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Biomass burning contribution to Beijing aerosol

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Abstract. Biomass burning, the largest global source of elemental carbon (EC) and primary organic carbon (OC), is strongly associated with many subjects of great scientific concern, such as secondary organic aerosol and brown carbon which exert important effects on the environment and on climate in particular. This study investigated the relationships between levoglucosan and other biomass burning tracers (i.e., water soluble potassium and mannosan) based on both ambient samples collected in Beijing and source samples. Compared with North America and Europe, Beijing was characterized by high ambient levoglucosan concentrations and low winter to summer ratios of levoglucosan, indicating significant impact of biomass burning activities throughout the year in Beijing. Comparison of levoglucosan and water soluble potassium (K^+) levels suggested that it was acceptable to use K^+ as a biomass burning tracer during summer in Beijing, while the contribution of fireworks to K^+ could be significant during winter. Moreover, the levoglucosan to K^+ ratio was found to be lower during the typical summer period (0.21 ± 0.16) compared with the typical winter period (0.51 ± 0.15). Levoglucosan correlated strongly with mannosan ($R^2 = 0.97$) throughout the winter and the levoglucosan to mannosan ratio averaged 9.49 ± 1.63, whereas levoglucosan and mannosan exhibited relatively weak correlation ($R^2 = 0.73$) during the typical summer period when the levoglucosan to mannosan ratio averaged 12.65 ± 3.38. Results from positive matrix factorization (PMF) model analysis showed that about 50 % of the OC and EC in Beijing were associated with biomass burning processes. In addition, a new source identification method was developed based on the comparison of the levoglucosan to K^+ ratio and the levoglucosan to mannosan ratio among different types of biomass. Using this method, the major source of biomass burning aerosol in Beijing was suggested to be the combustion of crop residuals, while the contribution from softwood burning was also non-negligible, especially in winter.

1 Introduction

Biomass burning processes, including wildfires, prescribed burning (of forest, agricultural waste, etc.) and domestic biofuel combustion (in fireplaces, stoves, etc.), contribute large amounts of trace gases (e.g., greenhouse gases and precursors of ozone) and particulate matter to the troposphere (Andreae and Merlet, 2001; van der Werf et al., 2006). These pollutants can be transported many thousands of kilometers downwind from the source areas. For example, forest fires in the southern Siberia/Lake Baikal area and agricultural burning in Kazakhstan and southern Russia were shown to be an important source of haze over the Arctic during an airborne experiment in April 2008 (Warneke et al., 2009), while it was found that ozone production in the mid-troposphere over the Atlantic was enhanced due to cross-hemispheric transport of African biomass burning plumes (Real et al., 2010). In addition to long-range transport, biomass burning is strongly associated with many other subjects that are of great scientific concern, such as secondary organic aerosol (SOA) production and release of light-absorbing organic carbon (i.e., brown carbon). Results from source emission studies

showed that fresh biomass burning aerosol is mainly comprised of carbonaceous species (e.g., Fine et al., 2001), which are expected to undergo atmospheric reactions (i.e., aging) during transport. Laboratory studies (Grieshop et al., 2009a, b) found that organic aerosol concentrations in diluted wood burning emissions increased by a factor of 1.5 to 2.8 after several hours of exposure to UV light and typical summertime hydroxyl radical (OH) concentrations, indicating significant production of SOA. However, a substantial challenge was that the oxidation of traditional precursors could only explain less than 20 % of the SOA formed. Formation of SOA from biomass burning emissions during aging processes was also confirmed by field observations (Lee et al., 2008; Adler et al., 2011). There were also several recent investigations focusing on the precursors and formation pathways of SOA from biomass burning. For example, it was found that aqueous-phase reactions of phenolic compounds, which are emitted in large amounts from wood combustion, can form SOA at high yields (Sun et al., 2010). In another chamber study, methyl-nitrocatechols were identified as atmospheric tracers for SOA from biomass burning, and *m*-cresol was suggested to be a precursor for methyl-nitrocatechols (Iinuma et al., 2010).

Inventory studies suggested that biomass burning is the largest source of global black carbon emission (Bond et al., 2004), while it was recently recognized that biomass burning is also an important source of brown carbon. Kirchstetter et al. (2004) found that the wavelength dependence of light absorption by biomass smoke aerosols was largely reduced when much of the organic carbon was extracted with acetone, indicating that organic carbon in the biomass smoke aerosols may appreciably absorb solar radiation. Studies based on the transmission electron microscope (TEM) technique provide additional evidence for the connection between biomass burning and brown carbon. A distinct group of organic particles termed tar balls, which have a brown appearance, was frequently observed in ambient aerosol samples impacted by biomass burning (Pósfai et al., 2004; Hand et al., 2005; Alexander et al., 2008; Adachi and Buseck, 2011) as well as in source samples from biomass combustion (Chakrabarty et al., 2010). Light absorption spectra of humic-like substances (HULIS) isolated from biomass burning aerosol (Hoffer et al., 2005) and those of methanol extracts of wood smoke samples (Chen and Bond, 2010) also demonstrate the importance of biomass burning as sources of brown carbon. In addition, a field study conducted in the southeastern US found that more than 50 % of the light absorption by PM$_{2.5}$ (fine particulate matter) water extracts could be attributed to biomass burning (Zhang et al., 2010).

Other important impacts of biomass burning emissions are the possibility of biomass smoke particles to act as cloud condensation nuclei (Reid et al., 2005a; Andreae and Rosenfeld, 2008), the strong radiative forcing caused by biomass burning aerosols (Haywood and Boucher, 2000; Reid et al., 2005b), and the adverse effects on human and environmen-

tal health (Naeher et al., 2007). Therefore, biomass burning has been the focus of extensive studies since the 1970s, and more recently, a series of international research initiatives were conducted, such as the SAFARI (the Southern Africa Fire Atmosphere Research Initiative) and the LBA-SMOCC (the Large Scale Biosphere-Atmosphere Experiment in Amazonia: Smoke, Aerosols, Clouds, Rainfall and Climate) campaigns.

Levoglucosan (1,6-anhydro-β-D-glucopyranose, $C_6H_{10}O_5$) is commonly used as tracer for biomass burning. As the main pyrolysis product from cellulose, levoglucosan is source specific and emitted in dominant amounts during the combustion of biomass; more importantly, the combustion of other materials, such as fossil fuels, does not produce levoglucosan (Elias et al., 2001). Therefore, levoglucosan is a unique tracer for biomass burning processes (Simoneit et al., 1999, 2004; Simoneit, 2002), and quantification of levoglucosan in aerosol samples provides valuable information regarding their emission sources. Measurement of levoglucosan usually relies on gas chromatography–mass spectrometry (GC-MS; e.g., Schauer et al., 2001) or high-performance liquid chromatography (HPLC, Schkolnik et al., 2005; Puxbaum et al., 2007; Yttri et al., 2007), both of which involve complex sample preparation and/or analytical procedures. A new method termed high-performance anion-exchange chromatography coupled to pulsed amperometric detection (HPAEC-PAD) was developed recently, and showed good agreement with traditional analytical methods (Engling et al., 2006; Caseiro et al., 2007; Iinuma et al., 2009). This new method, which directly quantifies levoglucosan as well as various other carbohydrates of atmospheric relevance using water extracts of aerosol samples, is simple and cost effective, and thus enables the analysis of a large number of samples.

Several investigators attempted to use the levoglucosan to organic carbon (OC) ratios as well as the levoglucosan to PM ratios measured in source samples to estimate the biomass burning contribution to ambient aerosol. Fine et al. (2002) found that an average of 136 mg levoglucosan per gram of OC was emitted from the fireplace combustion of four hardwood species grown in the southern US, which corresponds to an OC to levoglucosan ratio of 7.35. This ratio was used by Puxbaum et al. (2007) to estimate the contribution of biomass burning to OC measured at background sites in Europe:

$$\text{biomass burning OC} = \text{levoglucosan} \times 7.35. \quad (1)$$

Schmidl et al. (2008a) suggested a factor of 10.7 for converting levoglucosan concentration to PM mass based on the stove combustion of common woods grown in central Europe, while a substantially lower convention factor (7.6) was determined based on the main wood species burned in Portugal (Gonçalves et al., 2010). More recently, a conversion factor of 11.2 from levoglucosan to wood smoke mass, which was calculated as the mean value from published data (varying from 4.5 to 24.6), was used in a study conducted in the

UK (Harrison et al., 2012). This type of estimation may be problematic since the OC to levoglucosan ratio as well as the PM to levoglucosan ratio have been shown to be highly variable in biomass burning emissions. For example, Fine et al. (2002) found that the OC to levoglucosan ratio of softwood smoke particles (23.81) was much higher than hardwood (7.35), and Schmidl et al. (2008b) showed that the PM to levoglucosan ratio in emissions from burning of leaves (46.9) was more than four times the value of that for wood burning (10.7). Large differences in the OC to levoglucosan ratio as well as in the PM to levoglucosan ratio among different types of biomass fuels (varying by a factor of up to about 10) were also observed by Sullivan et al. (2008) and Gonçalves et al. (2010). Moreover, the combustion conditions could also influence the OC to levoglucosan ratio significantly. For example, the OC to levoglucosan ratio differed by a factor of about 7 when the same kind of wood (Loblolly Pine) was burned in a stove (3.95, Fine et al., 2004b) and fireplace (27.94, Fine et al., 2002), respectively. In addition, the OC to levoglucosan ratio of biomass burning emissions is expected to be complicated by the semivolatile organic compounds which might evaporate with increasing dilution (Robinson et al., 2007).

