Chemical Characteristics and Light-absorbing Property of Water-soluble Organic Carbon in Beijing: Biomass Burning Contributions

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Abstract

Emissions from biomass burning contribute significantly to water-soluble organic carbon (WSOC) and light-absorbing organic carbon (brown carbon). Ambient atmospheric samples were collected at an urban site in Beijing during winter and summer, along with source samples from residential crop straw burning. Carbonaceous aerosol species, including organic carbon (OC), elemental carbon (EC), WSOC and multiple saccharides as well as water-soluble potassium (K^+) in $PM_{2.5}$ (fine particulate matter with size less than $2.5\mu m$) were measured. Chemical signatures of atmospheric aerosols in Beijing during winter and summer days with significant biomass burning influence were identified. Meanwhile, light absorption by WSOC was measured and quantitatively compared to EC at ground level. The results from this study indicated that levoglucosan exhibited consistently high concentrations ($209\pm145\text{ ng m}^{-3}$) in winter. Ratios of levoglucosan/mannosan (L/M) and levoglucosan/galactosan (L/G) indicated that residential biofuel use is an important source of biomass burning aerosol in winter in Beijing. Light absorption coefficient per unit ambient WSOC mass calculated at 365 nm is approximately $1.54\pm0.16\text{ m}^2\text{ g}^{-1}$ in winter and $0.73\pm0.15\text{ m}^2\text{ g}^{-1}$ in summer. Biomass burning derived WSOC accounted for $23\pm7\%$ and $16\pm7\%$ of total WSOC mass, and contributed to $17\pm4\%$ and $19\pm5\%$ of total WSOC light absorption in winter and summer, respectively. It is noteworthy that, up to 30% of total WSOC light absorption was attributed to biomass burning in significant biomass-burning-impacted summer day. Near-surface light absorption (over the range 300-400 nm) by WSOC was about ~40% of that by EC in winter and ~25% in summer.

Keywords: Biomass burning, WSOC, saccharides, levoglucosan, light absorption

1. Introduction

Biomass burning, including domestic biofuel combustion and open field burning, has drawn increasing global attention and concern. It has been identified as a significant air pollution source with large emissions of gases (including greenhouse gases like CH_4 and CO_2) and fine particles (especially organic carbon, OC, and black carbon, BC) co-emitted, which can cause adverse health effects, deteriorate air quality, and impact climate (Jacobson, 2014). Water-soluble organic compounds emitted from biomass burning have been shown to have a pronounced indirect impact on climate by altering the cloud condensation nuclei activity of aerosols (Gao et al., 2003). In addition, BC and light-absorbing OC (brown carbon) emitted from biomass burning source can strongly absorb incident solar radiation, act as a major

contributor for light extinction, and lead to warming effects (Bond et al., 2013).

Open biomass burning and domestic biofuel combustion can be strong contributors to light-absorbing OC (Bosch et al., 2014; Chen et al., 2010; Hecobian et al., 2010; Kirchstetter et al., 2004; Kirillova et al., 2013, 2014a, 2014b; Lucás et al., 2007). Ground-based observations and model simulations show that columnar light-absorbing OC levels in biomass burning-active regions (e.g. South America and Africa) are most abundant, whereas, newly industrialized countries like China and India showed peak seasonal values during the coldest season due to domestic coal and biofuel used for heating (Arola et al., 2011; Feng et al., 2013). Lu et al. (2011) demonstrated that the residential sector (especially for biofuel combustions) was the dominant contributor to anthropogenic OC (69%) and EC ($51 \pm 3\%$) emissions in China through investigation of primary carbonaceous aerosol emissions in China from 1996 to 2010.

Although model- and observation-based biomass burning studies have been conducted in China (Cheng et al., 2013, 2014; Du et al., 2014; Ho et al., 2014; Huang et al., 2012a, 2012b; Zhang et al., 2008; Zhang et al., 2014), up to now, only two preliminary studies investigated light absorption of biomass burning related aerosols in this country. Thus, research in this area is very limited. Cheng et al. (2011) first presented optical properties of water-soluble organic carbon (WSOC) during winter and summer in Beijing, and investigated the mass absorption efficiency (MAE, at 632 nm) of elemental carbon (EC) from several biomass smoke samples. Du et al. (2014) calculated MAE for WSOC from a biomass burning factor derived from positive matrix factorization (PMF) receptor model and showed biomass burning source contributed 58% of total light absorption by WSOC at 365 nm. However, in these two studies, biomass burning aerosols are not chemically characterized, and mass and light absorption contributions by biomass burning aerosol are not quantified. In addition, biomass types are not identified.

