Effect of biomass burning over the western North Pacific Rim: wintertime maxima of anhydrosugars in ambient aerosols from Okinawa

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Abstract

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

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

1 Introduction

Biomass burning (BB) is a large source of atmospheric trace gases and aerosols. During the burning, numerous organic and inorganic gases and particles are emitted to the atmosphere (Andreae and Merlet, 2001; Mkoma et al., 2013). Most of the burning-emitted organic compounds and inorganic ions are water-soluble (Graham et al.; 2002; Mayol-Bracero et al., 2002; Kundu et al., 2010). They can act as cloud condensation nuclei (CCN) and ice nuclei (IN) (Penner et al., 1992; Lin et al., 2006; Prenni et al., 2012), affecting climate by altering the hygroscopic properties of aerosols. Emissions of CO and NO_x during BB affect O_3 formation and hence force the oxidation capability of the troposphere (Galanter et al., 2000; Honrath et al., 2004; Tanimoto et al., 2009). Along with direct emission of CO_2 (Goode et al., 2000; Konovalov et al., 2014), other greenhouse gases and particles emitted from BB affect radiative forcing (Langenfelds et al., 2002). Moreover, carbonaceous components and trace gases in the smoke contribute to respiratory diseases (Laumbach and Kipen, 2012).

There are different types of BB including open field fires in forest, savannas, peat lands, burning and land cultivation practices, burning of agricultural wastes in the fields and residential heating and cooking, as well as industrial biofuel burning (Akagi et al., 2011, 2014; Engling et al., 2014). The burning materials range from litters of forest trees and grasses to biofuels such as crop residues, dung and charcoal (Yevich and Logan, 2003; Hays et al., 2005; Yan et al., 2006). Emission parameters of burning materials are frequently represented by emission ratios of a particular species to that of a reference species such as CO_2 or CO, or to the amount of fuel burned (emission factor) (Andreae and Merlet, 2001; Akagi et al., 2011). It is difficult, however, to obtain either of these two emission indices because extensive measurements are needed with respect to different burning materials and emitted trace components.

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

Recent studies, however, demonstrated that degradation of levoglucosan occurred on the exposure to high levels of hydroxyl radicals (OH). Kinetic studies on the reactivity of levoglucosan with OH, NO_3, and SO_4^- radicals in aqueous phase and model simulations indicated that levoglucosan can be oxidized by OH radicals in daytime by rates of 7.2 ng m^{-3} h^{-1} in summer and 4.7 ng m^{-3} h^{-1} in winter for a polluted continental plume (Hoffmann et al., 2010). Based on the chamber experiment on levoglucosan oxidation by OH, Hennigan et al. (2010) reported that levoglucosan has an atmospheric lifetime of 0.7–2.2 days when BB particles are exposed to 1.0×10^6 molecules cm^{-3} of OH. A recent study by flow reactor indicated that pure levoglucosan is degrading by OH with a rate of $(9.17 \pm 1.16) \times 10^{-12}$ cm^3 $molecules^{-1}$ s^{-1} at 25 °C and 40% relative humidity (RH), and the average atmospheric lifetime is 1.2–3.9 days (Lai et al., 2014). The effect of temperature on levoglucosan degradation had been reported consistently positive (Bai et al., 2013; Lai et al., 2014), while the effect of RH is divergent (Hennigan et al., 2010; Lai et al., 2014; Slade and Knopf, 2014). Nevertheless, the study by Bai et al. (2013) indicated that levoglucosan reacts with OH at a rate of 2.21×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 25 °C, resulting in an atmospheric lifetime of 26 days under the OH level of 2.0×10^6 molecule cm^{-3}. Although these results are divergent, levoglucosan is subjected to degradation in BB aerosols during atmospheric transport.

