1			
WSOC	0.21*	0.59***	0.32*	0.50***	0.57***	0.03	-0.18	1		
OC	-0.04	0.12	0.33***	0.09	0.32***	-0.09	-0.17	0.67***	1	
EC	0.31*	0.52***	0.02	0.54***	0.40***	0.16	0.16	0.64***	0.28***	1

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

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

875 Table 3. Linear correlation coefficients ( $r$ ) between levoglucosan and other parameters including other two anhydrosugars, major ions  
 876 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>

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

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

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

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

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

883 **Figure captions**

884

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

887 Fig. 2. Monthly distribution of air mass origins to Cape Hedo, Okinawa shown by clusters of  
888 5-day backward trajectories arriving at 500 m above ground level during December  
889 2009–November 2011. The numbers in each panel indicate the percentages of daily  
890 trajectories in the month with such origins. Fire spots in East Asia in each month of the  
891 same period are also shown.

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

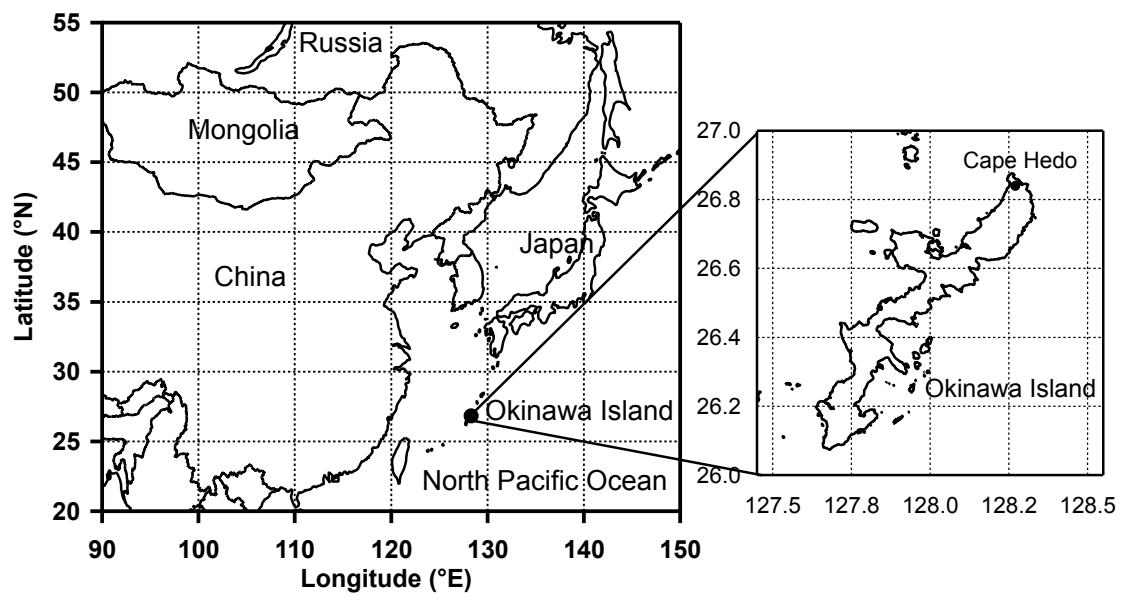
895 Fig. 4. Air mass origins for the events of elevated anhydrosugars corresponding to I and II in  
896 Figure 3 in (a) November 2–9, 2010 and (b) December 28, 2010–January 4, 2011,  
897 respectively. Clusters of 5-day backward trajectories arriving at 500 m above ground  
898 level at Cape Hedo, Okinawa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