Receptor models such as CMB (chemical mass balance model; e.g., Zheng et al., 2002; Robinson et al., 2006; Stone, 2008) and PMF (positive matrix factorization model; e.g., Ramadan et al., 2000; Kim et al., 2003) are most frequently used to estimate the contributions from biomass burning as well as other emission sources. Historically, organic tracer data sets (which are usually obtained by GC-MS measurements) have not been large enough for the PMF model, since PMF analysis typically requires at least 60–200 samples (Jaeckels et al., 2007). Therefore, the PMF model is usually driven by OC, elemental carbon (EC), inorganic ions, and trace elements, whereas organic tracer measurements are commonly limited to use in the CMB model (Jaeckels et al., 2007). When performing PMF analysis, water soluble potassium (K^+) is usually used as the tracer for biomass burning. However, the sources of K^+ are known to be complex such that in addition to biomass burning, sea salt and crustal materials also contribute to airborne K^+. A correction approach was suggested by Pio et al. (2007, 2008) in which sodium (Na^+) and calcium (Ca^{2+}) were used as tracers for sea salt and crustal materials, respectively. The approach also included several assumptions such as the crustal K^+ to Ca^{2+} ratio. Using this approach however, corrected K^+ was found to be occasionally negative for samples from the UK, indicating an overcorrection (Harrison et al., 2012). These results prove that the influence of sea salt and crustal materials on K^+ is difficult to account for, partly due to the inhomogeneity of crustal materials (i.e., the variability in the ratio of K^+ to Ca^{2+}). With the development of the HPAEC-PAD method, levoglucosan has been introduced to the PMF analysis. For example, levoglucosan was measured in more than 900 PM$_{2.5}$ samples collected in the southeastern US, and results from PMF analysis showed that biomass burn-
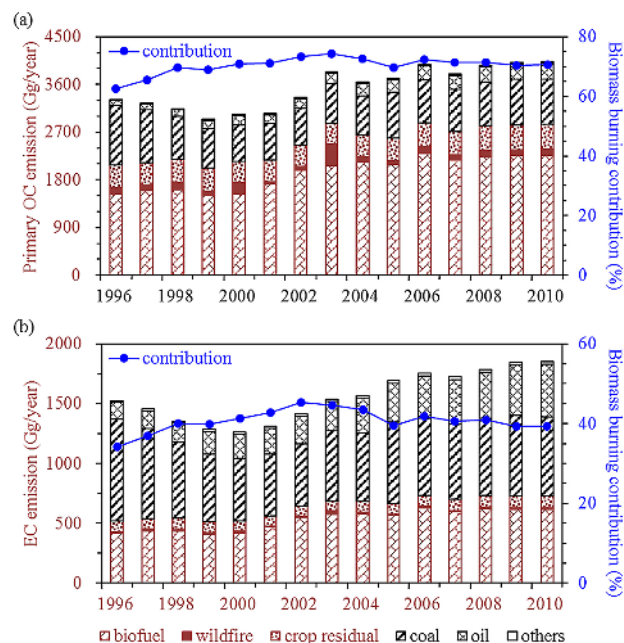
Fig. 1. Primary OC (**a**) and EC (**b**) emissions by fuel type in China during 1996 to 2010. The relative contributions of the total biomass burning sources are also shown. Data were obtained from Lu et al. (2011).

ing contributed 13 % to PM$_{2.5}$ mass annually (Zhang et al., 2010). This contribution (13%) was very close to that estimated for the same region using CMB (15 %; Zheng et al., 2002). Moreover, Zhang et al. (2010) found that K^+ exhibited poor correlation with levoglucosan during summer (R^2 was as low as 0.02), indicating that using K^+ as a biomass burning tracer can be problematic when biomass burning contributions are low and thus other sources of K^+ (e.g., mineral dust) become more important.

Air pollution in China has drawn continuous and increasing concerns not only from the scientific community, but also from the public. Compared with developed countries, the emission of pollutants (including both primary components such as black carbon and the gaseous precursors such as SO$_2$) are substantially higher in China and the emission sources are much more complex. While the sources of SO$_2$ and NO$_x$ (the precursors of sulfate and nitrate, respectively) are relatively well understood, it is more difficult to resolve the sources of particulate carbon. Figure 1 presents the EC and primary OC emissions by fuel type in China during 1996 to 2010 (data were obtained from Lu et al., 2011). Both EC and primary OC emissions tend to increase since 2000, while another noticeable feature is the high contribution of biomass burning emissions which include biofuel consumption, wildfires and burning of crop residuals. The biomass burning contributions to EC were in the range of 34–45 % during 1996 to 2010, whereas their contribution to primary OC was even higher (63–74 %). Moreover, biomass

burning contributions were relatively stable within the most recent five years (2006–2010), accounting for about 40 % and 70 % of EC and primary OC, respectively. In addition to emission inventories, several source apportionment studies have been conducted in China based on ambient measurements. Factor analysis, which was driven by inorganic ions and trace elements, was used in an early study to investigate the sources of $PM_{2.5}$ and PM_{10} in Beijing, although biomass burning was not included (Sun et al., 2004). Results from PMF analysis (using total K^+ as biomass burning tracer) showed that biomass burning contributions to $PM_{2.5}$ in Beijing were about 11 % in 2000 (Song et al., 2006), and the contribution increased to 18 % in 2004 (Song et al., 2007). Another study based on CMB modeling was also conducted for Beijing in 2000 (in which levoglucosan was used as biomass burning tracer; Zheng et al., 2005), revealing an estimated biomass burning contribution to $PM_{2.5}$ (6 %) that was much lower than the PMF results from the same year (11 %). In a more recent CMB study, the annual average of biomass burning contributions to $PM_{2.5}$ in Beijing was estimated to be about 17 % (Wang et al., 2009). It is also noteworthy that there have been several field studies focusing on biomass burning emissions in China. To our knowledge, the study by Duan et al. (2004) was the first of this kind. It was first assumed that the OC to K^+ ratio measured in ambient samples heavily impacted by prescribed burning of crop (wheat) residuals could be used as the source-specific conversion factor, by which the measured K^+ concentrations were converted to OC contributions from biomass burning. Using this approach, Duan et al. (2004) suggested that the biomass burning contribution could be as high as 70 % at a rural site in Beijing. More recently, ambient levoglucosan concentrations in Guangzhou and Beijing were measured by Wang et al. (2007) and Zhang et al. (2008), respectively; and a method similar to that described in Eq. 1 was used by both studies to investigate the biomass burning contribution. As mentioned above, however, this kind of estimation may be problematic. A substantial challenge is the large differences in the OC to levoglucosan ratios (or the PM to levoglucosan ratios) among emissions from different biomass species and from different combustion conditions, making it very difficult to determine the most suitable OC to levoglucosan ratio of biomass burning emissions for a given region.

In this study, we quantified levoglucosan as well as other chemical species in Beijing aerosol, and investigated the relationship between levoglucosan and other biomass burning tracers such as K^+ and mannosan. Moreover, the biomass burning contributions to OC and EC were estimated using a receptor model. Finally, the levoglucosan to K^+ ratios and the levoglucosan to mannosan ratios were compared among different types of biomass, and a new source identification method was developed.

2 Methods

2.1 Sample collection

2.1.1 Ambient samples

Daily $PM_{2.5}$ samples were collected using a high-volume sampler (Thermo Scientific, MA, USA; the flow rate was $1.13\,m^3\,min^{-1}$) at an urban site (the Tsinghua University campus) in Beijing, China. A total of 50 samples were collected during the summer of 2011 (from 3 June to 23 July), while there were 60 samples collected during the winter of 2011–2012 (from 1 December 2011 to 30 January 2012). Quartz fiber filters (8 × 10 in, 2500 QAT-UP; Pall Corporation, NY, USA) taken from the same lot were used for the entire sampling campaign. The filters had been pre-baked at 550 °C for 24 h before use.

