Atmos. Chem. Phys. Discuss., 14, 25581–25616, 2014
www.atmos-chem-phys-discuss.net/14/25581/2014/
doi:10.5194/acpd-14-25581-2014

Atmospheric Chemistry and Physics Discussions

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

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Received: 13 August 2014 – Accepted: 26 September 2014 – Published: 9 October 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Biomass burning (BB) largely modifies the chemical compositions 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 a 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. 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 agriculture 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.

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-

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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 smokes contribute to respiratory diseases (Laumbach et al., 2012).

There are different types of BB including open field fires in forest, savannas, peat lands, smack and planting practices, burning of agricultural wastes in the fields and residential heating and cooking, as well as industrial biofuel burnings (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 indexes 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 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). Recent studies, however, demonstrated that degradation of lev-

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oglucosan occurred on the exposure to high levels of hydroxyl radicals (OH) (Hennigan et al., 2010; Hoffmann et al., 2010). Even though, it is still the most reliable tracer for BB (Simoneit et al., 1999, 2004). The isomers of levoglucosan, mannosan and galactosan are also generated from pyrolysis of cellulose and hemicelluloses and used as BB tracers (Engling et al., 2009; Fabbri et al., 2009).

Moreover, the relative abundance of anhydrosugar isomers is used as diagnostic parameter for different BB substrates (Fu et al., 2012; Mkoma et al., 2013). Levoglucosan to mannosan (L/M) ratio differs from smokes 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 comprises 45 %, crop residues burning in the field comprises 34 %, and grassland and savanna burning comprises 20 % of the total burnt mass in East Asia (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

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(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 burnings 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 Measurement Station (CHAAMS) (26.9° N, 128.2° E) in the northwestern edge of Okinawa Island (Fig. 1). TSPs 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 of the 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 until constant weight to remove water. Two field blanks following all the collection procedures except for running sampling pump were collected on November 2009 and March 2011, respectively.

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Regions near CHAAMS are covered by subtropical evergreen broadleaf forest. There are industrial practices of biomass recycling to make biofuel pellet and apply to 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 quantified 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 on 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},

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followed by a final isothermal hold at 305 °C for 15 min. The mass spectrometer was operated on electron inoization (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 μL^{-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 injection^{-1}), 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.

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}. We used Na^+ to derive nss-K^+ and nss-SO_4^{2-} following the method of George et al. (2008), and discussed the results of nss-K^+, NH_4^+ and nss-SO_4^{2-} in this study. Water-soluble organic carbon (WSOC) was measured using a Shimadzu carbon/nitrogen analyzer (TOC–V_{CSH}), following the

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method of Miyazaki et al. (2011). The analytical errors in the measurements of water-soluble inorganic ions and WSOC during 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 trajectory starting at 500 m a.g.l. at 09:00 LT was 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 8 July 2014) were used as meteorology 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 spot, 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 8 July 2014).

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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 Fig. 2. In December and January, air masses are exclusively originating from the Asian continent (Fig. 2a and b). These are the months of the strongest influence of Asian outflow dominated by 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 generally locate 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, although dense fire spots were observed. From summer to winter, air masses shifted reversely to that of continental origin, until the highest influence of continental outflow from MNA in December–January.

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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 Fig. 3, and the annual and seasonal means and ranges are shown in Table 1. Among three isomers, levoglucosan is most abundant with the mean concentration of $3.09 \pm 3.70\,ng\,m^{-3}$ (mean $\pm 1\sigma$). Mannosan and galactosan are 1 order of magnitude less abundant than levoglucosan. Seasonally, levoglucosan clearly indicates winter maximum ($5.30 \pm 4.88\,ng\,m^{-3}$) and summer minimum ($0.57 \pm 0.84\,ng\,m^{-3}$). Specifically, monthly mean of levoglucosan in December ($7.21 \pm 7.14\,ng\,m^{-3}$) is > 20 times higher than that in July ($0.34 \pm 0.20\,ng\,m^{-3}$) (Fig. 2). Similar seasonal trend was observed for mannosan ($0.47 \pm 0.38\,ng\,m^{-3}$ in winter and $0.08 \pm 0.12\,ng\,m^{-3}$ in summer). However, galactosan did not show such a clear seasonal trend. Following the trend of levoglucosan, total anhydrosugars maximized in December ($7.91 \pm 7.63\,ng\,m^{-3}$) and minimized in August ($0.71 \pm 0.52\,ng\,m^{-3}$), with a mean of $3.53 \pm 3.91\,ng\,m^{-3}$ over the sampling period.