Information of biomass burning source contributions and understanding of their emission characteristics are important for air quality improvement and regulatory purposes. Inadequate knowledge of biomass burning contributions and microphysical properties such as emission size distributions, optical properties and mixing state of biomass burning particles impacts a good understanding of aerosol radiative forcing (Bauer et al., 2010). The knowledge of light absorption by organic aerosol is particularly needed (Bond et al., 2006; Feng et al., 2013; Lin et al., 2014). Therefore, the primary objectives of this study are to investigate chemical characteristics of biomass burning aerosol, and to quantify the mass and light absorption contributions of biomass burning aerosol to total WSOC.

2. Methodology

2.1 Sampling of ambient and source samples

PM_{2.5} (fine particulate matter with size less than 2.5 μm) was collected in the campus of Peking University (39°59'21"N, 116°18'25"E) in the northwestern area of Beijing city, with no obvious emission sources around except two major roads (150 m to the east and 200 m to the south). Situated in a mixed district of teaching, residential and commercial areas, the sampling site is representative of the Beijing urban area.

A high volume sampler (VFC-PM_{2.5}, Thermo Fisher Scientific Co., U.S., 1.13 m³ min⁻¹, 8 " ×10 " quartz filter) and a four-channel sampler (TH-16A, Tianhong, China, 16.7 L min⁻¹, 47 mm i.d. Teflon and quartz filters) were co-located at the site, mounted on the rooftop of a building approximately 20 m above ground level. Particles less than 2.5 micron in aerodynamic diameter were collected by both samplers. Quartz filters (Pallflex, Tissuquartz, 2500 QAT-UP) were used for EC and OC analysis and Teflon filters (Whatman Inc. Clifton, NJ, USA) were used for ion analysis. All quartz filters were pre-baked in a furnace at 550°C for 6 hours. After sampling, all filter samples were kept frozen at -20°C until analysis. PM_{2.5} samples were collected during January 11-18 and June 20-29, 2013. Each sample was collected for approximately 23.5 h.

Crop (e.g., wheat and rice) straws were provided by local residents in Shandong and Hunan provinces of China. Straws were burned in an improved cooking stove to simulate domestic biofuel burning. Source samples were collected using the system described by Zhang et al. (2013). Briefly, the stoves were connected to a system with hood, dilution tunnel and residence chamber, all of which are made of stainless steel. Particles were collected on two 47 mm quartz fiber filters and two 47 mm Teflon filters, connected to the dilution chamber through a cyclone with size cut of 2.5 μm .

2.2 Chemical and optical measurement

Ambient OC and EC concentrations were analyzed by a DRI Model 2001 thermal/optical carbon analyzer (Atmoslytic Inc., Calabasas, CA). IMPROVE temperature protocol was implemented in this study. Details of the methods are available in Cheng et al. (2011, 2013). One punch of 47 mm quartz filter taken from the same high-volume sample was extracted in 10 mL of deionized water (DI water, >18 M Ω) in a Nalgene amber HDPE bottle with ultra-sonication for 30 min without heating, and then filtered using 0.2 μm PTFE membrane filters (Whatman Inc.). Aliquots of extracts were taken for a series of following lab

analyses. A 1 mL aliquot was used to measure WSOC (Sievers Model 800 Turbo Total Organic Carbon (TOC) Analyzer). Another 1 mL aliquot was analyzed by high performance anion-exchange chromatography coupled with pulsed amperometric detection (HPAEC-PAD) to measure saccharides. A detailed description of saccharides analysis can be found in Sullivan et al. (2011). Twelve saccharides were simultaneously detected in this study, including three anhydrosugars (levoglucosan, mannosan and galactosan), five sugars (arabinose, galactose, glucose, mannose and xylose) and four sugar alcohols/polyols (glycerol, inositol, threitol and mannitol). Quartz filter samples collected for source testing also followed the above water-soluble organics analysis procedure. Ambient particles collected on Teflon filters were extracted with 10 mL DI water via 30 min sonication, and then aqueous solutions were filtered before instrumental analyses. Water-soluble potassium (K^+) was analyzed and quantified using an ion chromatograph (DIONEX, ICS-2500).