2.2 Source samples

Biomass smoke samples, including two kinds of crop residuals (wheat and corn, commonly found in northern China) and two kinds of wood (poplar and pine, both being softwood), were collected from a brick cooking stove as described by Shen et al. (2010). Briefly, biomass was burned in the stove following the typical practices of rural residents in northern China, with the smoke entering a mixing chamber ($4.5\,m^3$) equipped with a built-in mixing fan. Subsequently, the biomass smoke samples were collected from the chamber on quartz fiber filters using a low volume sampler (XQC-15E; Tianyue, Jiangsu, China) at a flow rate of $1.5\,L\,min^{-1}$. Three samples were collected for each kind of biomass. Smoldering and flaming combustion phases were not distinguished in this study. Although a size-selective inlet was not used, previous studies (Kleeman et al., 1999, 2008; Engling et al., 2006) have shown that the majority of biomass burning tracers, such as levoglucosan, mannosan and K^+, were emitted in the $PM_{2.5}$ fraction for non-field combustion (i.e., stove and chamber). It should also be mentioned that the size distribution of levoglucosan was more variable for field (i.e., open) burning, presumably due to the influences of suspended soil particles during the burning process. For example, levoglucosan emitted from the field burning of rice straw in Taiwan was found to exhibit a bimodal distribution such that a large fraction (up to 56 %) of the total levoglucosan mass was observed in particles with an aerodynamic diameter above 10 μm ($PM_{>10}$; Engling et al., 2009), whereas almost all of the levoglucosan mass emitted from the field burning of rice straw in Thailand was found in the $PM_{2.5}$ fraction (Oanh et al., 2011).

2.3 Sample analysis

2.3.1 Ambient samples

The ambient filters were analyzed for OC and EC using a DRI Model 2001 carbon analyzer (Atmoslytic Inc., CA, USA). OC and EC concentrations were quantified by the IMPROVE-A temperature protocol with transmittance charring correction. Briefly, a punch with an area of $0.5\,cm^2$ was taken from each sample and heated sequentially in inert (i.e., He) and oxidizing (i.e., He/O_2) atmospheres to volatilize and combust the loaded carbon, respectively. EC was measured as the carbon evolving after the filter transmittance (which is monitored at 632 nm) returned to its initial value.

The analysis of water-soluble ions was performed by ion chromatography (IC, DX-600, Dionex Corporation, CA, USA). Four anions (i.e., sulfate, nitrate, chloride and oxalate) and five cations (i.e., sodium, ammonium, potassium, magnesium and calcium) were quantified. The sample preparation procedure for IC analysis was similar to that described by Zhang et al. (2010). Briefly, a punch with a diameter of 47 mm was taken from each sample and placed in a 30 mL Nalgene amber HDPE bottle and extracted with 20 mL of deionized water ($> 18\,M\Omega$) via 30 min sonication. Finally, the water extract was filtered using a 0.45 μm PTFE syringe filter (Fisher Scientific, NH, USA) and stored in a refrigerator until analysis. The analysis was completed within three days after extraction.

Water soluble organic carbon (WSOC) was measured at the Georgia Institute of Technology using a Sievers Total Organic Carbon Analyzer (Model 900; GE Analytical Instruments, CO, USA). The pretreatment procedure was the same as that for IC analysis, except that a smaller punch ($1.5\,cm^2$) and a larger amount of deionized water (60 mL) were used for the WSOC measurement. The WSOC analysis was finished within one day after extraction. The WSOC analyzer was calibrated twice during the measurement period, using five sucrose solutions for each calibration. The variability in the linear regression slope was less than 1 % (with the intercept set as zero; $R^2 = 1.00$ and 1.00 for the two calibrations, respectively).

Levoglucosan and mannosan were quantified at the National Tsing Hua University (Taiwan) using the HPAEC-PAD method developed by Engling et al. (2006). The extraction and filtration procedure was also similar to the IC analysis. The current HPAEC-PAD method used a Dionex ICS-3000 Ion Chromatograph, with a Dionex CarboPak MA1 analytical column (4 mm × 250 mm) and sodium hydroxide solution (400 mM, 0.4 mL min^{-1}) as eluent (Engling et al., 2009). An autosampler was used for the injection, within which the water extracts were kept at 8 °C.

2.3.2 Source samples

Source samples were only analyzed for anhydrosugars (levoglucosan and mannosan) and K^+, mainly due to the small available filter area. K^+ was measured by IC, using a Dionex DX-120 system, from the same water extracts as the anhydrosugars which were quantified by HPAEC-PAD. The equivalence of K^+ measured by the DX-120 and DX-600 system (which was used for the ambient samples) was demonstrated by analysis of all the ambient samples ($n = 110$) on both IC systems. Linear regression analysis showed that K^+ measured by the DX-120 agreed well with the results from the DX-600 system (slope = 0.99, intercept = 0.05, $R^2 = 0.98$).

3 Results and discussion

Average concentrations of the major $PM_{2.5}$ components measured during summer and winter are summarized in Table 1. Summer aerosol was characterized by high contributions of secondary inorganic ions (SO_4^{2-}, NO_3^- and NH_4^+), whereas winter aerosol was dominated by carbonaceous fractions (OC and EC). In the following discussion, we will focus on the chemical species associated with biomass burning. Statistical results for the concentrations, ratios, regressions and comparisons included in the following discussion are presented as Supplement.

3.1 Relationship between levoglucosan and other biomass burning tracers: ambient samples

3.1.1 Levoglucosan concentrations

The ambient levoglucosan concentrations in Beijing averaged 0.23 ± 0.37 (varying from 0.06 to 2.30, $N = 50$) and 0.59 ± 0.42 (varying from 0.06 to 1.94, $N = 60$) μg m^{-3} during summer and winter, respectively (Table 1). The overall average levoglucosan concentration was 0.43 ± 0.44 μg m^{-3}, which provides an estimation of the annual average tracer level. Levoglucosan concentrations had been quantified in several previous studies conducted in Beijing, yet with variable results. The levoglucosan levels measured by He et al. (2006) (averaging 0.03 and 0.08 μg m^{-3} during summer and winter, respectively) were about an order of magnitude lower than those obtained during the present study, whereas more comparable values were observed by Zhang et al. (2008) (below 0.20 μg m^{-3} in summer and up to 0.81 μg m^{-3} in winter, with an annual average of 0.31 μg m^{-3}) and Wang et al. (2009) (0.17 and 0.68 μg m^{-3} in summer and winter, respectively). The significantly lower levoglucosan concentrations found by He et al. (2006) may be due to the small sample number, which was eleven and seven for summer and winter, respectively. Compared with American and European cities, Beijing was characterized by rather high levoglucosan concentrations, especially in

Table 1. Average concentrations of $PM_{2.5}$ components during summer and winter in Beijing. Values of OC, EC and WSOC are presented in $\mu g\,C\,m^{-3}$, whereas concentrations of the other species are presented in $\mu g\,m^{-3}$.

		Summer			Winter	
	Average	BB episode[a]	Typical summer[b]	Average	Firework episode[c]	Typical winter[d]
OC	12.04 ± 6.25	20.94 ± 8.62	10.09 ± 3.36	24.61 ± 17.06	26.11 ± 22.34	24.11 ± 15.19
EC	2.51 ± 1.16	4.02 ± 1.50	2.17 ± 0.76	8.09 ± 5.96	6.50 ± 4.89	8.62 ± 6.24
WSOC	7.77 ± 4.40	14.39 ± 5.75	6.32 ± 2.25	11.24 ± 8.02	12.48 ± 10.23	10.82 ± 7.23
levo.[e]	0.23 ± 0.37	0.75 ± 0.68	0.12 ± 0.05	0.59 ± 0.42	0.46 ± 0.29	0.64 ± 0.45
manno.[e]	0.01 ± 0.02	0.03 ± 0.04	0.01 ± 0.00	0.06 ± 0.04	0.04 ± 0.03	0.07 ± 0.05
K^+	1.74 ± 2.29	5.81 ± 2.75	0.84 ± 0.58	2.42 ± 5.86	6.03 ± 11.13	1.21 ± 0.81
Cl^-	1.43 ± 1.90	3.27 ± 3.41	1.03 ± 1.08	5.92 ± 4.47	7.52 ± 6.85	5.38 ± 3.28
$C_2O_4^{2-}$	0.44 ± 0.26	0.82 ± 0.28	0.36 ± 0.17	0.16 ± 0.10	0.19 ± 0.13	0.15 ± 0.08
SO_4^{2-}	23.67 ± 16.05	35.44 ± 8.53	21.09 ± 16.22	15.72 ± 14.44	22.63 ± 21.13	13.42 ± 10.77
NO_3^-	18.14 ± 15.51	24.87 ± 12.66	16.66 ± 15.82	12.71 ± 13.14	18.90 ± 21.20	10.64 ± 8.44
NH_4^+	12.45 ± 9.26	17.27 ± 5.96	11.39 ± 9.57	8.88 ± 8.44	11.08 ± 12.25	8.15 ± 6.76
Na^+	0.18 ± 0.14	0.34 ± 0.15	0.14 ± 0.10	0.68 ± 0.34	0.73 ± 0.38	0.67 ± 0.33
Ca^{2+}	0.46 ± 0.19	0.48 ± 0.20	0.45 ± 0.19	1.47 ± 0.77	0.91 ± 0.38	1.65 ± 0.79
Mg^{2+}	0.11 ± 0.05	0.14 ± 0.04	0.11 ± 0.05	0.24 ± 0.23	0.42 ± 0.40	0.18 ± 0.08

