Authors' Responses to editor's Comments

Comments to the Author:

Some minor alterations are still needed in the main text before the manuscript and its Supplement can be published in ACP.

Response: We truly appreciate the editor for the detailed corrections. We have altered the manuscript accordingly. A manuscript with highlighted corrections is placed following this response. The revised manuscript is uploaded online. We look forward to its publication in Atmospheric Chemistry and Physics.

Main text:

Line 406: Replace "level BC" by "BC level".

Response: Replaced in line 406.

Line 488: "Although clear" by "Although a clear".

Response: Replaced in line 488.

Line 489: "for longitudinal" by "for the longitudinal".

Response: Replaced in line 489.

Line 490: "(ratios of these" by "(the ratios for these".

Response: Replaced in line 490.

Line 491: ", longitudinal" by ", the longitudinal".

Response: Replaced in lines 491-492.

Line 493: "of air masses" by "of the air masses".

Response: Replaced in line 493.

Line 494: "higher emission" by "a higher emission".

Response: Replaced in line 494.

Line 495: "Comprising with" by "Compared to".

Response: Replaced in line 495.

Line 497: "with those of maritime" by "as those of the maritime".

Response: Replaced in line 497.

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)

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^+ ($r = 0.38$, $p < 0.001$); the latter is another BB tracer. The analyses

14   of air mass trajectories and fire spots demonstrated that the seasonal variations of

15   anhydrsosugsars 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

1   Introduction

30

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_x during

38   BB affect O_3 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_2 (Goode et al., 2000; Konovalov et al., 2014), other greenhouse gases and

41   particles emitted from BB affect radiative forcing (Langenfelds 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_2 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-β-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 1.0×10^6 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 2.21×10^{-13} cm^3 molecule^{-1} s^{-1} at 25 °C, resulting in an atmospheric

80 lifetime of 26 days under the OH level of 2.0×10^6 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 Loas, 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 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°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^3 h^{-1} 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^2, < 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^{-1} 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^2) 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 µl of N, O-bis-

151 (trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethyl chloride and 10 µl of

152 pyridine for 3 h at 70 °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 µl) 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 × 0.25 mm × 0.25

160 µm) was used with helium as a carrier gas at a flow rate of 1.0 ml min^{-1}. The sample was

161 injected in a splitless mode at 280 °C. The column temperature was programed from 50 °C

162 (2 min) to 120 °C at 15 °C min^{-1} and then to 305 °C at 5 °C min^{-1}, followed by a final

163 isothermal hold at 305 °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 µl^{-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 pg μl^{-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 ng m^{-3} for ambient aerosols under a typical sampling volume of 9000

180   m^3, and an aliquot of 10 cm^2 of the used filter. LODs of mannosan and galactosan are

181   considered the same as for levoglucosan, because levogucosan 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 ng m^{-3}. Based on IC-determined K^+,

188   SO_4^{2-} and Na^+, we estimated the fractions of 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-K^+,

190   NH_4^+ and nss-SO_4^{2-} are discussed in this study. We also investigated 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_{CSH}). 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) ($1° \times 1°$) 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 ± 3.70 ng m^{-3} (mean ± 1 σ). Mannosan

264   and galactosan are 1 order of magnitude less abundant than levoglucosan. Seasonally,

265   levoglucosan clearly shows a winter maximum (5.30 ± 4.88 ng m^{-3}) and summer minimum

266   (0.57 ± 0.84 ng m^{-3}). Specifically, the monthly mean of levoglucosan in December ($7.21 \pm$

267   7.14 ng m^{-3}) is > 20 times higher than that in July (0.34 ± 0.20 ng m^{-3}) (Fig. 2). A similar

268   seasonal trend was observed for mannosan (0.47 ± 0.38 ng m^{-3} in winter and 0.08 ± 0.12 ng

269   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 ± 7.63 ng m^{-3}) and minimized in August (0.71 ± 0.52 ng m^{-3}), with a mean

275   of 3.53 ± 3.91 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 9.6×10^7 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 ng

315   m^{-3}) 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 4×10^6 radicals 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 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^+ is another typical tracer of BB (Sullivan et al., 2011). Positive correlations were

361   found between nss-K^+ 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 levogucosan as a

363   representative BB tracer, the correlations between anhydrosugars and nss-K^+ 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 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 NH_4^+ (Andreae and Merlet et al., 2001; Akagi et al.,

391   2011). NH_4^+ could also be formed in the atmosphere by the protonation of 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   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 NH_3-derived

397   NH_4^+ from agricultural activities, and transformation and wet scavenging during

398   atmospheric transport. Levoglucosan did not correlate with 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 (4.6×10^{-3}) and minimum in May (0.3×10^{-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 (10.0×10^{-3}, 4.6×10^{-3}

468   ^{3} and 3.8×10^{-3} for Changdao, Okinawa and Chichijima, respectively), spring (9.3×10^{-3},

469   1.6×10^{-3} and 1.3×10^{-3}) and autumn (5.4×10^{-3}, 1.5×10^{-3} and 1.1×10^{-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 (1.2×10^{-3}) is the

474   highest among the three sites, the L/OC ratio at Okinawa (0.3×10^{-3}) is lower than that of

475   Chichijima (0.6×10^{-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 (14.5×10^{-3})

482   and summer minimum (3.3×10^{-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 (3.3×10^{-3}) and Chichijima (6.5×10^{-3}) were of the same order

487 as those of Changdao (4.0×10^{-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

563

564 **References**

565 Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T.,

566   Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass

567   burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039–4072,

568   doi:10.5194/acp–11–4039–2011, 2011.

569 Akagi, S. K., Burling, I. R., Mendoza, A., Johnson, T. J., Cameron, M., Griffith, D. W. T.,

570   Paton–Walsh, C., Weise, D. R., Reardon, J., and Yokelson, R. J.: Field measurements of

571   trace gases emitted by prescribed fires in southeastern US pine forests using an open–

572   path FTIR system, Atmos. Chem. Phys., 14, 199–215, doi:10.5194/acp–14–199–2014,

573   2014.

574 Andreae, M. O., and Merlet, P.: Emission of trace gases and aerosols from biomass burning,

575   Global Biogeochem. Cycles, 15, 955–966, doi:10.1029/2000gb001382, 2001.

576 Arimoto, R., Zhang, X. Y., Huebert, B. J., Kang, C. H., Savoie, D. L., Prospero, J. M., Sage,

577   S. K., Schloesslin, C. A., Khaing, H. M., and Oh, S. N.: Chemical composition of

578   atmospheric aerosols from Zhenbeitai, China, and Gosan, South Korea, during ACE-Asia,

579   J. Geophys. Res., 109, D19S04, 10.1029/2003JD004323, 2004.

580 Asman, W. A. H., Sutton, M. A., and Schjørring, J. K.: Ammonia: emission, atmospheric

581   transport and deposition, New Phytol., 139, 27–48, 10.1046/j.1469-8137.1998.00180.x,

582   1998.

