https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

An optimized tracer-based approach for estimating organic carbon emissions from biomass burning in Ulaanbaatar, Mongolia

Jayant Nirmalkar[1], Tsatsral Batmunkh[2], Jinsang Jung[1,*]
[1]Center for Gas Analysis, Korea Research Institute of Standards and Science (KRISS), Daejeon 34113, Republic of Korea
[2]Central Laboratory of Environment and Metrology, Ulaanbaatar, Mongolia

Correspondence to: Jinsang Jung (jsjung@kriss.re.kr)

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

Abstract

The impact of biomass burning (BB) on atmospheric particulate matter of <2.5 μm diameter ($PM_{2.5}$) at Ulaanbaatar, Mongolia, was investigated using an optimized tracer-based approach during winter and spring, 2017. Integrated 24 h $PM_{2.5}$ samples were collected on quartz filters using a 30 L min^{-1} air sampler at an urban site in Ulaanbaatar. The aerosol samples were analyzed for organic (OC) and elemental (EC) carbon, anhydrosugars (levoglucosan, mannosan, and galactosan), and water-soluble ions. OC was found to be the predominant species, contributing 64% and 56% to total aerosol compositions in winter and spring, respectively. BB was identified as a major source of $PM_{2.5}$, followed by dust and secondary aerosols. Levoglucosan/mannosan and levoglucosan/K^+ ratios indicate that softwood is the major fuel type in Ulaanbaatar. Because of the large uncertainty associated with quantitative estimates of OC emitted from BB (OC_{BB}), a novel approach was developed to optimize the OC/levoglucosan ratio for estimating OC_{BB}. The optimum OC/levoglucosan ratio was obtained by regression analysis between daily atmospheric concentrations of $OC_{non\text{-}BB}$ (OC_{total}–OC_{BB}) and levoglucosan, with the softwood OC/levoglucosan ratio that gives the lowest correlation coefficient (R^2) and slope in the regression analysis being treated as the optimum ratio. The optimum OC/levoglucosan ratio was found to be 27.6 and 18.0 for winter and spring, respectively, and these values were applied in quantifying OC_{BB}. It was found that 68% and 63% of OC originated from BB during winter and spring, respectively. In addition to OC_{BB}, sources of $OC_{non\text{-}BB}$ were investigated through multivariate correlation analysis, and indicate that $OC_{non\text{-}BB}$ originated mainly from coal burning, vehicles, and vegetative emissions.

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

***Keywords*:** Source identification, Biomass burning, Optimized organic-carbon/levoglucosan ratio

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

1. Introduction

Organic aerosol (OA; the organic fraction of particles) contributes a significant fraction (10%−90%) of atmospheric particulate matter (PM), which can affect human health and air quality (Jimenez et al., 2009; Maenhaut et al., 2011; Fu et al., 2012; Reche et al., 2012; Chen et al., 2018). An understanding of the sources of PM is highly relevant for air-quality remediation. Biomass burning (BB) is a major source of organic carbon (OC) in $PM_{2.5}$ (PM with aerodynamic diameter ≤2.5 μm) and it may become more significant in future as air-quality regulations restrict other anthropogenic emissions (Sullivan et al., 2019). Coal combustion, thermal power-plant, and traffic emissions also make significant contributions to the OC content of PM (Watson et al., 2001a, b), modifying PM characteristics such as hygroscopicity, light-attenuating properties, and health impacts (Jung et al., 2009; Sullivan et al., 2019). Previous studies have observed that the toxicity of $PM_{2.5}$ increases with the oxidation potential of BB species because of the water-soluble fraction of OC (Verma et al., 2014).