[a] BB episode refers to the sampling period between 14 and 23 June 2011 ($N = 9$).
[b] Typical summer period indicates the remaining sampling days of summer ($N = 41$).
[c] Firework episode refers to the sampling period between 15 and 30 January 2012 ($N = 15$).
[d] Typical winter period indicates the remaining sampling days of winter ($N = 45$).
[e] Levoglucosan and mannosan are referred to as levo. and manno., respectively.

summer. Results from fifteen sites throughout the southeastern US showed that the annual average levoglucosan concentration was $107.5\,ng\,m^{-3}$ (Zhang et al., 2010), which was comparable with the two-year average value ($95.2\,ng\,m^{-3}$) measured at a Midwestern site (St. Louis, MO; Jaeckels et al., 2007). Much lower results were observed in Pittsburgh, PA (in the northeastern US), with an annual average levoglucosan concentration of only about $20\,ng\,m^{-3}$ (Robinson et al., 2006). In a recent study conducted in Europe, levoglucosan was measured in four cities (Helsinki, Finland; Copenhagen, Denmark; Birmingham, UK; and Oporto, Portugal) during summer and winter, showing concentrations below $150\,ng\,m^{-3}$ at all sites with a majority of the values even lower than $50\,ng\,m^{-3}$ (Caseiro and Oliveira, 2012). It should be noted that higher levoglucosan concentrations had been observed in European cities during winter, which were comparable with our results from Beijing. For example, ambient levoglucosan was about $0.48\,\mu g\,m^{-3}$ during winter in Gent, Belgium (measured in total suspended particulate matter, TSP; Zdráhal et al., 2002), about $0.82\,\mu g\,m^{-3}$ during winter in an Alpine city in France (Favez et al., 2010), between 0.22 and $0.68\,\mu g\,m^{-3}$ during winter in three Austrian cities (measured in PM_{10}; Caseiro et al., 2009), and about $0.61\,\mu g\,m^{-3}$ during winter in Elverum, Norway (measured in PM_{10}; Yttri et al., 2007). However, the summertime levoglucosan concentrations measured in all of these studies (typically below $50\,ng\,m^{-3}$) were much lower than those observed in Beijing. Therefore, Beijing was characterized by a much smaller difference in levoglucosan concentrations between winter and summer, compared with American

and European cities. The winter to summer ratio of levoglucosan was 2.6 for Beijing, whereas the ratio was 24.6 and 12.9 for Gent, Belgium (Zdráhal et al., 2002), and Elverum, Norway (Yttri et al., 2007), respectively. Although this ratio was relatively smaller in three Austrian cities (averaging 7.3, Caseiro et al., 2009), it was still substantially higher than the Beijing ratio. Results from the southeastern US also suggested a substantially higher winter to summer ratio of levoglucosan (9.1) compared with Beijing (Zhang et al., 2010). The high summertime levoglucosan concentrations and the low winter to summer ratio of levoglucosan in Beijing indicate that biomass burning contributions to Beijing aerosol are significant throughout the year. As suggested by Zhang et al. (2008), the most likely cause of this phenomenon is the domestic use of biofuel, which prevails all year round, in the rural areas of Beijing and in the surrounding provinces. In Sect. 3.3, we will further identify the kinds of biofuel that are most accountable for the biomass burning aerosol in Beijing.
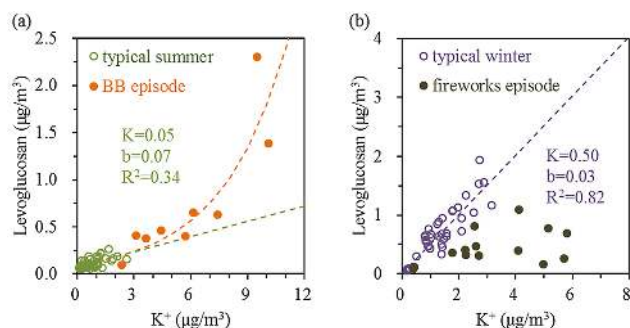
3.1.2 Comparison of levoglucosan and K^+ as biomass burning tracer

Figure 2a presents the daily variations of levoglucosan during summer of 2011, in which K^+ concentrations are also shown for comparison. In general, the temporal trend of levoglucosan coincided with that of K^+, indicating that it should be acceptable to use K^+ as a biomass burning tracer during summer in Beijing. Moreover, it was found that levoglucosan concentrations were substantially higher during 14 June to 23 June (averaging $0.75 \pm 0.68\,\mu g\,m^{-3}$) compared with the
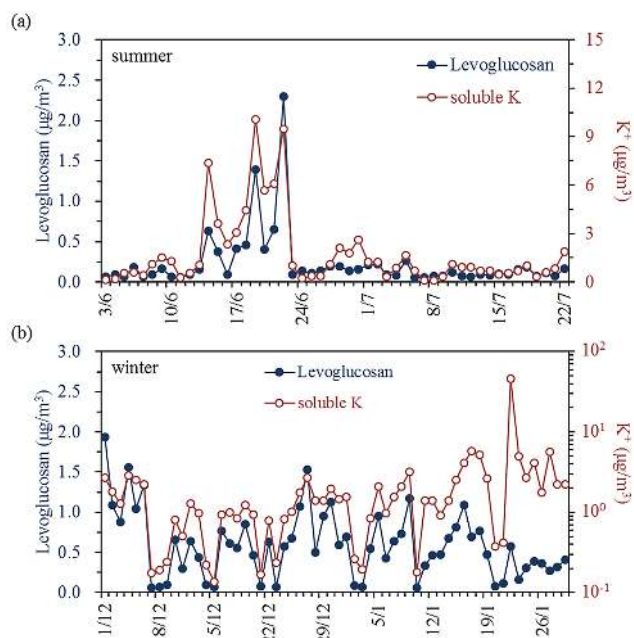
Fig. 2. Daily variation of levoglucosan and K^+ concentrations during summer **(a)** and winter **(b)** in Beijing.

Fig. 3. The dependence of levoglucosan on K^+ during summer **(a)** and winter **(b)** in Beijing. Linear regression results for the typical summer and typical winter period are shown in **(a)** and **(b)**, respectively. K indicates the regression slope, while b is the intercept. In **(a)**, an exponential fit ($R^2 = 0.79$) was shown for the comparison of levoglucosan and K^+ during the BB episode, whereas the correlation between levoglucosan and K^+ tended to be linear if removing the two points with extremely high levoglucosan concentrations (slope = 0.09 ± 0.02, intercept = 0.03 ± 0.12, $R^2 = 0.71$).

other sampling days (averaging $0.12 \pm 0.05 \, \mu g \, m^{-3}$). The period between 14 June to 23 June was also characterized by a much higher levoglucosan to OC ratio (0.014 ± 0.007, $\mu g C / \mu g C$), whereas that ratio was only 0.005 ± 0.002 on average for the other samples. The levoglucosan to OC ratios were calculated on a basis of carbon mass to avoid the complications of the conversion factor from organic carbon ($\mu g C \, m^{-3}$) to organic matter ($\mu g \, m^{-3}$). The harvest season of wheat in the North China Plain (where Beijing is located) is typically in late June. Although prohibited, field burning of wheat straw after the harvest is very common in the surrounding provinces (e.g., Hebei) as well as in the rural areas of Beijing, which likely is responsible for the elevated levoglucosan concentrations observed between 14 June and 23 June. In the following discussion, the period between 14 June and 23 June will be referred to as biomass burning (BB) episode, whereas the remaining sampling days will be termed typical summer period. Concentrations of K^+ also peaked during the BB period with an average of $5.81 \pm 2.75 \, \mu g \, m^{-3}$, which was about 6.9 times the average of the K^+ levels measured in the typical summer period ($0.84 \pm 0.58 \, \mu g \, m^{-3}$). Therefore, K^+ could also be used to identify BB episodes caused by post-harvest field burning of wheat straw during summer in Beijing. In the typical summer period, levoglucosan and K^+ correlated weakly ($R^2 = 0.34$) with a slope of 0.05 ± 0.01 and an intercept of 0.07 ± 0.01 (Fig. 3a). During the BB episode, however, the relationship between levoglucosan and K^+ appeared to be non-linear, and an exponential fit ($R^2 = 0.79$) was shown in Fig. 3a. Non-linear correlation between levoglucosan and K^+ was also observed by

Schkolnik et al. (2005) at an Amazon site during the deforestation fire season. It was found that levoglucosan exhibited a polynomial relationship (second degree) with K^+ at nighttime, whereas levoglucosan and K^+ correlated linearly during daytime. Schkolnik et al. (2005) attributed the difference to the influences of the combustion stage. It was suggested that flaming combustion prevailed during daytime when the deforestation fires were set, while smoldering processes were more dominant at nighttime when the fires had subsided; moreover, compared with flaming processes, smoldering combustion would give rise to more unbroken organic compounds, thus producing more levoglucosan in comparison to K^+.