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

East Asia is one of the most active BB regions in the world with high aerosol loadings (van der Werf et al., 2006). Forest burning resulting from both natural and man-made fires for land clearing or other purposes comprises 16%, crop residue burning in the agriculture field comprises 12%, grassland and savanna burning arising from prescribed burning, natural fires, and grassland conversion comprises 7%, and biofuel consumption of fuelwood, agricultural residues, and dried animal waste for cooking and heating comprises 64% of the total burnt biomass across the Asian continent (Streets et al., 2003). Regionally, the largest contributions to BB emissions are from Southeast Asian countries (Philippines, Thailand, Loas, Malaysia, Myanmar, Vietnam and Indonesia), China and Mongolia, and boreal Asia (Russia) (Streets et al., 2003; van der Werf et al., 2006, 2010). On the other hand, open burning (mostly of forest) is a dominant source in Southeast Asia and boreal Asia, while burning of crop residues is dominant in China and of grassland in Mongolia (Streets et al., 2003). A recent estimate of 2.33 Tg y^{-1} for nonmethane volatile organic compounds (NMVOCs) is obtained from the burning of crop residues in China (Kudo et al., 2014). Emissions from such burning may be submitted to long distance transport affecting regional air quality and climate (Mochida et al., 2010; Kawamura et al., 2012; Chen et al., 2013).

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

2 Experimental methods

2.1 Site and sampling

We collected total suspended particle (TSP) samples from October 2009 to February 2012 at Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS) (26.9°N, 128.2°E) in the northwestern edge of Okinawa Island (Fig. 1). TSP samples were collected on pre-combusted (450 °C, 3 h) quartz filters (Pallflex 2500QAT, 20 cm × 25 cm) using a high-volume air sampler (Kimoto AS-810B) at a flow rate of 60 m^3 h^{-1} on a weekly basis (n = 112). Each aerosol-loaded filter was placed in a pre-combusted (450 °C, 6 h) glass jar with a Teflon-lined screw cap and stored in darkness at –20 °C. Before weighing and analysis, each filter was placed in a desiccator for 24–72 h at ~20 °C until constant weight to remove water. Two field blanks following the entire collection procedure except for running the sampling pump were collected on November 2009 and March 2011, respectively. The OC levels in the field blanks were consistently low (1.16 and 1.54 µg per measured unit of 1.54 cm^2, < 5% of OC levels in most samples), indicating negligible contamination of the samples.

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

2.2 Measurement of anhydrosugars

2.2.1 Extraction and derivatization

A small filter section (ca. 10 cm^2) was sonicated three times for 10 min in a mixture (7 ml) of dichloromethane/methanol (2:1; v/v). The solvent extracts were filtered through quartz wool packed in a Pasteur pipette to remove particles. The filtrate was concentrated in a pear-shape flask by a rotary evaporator under vacuum down to 1 ml, and then dried with pure nitrogen gas in a 1.5 ml glass vial. Compounds in the extracts were then converted to their trimethylsilyl (TMS) derivatives by reacting with 50 µl of N, O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethyl chloride and 10 µl of pyridine for 3 h at 70 °C. OH groups of anhydrosugars in the extracts were derivatized to trimethylsilyl (TMS) ethers before GC/MS quantification (Medeiros and Simoneit, 2007; Fu et al., 2008).

2.2.2 Gas chromatography-mass spectrometry

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

Mass spectral data were acquired and processed using the HP-Chemstation software. Individual anhydrosugars were identified by comparison with the retention times and mass spectra of authentic standards and the mass spectral library of HP-Chemstation (Medeiros and Simoneit, 2007). Relative response factor of levoglucosan was obtained by comparing the peak area differences of the authentic standards to the internal standard (tridecane in n-hexane, ca. 1 ng $\mu\mathrm{l}^{-1}$ in the extracts before injection). Concentration of levoglucosan in each of the ambient samples was determined by comparing its relative response factor with that of the authentic standard. The relative response factor for levoglucosan was also applied in mannosan and galactosan. Recoveries for levoglucosan were 83–97% for four replicates as obtained by spiking standards to pre-combusted quartz filters following the extraction and derivatization described above. No peaks were found for anhydrosugars in the laboratory and field blank filters. The analytical errors by duplicate sample analyses were less than 15%. The limit of detection (LOD) of levoglucosan was 520 pg μl^{-1}, under a mean signal to noise ratio (S/N) of 84 in three replicate injections (279 pg per injection), which corresponds to 0.005 ng m^{-3} for ambient aerosols under a typical sampling volume of 9000 m^3, and an aliquot of 10 cm^2 of the used filter. LODs of mannosan and galactosan are considered the same as for levoglucosan, because levogucosan was used as surrogate standard for mannosan and galactosan.