Previous studies have identified and quantified OC emitted from BB (OC_{BB}) using the BB tracers (levoglucosan, mannosan, galactosan, and K^+). Levoglucosan is produced by the pyrolysis of cellulose at temperatures >300°C (Simoneit et al., 1999; Claeys et al., 2010; Maenhaut et al., 2011; Nirmalkar et al., 2015; Achad et al., 2018); and two isomers of levoglucosan, mannosan and galactosan, are produced by the burning of hemicellulose (Reche et al., 2012). The atmospheric concentration of levoglucosan is higher than those of the two isomers because of the lower content of hemicellulose (20%−30%, dry weight) than cellulose (40%−50%) in softwood and hardwood (Reche et al., 2012; Sharma et al., 2015). Water-soluble K^+ can also be used as a BB tracer (Cheng et al., 2013; Nirmalkar et al., 2015; Chen et al., 2018; Chantara et al., 2019). The proportion of these BB tracers

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

in PM depends on various factors such as the type of biomass (softwood, hardwood, crop, grass, etc.), where it is burnt (traditional stoves, fireplaces, field burning, burning in closed chambers, etc.), the type of burning (smoldering, flaming, etc.), and the burning season (Fu et al., 2012; Cheng et al., 2013; Jung et al., 2014). Levoglucosan/mannosan, levoglucosan/K^+, and OC/levoglucosan ratios were used to identify major biomass types and quantify OC_{BB} in previous studies (Reche et al., 2012; Cheng et al., 2013; Jung et al., 2014; Chen et al., 2018). However, OC/levoglucosan ratios are quite variable even with the same type of BB because of variations in burning type, place, and season (Cheng et al., 2013; Thepnuan et al., 2019 and references therein). It is therefore essential to optimize the OC/levoglucosan ratio to better estimate OC_{BB}.

Ulaanbaatar, with a population of about 1 million, is an atmospheric pollution 'hotspot' because of its topography, being situated in the Tuul river valley and surrounded by the Khentei mountains, with a high elevation (1300 m−1949 m above sea level) and large variations in temperature (–28°C to +16°C) and relative humidity (17.7%–72.7%; Table 1; Batmunkh et al., 2013; Jung et al., 2014). As the world's coldest capital city during winter, it requires additional fuel for space heating. The topography and low-temperature conditions cause an increase in PM concentrations, which are exacerbated by low wind speeds and atmospheric temperature inversions (Jung et al., 2010). Coal consumption (~5 million tons per year) by 3 large power plants and 250 heat-only boilers accounts for much of the anthropogenic OC emissions (Jung et al., 2010; Batmunkh et al., 2013). Furthermore, about half of the population of Ulaanbaatar lives in traditional Mongolian dwellings (Gers), with wood and coal being used for cooking and heating with no pollution control devices (Jung et al., 2010; Batmunkh et al., 2013). About 93,000 motor vehicles are registered in Ulaanbaatar, with most being second-hand and with ~80%

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

not satisfying current emission standards due to their age (54% are older than 11 years; Jung et al., 2010; Batmunkh et al., 2013).

Few studies have investigated the chemical characteristics of organic aerosol in Ulaanbaatar (Jung et al., 2010; Batmunkh et al., 2013), with none examining the contribution of OC_{BB}. In this study, we quantified the BB tracers levoglucosan, mannosan, galactosan, K^+, and other chemical species. Potential sources of $PM_{2.5}$ were identified by principal component analysis (PCA), with levoglucosan/K^+ and levoglucosan/mannosan ratios being used to identify major biomass types.

OC_{BB} can be quantified from OC/levoglucosan ratios and levoglucosan concentrations in PM. However, OC_{BB} uncertainties are large because OC/levoglucosan ratios vary with fuel type, burning conditions, place, and type. Therefore, it is difficult to determine the most suitable OC/levoglucosan ratio of BB emissions (Duan et al., 2004; Cheng et al., 2013; Jung et al., 2014). Here, for perhaps the first time, optimized OC/levoglucosan ratios were investigated for estimating concentrations of OC_{BB} during winter and spring. $OC_{non\text{-}BB}$ sources were also investigated using multivariate correlation analysis with ions and elemental carbon (EC).