583 Bai, J., Sun, X., Zhang, C., Xu, Y., and Qi, C.: The OH-initiated atmospheric reaction

584   mechanism and kinetics for levoglucosan emitted in biomass burning, Chemosphere, 93,

585   2004–2010, 10.1016/j.chemosphere.2013.07.021, 2013.

586 Birch, M. E., and Cary, R. A.: Elemental carbon–based method for occupational monitoring

587   of particulate diesel exhaust: methodology and exposure issues, Analyst, 121, 1183–1190,

588   doi:10.1039/an9962101183, 1996.

589 Cao, J. J., Wu, F., Chow, J. C., Lee, S. C., Li, Y., Chen, S. W., An, Z. S., Fung, K. K.,

590   Watson, J. G., Zhu, C. S., and Liu, S. X.: Characterization and source apportionment of

591   atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China,

592   Atmos. Chem. Phys., 5, 3127–3137, 10.5194/acp–5–3127–2005, 2005.

593 Chen, J., Kawamura, K., Liu, C. Q., and Fu, P.: Long–term observations of saccharides in

594   remote marine aerosols from the western North Pacific: A comparison between 1990–

595   1993 and 2006–2009 periods, Atmos. Environ., 67, 448–458,

596   doi:10.1016/j.atmosenv.2012.11.014, 2013.

597   Draxler, R.R., and G. D. Rolph: HYSPLIT (HYbrid Single–Particle Lagrangian Integrated

598   Trajectory) Model, access via NOAA ARL READY Website,

599   http://www.arl.noaa.gov/HYSPLIT.php (accessed July 8, 2014), NOAA Air Resources

600   Laboratory, College Park, MD, 2013.

601   Duvall, R. M., Majestic, B. J., Shafer, M. M., Chuang, P. Y., Simoneit, B. R. T., and

602   Schauer, J. J.: The water-soluble fraction of carbon, sulfur, and crustal elements in Asian

603   aerosols and Asian soils, Atmos. Environ., 42, 5872–5884,

604   doi:10.1016/j.atmosenv.2008.03.028, 2008.

605   Engling, G., Carrico, C. M., Kreidenweis, S. M., Collett Jr, J. L., Day, D. E., Malm, W. C.,

606   Lincoln, E., Min Hao, W., Iinuma, Y., and Herrmann, H.: Determination of levoglucosan

607   in biomass combustion aerosol by high–performance anion–exchange chromatography

608   with pulsed amperometric detection, Atmos. Environ., 40, 299–311,

609   doi:10.1016/j.atmosenv.2005.12.069, 2006.

610   Engling, G., Lee, J. J., Tsai, Y. W., Lung, S. C. C., Chou, C. C. K., and Chan, C. Y.: Size-

611   resolved anhydrosugar composition in smoke aerosol from controlled field burning of

612   rice straw, Aerosol Sci. Technol., 43, 662–672, doi:10.1080/02786820902825113, 2009.

613   Engling, G., He, J., Betha, R., and Balasubramanian, R.: Assessing the regional impact of

614   indonesian biomass burning emissions based on organic molecular tracers and chemical

615   mass balance modeling, Atmos. Chem. Phys., 14, 8043–8054, doi:10.5194/acp-14-8043-

616   2014, 2014.

617   Fabbri, D., Torri, C., Simoneit, B. R. T., Marynowski, L., Rushdi, A. I., and Fabiańska, M.

618   J.: Levoglucosan and other cellulose and lignin markers in emissions from burning of

619   Miocene lignites, Atmos. Environ., 43, 2286–2295, doi:10.1016/j.atmosenv.2009.01.030,

620   2009.

621   Feng, J., Guo, Z., Chan, C. K., and Fang, M.: Properties of organic matter in $PM_{2.5}$ at

622   Changdao Island, China-A rural site in the transport path of the Asian continental

623   outflow, Atmos. Environ., 41, 1924–1935, doi:10.1016/j.atmosenv.2006.10.064, 2007.

624   Fine, P. M., Cass, G. R., and Simoneit, B. R.: Chemical characterization of fine particle

625   emissions from the fireplace combustion of wood types grown in the Midwestern and

626   Western United States, Environ. Eng. Sci., 21, 387–409, 2004.

627   Fu, P., Kawamura, K., Okuzawa, K., Aggarwal, S. G., Wang, G., Kanaya, Y., and Wang,

628   Z.: Organic molecular compositions and temporal variations of summertime mountain

629   aerosols over Mt. Tai, North China Plain, J. Geophys. Res., 113, D19107,

630   doi:10.1029/2008jd009900, 2008.

631   Fu, P., Kawamura, K., Chen, J., and Miyazaki, Y.: Secondary Production of Organic

632   Aerosols from Biogenic VOCs over Mt. Fuji, Japan, Environ. Sci. Technol., 48, 8491–

633   8497, 10.1021/es500794d, 2014.

634   Fu, P. Q., Kawamura, K., Chen, J., Li, J., Sun, Y. L., Liu, Y., Tachibana, E., Aggarwal, S.

635   G., Okuzawa, K., Tanimoto, H., Kanaya, Y., and Wang, Z. F.: Diurnal variations of

636   organic molecular tracers and stable carbon isotopic composition in atmospheric aerosols

637   over Mt. Tai in the North China Plain: an influence of biomass burning, Atmos. Chem.

638   Phys., 12, 8359–8375, 10.5194/acp-12-8359-2012, 2012.

639   Galanter, M., Levy, H., and Carmichael, G. R.: Impacts of biomass burning on tropospheric

640   CO, NO_x, and O_3, J. Geophys. Res., 105, 6633–6653, doi:10.1029/1999jd901113, 2000.

641   George, S. K., Nair, P. R., Parameswaran, K., Jacob, S., and Abraham, A.: Seasonal trends

642   in chemical composition of aerosols at a tropical coastal site of India, J. Geophys. Res.,

643   113, D16209, doi:10.1029/2007jd009507, 2008.

644   Goode, J. G., Yokelson, R. J., Ward, D. E., Susott, R. A., Babbitt, R. E., Davies, M. A., and

645   Hao, W. M.: Measurements of excess O_3, CO_2, CO, CH_4, C_2H_4, C_2H_2, HCN, NO, NH_3,

646   HCOOH, CH_3COOH, HCHO, and CH_3OH in 1997 Alaskan biomass burning plumes by

647   airborne Fourier transform infrared spectroscopy (AFTIR), J. Geophys. Res., 105,

648   22147–22166, doi:10.1029/2000jd900287, 2000.