2.3 Water-soluble inorganic ions and carbonaceous components

Major water-soluble inorganic ions were determined using an ion chromatograph (IC) (761 Compact IC, Metrohm, Switzerland) following Kunwar and Kawamura (2014). The detection limits for anions and cations were ca. 0.1 ng m^{-3}. Based on IC-determined K$^+$, SO_4^{2-} and Na$^+$, we estimated the fractions of K$^+$ ion derived from sea salt (ss) and none-sea-salt (nss-) sources following the method of George et al. (2008). The results of nss-K$^+$, NH_4^+ and nss-SO_4^{2-} are discussed in this study. We also investigated K$^+$ components using a tracer-based method (Pio et al., 2008) and positive matrix factorization (PMF) model (Paatero and Tapper, 1994) (Supplementary materials). Water-soluble organic carbon (WSOC) was measured using a Shimadzu carbon/nitrogen analyzer (TOC–V$_{CSH}$). following Miyazaki et al. (2011). The analytical errors for water-soluble inorganic ions and WSOC in duplicate analyses of laboratory standards were both within 5%. The concentrations of ions and WSOC in the samples were corrected for field blanks.

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

2.4 Backward trajectories and fire counts

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

3 Results and discussions

3.1 Air mass origins and fire counts

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

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

Based on satellite observation and model simulation, Van der Werf et al. (2006) reported that BB emissions in boreal East Asia (most of Russia) maximized in summer, whereas in central Asia (Mongolia, China and Japan) they showed a bimodal pattern with two maxima in spring and autumn. Monthly total fire counts in MNA indicated a consistent pattern with a major peak in May (total counts 45020) and a secondary peak in October (total counts 17838) (Fig. S1). In Southeast Asia, they maximized in spring. Furthermore, Van der Werf et al. (2010) reported that the dominant type was forest fire in Russia and part of northeast China, savanna in Mongolia and Inner Mongolia of China, agricultural wastes in north and northeast China, and deforestation in south China and Southeast Asia. With considerations of such seasonality and fire types, the biomass burning types that affect Okinawa aerosols could be summarized as follows: both indoor and open field burning of woods and agricultural wastes in MNA in winter, open burning of wheat straw in north China in spring, and open burning of maize straw in north and northeast China in autumn. There is little influence of BB on Okinawa aerosols from South China and Southeast Asia where deforestation is the main BB source.

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

3.2.1 Seasonal variation of anhydrosugars

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

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

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

3.2.2 Effect of continental outflow on high anhydrosugar concentrations in winter

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

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

3.2.3 Anhydrosugar levels in summer

There is little air mass delivery from the Asian continent that directly affects anhydrosugars in Okinawa aerosols during summer (Fig. 2g–i, 3). Air masses from the western North Pacific in summer are expected to bring “clean” air without the contribution of anhydrosugars. Moreover, the summer minimum of levoglucosan at Okinawa (0.32 ng m^{-3}) was 78% higher than that at Chichijima, a remote oceanic site in the western North Pacific, ca. 1400 km east of Okinawa (Mochida et al., 2010). Other than the dilution and deposition during long-range transport, the gradient of anhydrosugars from Okinawa to Chichijima suggests that levoglucosan may undergo photochemical degradation in the troposphere. A higher level of OH in the troposphere is expected in summer as a result of higher temperature and stronger ultraviolet light (Stone et al., 2012), which would lead to the degradation of levoglucosan (Hennigan et al., 2010; Hoffmann et al., 2010; Mochida et al., 2010).