Aliquots of aqueous quartz filter extracts were used for light absorption measurement by a Hitachi U2010 ultraviolet-visible absorption spectrophotometer with a scanning wavelength range of 190-1100 nm as described in Kirillova et al. (2014a, 2014b) and Bosch et al. (2014). Mass absorption efficiency (MAE, $m^2 g^{-1}$) at 365 nm was calculated based on equation (1):

$$MAE_{\lambda} = \frac{Abs_{\lambda}}{[WSOC]} = \frac{(ATN_{\lambda} - ATN_{700}) \times \frac{V_w}{V_a \times l} \times \ln(10)}{[WSOC]} \quad (1)$$

Where Abs_{λ} is the light absorption coefficient (Mm^{-1}); $[WSOC]$ is the mass concentration of WSOC in the air ($\mu g m^{-3}$); ATN_{λ} is the light attenuation at wavelength λ measured by the spectrophotometer; V_w is the volume of aqueous extract (mL); V_a is the air volume (m^3); and l is the optical length (0.01 m). The reference wavelength λ is chosen as 365 nm to represent light absorption of organic aerosol in order to be consistent with previous studies, and to avoid light-absorbing disturbance by other substances (e.g. inorganic compounds like nitrate) in the aqueous filter extract. Absorbance at 700 nm (ATN_{700}) is the average between 695 and 705 nm, and used to account for baseline drift during analysis. The reasons for choosing wavelength 365 nm and 700 nm have been further discussed in previous studies (Bosch et al., 2014; Cheng et al., 2011; Hecobian et al. 2010).

In this study, all ambient chemical species and light absorbing measurements (including OC, EC, WSOC, saccharides, and light absorption) were made with the same quartz filter from the high-volume sampler. Only K^+ data were from Teflon filter installed on the four-channel sampler. The choice of filter for specific chemical analysis follows what has been widely used in the literature for reasons such as low blank levels

and the requirement for pretreatment or processing before sampling.

2.3 Light absorbance of WSOC relative to EC

The solar energy absorbance of WSOC relative to EC at ground level is estimated using equation (2).

$$f_{WSOC/EC} = \frac{\int I(\lambda) \left\{ 1 - e^{-\left(MAE_{365, WSOC} \left(\frac{365}{\lambda} \right)^{AAE_{WSOC}} \cdot [WSOC] \cdot h_{ABL} \right)} \right\} d\lambda}{\int I(\lambda) \left\{ 1 - e^{-\left(MAE_{550, EC} \left(\frac{550}{\lambda} \right)^{1} \cdot [EC] \cdot h_{ABL} \right)} \right\} d\lambda} \quad (2)$$

where, $I(\lambda)$ is the clear sky Air Mass 1 Global Horizontal (AM1GH) solar radiance spectrum at the surface; $MAE_{365, WSOC}$ is the mass absorption efficiency of WSOC at 365 nm, $MAE_{550, EC}$ is the mass absorption efficiency of EC at 550 nm, we use $MAE_{550} = 7.5 \pm 1.2 \text{ m}^2 \text{g}^{-1}$ following Bosch et al. (2014) and Kirillova et al. (2014b); AAE_{WSOC} is the Absorption Ångström Exponent (AAE) for WSOC; h_{ABL} is the vertical height of the aerosol layer (here estimated as the height of the boundary layer, 1000 m, little variability (within 1%) is seen from this parameter in the range of 100 to 2000 m). The fraction $f_{WSOC/EC}$ was computed in MATLAB version R012b with numerical integration (integration step 1 nm, integration interval 300-2500 nm) with measured WSOC and EC concentrations for each sample (Bosch et al., 2014; Kirillova et al., 2014). In this study, AAE for WSOC was fitted within the range of 330-400 nm in consideration of avoiding interference from other light-absorbing substances (e.g., ammonium nitrate, sodium nitrate, and nitrate ions) and negligible light absorption at wavelength greater than 500 nm, while AAE for EC is set to 1 (Bond and Bergstrom, 2006).

3. Results and discussion

3.1 Characterization of $PM_{2.5}$

3.1.1 Carbonaceous compounds

Mass concentrations of $PM_{2.5}$ and carbonaceous components are summarized in **Table 1**. During the study periods, daily averaged $PM_{2.5}$ mass concentrations using the filter based gravimetric method were about 2.5-fold higher in winter than in summer, but both exceeded the China national 24-hr average ambient air quality class II standard (NAAQS) ($75 \text{ } \mu\text{g m}^{-3}$). Higher $PM_{2.5}$ concentrations in winter in Beijing have also been reported in previous studies (Zhao et al., 2009; Yu et al., 2013). Total Carbon (TC, the sum of OC and EC) accounted for $21 \pm 7\%$ (average $\pm$ standard deviation, $\mu\text{gC } \mu\text{g}^{-1}$) and $17 \pm 8\%$ of total $PM_{2.5}$ mass during winter and summer periods, respectively. OC and EC were approximately 3.4-fold and 2.9-fold higher in winter compared to summer. However, the OC/EC ratio was comparable in both seasons (larger than 5). It has been reported that OC/EC ratios from biomass burning sources (larger than 5)

are usually higher than those from fossil fuel sources (Zeng et al., 2011 and references therein). High OC/EC ratios in Beijing might be attributed to OC-rich source emissions (such as biomass burning and coal combustion) as well as secondary organic aerosol (SOA) formation.