649   Graham, B., Mayol–Bracero, O. L., Guyon, P., Roberts, G. C., Decesari, S., Facchini, M. C.,

650   Artaxo, P., Maenhaut, W., Köll, P., and Andreae, M. O.: Water–soluble organic

651   compounds in biomass burning aerosols over Amazonia 1. Characterization by NMR and

652   GC-MS, J. Geophys. Res., 107, D20, doi:10.1029/2001jd000336, 2002.

653   Hays, M. D., Fine, P. M., Geron, C. D., Kleeman, M. J., and Gullett, B. K.: Open burning of

654   agricultural biomass: Physical and chemical properties of particle-phase emissions,

655   Atmos. Environ., 39, 6747–6764, doi:10.1016/j.atmosenv.2005.07.072, 2005.

656   Hennigan, C. J., Sullivan, A. P., Collett, J. L., and Robinson, A. L.: Levoglucosan stability

657   in biomass burning particles exposed to hydroxyl radicals, Geophys. Res. Lett., 37,

658   L09806, doi:10.1029/2010gl043088, 2010.

659 Ho, K. F., Engling, G., Ho, S. S. H., Huang, R., Lai, S., Cao, J., and Lee, S. C.: Seasonal

660   variations of anhydrosugars in $PM_{2.5}$ in the Pearl River Delta Region, China, Tellus, 66B,

661   22577, doi:10.3402/tellusb.v66.22577, 2014.

662 Hoffmann, D., Tilgner, A., Iinuma, Y., and Herrmann, H.: Atmospheric stability of

663   levoglucosan: a detailed laboratory and modeling study, Environ. Sci. Technol., 44, 694–

664   699, doi:10.1021/es902476f, 2010.

665 Honrath, R. E., Owen, R. C., Val Martín, M., Reid, J. S., Lapina, K., Fialho, P., Dziobak, M.

666   P., Kleissl, J., and Westphal, D. L.: Regional and hemispheric impacts of anthropogenic

667   and biomass burning emissions on summertime CO and O_3 in the North Atlantic lower

668   free troposphere, J. Geophys. Res., 109, D24310, doi:10.1029/2004jd005147, 2004.

669 Hu, Q. H., Xie, Z. Q., Wang, X. M., Kang, H., and Zhang, P.: Levoglucosan indicates high

670   levels of biomass burning aerosols over oceans from the Arctic to Antarctic, Sci. Rep., 3,

671   doi:10.1038/srep03119, 2013

672 Huang, X., Song, Y., Li, M., Li, J., Huo, Q., Cai, X., Zhu, T., Hu, M., and Zhang, H.: A

673   high-resolution ammonia emission inventory in China, Global Biogeochem. Cycles, 26,

674   GB1030, 10.1029/2011GB004161, 2012.

675 Iinuma, Y., Brüggemann, E., Gnauk, T., Müller, K., Andreae, M. O., Helas, G., Parmar, R.,

676   and Herrmann, H.: Source characterization of biomass burning particles: The combustion

677   of selected European conifers, African hardwood, savanna grass, and German and

678   Indonesian peat, J. Geophys. Res., 112, D08209, doi:10.1029/2006jd007120, 2007.

679 Itahashi, S., Uno, I., Irie, H., Kurokawa, J. I., and Ohara, T.: Regional modeling of

680   tropospheric NO_2 vertical column density over East Asia during the period 2000–2010:

681   comparison with multisatellite observations, Atmos. Chem. Phys., 14, 3623–3635,

682   10.5194/acp-14-3623-2014, 2014.

683 Kanaya, Y., Sadanaga, Y., Nakamura, K., and Akimoto, H.: Behavior of OH and HO_2

684   radicals during the Observations at a Remote Island of Okinawa (ORION99) field

685   campaign: 1. Observation using a laser-induced fluorescence instrument, J. Geophys.

686   Res., 106, 24197–24208, doi:10.1029/2000jd000178, 2001.

687 Kawamura, K., Izawa, Y., Mochida, M., and Shiraiwa, T.: Ice core records of biomass

688   burning tracers (levoglucosan and dehydroabietic, vanillic and p-hydroxybenzoic acids)

689   and total organic carbon for past 300 years in the Kamchatka Peninsula, Northeast Asia,

690   Geochim. Cosmochim. Ac., 99, 317–329, doi:10.1016/j.gca.2012.08.006, 2012.

691 Konovalov, I. B., Berezin, E. V., Ciais, P., Broquet, G., Beekmann, M., Hadji–Lazaro, J.,
692   Clerbaux, C., Andreae, M. O., Kaiser, J. W., and Schulze, E. D.: Constraining CO_2
693   emissions from open biomass burning by satellite observations of co–emitted species: a
694   method and its application to wildfires in Siberia, Atmos. Chem. Phys. Discuss., 14,
695   3099–3168, doi:10.5194/acpd-14-3099-2014, 2014.

696 Kudo, S., Tanimoto, H., Inomata, S., Saito, S., Pan, X., Kanaya, Y., Taketani, F., Wang, Z.,
697   Chen, H., Dong, H., Zhang, M., and Yamaji, K.: Emissions of nonmethane volatile
698   organic compounds from open crop residue burning in the Yangtze River Delta region,
699   China, J. Geophys. Res., 119, 7684–7698, doi:10.1002/2013jd021044, 2014.

700 Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Diurnal
701   variation in the water–soluble inorganic ions, organic carbon and isotopic compositions
702   of total carbon and nitrogen in biomass burning aerosols from the LBA-SMOCC
703   campaign in Rondônia, Brazil, J Aerosol Sci., 41, 118–133,
704   doi:10.1016/j.jaerosci.2009.08.006, 2010.

705 Kunwar, B., and Kawamura, K.: One-year observations of carbonaceous and nitrogenous
706   components and major ions in the aerosols from subtropical Okinawa Island, an outflow
707   region of Asian dusts, Atmos. Chem. Phys., 14, 1819–1836, doi:10.5194/acp-14-1819-
708   2014, 2014.

709 Křůmal, K., Mikuška, P., Vojtěšek, M., and Večeřa, Z.: Seasonal variations of
710   monosaccharide anhydrides in PM_1 and $PM_{2.5}$ aerosol in urban areas, Atmos. Environ.,
711   44, 5148–5155, doi:10.1016/j.atmosenv.2010.08.057, 2010.

712 Lai, C., Liu, Y., Ma, J., Ma, Q., and He, H.: Degradation kinetics of levoglucosan initiated
713   by hydroxyl radical under different environmental conditions, Atmos. Environ., 91, 32–
714   39, 10.1016/j.atmosenv.2014.03.054, 2014.

715 Langenfelds, R. L., Francey, R. J., Pak, B. C., Steele, L. P., Lloyd, J., Trudinger, C. M., and
716   Allison, C. E.: Interannual growth rate variations of atmospheric CO_2 and its $\delta^{13}C$, H_2,
717   CH_4, and CO between 1992 and 1999 linked to biomass burning, Global Biogeochem.
718   Cycles, 16, 1048, doi:10.1029/2001gb001466, 2002.