The primary cause of the seasonality of levoglucosan and mannosan 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 (Figs. 2a–c and 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 anhydrosugars 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

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spots in north and northeast China indicate the burning in the open fields (Fig. 2a–e and l). Most of the air masses arriving at Okinawa passed through such regions. One example is the high anhydrosugar event observed in 2–9 November 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 burnings or small sizes of field burning that could not be detected by satellite. Therefore, domestic burning for heating and cooking in MNA largely contributes 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 28 December 2010–4 January 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 are associated with indoor biofuel burnings. 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 Background anhydrosugar levels in summer

There is little air mass delivery from the Asian continent that directly affects anhydrosugars in Okinawa aerosols during summer (Figs. 2g–i and 3). Air masses from the western North Pacific in summer are expected to bring “clean” air without the contribution of anhydrosugars. Therefore, the observed low levels of anhydrosugars represent a regional background level. Moreover, the summer minimum of levoglucosan at Oki-

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nawa (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. Higher level of OH in the troposphere is expected in summer as a result of higher temperature and stronger ultraviolet light (Kanaya et al., 2001, 2002; Stone et al., 2012), which would lead to the degradation of levoglucosan (Hennigan et al., 2010; Hoffmann et al., 2010; Mochida et al., 2010).

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 Philipines did not seriously affect the aerosols in the northeast region where Okinawa locates. Anhydrosugars emitted from the Philippine region are likely decomposed in summer during the atmospheric transport, as well as dilution and dry/wet deposition.

3.2.4 Biomass burning types in East Asia

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 bimodal pattern with two maxima in spring and autumn. 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

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Southeast Asia. With considerations of such seasonality and fire types, the biomass burning types that affect anhydrosugars in 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.

3.3 Relations between anhydrosugars with inorganic ions and EC

Linear correlations among anhydrosugars and with major ions that 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. It is interesting to note that galactosan did not co-vary with other anhydrosugars. Further investigations are needed to clarify the factors regulating the seasonal variation of galactosan.

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. Nevertheless, 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 NH_4^+ is either emitted through BB directly, or formed in the atmosphere from plant nitrogen precursor, as NO_x was a more common nitrogen form emitted during biomass burning (Andreae and Merlet et al., 2001; Akagi et al., 2011). Levoglucosan did not correlate with nss-SO_4^{2-} ($r = 0.12$), indicating that sulfur emission from BB was not significant.

Using levogucosan as a representative BB tracer, the correlations between anhydrosugars and possible ion tracers for biomass burning 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

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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. On the other hand, 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 transformation and wet scavenging of nitrogenous components during transport.

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 are significantly derived from BB. Meanwhile, air masses with mixed sources from emissions of BB and fossil fuel would also result in such relations. Seasonally, levoglucosan significantly correlates with EC in summer, autumn and winter. However, no correlation in spring suggests that EC originates from other sources including fossil fuel combustion in the upwind Asian continent.

3.4 Implication for burning substrates based on L/M ratios

Levoglucosan/Mannosan (L/M) ratio has been used to differentiate the burning substrates (Table 1, Fig. 5). 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. 5b). 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, 2014; Fu et al., 2012; Mkoma et al., 2013). Higher monthly means of L/M ratios in November–January suggest that the burning substrates were hardwood, mixture of softwood and hardwood, or 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. 2f and g).