Concentrations of WSOC, which mainly originates from primary biomass burning emission or SOA formation (Snyder et al., 2009; Weber et al., 2007), averaged 1.7-fold higher in winter, accounting for an average of 38.7% of OC mass in winter and 66.2% in summer. Aggarwal et al. (2009) pointed out that sources of fine particles and their atmospheric processing (e.g. photochemical aging) could affect the ratio of WSOC to OC and the associated chemical composition. A high WSOC fraction in summer in Beijing is most likely due to high contributions from biomass burning and/or SOA formation. Lower percentages in winter could be due to increased influence of sources with low WSOC emission, such as vehicle exhaust (Ram et al., 2012; Saarikoski et al., 2008), and other primary sources.

3.1.2 *Saccharides*

A series of anhydrosugars, sugars and sugar alcohols/polyols, were simultaneously identified and quantified in PM_{2.5} samples. Average concentrations of these compounds measured in Beijing winter and summer samples are shown in **Figure 1** and listed in **Table S1**. All the identified sugars and sugar alcohols/polyols (except for glycerol) showed higher concentrations in summer than winter. This could reflect the fact that sugar alcohols/polyols are mainly generated from airborne fungal spores and plant materials (like pollen, fruits, fragments) (Bauer et al., 2008; Fu et al., 2012 and references therein), as well as biomass burning (Sullivan et al., 2011), which are active in summer in North China Plain (Huang et al., 2012a). Anhydrosugars, including levoglucosan (L) and its two isomers (mannosan, M and galactosan, G), which are produced from pyrolysis of cellulose and hemicellulose and widely used as tracers for biomass burning source (Engling et al., 2009; Piot et al., 2012), exhibited an opposite seasonal pattern with higher abundance in winter (except for galactosan).

Mass concentrations and relative abundance of various sugar compounds in each winter and summer sample are shown in **Figure S1 (a-d)**. It can be seen that anhydrosugars were the most abundant, accounting for about 64% and 44% of the total measured saccharides in winter and summer, respectively. Maxima of anhydrosugars in winter might be associated with biomass burning (Sullivan et al., 2011), which was mainly used for residential heating in the northern and northeastern China during cold seasons. In winter samples, the relative fraction of each sugar species remained relatively constant, in contrast to summer samples (Figure S1(d)), suggesting source types did not vary much in winter (Figure S1(b)).

Higher concentrations of these sugars indicated higher impacts of biomass burning on ambient air quality in winter as well.

Levoglucosan dominated not only concentrations of the three anhydrosugars (~83% and ~91%) but all of the 12 measured saccharides (~53% and ~40%) in both winter and summer, followed by glycerol, which has also been reported from biomass burning (Jia et al., 2007) and found in wood combustion source samples (Schauer et al., 2001).

3.1.3 Correlation between carbonaceous components and biomass burning tracers

Correlations between concentrations of OC, EC, and water-soluble species (including WSOC, saccharides and K^+) are summarized in **Table S2**. Significant correlation ($r=0.993$ and $r=0.985$ for L & M and L&G in winter; $r=0.974$ and $r=0.963$ in summer, respectively, $p<0.001$) among the three anhydrosugar concentrations suggests their common sources from burning of biomass in the field or biofuels for residential heating or cooking. During winter, glucose and sugar alcohol (inositol, threitol and glycerol) concentrations were well correlated with each other ($r: 0.815 - 0.942$, $p<0.05$) and also with the anhydrosugar concentrations, also suggesting influence from biomass burning emissions. OC and EC concentrations were both correlated with anhydrosugar concentrations ($r: 0.866 - 0.913$, $p<0.01$). During summer, good correlations were found between concentrations of threitol, arabinose, and xylose vs. anhydrosugar concentrations. Arabinose has previously been reported to be derived from hemicellulose and pectin, and xylose was found in most woods and straws (Sullivan et al., 2011). WSOC and OC concentrations both correlated well with anhydrosugars and threitol, arabinose and xylose, and in particular, WSOC presented more significant correlation with anhydrosugars ($r: 0.904 - 0.930$, $p<0.001$) in summer. It's noteworthy that significant correlation among K^+ and anhydrosugar concentrations were found in summer ($r: 0.840 - 0.895$, $p<0.01$) compared to winter ($r<0.48$), suggesting there might be other sources of K^+ in winter in Beijing. Potassium could come from multiple sources including biomass burning, soil, sea salts, fireworks, etc. (Cheng et al., 2013, 2014); therefore, one should be careful when using K^+ as the only biomass burning indicator, especially during wintertime. Evident correlation between concentrations of levoglucosan and other biomass or biofuel burning related species (e.g. WSOC, mannosan, galactosan, arabinose, xylose, threitol, and glycerol) proved its effectiveness as a biomass burning tracer.