719 Laumbach, R. J., and Kipen, H. M.: Respiratory health effects of air pollution: Update on
720   biomass smoke and traffic pollution, J. Allergy Clin. Immunol., 129, 3–11,
721   doi:10.1016/j.jaci.2011.11.021, 2012.

722 Lin, J. C., Matsui, T., Pielke, R. A., and Kummerow, C.: Effects of biomass-burning-
723   derived aerosols on precipitation and clouds in the Amazon Basin: a satellite-based
724   empirical study, J. Geophys. Res., 111, D19204, doi:10.1029/2005jd006884, 2006.

725 Mayol–Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari, S.,
726   Facchini, M. C., Fuzzi, S., and Artaxo, P.: Water-soluble organic compounds in biomass
727   burning aerosols over Amazonia 2. Apportionment of the chemical composition and
728   importance of the polyacidic fraction, J. Geophys. Res., 107, 8091,
729   doi:10.1029/2001jd000522, 2002.

730 Medeiros, P. M., and Simoneit, B. R. T.: Analysis of sugars in environmental samples by
731   gas chromatography-mass spectrometry, J. Chromatogr. A, 1141, 271–278,
732   doi:10.1016/j.chroma.2006.12.017, 2007.

733 Miyazaki, Y., Kawamura, K., Jung, J., Furutani, H., and Uematsu, M.: Latitudinal
734   distributions of organic nitrogen and organic carbon in marine aerosols over the western
735   North Pacific, Atmos. Chem. Phys., 11, 3037–3049, doi:10.5194/acp-11-3037-2011,
736   2011.

737 Mkoma, S. L., Kawamura, K., and Fu, P. Q.: Contributions of biomass/biofuel burning to
738   organic aerosols and particulate matter in Tanzania, East Africa, based on analyses of
739   ionic species, organic and elemental carbon, levoglucosan and mannosan, Atmos. Chem.
740   Phys., 13, 10325–10338, doi:10.5194/acp-13-10325-2013, 2013.

741 Mochida, M., Kawamura, K., Fu, P., and Takemura, T.: Seasonal variation of levoglucosan
742   in aerosols over the western North Pacific and its assessment as a biomass-burning tracer,
743   Atmos. Environ., 44, 3511–3518, doi:10.1016/j.atmosenv.2010.06.017, 2010.

744 Okinawa prefecture: Integrative usage plan of biomass in Okinawa (in Japanese), Okinawa
745   prefecture website,
746   http://www.pref.okinawa.jp/site/norin/norinkikaku/kikaku/documents/biomass.pdf
747   (accessed July 8, 2014), 2005.

748 Paatero, P., and Tapper, U.: Positive Matrix Factorization – a nonnegative factor model with
749   optimal utilization of error–estimates of data values, Environmetrics, 5(2), 111–126,
750   1994.

751 Paulot, F., Jacob, D. J., Pinder, R. W., Bash, J. O., Travis, K., and Henze, D. K.: Ammonia
752   emissions in the United States, European Union, and China derived by high-resolution
753   inversion of ammonium wet deposition data: Interpretation with a new agricultural

754   emissions inventory (MASAGE_NH3), J. Geophys. Res., 119, 4343–4364,

755   doi:10.1002/2013JD021130, 2014.

756   Penner, J. E., Dickinson, R. E., and O'Neill, C. A.: Effects of Aerosol from Biomass

757   Burning on the Global Radiation Budget, Science, 256, 1432–1434,

758   doi:10.1126/science.256.5062.1432, 1992.

759   Pio, C. A., Legrand, M., Oliveira, T., Afonso, J., Santos, C., Caseiro, A., Fialho, P., Barata,

760   F., Puxbaum, H., Sanchez-Ochoa, A., Kasper-Giebl, A., Gelencsér, A., Preunkert, S., and

761   Schock, M.: Climatology of aerosol composition (organic versus inorganic) at nonurban

762   sites on a west-east transect across Europe, J. Geophys. Res., 112, D23S02,

763   10.1029/2006JD008038, 2007.

764   Pio, C. A., Legrand, M., Alves, C. A., Oliveira, T., Afonso, J., Caseiro, A., Puxbaum, H.,

765   Sanchez-Ochoa, A., and Gelencsér, A.: Chemical composition of atmospheric aerosols

766   during the 2003 summer intense forest fire period, Atmos. Environ., 42, 7530–7543,

767   doi:10.1016/j.atmosenv.2008.05.032, 2008.

768   Prenni, A. J., DeMott, P. J., Sullivan, A. P., Sullivan, R. C., Kreidenweis, S. M., and Rogers,

769   D. C.: Biomass burning as a potential source for atmospheric ice nuclei: Western

770   wildfires and prescribed burns, Geophys. Res. Lett., 39, L11805,

771   doi:10.1029/2012gl051915, 2012.

772   Sang, X. F., Chan, C. Y., Engling, G., Chan, L. Y., Wang, X. M., Zhang, Y. N., Shi, S.,

773   Zhang, Z. S., Zhang, T., and Hu, M.: Levoglucosan enhancement in ambient aerosol

774   during springtime transport events of biomass burning smoke to Southeast China, Tellus,

775   63B, 129–139, doi:10.1111/j.1600-0889.2010.00515.x, 2011.

776   Schkolnik, G., and Rudich, Y.: Detection and quantification of levoglucosan in atmospheric

777   aerosols: a review, Anal. Bioanal. Chem., 385, 26–33, doi:10.1007/s00216-005-0168-5,

778   2006.

779   Schmidl, C., Bauer, H., Dattler, A., Hitzenberger, R., Weissenboeck, G., Marr, I. L., and

780   Puxbaum, H.: Chemical characterisation of particle emissions from burning leaves,

781   Atmos. Environ., 42, 9070–9079, doi:10.1016/j.atmosenv.2008.09.010, 2008a.

782   Schmidl, C., Marr, I. L., Caseiro, A., Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A.,

783   and Puxbaum, H.: Chemical characterisation of fine particle emissions from wood stove

784   combustion of common woods growing in mid-European Alpine regions, Atmos.

785   Environ., 42, 126–141, doi:10.1016/j.atmosenv.2007.09.028, 2008b.

786 Sheesley, R. J., Schauer, J. J., Chowdhury, Z., Cass, G. R., and Simoneit, B. R. T.:

787   Characterization of organic aerosols emitted from the combustion of biomass indigenous

788   to South Asia, J. Geophys. Res., 108, 4285, doi:10.1029/2002jd002981, 2003.

789 Shen, Z., Cao, J., Arimoto, R., Han, Z., Zhang, R., Han, Y., Liu, S., Okuda, T., Nakao, S.,

790   and Tanaka, S.: Ionic composition of TSP and $PM_{2.5}$ during dust storms and air pollution

791   episodes at Xi'an, China, Atmos. Environ., 43, 2911–2918,

792   doi:10.1016/j.atmosenv.2009.03.005, 2009.