Figure 2b presents the daily variations of levoglucosan and K^+ during winter of 2011–2012. It was found that K^+ coincided well with levoglucosan for the samples collected between 1 December 2011 and 15 January 2012 (period 1; $N = 45$). During this period, linear regression of levoglucosan on K^+ resulted in a slope of 0.50 ± 0.04 and an intercept of 0.03 ± 0.05 ($R^2 = 0.82$; Fig. 3b). For the samples collected after 15 January 2012 (period 2; $N = 15$), K^+ did not show any apparent dependence on levoglucosan, and there was more K^+ in comparison to levoglucosan (Fig. 3b). Levoglucosan concentrations were comparable during period 1 (averaging $0.64 \pm 0.45 \, \mu g \, m^{-3}$) and period 2 (averaging $0.46 \pm 0.29 \, \mu g \, m^{-3}$), whereas the average concentration of K^+ measured during period 2 ($6.03 \pm 11.13 \, \mu g \, m^{-3}$) was about 5 times the value of that found in period 1 ($1.21 \pm 0.81 \, \mu g \, m^{-3}$), indicating that in addition to biomass burning, other sources contributed to the K^+ abundance during period 2. The K^+ concentrations peaked at $45.76 \, \mu g \, m^{-3}$ in the sample collected from 22 to 23 January 2012, which coincided with the Chinese New Year (i.e., the so-called
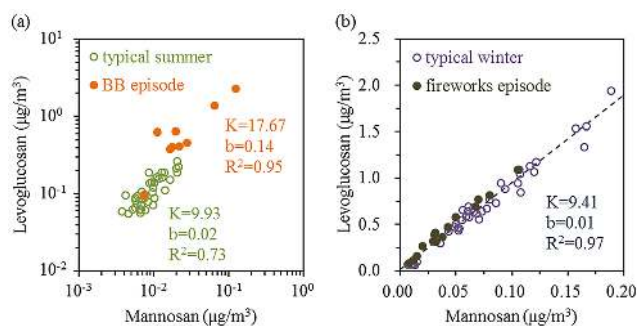
Fig. 4. The dependence of levoglucosan on mannosan during summer **(a)** and winter **(b)** in Beijing. Linear regression results are shown with K as slope and b as intercept. In **(a)**, linear regression results of the BB episode (marked with orange font) and the typical summer period (marked with green font) are shown separately, whereas the regression results in **(b)** are for the whole winter.

Spring Festival) and New Year's Eve on 23 January and 22 January, respectively. The Chinese New Year is the most important national festival in China. People usually start to set off fireworks several days before the Chinese New Year's Eve, and the fireworks typically last for two weeks after the beginning of the new year. Previous studies have shown that firework aerosols are rich in K^+ (Drewnick et al., 2006; Wang et al., 2007). Therefore, elevated K^+ concentrations during period 2 should be mainly due to fireworks. In the following discussion, period 2 will be referred to as firework episode, whereas period 1 is termed typical winter period. Comparison of levoglucosan and K^+ levels in winter suggests that emissions from fireworks can significantly bias the use of K^+ as biomass burning tracer.

Comparison of Fig. 3a and b showed that the levoglucosan to K^+ ratios were lower during the typical summer period (averaging 0.21 ± 0.16) compared with the typical winter period (averaging 0.51 ± 0.15), while during the BB episode the levoglucosan to K^+ ratios averaged 0.11 ± 0.06. It is also noteworthy that the levoglucosan to K^+ ratio (0.24) of the sample with the highest levoglucosan concentration was substantially higher than those for the other samples of the BB episode (averaging 0.10 ± 0.03). This phenomenon could be attributed to the non-linear dependence of levoglucosan on K^+ during the BB episode. Factors responsible for the seasonal variations in the levoglucosan to K^+ ratio are discussed in Sect. 3.3 based on the results from source samples.

3.1.3 Comparison of levoglucosan and mannosan

Ambient levoglucosan and mannosan concentrations are compared in Fig. 4. It was found that levoglucosan and mannosan correlated strongly ($R^2 = 0.97$) with a slope of 9.41 ± 0.22 and a small intercept of 0.01 ± 0.02 throughout winter, indicating fireworks do not impact the dependence of levoglucosan on mannosan. In summer, the BB episode and the typical summer period exhibited a different relation-

ship between levoglucosan and mannosan. During the typical summer period, levoglucosan and mannosan showed relatively weak correlation with a slope of 9.93 ± 0.97 and a small intercept of 0.02 ± 0.01 ($R^2 = 0.73$), whereas during the BB episode regression of levoglucosan on mannosan resulted in a slope of 17.67 ± 1.61 and a relatively large intercept of 0.14 ± 0.08 ($R^2 = 0.95$). The levoglucosan to mannosan ratios averaged 25.01 ± 13.20 and 12.65 ± 3.38 during the BB episode and typical summer period, respectively, whereas an average value of 9.49 ± 1.63 was observed during winter (Table 2). Factors responsible for the seasonal variations in the levoglucosan to mannosan ratio are discussed in Section 3.3 based on the results from source samples.

### 3.2 Source apportionment based on PMF analysis

Biomass burning contributions to Beijing aerosol were estimated using the PMF model developed by the US EPA (version 3.0; see US EPA website for a detailed description of the model: http://www.epa.gov/heasd/products/pmf/pmf.html). OC, EC, WSOC, levoglucosan, K^+, sulfate and oxalate measured during the typical summer and winter periods were included in the PMF analysis, whereas the two unusual events (i.e., the BB episode and the firework episode) were excluded as suggested by the user guide for PMF analysis (US EPA, 2008). The uncertainties of OC, EC, and water soluble ions were estimated based on our previous studies regarding the measurement methods for ambient aerosol, which are described in detail in the Supplement. A value of 5 % was used for the uncertainty of the levoglucosan data as suggested by Engling et al. (2006). The uncertainty of WSOC was estimated to be 5 % based on parallel analysis of both ambient filters and sucrose solutions (see Supplement). A solution with six factors was identified as the optimal solution of the Beijing data set. The agreement of the Q (robust) and Q (true) parameters indicated that the model fits the input data well. Q (robust) is the goodness-of-fit parameter calculated excluding outliers (defined as samples for which the scaled residual is greater than 4), whereas Q (true) is calculated including all data points. The distribution of residuals was narrow and close to normal. Moreover, the input concentrations and the modeled values correlated strongly (R^2 was between 0.98 and 1.00) with a slope very close to 1 (between 0.99 ± 0.00 and 1.03 ± 0.01; intercept was set as zero) for all of the components, indicating that the model also fits the individual species well.

Factor profiles resolved by the PMF analysis are shown in Fig. 5. Factor 1 was characterized by high levels of K^+, sulfate and oxalate, such that 37 % of K^+, 17 % of sulfate and 22 % of oxalate were in this factor, suggesting a secondary nature of this factor. Little levoglucosan was found in factor 1, indicating that K^+ associated with this factor should be from other sources in addition to biomass burning (e.g., crustal material). Factor 2 was characterized by levoglucosan (48 %), OC (42 %), WSOC (35 %), K^+ (24 %) and sulfate

Table 2. Levoglucosan (levo.) to K^+ and levoglucosan to mannosan (manno.) ratios of ambient and source samples.

	Ambient samples			
	BB episode	Typical summer	Firework episode	Typical winter
levo./K^+	0.11 ± 0.06	0.21 ± 0.16	0.16 ± 0.09	0.51 ± 0.15
levo./manno.	25.01 ± 13.20	12.65 ± 3.38	10.88 ± 1.23	9.01 ± 1.47
	Source samples			
	Wheat straw	Corn straw	Pine wood	Poplar wood
levo./K^+	0.10 ± 0.00	0.21 ± 0.08	23.96 ± 1.82	5.89 ± 0.53
levo./manno.	12.71 ± 1.53	19.48 ± 3.37	2.69 ± 0.03	5.98 ± 1.40
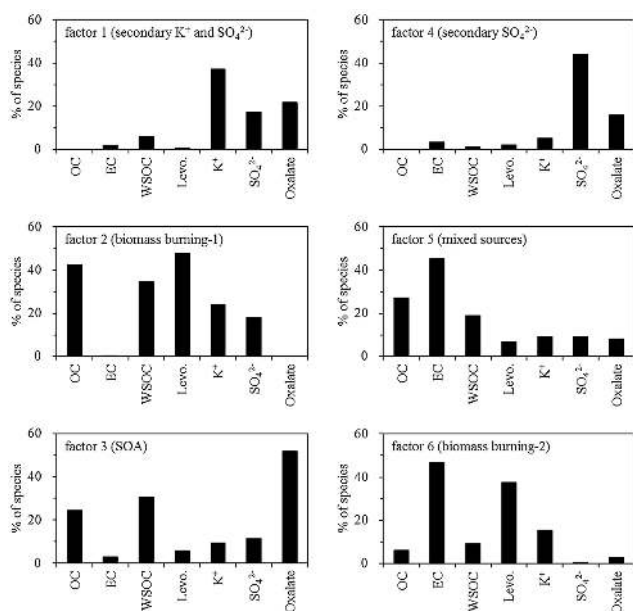
Fig. 5. Composition profiles for the six factors resolved by PMF based on data from the typical summer and winter period.