3.2 Identification of significant biomass-burning-impacted days and associated chemical signatures

3.2.1 Significant biomass-burning-impacted days

Figure 2 shows temporal variations of $PM_{2.5}$ and levoglucosan concentrations. Higher levoglucosan

levels are found in winter (ranging from 140 to 317 ng m⁻³ with an average of 209±145 ng m⁻³) compared to summer (89.6-499 ng m⁻³ with an average of 180±143 ng m⁻³). Active burning hot spot fire information from the Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA satellites (<https://firms.modaps.eosdis.nasa.gov/firemap/>) can be seen during summer, but not in winter (see **Figure S2(a)**), providing supportive evidence that high levoglucosan concentrations might be largely associated with extensive residential heating burning activities emissions. In addition, stable synoptic conditions (e.g. low wind speed and mixed layer height (<500 m), temperature inversion) in winter do not favor dispersion of air pollutants and could enhance accumulation of these directly emitted fine particles (Wang et al., 2014). During the winter period, days with high PM_{2.5} (>75 µg m⁻³) and levoglucosan (>200 ng m⁻³) concentrations were defined as “high PM days” (named as “W-Ep”) and days with PM_{2.5} lower than 75µg m⁻³ were defined as “low PM days” (named as “W-NEp”).

Apparent fires are shown by MODIS images during the summer period (see **Figure S2(b)**). It’s well known that June is a harvest month in China. Huang et al. (2012a, 2012b) reported that crop fires sweeping from the south to north were sometimes responsible for extensive air pollution during the harvest season, and agricultural open fires were concentrated in North China Plain (including Henan Province, Shandong Province, etc.). On June 28th 2013, levoglucosan concentration was increased by 3-5 times compared to other summer days, and PM_{2.5} also showed an obvious increase (~2 times). Based on active fire locations and brightness obtained from MODIS images (**Figure S2(c)**), there were numerous fire counts distributed in Hebei province and Tianjin province, which are located to the south of Beijing (the so called Jing-Jin-Ji region). Likewise, fires could also be clearly found in Henan, Jiangsu, Anhui and Hubei provinces, even farther south. The 48-h back trajectory calculated using the NOAA Hybrid Single-particle Lagrangian Integrated Trajectory (HYSPLIT) (Dröler and Rolph, NOAA Air Resources Laboratory, College Park, MD) model with a starting elevation of 500 m indicated that the air masses sampled in Beijing were originated from south of the city, passing through the active fire regions (see **Figure S3**). Thus, June 28th with highest levoglucosan (around 500 ng m⁻³) was identified as a biomass burning episode (named as “S-Ep”).

3.2.2 Chemical signatures of biomass-burning-impacted days

Chemical signatures could help to identify sources of particles. During the summer biomass burning episode, K⁺ and levoglucosan both exhibited dramatic increases (3.4 and 4.8 times, respectively), along with substantial increase of WSOC and OC. However, in winter, compared to low PM days, PM_{2.5} and OC increased obviously about 5- and 4-fold in high PM days. WSOC and levoglucosan (as well as other

saccharides except for glucose and mannose) exhibited similar extent of increase (2-fold). The lower increase of levoglucosan in winter than in summer suggested that high PM days were not mainly resulted from biomass burning. In addition, K^+ exhibited a more significant higher extent of increase (~6.6 times), which also suggested other non-biomass burning sources influence (e.g. mineral dust) in winter high PM days.

The highest levoglucosan/OC ($0.036 \mu\text{g}/\mu\text{gC}$) and levoglucosan/WSOC ($0.048 \mu\text{g}/\mu\text{gC}$) ratios occurred in summer biomass burning episode, but they are lower than the reported ratios from fireplace or stove wood burning testing (Fine et al., 2001, 2002, 2004a, 2004b; Schmidl et al., 2008a). However, the levoglucosan/WSOC ratio was comparable to that of burning of crop straw (below or about 10%, Hays et al., 2005; Sheesley et al., 2003). Excellent correlation is found between K^+ and levoglucosan ($r^2=0.98$) during 26-28 June (with obvious fire counts), and the levoglucosan/ K^+ ratio is similar to those from Asian crop residue and grass burning (Sullivan et al., 2008). Lower levoglucosan/OC and levoglucosan/WSOC ratios in winter might reflect enhanced contribution of non-biomass burning sources such as coal combustion and vehicle exhaust during the winter period which are enriched in OC but not in levoglucosan. Lower levoglucosan/EC ratio in winter (0.04 ± 0.01 compared to 0.09 ± 0.05 in summer) also provides supportive evidence.