793 Shen, Z. X., Cao, J. J., Arimoto, R., Zhang, R. J., Jie, D. M., Liu, S. X., and Zhu, C. S.:

794   Chemical composition and source characterization of spring aerosol over Horqin sand

795   land in northeastern China, J. Geophys. Res., 112, D14315, 10.1029/2006JD007991,

796   2007.

797 Simoneit, B. R. T.: Biomass burning - a review of organic tracers for smoke from

798   incomplete combustion, Appl. Geochem., 17, 129–162, doi:10.1016/S0883-

799   2927(01)00061-0, 2002.

800 Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P.,

801   Rogge, W. F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning

802   and atmospheric particles, Atmos. Environ., 33, 173–182, doi:10.1016/S1352–

803   2310(98)00145–9, 1999.

804 Simoneit, B. R. T., Elias, V. O., Kobayashi, M., Kawamura, K., Rushdi, A. I., Medeiros, P.

805   M., Rogge, W. F., and Didyk, B. M.: SugarsDominant Water-Soluble Organic

806   Compounds in Soils and Characterization as Tracers in Atmospheric Particulate Matter,

807   Environ. Sci. Technol., 38, 5939–5949, doi:10.1021/es0403099, 2004.

808 Slade, J. H., and Knopf, D. A.: Multiphase OH oxidation kinetics of organic aerosol: The

809   role of particle phase state and relative humidity, Geophys. Res. Lett., 41, 5297–5306,

810   10.1002/2014GL060582, 2014.

811 Stone, D., Whalley, L. K., and Heard, D. E.: Tropospheric OH and HO_2 radicals: field

812   measurements and model comparisons, Chem. Soc. Rev., 41, 6348–6404,

813   doi:10.1039/c2cs35140d, 2012.

814 Streets, D. G., Yarber, K. F., Woo, J. H., and Carmichael, G. R.: Biomass burning in Asia:

815   Annual and seasonal estimates and atmospheric emissions, Global Biogeochem. Cycles,

816   17, 1099, doi:10.1029/2003gb002040, 2003.

817　Sullivan, A. P., Holden, A. S., Patterson, L. A., McMeeking, G. R., Kreidenweis, S. M.,

818　　　Malm, W. C., Hao, W. M., Wold, C. E., and Collett, J. L.: A method for smoke marker

819　　　measurements and its potential application for determining the contribution of biomass

820　　　burning from wildfires and prescribed fires to ambient $PM_{2.5}$ organic carbon, J. Geophys

821　　　Res., 113, D22302, doi:10.1029/2008JD010216, 2008.

822　Sullivan, A. P., Frank, N., Onstad, G., Simpson, C. D., and Collett, J. L.: Application of

823　　　high-performance anion-exchange chromatography-pulsed amperometric detection for

824　　　measuring carbohydrates in routine daily filter samples collected by a national network: 1.

825　　　Determination of the impact of biomass burning in the upper Midwest, J. Geophys. Res.,

826　　　116, D08302, doi:10.1029/2010jd014166, 2011.

827　Sutton, M. A., Erisman, J. W., Dentener, F., and Möller, D.: Ammonia in the environment:

828　　　From ancient times to the present, Environ. Pollut., 156, 583–604,

829　　　doi:10.1016/j.envpol.2008.03.013, 2008.

830　Tanimoto, H., Sato, K., Butler, T. I. M., Lawrence, M. G., Fisher, J. A., Kopacz, M.,

831　　　Yantosca, R. M., Kanaya, Y., Kato, S., Okuda, T., Tanaka, S., and Zeng, J.: Exploring

832　　　CO pollution episodes observed at Rishiri Island by chemical weather simulations and

833　　　AIRS satellite measurements: long–range transport of burning plumes and implications

834　　　for emissions inventories, Tellus, 61B, 394–407, doi:10.1111/j.1600–0889.2008.00407.x,

835　　　2009.

836　Urban, R. C., Lima-Souza, M., Caetano-Silva, L., Queiroz, M. E. C., Nogueira, R. F. P.,

837　　　Allen, A. G., Cardoso, A. A., Held, G., and Campos, M. L. A. M.: Use of levoglucosan,

838　　　potassium, and water–soluble organic carbon to characterize the origins of biomass–

839　　　burning aerosols, Atmos. Environ., 61, 562–569, doi:10.1016/j.atmosenv.2012.07.082,

840　　　2012.

841　van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Kasibhatla, P. S., and

842　　　Arellano Jr, A. F.: Interannual variability in global biomass burning emissions from 1997

843　　　to 2004, Atmos. Chem. Phys., 6, 3423–3441, doi:10.5194/acp-6-3423-2006, 2006.

844　van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S.,

845　　　Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and

846　　　the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009),

847　　　Atmos. Chem. Phys., 10, 11707–11735, doi:10.5194/acp-10-11707-2010, 2010.

848   Waked, A., Favez, O., Alleman, L. Y., Piot, C., Petit, J. E., Delaunay, T., Verlinden, E.,

849   Golly, B., Besombes, J. L., Jaffrezo, J. L., and Leoz-Garziandia, E.: Source

850   apportionment of PM10 in a north-western Europe regional urban background site (Lens,

851   France) using positive matrix factorization and including primary biogenic emissions,

852   Atmos. Chem. Phys., 14, 3325–3346, doi:10.5194/acp–14–3325–2014, 2014.

853   Wang, H., Kawamura, K., and Shooter, D.: Carbonaceous and ionic components in

854   wintertime atmospheric aerosols from two New Zealand cities: Implications for solid fuel

855   combustion, Atmos. Environ., 39, 5865–5875, doi:10.1016/j.atmosenv.2005.06.031,

856   2005.

857   Yan, X., Ohara, T., and Akimoto, H.: Bottom-up estimate of biomass burning in mainland

858   China, Atmos. Environ., 40, 5262–5273, doi:10.1016/j.atmosenv.2006.04.040, 2006.

859   Yevich, R., and Logan, J. A.: An assessment of biofuel use and burning of agricultural

860   waste in the developing world, Global Biogeochem. Cycles, 17, 1095,

861   doi:10.1029/2002gb001952, 2003.

862   Yttri, K. E., Lund Myhre, C., Eckhardt, S., Fiebig, M., Dye, C., Hirdman, D., Ström, J.,

863   Klimont, Z., and Stohl, A.: Quantifying black carbon from biomass burning by means of

864   levoglucosan – a one-year time series at the Arctic observatory Zeppelin, Atmos. Chem.

865   Phys., 14, 6427-6442, doi:10.5194/acp-14-6427-2014, 2014.

866   Zhang, H., Ye, X., Cheng, T., Chen, J., Yang, X., Wang, L., and Zhang, R.: A laboratory

867   study of agricultural crop residue combustion in China: Emission factors and emission

868   inventory, Atmos. Environ., 42, 8432–8441, doi:10.1016/j.atmosenv.2008.08.015, 2008.