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

On the contrary to our expectation, there was little influence of biomass burning in Southeast Asia to anhydrosugars in Okinawa aerosols (Fig. 2). In August 26% of the air masses originated from the Philippine islands, however very few fire spots were detected by satellite (84 and 9 counts in the whole Philippines and close to the trajectory centroid, respectively). Previous studies indicated that biomass burning in the Philippine islands control the levels of anhydrosugars in the northwest aerosols at Hok Tsui, Hong Kong and Hainan in coastal southeast China in spring (Zhang et al., 2012). However, the biomass burning in the Philippines did not seriously affect the aerosols in the northeast region where Okinawa is located. Anhydrosugars emitted from the Philippine region are likely decomposed and/or scavenged from the atmosphere by dry/wet deposition in summer before arriving at Okinawa, given the long travel distance of ~2000 km, more frequency of precipitation and short lifetime of levoglucosan (roughly 1 day, corresponding to 663 km in the trajectory cluster).

3.3 Relations between anhydrosugars and inorganic ions and EC

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

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

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

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

On the other hand, positive relations were found between NH_4^+ and levoglucosan (r = 0.39, $p < 0.001$) and mannosan ($r = 0.20$, $p < 0.05$). These results imply that BB in MNA could be an important direct source of NH_4^+ (Andreae and Merlet et al., 2001; Akagi et al., 2011). NH_4^+ could also be formed in the atmosphere by the protonation of NH_3, which is abundantly emitted from livestock excreta, fertilizer application, agricultural soil and plants, biomass burning, and so on (Asman et al., 1998; Huang et al., 2012; Paulot et al., 2014; Sutton et al., 2008; Zhang et al., 2010). The seasonal relations between levoglucosan and NH_4^+ showed no correlation in summer and autumn although there is a weak positive correlation in winter and spring. This may be caused by the enrichment of NH_3-derived NH_4^+ from agricultural activities, and transformation and wet scavenging during atmospheric transport. Levoglucosan did not correlate with nss-SO_4^{2-} (r=0.12), indicating that sulfur emission from BB may not be significant.

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

3.4 Implication for burning substrates based on L/M ratios

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

Sporadically high L/M ratio events were observed. The highest ratio of 38.9 was observed in the sample collected on October 27–November 3, 2009. Elevated concentrations of OC, EC and water-soluble ions were also observed for this sample. On these days, 44% of the air masses originated from the North China Plain, while another 28% originated from west Siberia, en route Mongolia and north China to Okinawa (Fig. 7). October–November are the harvest season of maize in the North China Plain where fire spots were observed. This event indicates that emissions of particulate matter from burning of maize straw residues were transported to the western North Pacific. High L/M ratios had been reported for smoke from chamber burning of rice straw (40–42) and ambient aerosols affected by burning of wheat straw (40–46) (Engling et al., 2009; Fu et al., 2008). A higher average L/M ratio of 55 was obtained for the burning of rice straw, wheat straw and maize straw by chamber experiment (Zhang et al., 2007). These results implied that maize straw smoke may have a higher L/M ratio. Our results gave a relatively high L/M ratio of 38.9 even after long-range transport to Okinawa, supporting the above proposition.

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

3.5 L/OC and L/EC ratios

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

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

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

EC is emitted primarily via coal combustion, motor vehicle exhaust and BB (Cao et al., 2005; Waked et al., 2014, Yttri et al., 2014). The ratio between levoglucosan and EC (L/EC) was also investigated (Fig. 5 e–f, Table 1). Showing a similar behavior as the L/OC ratios, the L/EC ratios indicate a clear seasonal trend with winter maximum (14.5×10^{-3}) and summer minimum (3.3×10^{-3}). Moreover, the L/EC ratios in Okinawa and Chichijima are one order of magnitude lower than those of Changdao in winter, spring and autumn (Feng et al., 2007; Mochida et al., 2010). As there was little source of EC in the ocean, this result may imply a degradation of levoglucosan during atmospheric transport. In summer, the L/EC ratios in Okinawa (3.3×10^{-3}) and Chichijima (6.5×10^{-3}) were of the same order as those of Changdao (4.0×10^{-3}). Other than levoglucosan degradation, this is also likely related to the relatively high level of EC in summer at Changdao. Although clear seasonal variation was found for longitudinal gradient of levoglucosan between Changdao and Okinawa (ratios of these two sites are 27.9, 25.3, 7.5 and 18.3 for winter, spring, summer and autumn, respectively) with winter maximum and summer minimum, longitudinal gradient of EC (6.9, 2.6, 6.5, 5.0) was similar between winter and summer. As long as the majorities of air masses are from the ocean for all these three sites in summer, there is higher emission of EC from local fossil fuel combustion at Changdao, whereas EC at Okinawa and Chichijima might represent a regional background level. Comprising with other seasons, the elevated EC at Changdao in summer lowered the L/EC ratio to a comparative level with those of maritime sites.