3.2.3 Biomass burning source types

Ratios of emitted biomass burning tracers can vary with fuel types (Jung et al., 2014; Sullivan et al., 2008, 2014). For example, ratios between levoglucosan (L), mannosan (M) and galactosan (G) have been used to track the possible sources of biomass burning (Jung et al., 2014). L/M and L/G ratios in different biomass types (hardwoods, softwood, briquettes, straw, needle, leaves) have been reported and are shown in **Figure 3**. Ratios in ambient samples of different sampling periods, along with residential crop straw burning test samples collected and analyzed in this study are also plotted in the same scatter plots.

L/M and L/G ratios in all winter samples were similar and close to that from softwoods and needles. The Chinese Environmental Exposure-related Human Activity Patterns Survey (CEERHAPS) reveals that biomass (~48%) is predominantly used by rural populations for cooking, coal (21%) and biomass (19%) for their household heating, and coal (11%) as fuels in urban areas (Duan et al., 2012). Therefore increased emissions from daily heating and cooking in winter in Beijing and its upwind rural areas (e.g. Northeast, Northwest and North) could contribute to high concentration of fine particles at our sampling site in winter.

In summer S-Ep samples, L/G and L/M ratios were similar to rice straw source sample ratios in this

study, but even closer to wheat straw source sample ratios during normal summer days. As described in section 3.2.1, the air mass reaching the sampling site on the S-Ep day originated from south of Beijing. Particles emitted from crop residue burning in Shandong, Henan, Anhui and even Hubei provinces (see Figure S3), therefore, likely impacted air quality in Beijing. Major crop residues from north to south China are maize straws, followed by wheat straws and rice straws reported by Huang et al. (2012a).

3.3 Contribution of biomass burning to WSOC and the bulk light absorption of WSOC

Here we assume levoglucosan is a stable tracer and the discussion of its stability in the atmosphere is included in the supplementary material. Absorption coefficient of WSOC averaged between 360 and 370 nm (Abs_{365}) showed higher absorbance in wintertime ($14.0 \pm 5.17 \text{ Mm}^{-1}$) and lower values ($4.62 \pm 2.20 \text{ Mm}^{-1}$) in summertime. Abs_{365} correlated better with WSOC than EC and levoglucosan in both winter and summer (Figure 4). It is possible that the absorption is primarily related to SOA or aged OC from primary emissions. The WSOC from primary biomass burning emissions ($WSOC_{BB}$) was calculated based on the ([levoglucosan]/[WSOC])_{source} ratio of 0.17 ($\mu\text{g } \mu\text{gC}^{-1}$) from the test burns of rice straws and wheat straw in this study for summer samples. And ratios of 0.1 ($\mu\text{g } \mu\text{gC}^{-1}$) from wood burning (Ding et al., 2008) was used for winter period samples. Calculations were based on equation (3):

$$\text{Contributions of biomass burning to WSOC} = \frac{([Levoglucosan]/[WSOC])_{\text{ambient}}}{([Levoglucosan]/[WSOC])_{\text{source}}} \quad (3)$$

Results showed that WSOC from biomass burning contribution accounted for $23 \pm 7 \%$ in wintertime and $16 \pm 7 \%$ in summertime, with highest contribution of 28% on June 28, 2013 (S-Ep). Assuming WSOC is exclusively generated from biomass burning and production of SOA (Snyder et al., 2009), the large fraction of non- $WSOC_{BB}$ provide supportive evidence for an important influence of SOA.

Normalizing Abs_{365} (without interfering absorbance by EC and inorganics) to WSOC mass yields a mass absorption efficiency (MAE_{365}), which characterizes the efficiency of absorbing solar energy by WSOC. In this study, the MAE_{365} of WSOC was about 2-fold higher in winter ($1.54 \pm 0.16 \text{ m}^2 \text{ g}^{-1}$) compared to summer ($0.73 \pm 0.15 \text{ m}^2 \text{ g}^{-1}$), confirming the findings by Cheng et al. (2011). The higher MAE_{365} value in winter represented a stronger absorbing ability of WSOC, which probably reflected the different chemical compositions and sources of fine PM in winter and summer. The average AAE of WSOC was 5.30 ± 0.44 in winter and 5.83 ± 0.51 in summer. Comparisons between MAE values of WSOC measured at 365 nm and Ångström exponent calculated in this study and other previous studies are shown in Figure S4. AAE of WSOC in this study was similar to previous studies. MAE_{365} of WSOC in Beijing winter was higher than

reported in south Asia and some U.S. cities, but comparable to values in Delhi, India, where biomass burning was a major source of WSOC based on ^{14}C isotope analysis (Kirillova et al., 2014b). MAE_{365} of WSOC in summer in Beijing exhibited a similar MAE_{365} value to Los Angeles, where SOA formation from anthropogenic emissions was concluded to be the source of the strong light-absorbing WSOC.