869   Zhang, Y., Dore, A. J., Ma, L., Liu, X. J., Ma, W. Q., Cape, J. N., and Zhang, F. S.:

870   Agricultural ammonia emissions inventory and spatial distribution in the North China

871   Plain, Environ. Pollut., 158, 490–501, doi:10.1016/j.envpol.2009.08.033, 2010.

872   Zhang, Y., Obrist, D., Zielinska, B., and Gertler, A.: Particulate emissions from different

873   types of biomass burning, Atmos. Environ., 72, 27–35,

874   doi:10.1016/j.atmosenv.2013.02.026, 2013.

875   Zhang, Y. N., Zhang, Z. S., Chan, C. Y., Engling, G., Sang, X. F., Shi, S., and Wang, X. M.:

876   Levoglucosan and carbonaceous species in the background aerosol of coastal southeast

877   China: case study on transport of biomass burning smoke from the Philippines, Environ.

878   Sci. Pollut. Res., 19, 244–255, doi:10.1007/s11356–011–0548–7, 2012.

879   Zhang, Y. X., Shao, M., Zhang, Y. H., Zeng, L. M., He, L.Y., Zhu, B., Wei, Y. J., and Zhu,

880   X. L.: Source profiles of particulate organic matters emitted from cereal straw burnings, J.

881   Environ. Sci., 19, 167–175, doi:10.1016/S1001–0742(07)60027–8, 2007.

882   Zhu, C., Kawamura K., and Kunwar B.: Seasonal variations of organic tracers of primary

883   biological aerosol particles and soil dust at subtropical Okinawa Island in the western

884   North Pacific rim: Asian outflow and local sources, J. Geophys. Res., under review,

885   2015a.

886   Zhu, C., Yoshikawa-Inoue, H., Tohjima, Y., and Irino, T.: Variations in black carbon on

887   Rishiri Island, northern Japan, Geochem. J., 49, doi:10.2343/geochemj.2.0356, 2015b.

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) [a]		spring (n = 23)		summer (n = 23)		autumn (n = 30)	
	Mean ± sd. [b]	Range	Mean ± sd.	Range	Mean ± sd.	Range	Mean ± sd.	Range	Mean ± sd.	Range
Levoglucosan	3.09±3.70	nd–27.18 [c]	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^{-3}	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^{-3}	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   [a] Seasons are divided as December–February in winter, March–May in spring, June–August in summer, and September–November in autumn.

890   [b] sd. denotes standard deviation (1σ).

891   [c] 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$^+$	NH$_4^+$	nss-SO$_4^{2-}$	WSOC	OC	EC
Levoglucosan	1									
Mannosan	0.34[***]	1								
Galactosan	-0.19 [a]	0.17	1							
Anhydrosugars	0.42	0.80	-0.06	1						
nss-K$^+$	0.38[***]	0.36[***]	0.08	0.35[***]	1					
NH$_4^+$	0.39[***]	0.20[*]	-0.10	0.32[***]	-0.03	1				
nss-SO$_4^{2-}$	0.12	-0.05	-0.19	0.04	-0.18	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

894   [*] denotes p < 0.05; [**] denotes p < 0.01; [***] denotes p < 0.001.

895   [a] 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)[a]	Spring (n = 23)	Summer (n = 23)	Autumn (n = 30)
Mannosan	0.82[***]	0.50[*]	0.90[***]	0.61[***]
Galactosan	0.07	-0.31[b]	0.73[***]	0.22
nss-K^+	0.49[**]	0.59[**]	0.86[***]	-0.03
NH_4^+	0.23	0.31	0.02	-0.21
nss-SO_4^{2-}	0.26	0.25	-0.19	-0.04
WSOC	0.47[**]	0.47[*]	0.95[***]	0.48[*]
OC	0.26	0.43	0.65[**]	0.16
EC	0.61[***]	0.17	0.68[**]	0.65[***]

898 [*] denotes $p < 0.05$; [**] denotes $p < 0.01$; [***] denotes $p < 0.001$.

899 [a] Seasons are divided as December–February in winter, March–May in spring, June–August in summer, and September–November in autumn.

900 [b] 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) [a]		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   [a] 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.
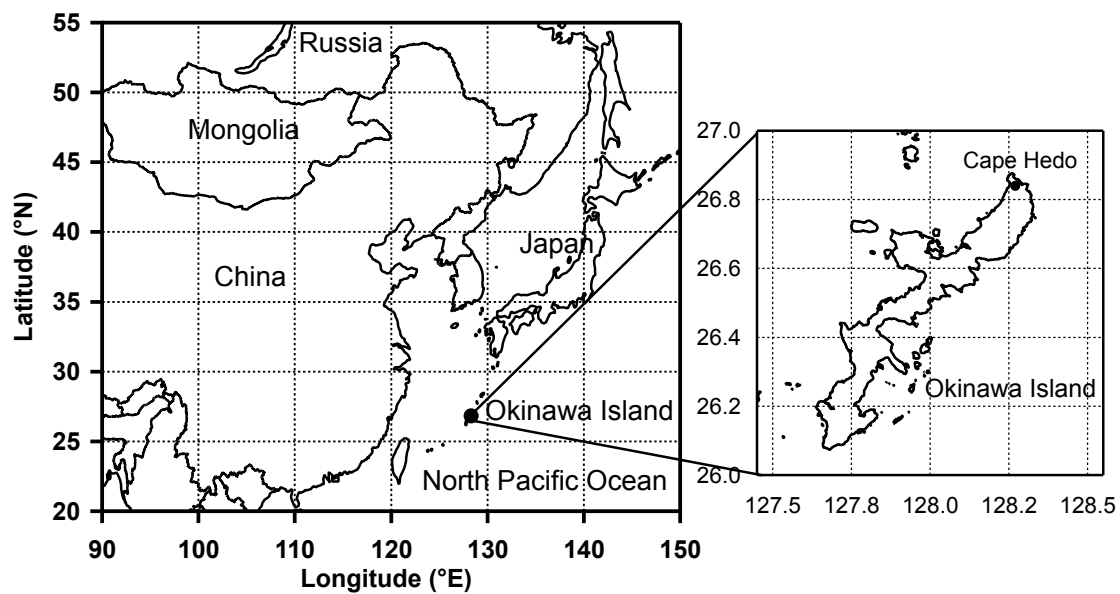
934