2. Methods

2.1 Sampling site and aerosol sampling

Aerosol sampling was carried out in Ulaanbaatar during the winter (17 January to 03 February) and spring (17 April to 4 May) of 2017, with 24 h periods commencing daily at 11:00 local time. An aerosol sampler was installed on the rooftop of the National Agency for Meteorology and Environmental Monitoring station in Ulaanbaatar (47°92' N, 106°90' E), 10 m above ground level. The sampling site was located between

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

crossroads 8 km–10 km from two large thermal power plants to the west. $PM_{2.5}$ samples were collected on 47 mm diameter quartz filters (Pall-Life Sciences, USA) using an aerosol sampler (Murata Keisokuki Service, Japan) at a flow rate of 30 L min^{-1}. Filters were wrapped in aluminum foil and heated at 550°C for 12 h to remove adsorbed impurities before use and stored at –20°C before and after sampling.

2.2 Filter analysis

A one-fourth part of quartz filter sample was extracted in 10 mL ultrapure water (resistivity 18.2 MΩ, total OC content < 1 ppb,) under ultrasonication for 30 min. The liquid was then filtered using a syringe filter (Millipore, Millex−GV, 0.45μm) and the extract stored at 4°C pending analysis. Water-soluble cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, and NH_4^+) were quantified by an ion chromatograph (Dionex ICS 5000, Thermo Fisher Scientific, USA). Water-soluble cations were separated using an IonPac CS−12A column (Thermo Fisher Scientific, USA) with 20 mM methanesulfonic acid as eluent at a flow rate of 1.0 mL min^{-1}. Water-soluble anions (Cl^-, NO_3^-, and SO_4^{2-}) were separated using an IonPac AS−15 column (Thermo Fisher Scientific, USA) with 40 mM KOH as eluent at a flow rate of 1.2 mL min^{-1}. The detection limits for major inorganic ions (based on 3σ of blanks) were 0.01 μg m^{-3}, 0.01 μg m^{-3}, and 0.03 μg m^{-3} for NO_3^-, SO_4^{2-}, and NH_4^+, respectively.

Levoglucosan, mannosan, and galactosan were analyzed by a high-performance anion-exchange chromatograph (Dionex, ICS−5000, Thermo Fisher Scientific, USA) with pulsed amperometric detection involving an electrochemical detector with a gold working electrode. Details of the method are given elsewhere (Jung et al., 2014). In brief, separation involved a CarboPak MA1 (4 × 250 mm, Thermo Fisher Scientific, USA)

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

analytical column and NaOH eluent (360 mM, 0.4 mL min^{-1}). Limits of detection were 3.0 ng m^{-3}, 0.7 ng m^{-3}, and 1.0 ng m^{-3} for levoglucosan, mannosan, and galactosan, respectively.

Aerosol samples were analyzed for OC and EC using a thermal optical OC/EC analyzer (Sunset Laboratory Inc. Forest Grove, OR, USA) with laser transmittance-based correction of pyrolysis. Details of the analyzer and quality-control parameters are reported elsewhere (Jung et al., 2014). In brief, 1.5 cm^2 punch-core samples of quartz filter were placed in a quartz dish inside the thermal desorption oven of the analyzer. OC and EC were quantified using a temperature program developed by the US National Institute for Occupational Safety and Health (NIOSH) in an inert atmosphere (100% He) and in an oxidizing atmosphere (98% He + 2% O_2), respectively. Detection limits of OC and EC were 0.04 and 0.01 μg C m^{-3}, and analytical errors were 1.3% and 3.7%, respectively.

3. Results and Discussion

3.1 Chemical characteristics of $PM_{2.5}$ and source identification

Mass concentrations of carbonaceous aerosol, BB tracers, and water-soluble ions in $PM_{2.5}$ samples collected at Ulaanbaatar during winter and spring of 2017 are summarized in Table 1. OC contributed 65% and 57% of the total chemical species quantified in winter and spring, respectively (Table 1). Semi-volatile organic compounds (SVOCs) condensation is generally favored by low-temperature conditions during winter in urban atmospheres in China (Wang et al., 2018). Average concentrations of OC during winter were five times those obtained in spring (Fig. 2). This may be attributed to additional BB emission for home heating, increased condensation of SVOCs due to low temperatures,

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

and temperature inversions with low wind speeds (average wind speed 1.43 ± 0.73 m s^{-1}; Table 1 and Fig. 3a). During spring, OC concentrations increased with temperature (R^2 = 0.36; slope = 1.04) as shown in Fig. 3b, possibly due to volatilization of SVOCs during periods of elevated temperature. A similar correlation between OC and temperature was observed in the USA during the high-temperature months of 1998−2008 (Tai et al., 2010). OC concentrations decreased with increasing wind speed during winter (Fig. 3a) and spring (Fig. 3b), over all air temperature ranges. The inverse relationship between OC and wind speed during winter (Fig. 3a) and spring (Fig. 3b) suggests a predominance of local sources, with higher wind speeds flushing air pollutants out of the area whereas low wind speeds allow them to accumulate (Khan et al., 2010).