Parameters for light-absorbing properties in the observation days are listed in **Table 2**. The amount of solar energy (integrating over the solar spectrum) absorbed by light-absorbing WSOC relative to EC at ground level within the boundary layer in Beijing during our study periods was estimated using equation (2). The calculated WSOC to EC absorption percentage was $11\pm3\%$ in wintertime and $6\pm3\%$ in summertime over the whole solar spectrum, and up to $42\pm13\%$ and $24\pm10\%$ at shorter wavelengths (300-400 nm), respectively. It should be noted that the calculation is just for near surface cases, the fractional contribution of WSOC to light absorption might be different when integrated over a vertical column (Bosch et al., 2014; Liu et al., 2014). In addition, light-absorptive properties of solvent extracts might be different from that of ambient aerosol. A specific factor such as 0.7 (Sun et al., 2007) or 2 (Liu et al., 2013) have been applied to convert bulk solution absorption to particle light absorption. Here a factor of 1 was assumed in this study as size distribution information was unknown. We just attempt to give a first order estimate of the light absorption of WSOC. This simplistic estimate is based on several assumptions, for example, measurements at ground level represent the whole ABL; AAE of WSOC measured at 330-400 nm could represent the whole spectral range (Bosch et al., 2014; Kirillova et al., 2014); WSOC and EC are externally mixed, thus $\text{MAE}_{550,\text{EC}}=7.5\pm1.2\text{ m}^2\text{g}^{-1}$ and $\text{AAE}_{\text{EC}}=1$ was taken based on Bond and Bergstrom (2006) for uncoated EC particles. A sensitivity test on the assumptions and related parameters used in the model is shown in supporting information (**Figure S5**).

To further investigate light absorption by WSOC_{BB} relative to total WSOC at 365 nm, a simplified method is used as equation (4):

$$f = \frac{\text{MAE}_{365} \cdot \text{WSOC}_{\text{BB}}}{\text{Abs}_{365}} \times 100\% \quad (4)$$

Where Abs_{365} is the light absorption coefficient at 365 nm. $\text{MAE}_{365}=0.80\text{ m}^2\text{g}^{-1}$ is used for summer samples based on the wheat and rice straw burning tests in this study, and $\text{MAE}_{365}=0.97\text{ m}^2\text{g}^{-1}$ is used for winter samples (wood burning, Du et al. 2014). It shows that WSOC_{BB} contributed $17\pm4\%$ and $19\pm5\%$ of total light absorption by WSOC in winter and summer, respectively, and up to 30% during the day under obvious influence by biomass burning, indicating the significant contribution of biomass burning

emissions to light-absorption of water-soluble brown carbon in the region. Desyaterik et al. (2013) examined molecular contributions to light absorption by brown carbon in clouds strongly impacted by emissions from crop residue burning sampled in June at Mt. Tai in the North China Plain. Strongly absorbing organic nitrogen compounds observed in these samples suggest that secondary compounds formed during oxidative aging of biomass burning emissions probably further enhance the overall contribution of biomass burning (primary and secondary) to total light absorption in the 300-400 nm range. Assuming the non-primary-biomass burning WSOC came exclusively from secondary organic aerosol formation, then the mass absorption efficiency of water-soluble SOA at 365 nm was estimated as $1.41 \pm 0.46 \text{ m}^2 \text{ g}^{-1}$ in winter and $0.59 \pm 0.14 \text{ m}^2 \text{ g}^{-1}$ in summer. This value is similar to those estimated by Zhang et al. (2011). The mass absorption efficiency might also be influenced by sunlight bleaching, chromophore formation, aging or other atmospheric processing (Lee et al., 2014; Zhong et al., 2014).

4. Conclusions

In this study, saccharides (including anhydrosugar, sugar, and sugar alcohols/polyols) have been measured and used to determine biomass types that contribute to atmospheric fine particulate matter in Beijing. The light-absorption contribution of primary biomass-burning aerosol to that of total WSOC has also been evaluated and quantified.

WSOC was about 1.7-fold higher in Beijing winter than in summer, but it can contribute up to 66% of total OC in summer. Levoglucosan was the most abundant water-soluble sugar species with higher concentration in winter, which might be related to extensive residential biofuel used in winter in Beijing and its surrounding provinces. Our results suggest an important contribution of biomass/biofuel burning and influence of air mass transported from other regions to Beijing. Open field burning has significant influence in summertime in northern China. Primary particulate emissions from biomass burning contributed approximately $23 \pm 7\%$ and $16 \pm 7\%$ to total WSOC in Beijing winter and summer, respectively.