3.6 Contributions of biomass burning to WSOC, OC and TSP

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

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

4 Conclusions

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

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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, $\times 10^{-3}$	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, $\times 10^{-3}$	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

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

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

[c] nd denotes not detected.

Table 2. Linear correlation coefficients (*r*) among anhydrosugars, major ions and carbonaceous components in Okinawa aerosols from 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

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

[a] Negative values indicate negative correlations.

Table 3. Linear correlation coefficients (*r*) between levoglucosan and other parameters including the other two anhydrosugars, major 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^{***}

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

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

[b] Negative values indicate negative correlations.

Table 4. Annual and seasonal means of contributions of total carbon in the anhydrosugars to the WSOC and OC, of the total 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

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

Figure captions

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

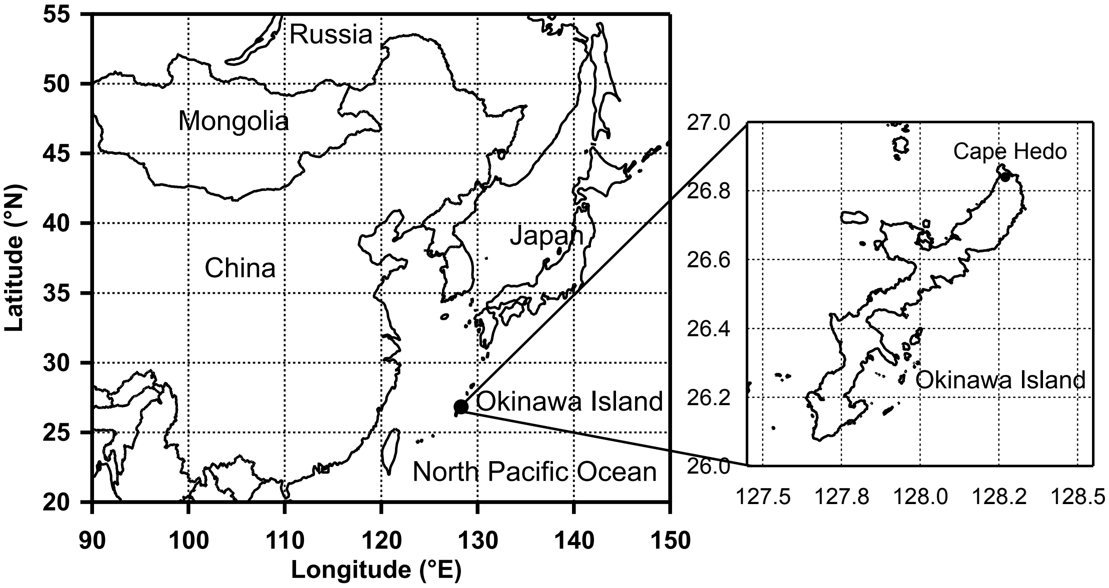
Fig. 3. Temporal variation (a, c, e, g) and monthly means (b, d, f, h) of anhydrosugars in aerosols at Cape Hedo, Okinawa from October 2009 to February 2012. Typical elevation events of anhydrosugars are marked I and II and analyzed in details.

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.

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

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.