(18 %), indicating emissions associated with biomass burning. The relative contribution of factor 2, which was obtained from the PMF output, was much more significant during winter compared with summer, whereas previous source apportionment studies conducted in Beijing showed that secondary organic carbon was more abundant in summer (when it is warm, humid and wind speeds are low) than winter (when it is cold, dry and wind speeds are high) (Zheng et al., 2005; Lin et al., 2009; Wang et al., 2010). Therefore, factor 2 was likely not secondary though little EC was detected in this factor. Bi et al. (2011) investigated a large number of biomass burning particles (BB particles) using a single particle aerosol mass spectrometer, in which BB particles were identified by the *m/z* ratios of levoglucosan as well as other species. It was found that although the number of BB particles rich in K^+, OC and EC was considerable, the BB particles rich in K^+ and OC were most abundant. Thus, Bi et al. (2011) provided solid evidence for the presence of biomass burning emissions with the characteristics of factor 2 (i.e., with little EC). It is hypothesized that factor 2 may be associated with the condensation processes which could be enhanced when temperatures are low. Factor 3 had high levels of oxalate, WSOC and OC, showing characteristics of secondary organic aerosol. Moreover, aqueous-phase reactions (or in-cloud processes) were suggested to be the primary mechanism for oxalate formation in ambient aerosols (Yao et al., 2002; Yu et al., 2005; Huang et al., 2006; Sorooshian et al., 2006), which was also strongly supported by the good correlation between oxalate and sulfate measured in this study (Fig. 6; in-cloud processes are the major production pathway of sulfate). Compared with factor 3, factor 4 exhibited a stronger link with secondary inorganic aerosol since more than 40 % of sulfate was found in this factor. Factor 5 was characterized by a high level of EC (45 %), whereas secondary species were also not negligible (about 10 % of sulfate and oxalate was associated with factor 5). Due to the lack of tracers for other primary sources besides biomass burning, it could only be suggested that factor 5 represented mixed sources dominated by primary emissions. High levels of EC and levoglucosan were observed in factor 6, while the levels of secondary species (sulfate and oxalate) were very low. Thus, factor 6 should represent primary emissions from biomass burning.
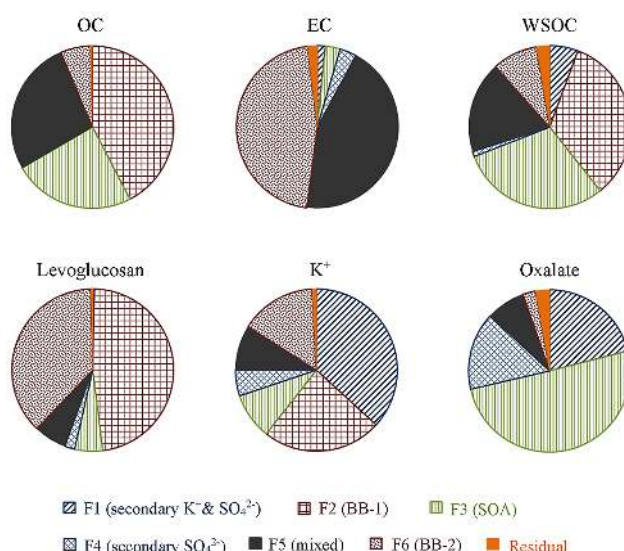
Contributions of the six sources to various components are shown in Fig. 7. Results from the whole data set showed that about 50 % (sum of factors 2 and 6) of OC was associated with biomass burning, while the biomass burning contribution to EC was also close to 50%. Moreover, it was estimated that about 10 % of WSOC and 3 % of oxalate was due to the primary emissions from biomass burning (factor 6). It was with expectation that the majority of levoglucosan (about 85 %, sum of factors 2 and 6) was attributed to biomass burning, while it was also noticed that a substantial fraction of K^+ (about 40 %, sum of factor 1 and factor 4) was linked with sulfate. In addition, the source apportionment results of K^+ exhibited significant seasonal variations such that factor 1 and factor 4 constituted about 70 % of K^+ during the typical summer period, whereas about 60 % of K^+ was contributed
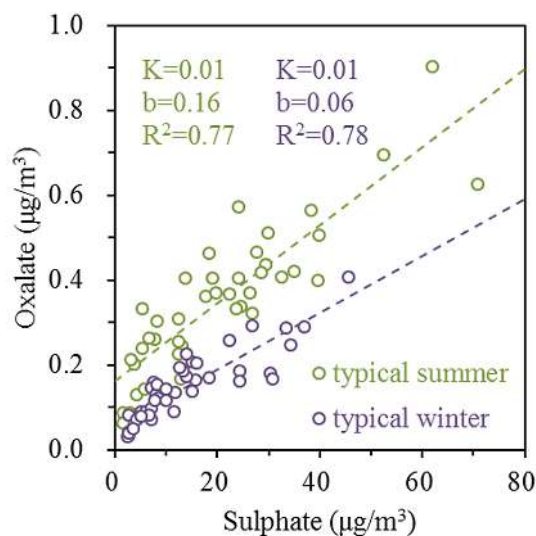
Fig. 6. Dependence of oxalate on sulfate during the typical summer and winter period. Linear regression results are shown with K as slope and b as intercept, and results for summer and winter are marked by green and purple font, respectively.

Fig. 7. Average source contributions to OC, EC, WSOC, levoglucosan, K^+ and oxalate estimated by PMF. Source apportionment results during the typical summer and typical winter periods are presented separately in the Supplement.

by factor 2 and factor 6 (i.e., biomass burning) during the typical winter period. The source apportionment results suggest that (1) K^+ was mainly associated with sulfate during the typical summer period when the correlation between levoglucosan and K^+ was found to be weak ($R^2 = 0.34$, Fig. 3a); and (2) biomass burning was the major source of K^+ during the typical winter period, which was also strongly supported by the high correlation between levoglucosan and K^+ observed in the typical winter period ($R^2 = 0.82$; Fig. 3b).

As mentioned in the introduction section, previous PMF studies conducted in Beijing usually estimated the biomass burning contributions to $PM_{2.5}$ mass rather than OC and EC (Song et al., 2006, 2007). Although $PM_{2.5}$ mass concentrations were not measured in this study, an estimation (reconstructed $PM_{2.5}$) could be provided by the sum of carbonaceous components ($1.6 \times OC + EC$) and inorganic ions ($SO_4^{2-} + NO_3^- + Cl^- + NH_4^+ + K^+ + Ca^{2+} + Mg^{2+} + Na^+$). The reconstructed $PM_{2.5}$ mass was on average 70.02 ± 45.40 and $88.51 \pm 55.74\,\mu g\,m^{-3}$ during the typical summer and winter periods, respectively. Subsequently, contributions of the six factors resolved by PMF to the reconstructed $PM_{2.5}$ mass could be estimated using multivariate linear regression (see Supplement for the detailed calculation process). It was found that the $PM_{2.5}$ mass concentrations calculated based on multivariate linear regression agreed well with the reconstructed $PM_{2.5}$ mass (slope = 0.97 ± 0.02, $b = 2.53 \pm 1.47$, $R^2 = 0.98$). The biomass burning contribution to the reconstructed $PM_{2.5}$ mass was estimated to be about 34 %. This estimation was substantially higher than those from previous source apportionment studies (less than 20 %; Song et al., 2007; Wang et al., 2009). On the other hand, speciation stud-
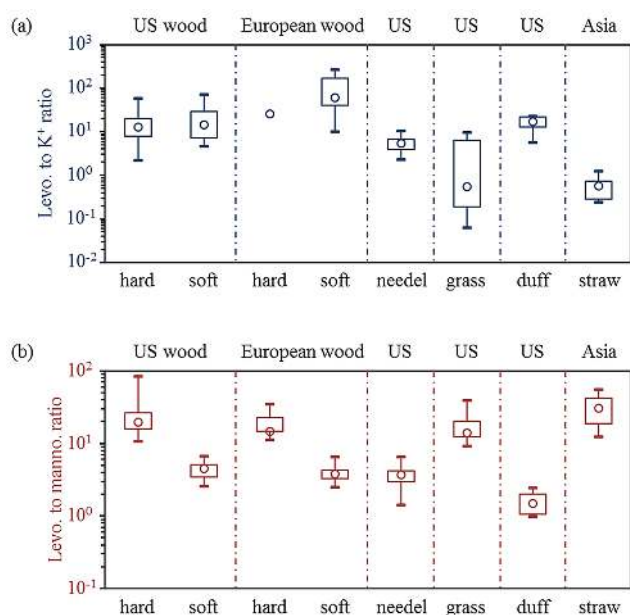
ies conducted in the urban area of Beijing had shown that the sum of carbonaceous components and inorganic ions (i.e., reconstructed $PM_{2.5}$ mass as defined in this study) usually accounted for only about 70 % of the $PM_{2.5}$ mass measured gravimetrically on Teflon filters (He et al., 2001; Duan et al, 2006). Therefore, the contribution of biomass burning to the "actual" $PM_{2.5}$ mass (i.e., that measured on Teflon filters) should be about 24 % (calculated as 34 % × 70 %), which was more comparable with previous studies.