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Sporadically high L/M ratio events were observed. The highest ratio of 38.9 was observed in the sample collect on 27 October–3 November 2009. Elevated concentrations of OC, EC and water-soluble ions were also observed for this sample. On these days, 44 % of air masses originated from the North China Plain, while another 28 % originated from west Siberia, en route Mongolia and north China to Okinawa (Fig. 6). 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. Nevertheless, two high L/M ratios (24.7 and 22.4) were observed on 15–27 July 2010 and 30 June–12 July 2011, respectively. During 15–27 July 2010, 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 entertainment. On the other hand, on 30 June–12 July 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 Lev/OC and Lev/EC ratios for possible degradation of levoglucosan

Levoglucosan to OC (Lev/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 Lev/OC, with a maximum in winter (4.6×10^{-3}) and minimum in May (0.3×10^{-3}) (Fig. 5c and d, Table 1). This seasonal trend is consistent with those reported for 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 remote maritime site (Chichijima) in the western North Pacific (Mochida et al., 2010). Interestingly, Lev/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),

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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 local terrestrial/maritime biosphere of Okinawa and Chichijima. In summer when Lev/OC ratio at Changdao (1.2×10^{-3}) is the highest among the three sites, Lev/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 large amount of primary organic aerosols (Zhu and Kawamura, 2014).

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 to EC (Lev/EC) was also investigated (Fig. 5e and f, Table 1). Being similar to Lev/OC, Lev/EC ratios indicate a clear seasonal trend with winter maximum (14.5×10^{-3}) and summer minimum (3.3×10^{-3}). Moreover, Lev/EC ratios in Okinawa and Chichijima are one order of magnitude lower than that 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, Lev/EC ratios in Okinawa (3.3×10^{-3}) and Chichijima (6.5×10^{-3}) were in the same order with that of Changdao (4.0×10^{-3}). This is likely related to the different EC sources at these sites. As long as the majorities of air masses are from the ocean for all these three sites, 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 in summer.

3.6 Contributions of biomass burning to WSOC, OC and TSP

Positive linear relations were found between total and each anhydrosugar component and WSOC (Table 2), as well as between levoglucosan and WSOC in each season

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(Table 3). Although the relations between levoglucosan and OC in most of the seasons are not significant (Tables 2 and 3), clear seasonal trend of Lev/OC ratios indicates that the contribution of anhydrosugars to OC varied depending on seasons (Fig. 5c and d). We further investigated the contributions of anhydrosugars to WSOC and OC, and total anhydrosugars mass to TSP (Table 4). Anhydrosugars account for 0.22 % of WSOC and 0.13 % of OC annually. The highest contributions of anhydrosugars to WSOC (0.37 %) and OC (0.25 %) were obtained in winter, indicating a strong influence of BB on winter aerosols. The contribution of anhydrosugars to WSOC in Okinawa is lower than those 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). Anhydrosugars accounted for 0.006 % of TSP on annual basis in Okinawa aerosols with maximum (0.01 %) in winter.

Lev/OC ratio has been used to estimate the contributions of BB to OC in aerosols as stated above. Lev/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 Lev/OC during the burning of wheat, corn and rice straws in China was derived as 8.27 % (Zhang et al., 2007). Using the Lev/OC of 8.2 % from the source of biomass burning, we estimated that biomass burning in East Asia contributes 2.9 % of OC in Okinawa aerosols on annual basis (Table 4). This is lower than the contribution of BB to 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 %. These results indicate that BB, especially from MNA in winter, significantly affects the regional air quality in Okinawa.

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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. 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 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, mixture of softwood and hardwood, or mixture of softwood and plant straws. Clear seasonal trends of the contributions of anhydrosugars to 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.

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

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

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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.

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Table 3. Linear correlation coefficients (r) between levoglucosan and other parameters including 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.