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



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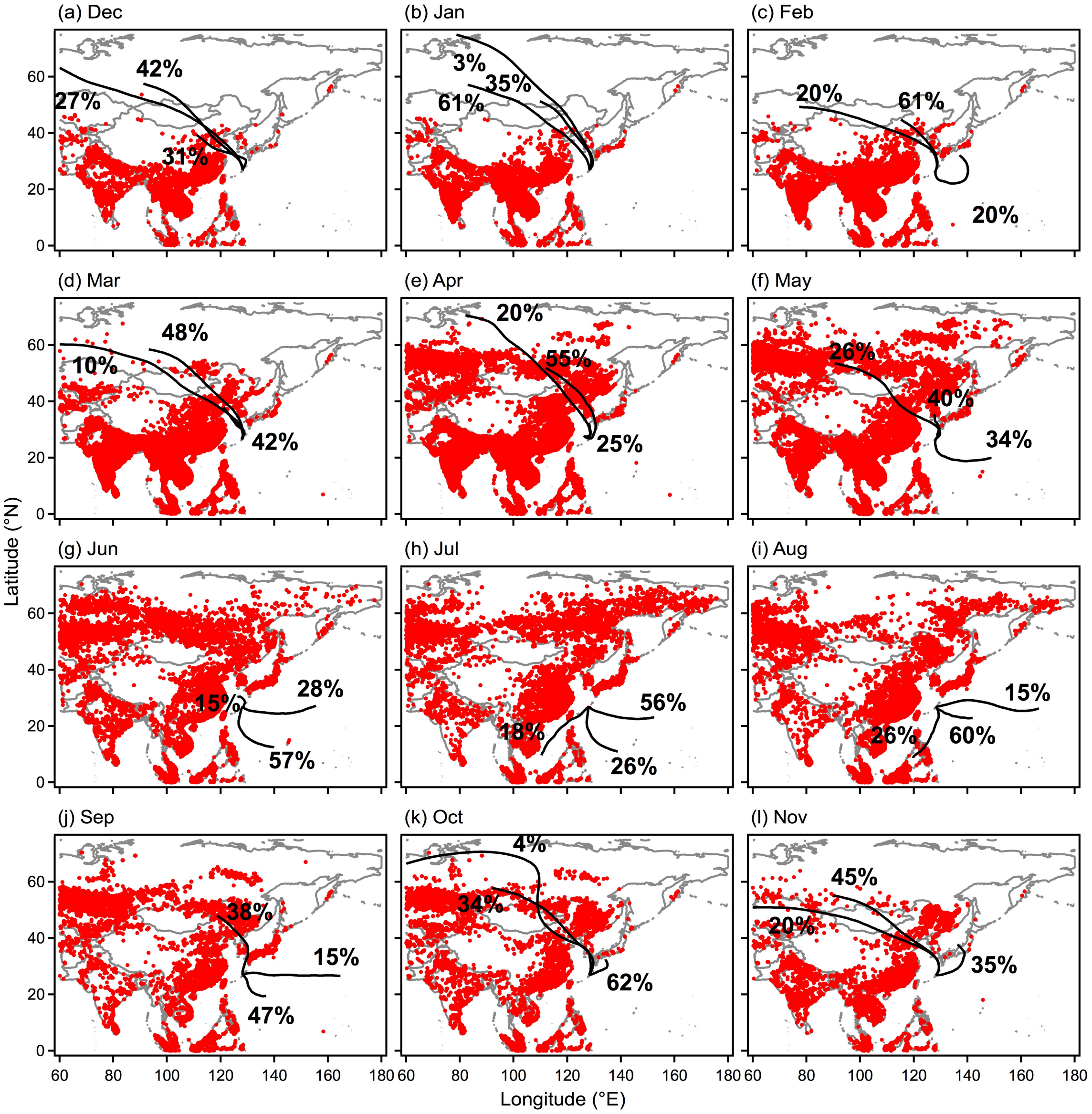