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

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

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

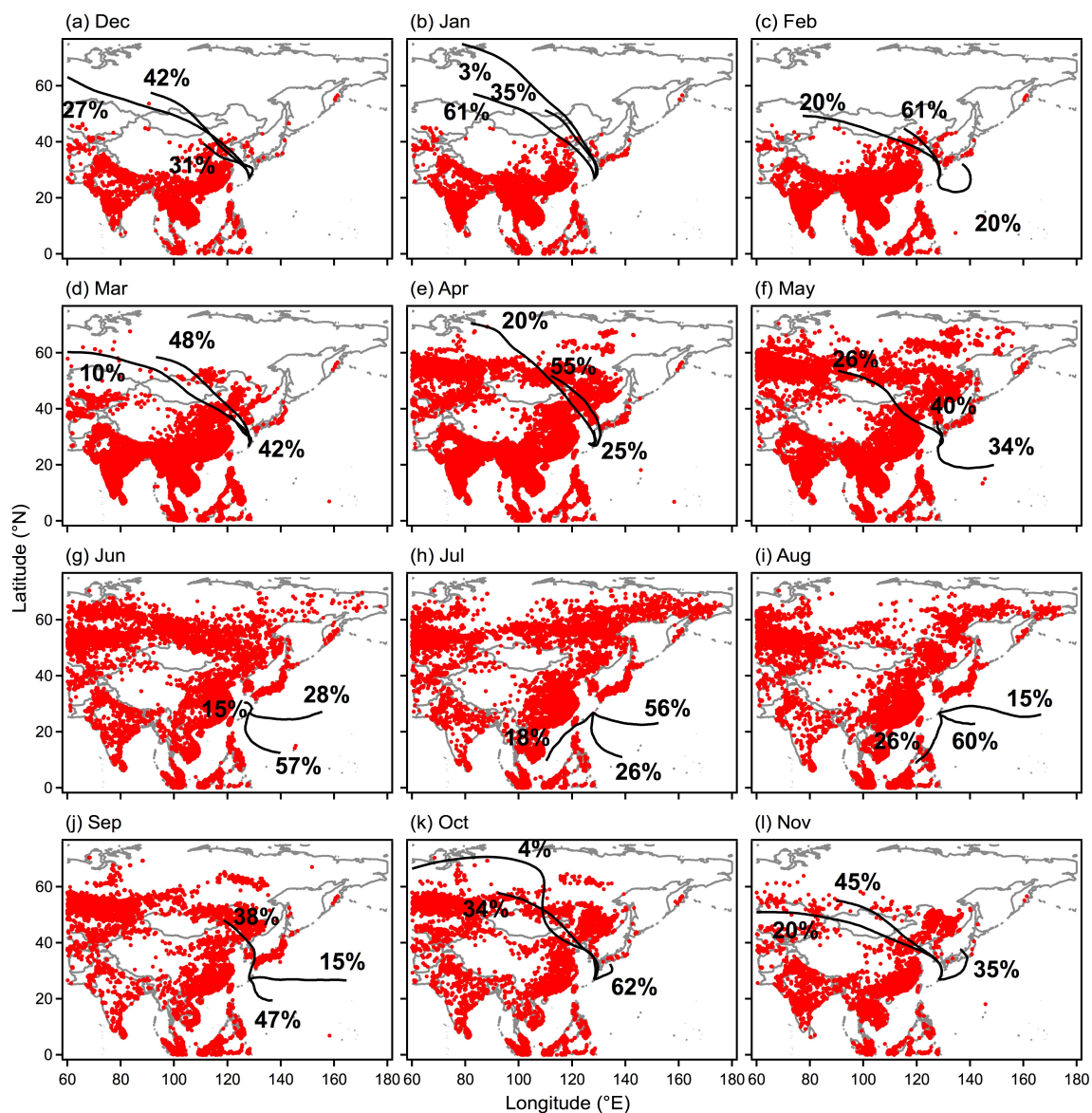




913

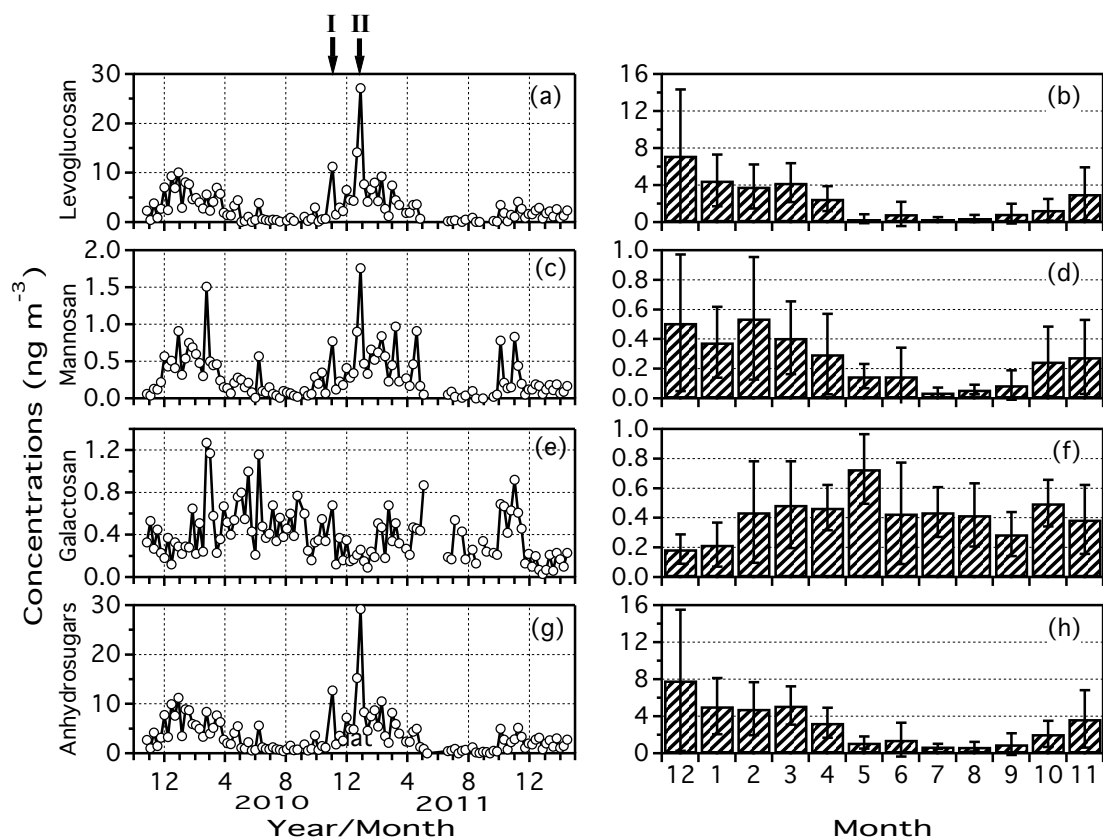
914 Fig. 1. Location of Cape Hedo, Okinawa in East Asia where total suspended particles (TSP)