3.3 Relationship between levoglucosan and other biomass burning tracers: source samples

The levoglucosan to K^+ and levoglucosan to mannosan ratios measured in source samples are summarized in Table 2. Distinct differences of those ratios were found between crop residuals and softwood. Compared with softwood burning emissions, biomass smoke emissions from the combustion of crop residuals were characterized by a significantly lower levoglucosan to K^+ ratio and a substantially higher levoglucosan to mannosan ratio. In the following discussion, we will first compare the levoglucosan to K^+ and levoglucosan to mannosan ratios across different kinds of biomass, and then we will try to identify the major kinds of biomass that are responsible for the biomass burning aerosol in Beijing.
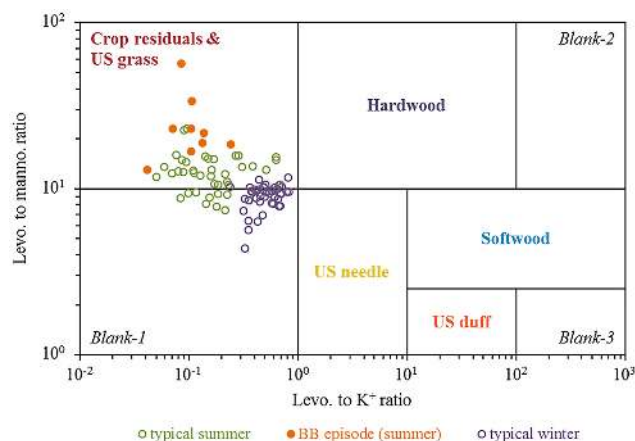
3.3.1 Levoglucosan to K^+ and levoglucosan to mannosan ratios: are they source specific?

Figure 8 summarizes the published levoglucosan to K^+ and levoglucosan to mannosan ratios measured in emissions from controlled biomass burning experiments. The ratios were

Fig. 9. Representative ranges of the levoglucosan to K^+ and the levoglucosan to mannosan ratios for different kinds of biomass. Results from the ambient samples collected in Beijing are also shown for comparison.

Fig. 8. Levoglucosan to K^+ **(a)** and levoglucosan to mannosan **(b)** ratios measured in source samples. The boundary of the box closest to and farthest from the x axis indicates the 25th and the 75th percentile, respectively, while the whiskers above and below the box indicate the maximum and minimum. The circle within the box marks the median. Only the average value is shown for the levoglucosan to K^+ ratio of European hardwood since few data are available.

obtained from studies by Schauer et al. (2001), Fine et al. (2001, 2002, 2004a, b), and Engling et al. (2006) for hardwood grown in the US; from Schauer et al. (2001), Hays et al. (2002), Fine et al. (2001, 2002, 2004a, b), and Engling et al. (2006) for US softwood; from Schmidl et al. (2008a), Bari et al. (2009) and Gonçalves et al. (2010) for hardwood grown in Europe; from Iinuma et al. (2007), Schmidl et al. (2008a), and Gonçalves et al. (2010) for European softwood; from Engling et al. (2006) and Sullivan et al. (2008) for needles and duff found in the US; from Sullivan et al. (2008) for US grass; and from Sheesley et al. (2003), Sullivan et al. (2008), Engling et al. (2009) and Oanh et al. (2011) for Asian rice straw. The raw data used for Fig. 8 are provided as Supplement. As shown in Fig. 8a, the levoglucosan to K^+ ratio was comparable for US hardwood and softwood with average values of 16.15 ± 13.04 and 22.03 ± 19.88, respectively, indicating that emissions from hardwood and softwood burning could not be well distinguished by the levoglucosan to K^+ ratio. With respect to the results from Europe, the levoglucosan to K^+ ratio averaged 25.69 ± 9.11 for hardwood burning, whereas a substantially higher average value was found for softwood (105.58 ± 102.60). However, all of the levoglucosan to K^+ ratios for European hardwood (varying from 19.25 to 32.13) were within the range of those for European softwood (varying from 10.12 to 260.87), also indicating that the levoglucosan to K^+ ratio could not be used to

reliably distinguish between hardwood and softwood burning. In terms of other kinds of biomass, the levoglucosan to K^+ ratio of US duff (averaging 16.03 ± 6.98) was comparable with that of US wood (either hard or soft). Although US needles had a slightly higher average levoglucosan to K^+ ratio (5.78 ± 2.78) compared with US grass (3.33 ± 4.27), the range of the ratios overlapped between the two kinds of biomass. Similarly, combustion of rice straw and US grass could not be well separated. Most of the values shown in Fig. 8 were based on studies conducted in America and Europe where wood burning is important, whereas in China, combustion of crop residuals is also significant. Rice straw is commonly burned in southern China, whereas wheat straw and corn straw prevail in northern China. Results from this study showed that the levoglucosan to K^+ ratio of wheat straw and corn straw averaged 0.10 ± 0.00 and 0.21 ± 0.08, respectively (Table 2), both of which were comparable with the ratio of rice straw grown in Asia (averaging 0.62 ± 0.32). Therefore, it could be concluded that (1) emissions from the combustion of crop residuals such as rice straw, wheat straw and corn straw exhibit comparable levoglucosan to K^+ ratios, typically below 1.0; (2) levoglucosan to K^+ ratios are capable of distinguishing emissions from the burning of crop residuals and wood; and (3) levoglucosan to K^+ ratios can not be used to separate hardwood and softwood burning.

Levoglucosan to mannosan ratios are compared in Fig. 8b for different kinds of biomass smoke. Burning of hardwood grown in the US and Europe resulted in similar levoglucosan to mannosan ratios (averaging 24.19 ± 15.65 and 19.07 ± 8.81, respectively), which were significantly higher than the ratios of softwood smoke (averaging 4.41 ± 1.17 and 3.98 ± 1.33 for US softwood and European softwood, respectively). The levoglucosan to mannosan ratio of US needles (averaging 3.56 ± 1.41) was found to be

comparable with that of softwood. Moreover, emissions from US needles and US grass could be well separated using the levoglucosan to mannosan ratio, as the ratio was much higher for the latter one (averaging 18.21 ± 10.20). In addition, US duff was characterized by the lowest levoglucosan to mannosan ratio (1.60 ± 0.59) among the biomass species shown in Fig. 8b. However, the range of levoglucosan to mannosan ratios overlapped between rice straw and US grass (although the overlap was less significant compared with the levoglucosan to K^+ ratio). Another noticeable feature of Fig. 8b was the overlap between the levoglucosan to mannosan ratios of rice straw and hardwood. The levoglucosan to mannosan ratios of wheat straw and corn straw (averaging 12.71 ± 1.53 and 19.48 ± 3.37, respectively; Table 2) also overlapped with the ratios of hardwood. Therefore, it could be concluded that (1) levoglucosan to mannosan ratios can be applied to reliably distinguish hardwood and softwood burning; (2) the levoglucosan to mannosan ratio shows stronger dependence on the type of wood (i.e., hard or soft) rather than where the wood is grown (i.e., America or Europe); and (3) levoglucosan to mannosan ratios can not be used to separate emissions from burning of crop residuals and hardwood.

Figure 8 demonstrates the limitation of using only one signature (either the levoglucosan to K^+ ratio or the levoglucosan to mannosan ratio) to distinguish emissions from the burning of different kinds of biomass. When using the two ratios together, new insights are provided such that each kind of biomass smoke is characterized by a distinct range of levoglucosan to K^+ and levoglucosan to mannosan ratios. As shown in Fig. 9, emissions from hardwood burning are characterized by high values of both the levoglucosan to K^+ ratio and the levoglucosan to mannosan ratio, which were typically in the range of 1–100 and 10–100, respectively. Compared with hardwood, softwood burning resulted in a lower levoglucosan to mannosan ratio (typically in the range of 2.5–10), whereas the levoglucosan to K^+ ratio (typically in the range of 10–1000) tended to be higher for softwood burning. US needles had a comparable but wider range of levoglucosan to mannosan ratios (typically between 1 and 10) compared with softwood, while they were better separated by the levoglucosan to K^+ ratio, which was generally lower for US needles (typically between 1 and 10). US duff differed from softwood by its lower levoglucosan to mannosan ratio (typically between 1 and 2.5) and differed from US needles by its higher levoglucosan to K^+ ratio, which was in general above 10. Crop residuals and US grass were distinguished from the other biofuel by their low levoglucosan to K^+ ratios (typically below 1), although crop residuals and US grass could not be further distinguished due to the overlap of both the levoglucosan to K^+ and the levoglucosan to mannosan ratios. It should be pointed out that the ranges shown in Fig. 9 were typical rather than absolute for each kind of biomass (see Supplement for details). For example, the levoglucosan to K^+ ratios overlapped slightly between softwood and US needles (Fig. 8a).