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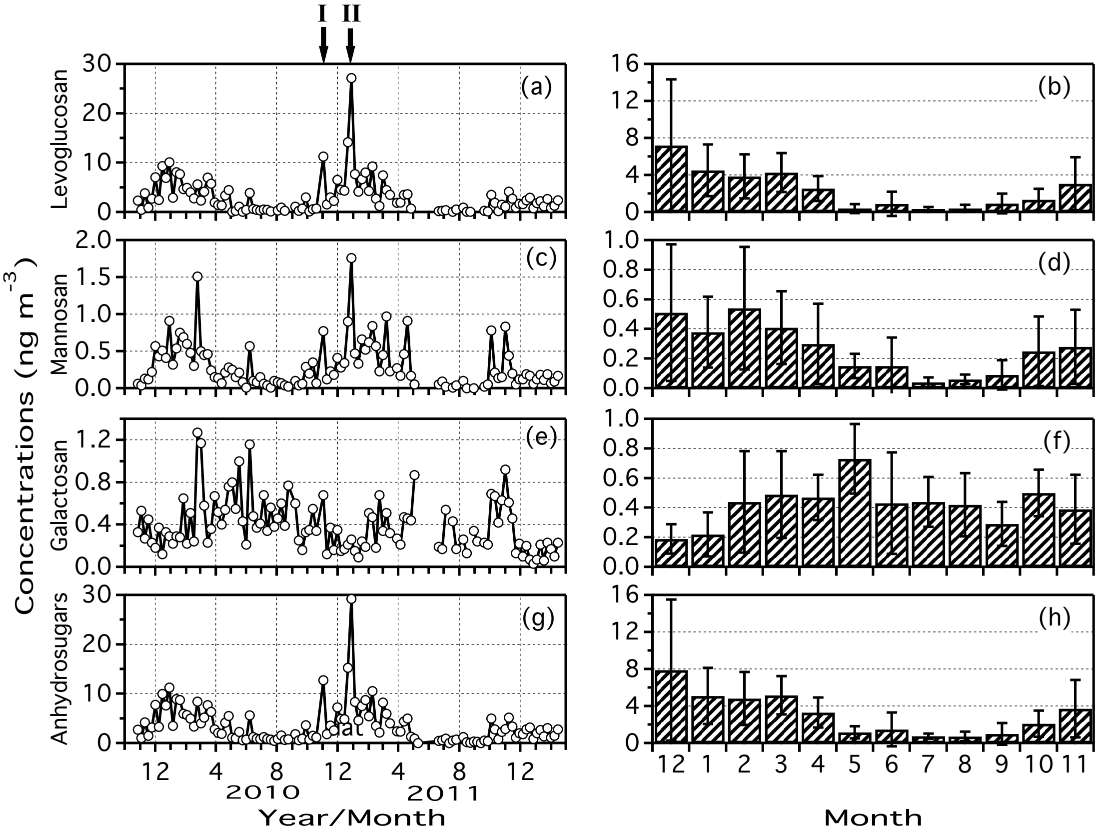

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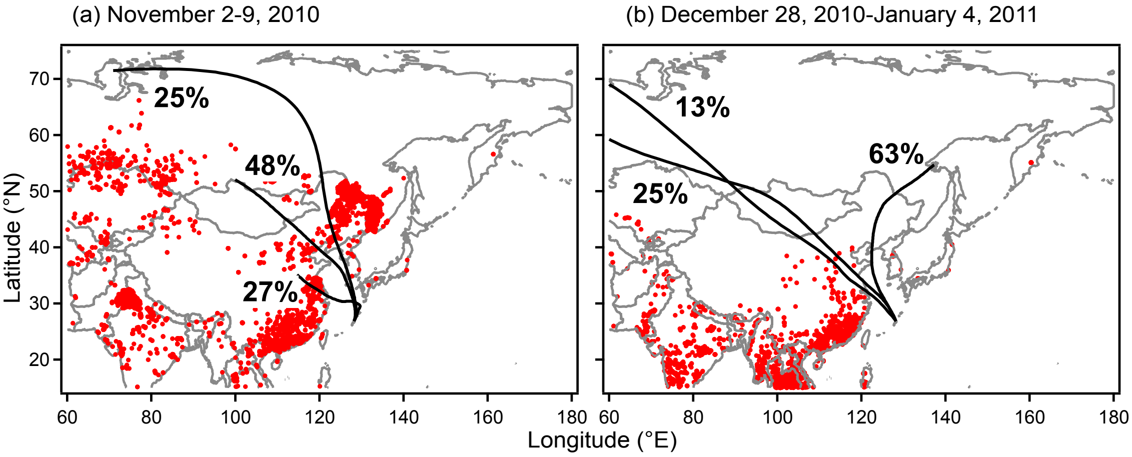