Average concentration of EC during winter (1.71 ± 0.58 μg m^{-3}) was higher than that in spring (1.11 ± 0.42 μg m^{-3}) (Table 1), consistent with general urban observations in cities of China (Ji et al., 2016) and India (Panda et al., 2016). In winter and spring, EC concentrations at the study site were lower than those observed in a suburban site (2.3 ± 1.0 μg m^{-3} and 3.1 ± 1.5 μg m^{-3}, respectively) and an urban site (2.3 ± 1.0 μg m^{-3} and 3.3 ± 1.2 μg m^{-3}, respectively) in Shanghai, China (Feng et al., 2009). EC is emitted mainly as primary particles during combustion and exists in an inert state in the atmosphere (Zhang et al., 2015). Winter increases in EC concentration are therefore due mainly to emissions from increased combustion of coal and biomass for space heating rather than to effects of temperature and relative humidity. In spring, however, a strong correlation was found between EC and temperature (Fig. 4; R^2 = 0.81), possibly due to increasing temperature causing an increase in resuspension of EC with soil particles. This is consistent with our observation of a strong correlation of Ca^{2+} concentration with temperature (R^2 = 0.83; Fig. 4) and EC (r = 0.90; Table 4) during spring.

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Daily concentrations of levoglucosan, mannosan and galactosan have similar trends during winter and spring (Fig. 2), possibly because of combustion of similar biomass fuels in both seasons. Changes in concentrations of these BB tracers might be attributed to changes in relative proportions of cellulose and hemicellulose in different biomass fuels (Zhu et al., 2015; Nirmalkar et al., 2015). Concentrations of anhydrosugars were four times higher in winter than in spring (Table 1) due to increased heating requirements in winter. The higher relative humidity (58.5%–72.7%) and lower temperature (–10.5°C to –27.8°C; Table 1) in winter can also contribute to longer atmospheric residence times due to increased levoglucosan stability (Lai et al., 2014). Higher concentrations of BB tracers in winter than spring have previously been observed in Beijing, China, (Liang et al., 2016) and were attributed to meteorological conditions similar to those of Ulaanbaatar.

Among water-soluble ions, SO_4^{2-} (9.7 ± 3.4 μg m^{-3}) was the most dominant $PM_{2.5}$ species during winter, followed by NH_4^+ (6.2 ± 2.4 μg m^{-3}) and NO_3^- (4.2 ± 1.7 μg m^{-3}), whereas SO_4^{2-} (1.9 ± 0.5 μg m^{-3}) was the dominant species during spring, followed by Ca^{2+} (0.9 ± 0.4 μg m^{-3}) and NH_4^+ (0.7 ± 0.3 μg m^{-3}). The total SO_4^{2-} + NH_4^+ + NO_3^- content accounted for 27% and 23% of the total measured chemical species during winter and spring, respectively (Fig. 2 and Table 1). SO_4^{2-} is the most prevalent water-soluble ion in $PM_{2.5}$ in Wuhan, Guangzhou, and Tianjin (China) due to industrial emissions and coal burning (Gu et al., 2011; Tao et al., 2014; Huang et al., 2016). This suggests that the higher SO_4^{2-} concentration in Ulaanbaatar may be attributable to emissions from the three major coal-fired thermal power plants near the study site.