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

936   were collected.
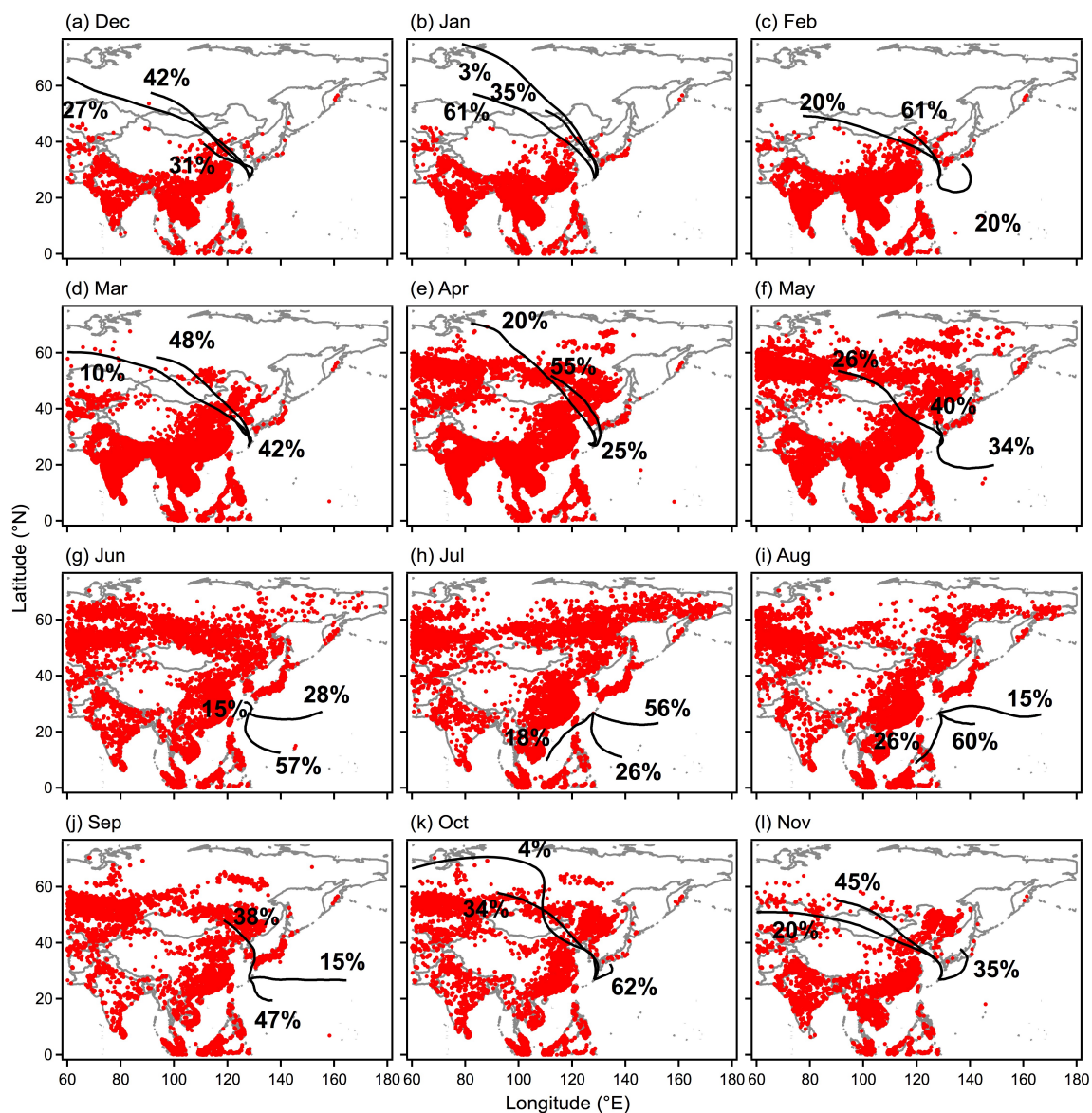
Fig. 2. Monthly distribution of air mass origins to Cape Hedo, Okinawa shown by clusters of 5–day backward trajectories arriving at 500 m above ground level during December 2009–November 2011. The numbers in each panel indicate the percentages of daily trajectories in the month with such origins. Fire spots in East Asia in each month of the same period are also shown.
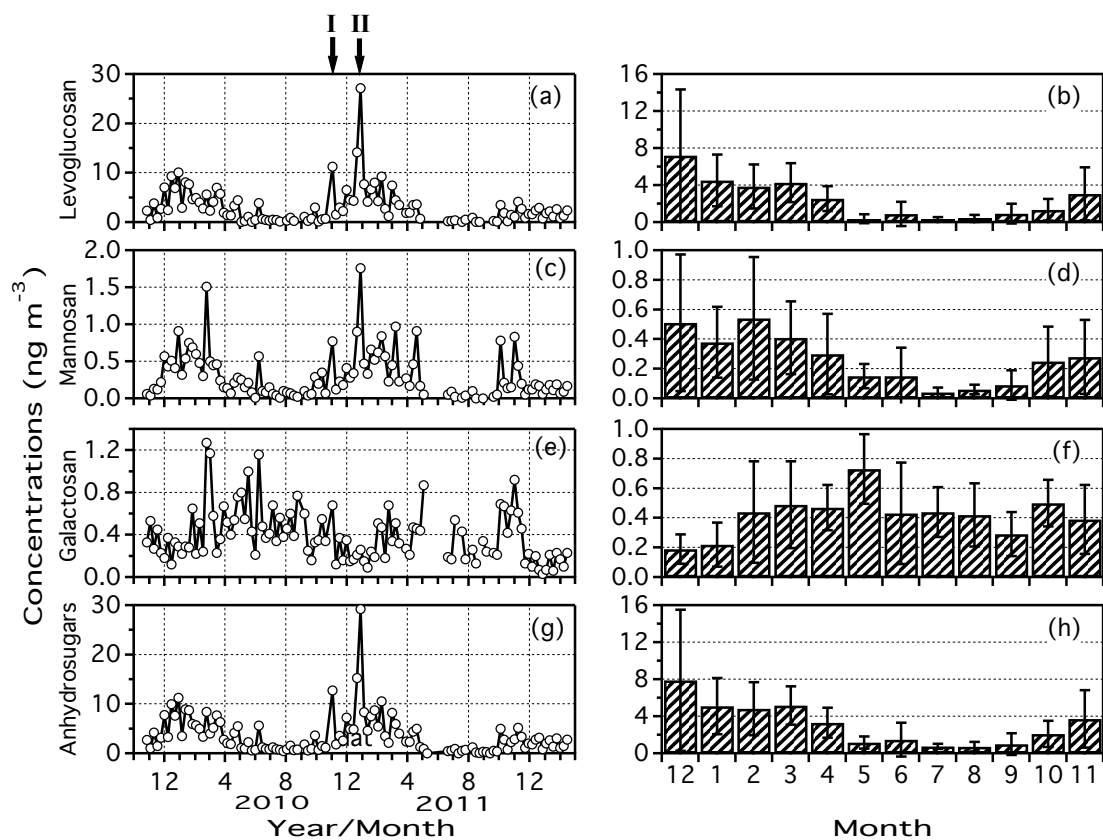
943