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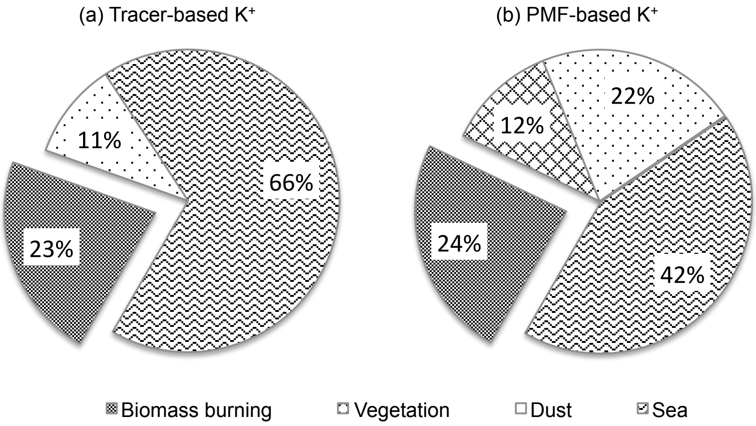

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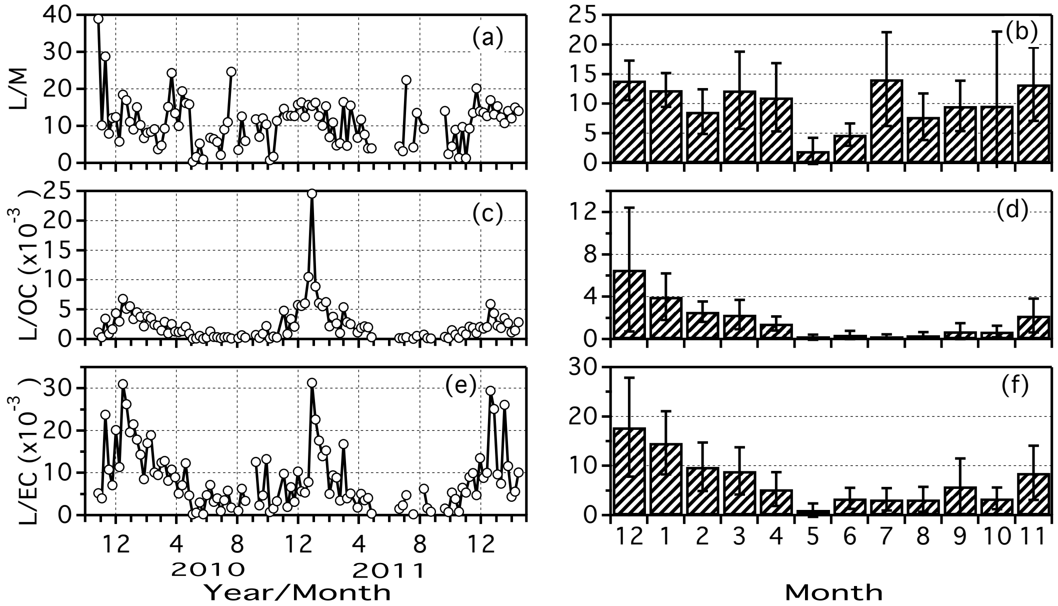

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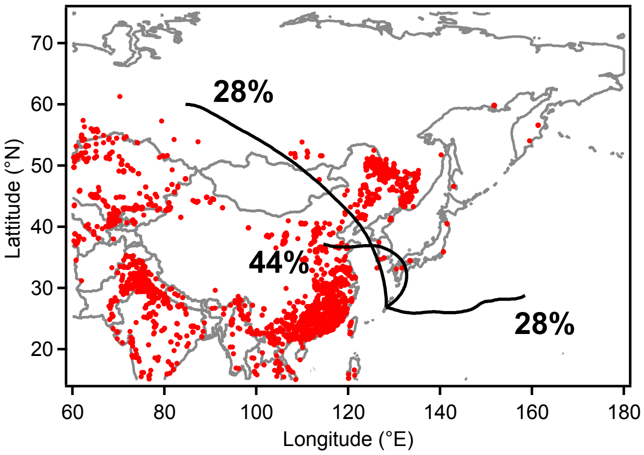

961

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.