915 were collected.



916

917 Fig. 2. Monthly distribution of air mass origins to Cape Hedo, Okinawa shown by clusters of  
 918 5-day backward trajectories arriving at 500 m above ground level during December 2009–  
 919 November 2011. The numbers in each panel indicate the percentages of daily trajectories in  
 920 the month with such origins. Fire spots in East Asia in each month of the same period are also  
 921 shown.

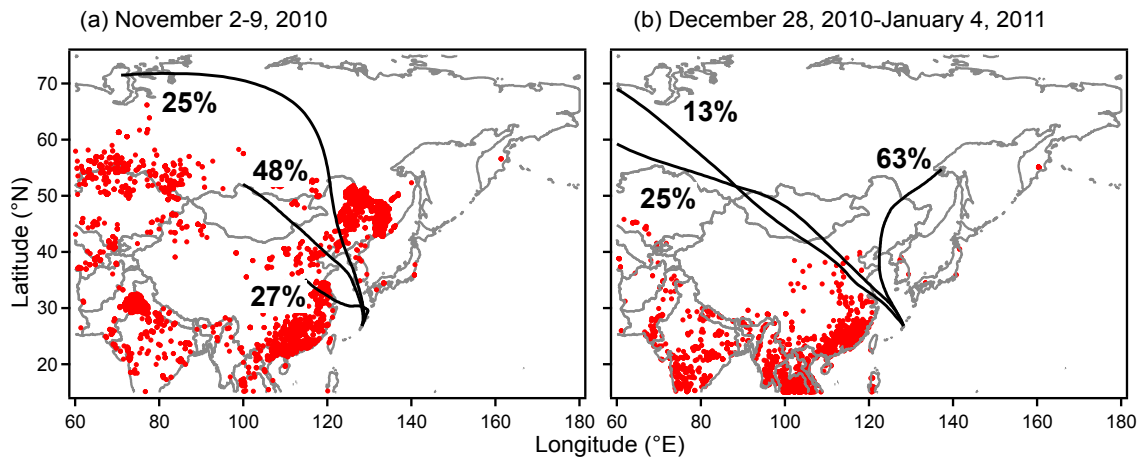


922

923 Fig. 3. Temporal variation (a, c, e, g) and monthly means (b, d, f, h) of anhydrosugars in

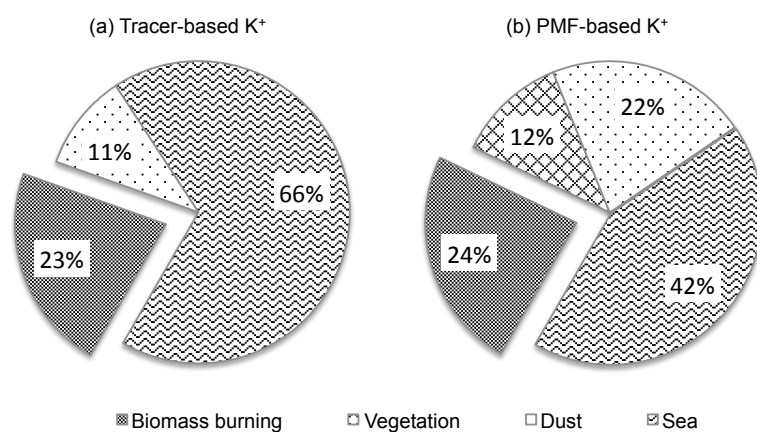
924 aerosols at Cape Hedo, Okinawa from October 2009 to February 2012. Typical elevation

925 events of anhydrosugars are marked I and II and analyzed in details.