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

Contributions	Annual (n = 112)		Winter (n = 36)*		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

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

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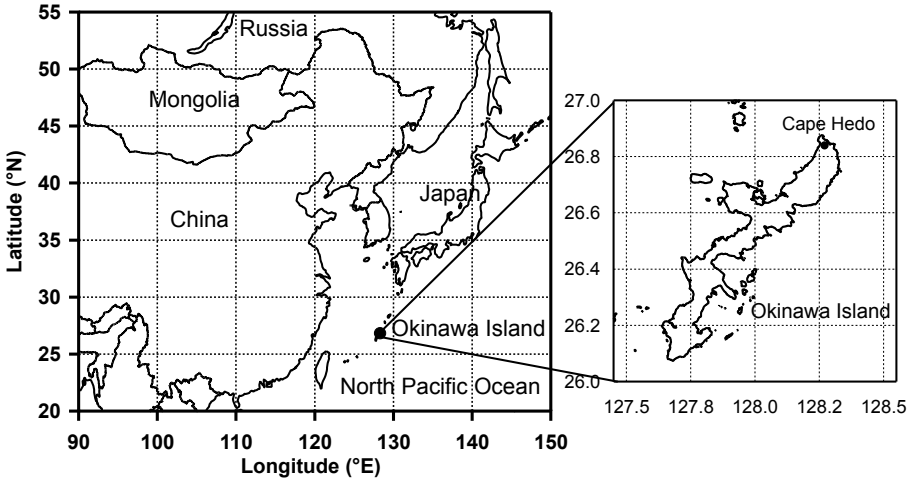

Figure 1. Location of Cape Hedo, Okinawa in East Asia where total suspended particles (TSP) were collected.

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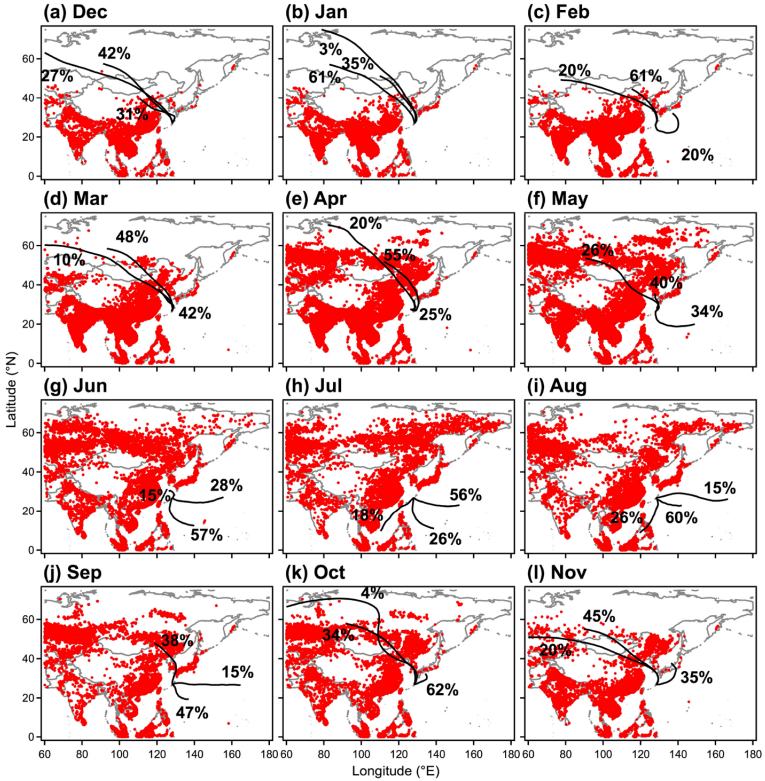

Figure 2. Monthly distribution of air mass origins to Cape Hedo, Okinawa shown by clusters of 5 day backward trajectories arriving at 500 m above ground level during December 2009–November 2011. The numbers in each panel indicate the percentages of daily trajectories in the month with such origins. Fire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