The mass absorption efficiency of WSOC at 365 nm was determined for Beijing and found to be higher in winter compared to summer. Light absorption (in the range of 300-400 nm) due to WSOC was up to $42 \pm 13\%$ of that by EC in winter and $24 \pm 10\%$ in summer. Differences in chemical signatures and light-absorbing properties were observed between significant biomass-burning-impacted day and normal days. It is important to conduct more light absorption analysis of source samples and to connect observed absorption to specific individual organic molecules in future work.

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Table and Figure Caption

Table 1 Averaged concentrations of PM_{2.5} and chemical species during this study in Beijing

Table 2 Light absorption parameters in different periods

Figure 1. Average concentration of sugar compounds measured in Beijing winter and summer samples

Figure 2. Temporal variation of levoglucosan (ng m⁻³) and PM_{2.5} concentrations (μg m⁻³) in (a) winter in Beijing and (b) summer in Beijing

Figure 3. Scatter plots of levoglucosan/mannosan ratios versus levoglucosan/galactosan ratios of ambient samples in this study and from different biomass burning source tests

Figure 4. Correlation of Abs₃₆₅ of WSOC with mass concentration of (a) WSOC and EC in winter, (b) WSOC and EC in summer, (c) levoglucosan in winter and (b) levoglucosan in summer

Table 1 Averaged concentrations of PM_{2.5} and chemical species during this study in Beijing

	Winter (Average±One Std Dev)	Summer (Average±One Std Dev)
PM _{2.5} (μg m ⁻³)	209±145	82.5±37.0
OC (μg m ⁻³)	32.9±16.8	9.65±2.87
EC (μg m ⁻³)	5.58±1.44	1.90±0.63
WSOC (μg m ⁻³)	10.8±3.13	6.42±2.17
Water soluble K ⁺ (μg m ⁻³)	3.12±2.52	2.60±1.52
WSOC/OC	38.7±15.6%	66.2±5.8%
OC/EC	5.73±2.47	5.29±1.32

Table 2 Light absorption parameters in different periods

	AAE (330-400 nm)	MAE _{365,WSOC} (m ² g ⁻¹)	MAE _{632,EC} (m ² g ⁻¹)	Absorbance WSOC/EC (%) (300-2500 nm)	Absorbance WSOC/EC (%) (300-400 nm)
S-Ep	6.30	0.84	11.6	9.6	41.6
S-NEp	5.72±0.68	0.66±0.16	10.8±0.60	5.3±2.2	21.7±7.2
Summer (Average)	5.83±0.51	0.73±0.15	11.1±0.50	5.7±2.5	23.6±10.2
Winter (Average)	5.30±0.44	1.54±0.16	9.38±2.63	10.7±3.0	42.4±12.8

Note: S-Ep, and S-NEp refers to significant biomass-burning-impacted summer day, and normal summer day, respectively. Values are listed as average ± one std. dev.

Figure 1. Average concentration of sugar compounds measured in Beijing winter and summer samples
(Note: levoglucosan concentration is divided by 4)

Figure 2. Temporal variation of levoglucosan (ng m^{-3}) and $\text{PM}_{2.5}$ concentrations ($\mu\text{g m}^{-3}$) in (a) winter in Beijing and (b) summer in Beijing

Figure 3. Scatter plots of levoglucosan/mannosan ratios versus levoglucosan/galactosan ratios of ambient

samples in this study and from different biomass burning source tests. **Hardwood:** Bari et al. (2009), Fine et al. (2002, 2004a, 2004b), Engling et al. (2006), Schmidel et al. (2008a); **Softwood:** Bari et al. (2009), Fine et al. (2001, 2002, 2004a, 2004b), Iinuma et al. (2007), Schmidel et al. (2008a); **Briquettes:** Schmidel et al. (2008a); **Needle:** Engling et al. (2006), Sullivan et al. (2014); **Leaves:** Schmidel et al. (2008b), Sullivan et al. (2014); **Rice straw:** Engling et al. (2009), Sheesley et al. (2003). (Note: “*” denotes results from this study; “BJ W-Ep” denotes high PM days in winter; “BJ W-NEp” denotes low PM days in winter; “BJ W-days” denotes other winter days; “BJ S-Ep” denotes significant biomass-burning-impacted summer day; “BJ S-NEp” denotes other summer days”)

Figure 4. Correction of Abs₃₆₅ of WSOC with mass concentration of (a) WSOC and EC in winter, (b) WSOC and EC in summer (c) levoglucosan in winter and (d) levoglucosan in summer