926

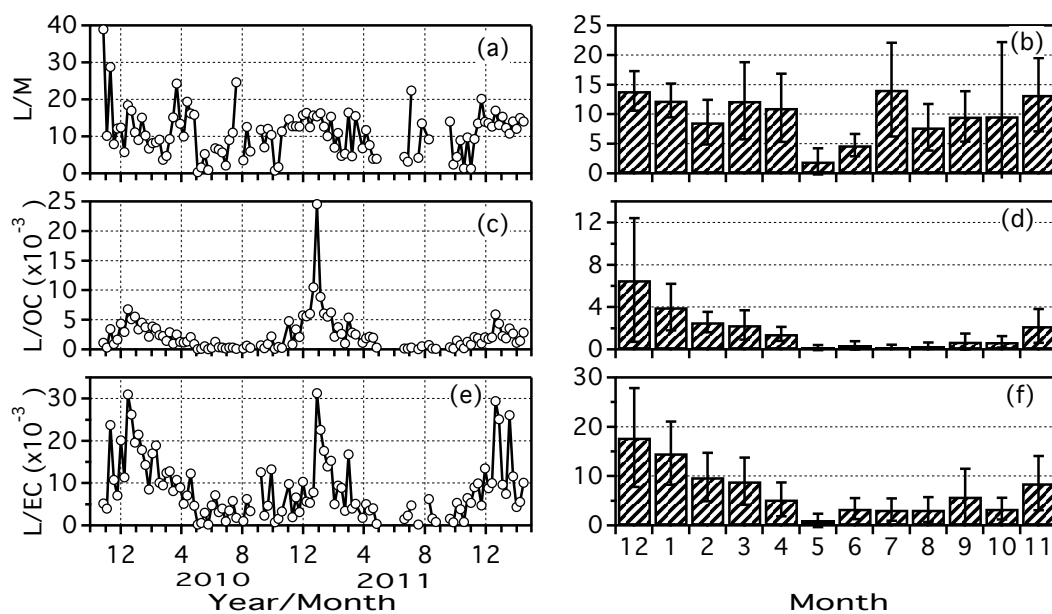
927 Fig. 4. Air mass origins for the events of elevated anhydrosugars corresponding to I and II in  
 928 Figure 3 in (a) November 2–9, 2010 and (b) December 28, 2010–January 4, 2011, respectively.  
 929 Clusters of 5–day backward trajectories arriving at 500 m above ground level at Cape Hedo,  
 930 Okinawa are given. The numbers in each panel indicate the percentages of hourly trajectories  
 931 in the events with such origins. Fire spots in East Asia during (a) October 28–November 9,  
 932 2010 and (b) December 23, 2010–January 4, 2011 are also shown.



933

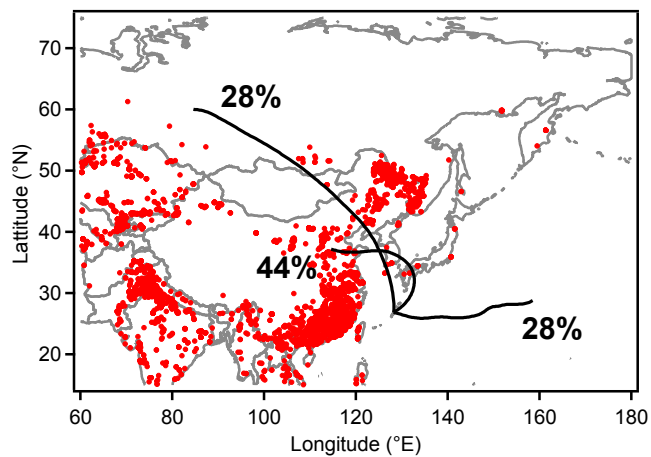
934 Fig. 5. Components of water-soluble  $K^+$  derived by (a) tracer-based method (Pio et al., 2008)

935 and (b) PMF analysis. Details on PMF analysis can be found in the supplementary material.



936

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



940

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