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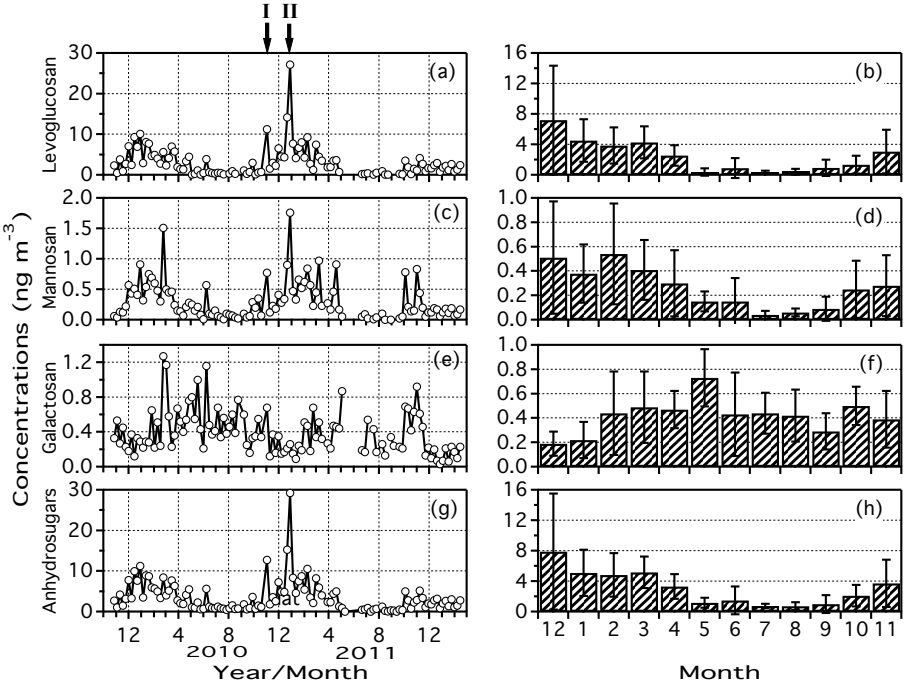

Figure 3. Temporal variation **(a, c, e, g)** and monthly means **(b, d, f, h)** of anhydrosugars in aerosols at Cape Hedo, Okinawa from October 2009 to February 2012. Typical elevation events of anhydrosugars are marked I and II and analyzed in details.

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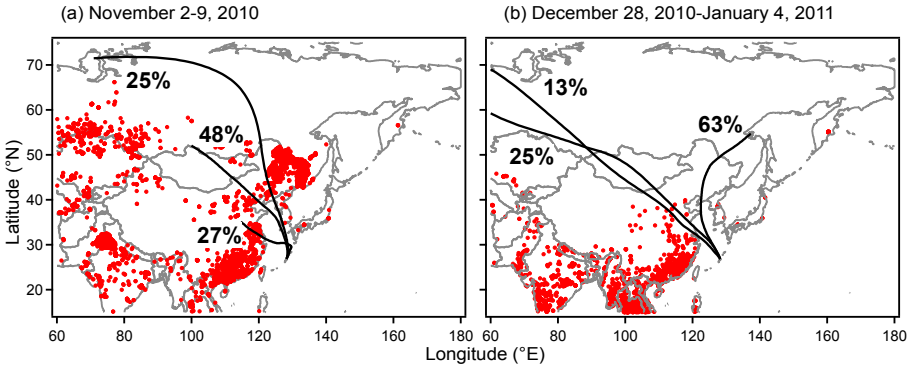

Figure 4. Air mass origins for the events of elevated anhydrosugars corresponding to I and II in Fig. 3 in **(a)** 2–9 November 2010 and **(b)** 28 December 2010–4 January 2011, respectively. Clusters of 5 day backward trajectories arriving at 500 m a.g.l. at Cape Hedo, Okinawa are given. The numbers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