Smoke emissions from other kinds of biomass in addition to those shown in Fig. 8 have also been investigated, although less frequently. For example, the levoglucosan to K^+ and levoglucosan to mannosan ratios of Musasa (a type of hardwood grown in Africa) was found to be 81.97 and 22.73, respectively (Iinuma et al., 2007), placing it in the hardwood region of Fig. 9. Results from Sullivan et al. (2008) suggested that branches from US softwood (fir and pine) would fall within either the US needle or the softwood regions. Moreover, the levoglucosan to K^+ (20.00) and levoglucosan to mannosan ratios (21.74) of savannah grass (grown in Africa) measured by Iinuma et al. (2007) place it in the hardwood region. However, it has to be mentioned that the ratios retrieved from Iinuma et al. (2007) were substantially different from those obtained by other studies. For example, Engling et al. (2006) found much higher levoglucosan to mannosan ratios for savannah grass (above 100), whereas much lower levoglucosan to K^+ ratios (about 1.0) were observed by Gao et al. (2003). It is also noteworthy that there are three "blank" regions in Fig. 9. The blank-1 region might be associated with the mixed emissions from crop residuals and softwood. Moreover, based on the published data, it was found that the burning of some kinds of leaves (e.g., sage) could give rise to low values of both the levoglucosan to K^+ and levoglucosan to mannosan ratios (between 0.1 and 1 and 1 and 10, respectively; Sullivan et al., 2008), which were the characteristics of the blank-1 region. In addition, high values of both the levoglucosan to K^+ (192.31) and levoglucosan to mannosan ratios (11.36) would make the Indonesian peat (Iinuma et al., 2007) appear in the blank-2 region.

3.3.2 Major sources of biomass burning aerosol in Beijing

During the typical summer period, the levoglucosan to K^+ and levoglucosan to mannosan ratios were found to fall within the crop residuals and grass region for the majority of the Beijing samples investigated in this study. Combustion of wheat and corn residuals should be the major sources of biomass burning aerosol during the typical summer period, because (1) the contribution of grass to total biomass (including wild fires) consumed in China was shown to be negligible (less than 1 %; Streets et al., 2003), and (2) the land areas planted with rice account for only a few percent of the areas used for wheat and corn in Beijing and the surrounding provinces, such as Hebei, Henan, Shanxi, Shangdong, and Inner Mongolia (National Bureau of Statistics, 2011). In addition, a few samples from the typical summer period were within the blank-1 region, indicating that the burning of softwood and/or other materials from softwood (such as branches and needles) were non-negligible. It was with expectation that all of the samples collected during the BB episode appeared in the crop residuals and grass region. Compared with the typical summer period, the BB episode was characterized by higher

levoglucosan to mannosan ratios, presumably due to the distinct burning style (i.e., open burning). Although mannosan was not measured, results from a study conducted in the US also showed that emissions from field burning of wheat straw were more abundant in levoglucosan (77.8, expressed as $\mu g\,mg^{-1}PM_{2.5}$) compared with chamber combustion (20, expressed as $\mu g\,mg^{-1}PM_{2.5}$; Jimenez et al., 2007). During the typical winter period, the levoglucosan to K^+ ratios increased substantially to 0.51 ± 0.15, whereas the levoglucosan to mannosan ratios decreased moderately to 9.01 ± 1.47 (Table 2), making most of the samples appear in the blank-1 region. Therefore, the influence of softwood and/or other materials from softwood should be larger during winter, although emissions from crop residuals are still expected to be dominant due to the low levoglucosan to K^+ ratios (0.51 ± 0.15).

Besides the less significant contributions from softwood burning, there are several other possible factors responsible for the lower levoglucosan to K^+ ratios in summer, such as (1) enhanced loss of levoglucosan in summer due to atmospheric reactions and (2) contribution of K^+ by other sources besides biomass burning. Levoglucosan has long been considered to be inert under ambient conditions, while several recent laboratory studies indicated that levoglucosan may not be as stable as previously thought, because decay of levoglucosan was observed when exposed to hydroxyl radicals (Holmes and Petrucci, 2006; Hoffmann et al., 2010; Hennigan et al., 2010). Moreover, results from the western North Pacific showed that measured and modeled levoglucosan was comparable during winter, whereas measured levoglucosan was significantly lower in summer (Mochida et al., 2010). If the atmospheric degradation of levoglucosan was considerable during summer in Beijing, the summertime levoglucosan to mannosan ratio might also be biased. However, this bias can not be evaluated at present, since to our knowledge, it is still not known whether mannosan, an isomer of levoglucosan, will undergo similar atmospheric reactions as levoglucosan. As for other sources of K^+ besides biomass burning, fireworks should be negligible during summer in Beijing, and sea salt should also be negligible as well, since Beijing is an inland city. Thus, crustal material is the most likely additional source of K^+. However, influence of crustal material on the levoglucosan to K^+ ratio is also difficult to estimate. This is because the heterogeneous atmospheric reactions are expected to be more active in summer, which can increase the solubility of potassium, although the concentration of crustal material was usually higher during winter and spring compared with summer and autumn in Beijing (He et al., 2001; Duan et al., 2006).

3.3.3 Major sources of biomass burning aerosol at other locations: analysis of published data

As shown in Fig. 9, major sources of biomass burning aerosol could be estimated using levoglucosan to K^+ ratios in com-

bination with the levoglucosan to mannosan ratios. Based on this method, we have shown that biomass burning aerosol in Beijing was mainly derived from the combustion of crop residuals, while the contribution of softwood burning was also non-negligible (especially in winter). In the following discussion, this method will be used to analyze published data measured at other locations. Results from two severe pollution episodes in Missoula, MT, showed that the levoglucosan to K^+ ratio (5.04–24.74) and levoglucosan to mannosan ratio (4.78–5.60) would appear in either the US needle region or the softwood region (Ward et al., 2006), indicating emissions from the burning of softwood and other materials derived from softwood. This conclusion is consistent with the description of Ward et al. (2006), such that the episodes were due to forest fires burning throughout western Montana, where the predominant tree species was softwood. In a recent study conducted in the Chiang Mai basin, Thailand, the levoglucosan to K^+ and levoglucosan to mannosan ratios averaged 0.51 and 14.12, respectively, during a PM_{10} episode occurring in the dry season (Tsai et al., 2012). According to Fig. 9, the two ratios were characteristic of the combustion of crop residuals or US grass. Consequently, it is reasonable to conclude that the PM_{10} episode observed by Tsai et al. (2012) was due to burning of crop residuals, which was confirmed by Tsai et al. (2012) who mentioned that farmers in the mountains surrounding the Chiang Mai basin often burn agricultural waste.

4 Conclusions

The characteristics of biomass burning aerosol, including respective molecular tracers, were investigated based on both ambient samples collected in Beijing and sources emission samples derived from stove combustion. The ambient levoglucosan concentration averaged 0.23 ± 0.37 and $0.59 \pm 0.42\,\mu g\,m^{-3}$ during summer and winter, respectively. The high levoglucosan concentration and the low winter to summer ratio (2.6) of levoglucosan in Beijing indicated that the biomass burning contribution to Beijing aerosol was significant throughout the year. The trend of K^+ coincided with that of levoglucosan in summer, suggesting that it was acceptable to use K^+ as a biomass burning tracer during summer in Beijing, while the contribution of fireworks to K^+ could be significant during winter (e.g., the Spring Festival period). Moreover, the levoglucosan to K^+ ratio was found to be lower during the typical summer period (0.21 ± 0.16) compared with the typical winter period (0.51 ± 0.15). As to the relationship between levoglucosan and mannosan, levoglucosan correlated strongly with mannosan ($R^2 = 0.97$) throughout the winter and the levoglucosan to mannosan ratio averaged 9.49 ± 1.63, whereas levoglucosan and mannosan exhibited relatively weak correlation ($R^2 = 0.73$) during the typical summer period and the levoglucosan to mannosan ratio averaged 12.65 ± 3.38.

Results from PMF modeling showed that 50 % of OC was associated with biomass burning, while the biomass burning contribution to EC was also close to 50 %. Based on published data and the results from the source samples measured in this study, the levoglucosan to K^+ ratio and the levoglucosan to mannosan ratio were compared among different kinds of biomass. The comparison showed that the levoglucosan to K^+ ratio is capable of distinguishing emissions from the burning of crop residuals and wood, whereas the levoglucosan to mannosan ratio can reliably separate hardwood and softwood burning. A new source identification method that uses the levoglucosan to K^+ ratio in combination with the levoglucosan to mannosan ratio was developed. Using this method, it was suggested that biomass burning aerosol in Beijing mainly came from the combustion of crop residuals (i.e., wheat and corn residuals) while the contribution of softwood burning was non-negligible.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/13/7765/2013/acp-13-7765-2013-supplement.pdf.

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