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

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

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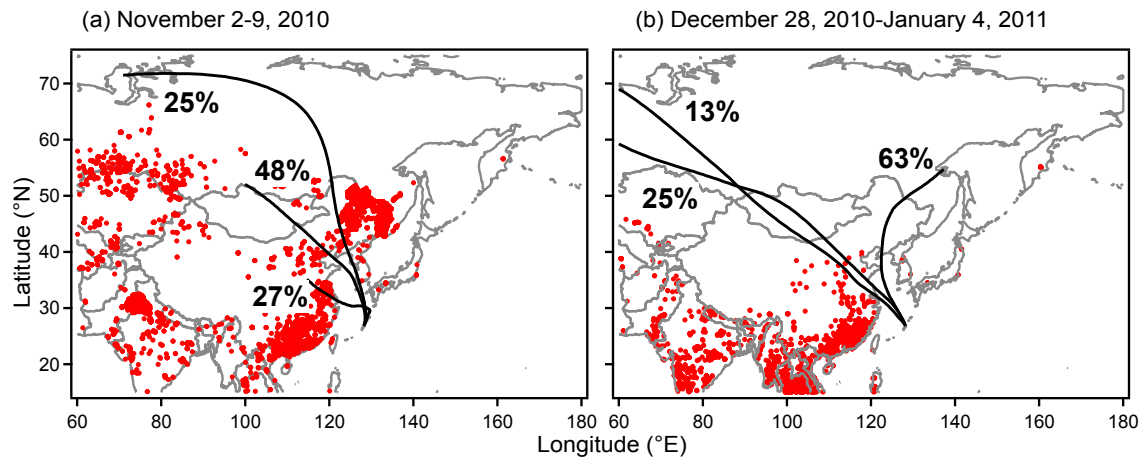
Fig. 4. Air mass origins for the events of elevated anhydrosugars corresponding to I and II in Figure 3 in (a) November 2–9, 2010 and (b) December 28, 2010–January 4, 2011, respectively. Clusters of 5–day backward trajectories arriving at 500 m above ground level at Cape Hedo, Okinawa are given. The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

(a) Tracer-based K$^+$

(b) PMF-based K$^+$

□ Biomass burning　□ Vegetation　□ Dust　□ Sea
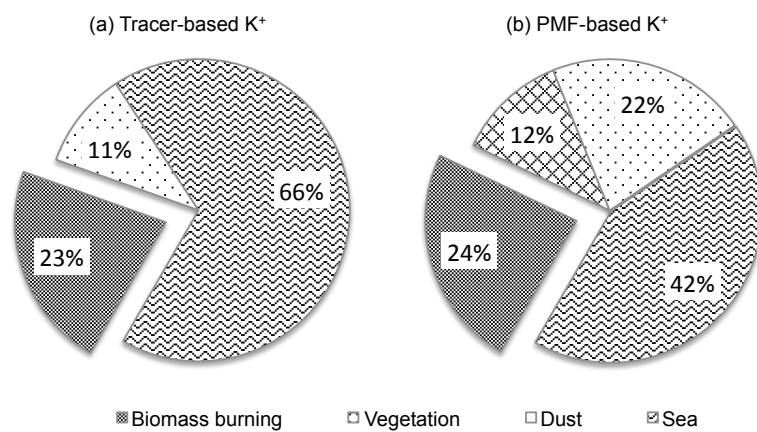
954

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

956　and (b) PMF analysis. Details on PMF analysis can be found in the supplementary material.
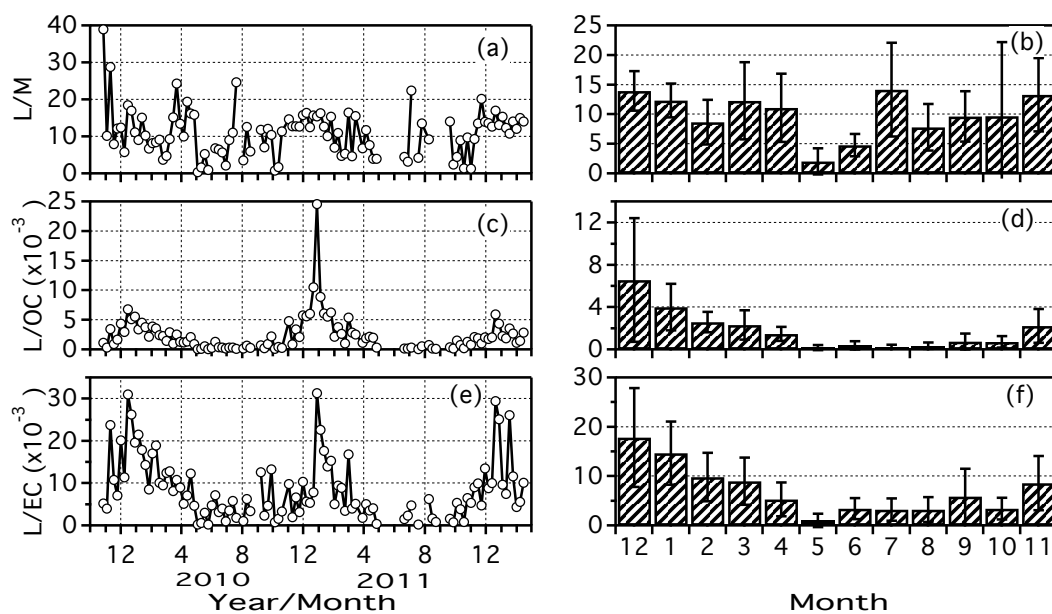
957

Fig. 6 Temporal variations (a, c, e) and monthly means (b, d, f) of the ratios of levoglucosan to mannosan (L/M), OC (L/OC) and EC (L/EC) in aerosols at Cape Hedo, Okinawa from October 2009 to February 2012.
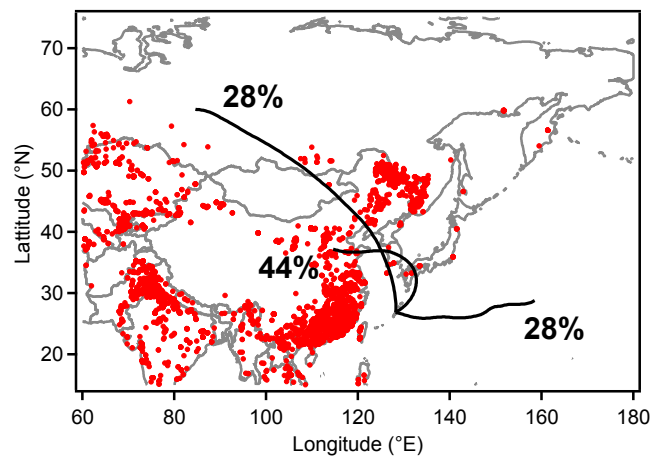
961

962   Fig. 7 Air mass origins for the event of elevated ratio of levoglucosan to mannosan (L/M) in

963   October 27–November 3, 2009. Clusters of 5–day backward trajectories arriving at 500 m

964   above ground level at Cape Hedo, Okinawa are given. The numbers in the panel indicate the

965   percentages of hourly trajectories with such origins. Fire spots in East Asia over October 22–

966   November 3, 2009 are also shown.