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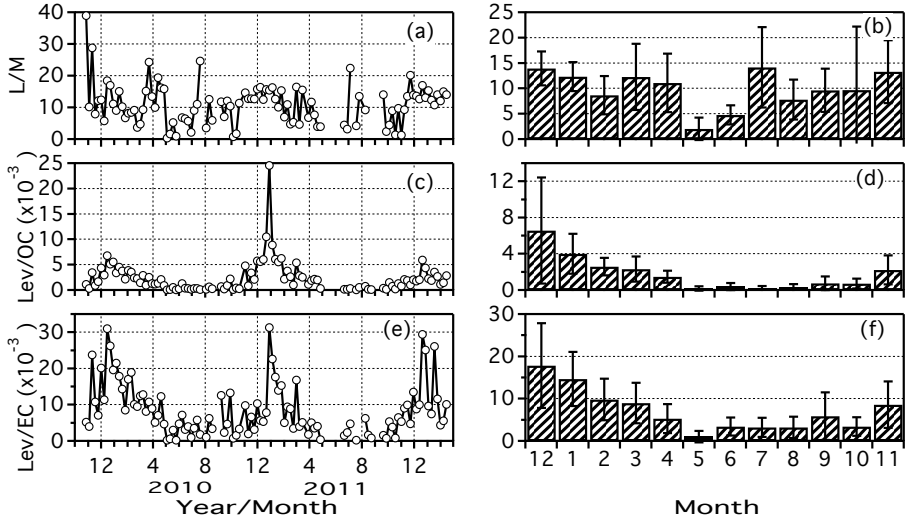

Figure 5. Temporal variations **(a, c, e)** and monthly means **(b, d, f)** of ratios of levoglucosan over mannosan (L/M), OC (Lev/OC) and EC (Lev/EC) in aerosols at Cape Hedo, Okinawa from October 2009 to February 2012.

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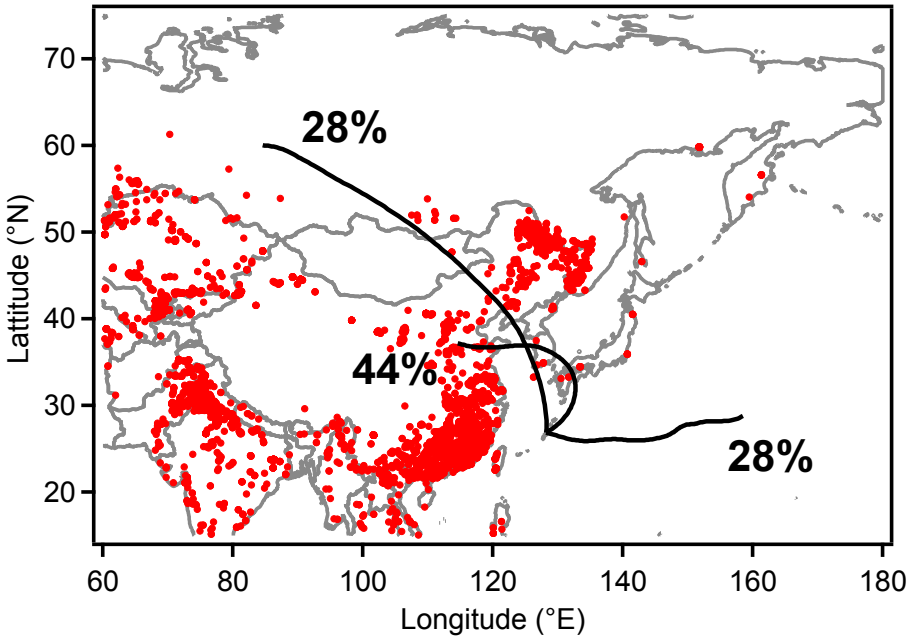

Figure 6. Air mass origins for the event of elevated ratio of levoglucosan over mannosan (L/M) in 27 October–3 November 2009. Clusters of 5 day backward trajectories arriving at 500 m a.g.l. at Cape Hedo, Okinawa are given. The numbers in the panel indicate the percentages of hourly trajectories with such origins. Fire spots in East Asia over 22 October–3 November 2009 are also shown.

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