The atmospheric concentrations of OC (11–17 μg m^{-3}) and levoglucosan (0.46–0.73 μg m^{-3}) were higher for samples collected during 27–30 April 2017 than on almost all remaining days in spring (Fig. 2b). Backward atmospheric trajectories based on the

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model provided by the US National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) indicate that during those days air masses originated from a region where a significant number of fires were detected [US Fire Information for Resource Management System (FIRMS); National Aeronautics and Space Administration (NASA); Fig. 5a, b)]. The elevated OC and levoglucosan concentrations during 27–30 April may thus have been influenced by long-range transport from BB north of Mongolia.

Principal component analysis (PCA) is a useful tool for reducing the dimensionality of large aerosol datasets to principal components using varimax rotation for source identification (Cao et al., 2005; Lin et al., 2018; Nirmalkar et al., 2019). Four principal components (PCs) in winter and three in spring were identified with eigenvalues >1 explaining 96% and 92%, respectively, of the total variance (Tables 2 and 3). The PCs were categorized on the basis of loadings of chemical components as follows. In winter, PC1 includes BB characterized by high loadings of levoglucosan, mannosan, and galactosan; PC2 includes dust characterized by Ca^{2+} and Mg^{2+} content; PC3 includes secondary formation characterized by SO_4^{2-}, NO_3^-, and NH_4^+ content; and PC4 includes vehicular sources characterized by EC. In spring, PC1 includes BB (levoglucosan, mannosan, and galactosan); PC2 includes dust (Ca^{2+} and Mg^{2+}) and vehicular emissions (EC); and PC3 includes secondary formation (SO_4^{2-}, NO_3^-, and NH_4^+). In both in winter and spring, BB was a major source of OC as indicated by high loadings of levoglucosan, mannosan, and galactosan in PC1 (explaining 35% of the total variance). PCA results thus indicate that BB is the major source of OC in Ulaanbaatar, with high positive loadings of PC1 during both winter (0.82; Table 2) and spring (0.77; Table 3). Interestingly, the source of K^+ changes with season, being associated with BB in winter (PC1 loading 0.70) and

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

dust re-suspension in spring (PC2 loading 0.65).

3.2 Relationship between BB tracers

The correlations among the three BB tracers levoglucosan, mannosan, and galactosan are shown in Fig. 6a (winter) and 6b (spring). The correlations between levoglucosan and mannosan and between levoglucosan and galactosan are strong during winter ($R^2 = 0.99$ for both pairs) and spring ($R^2 = 0.95$ and 0.83, respectively; Fig. 6a, b). Concentrations of levoglucosan and OC are strongly correlated in both winter ($R^2 = 0.78$) and spring ($R^2 = 0.86$; Fig. 7a), suggesting a major fraction of OC originates from BB in Ulaanbaatar. The similar strong correlation and steep slope observed in OC–levoglucosan plots for PM collected in Chiang Mai Province (Thailand) and Daejeon (Korea) were attributed mainly to BB (Jung et al., 2014; Thepnuan et al., 2019). The substantial intercept values during winter (6.5 μg C m^{-3}) and spring (2.9 μg C m^{-3}; Fig. 7a) can be explained by the emission of OC from fossil-fuel combustion and other primary organic aerosol sources, and secondary organic aerosol formation via gas–particle conversion in the atmosphere, with the contribution of non-BB sources thus also being substantial.

The strong correlation between levoglucosan and K^+ concentrations ($R^2 = 0.68$) in winter indicates they are produced from similar sources (Fig. 7b), with BB contributing most of the K^+. The higher concentration of K^+ in winter than spring in Hong Kong is attributed to nearby residential and agricultural BB activities (Louie et al., 2005). At Ulaanbaatar, the correlation between levoglucosan and K^+ is weaker in spring ($R^2 = 0.49$; Fig. 7b), suggesting emission of K^+ from other sources together with BB. In spring, K^+ may be also derived from soil dust re-suspension due to high wind speeds (up to 2.6 m s^{-1}) and dry atmospheric conditions (RH = 35%) in

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Ulaanbaatar (Table 1).

OC and K^+ concentrations are strongly correlated during winter ($R^2 = 0.79$; Fig. 8a) and spring ($R^2 = 0.73$; Fig. 8b). As most of the aerosol particles emitted from BB occur in $PM_{2.5}$, the correlation between OC and K^+ suggests that BB is one of the major sources of ambient aerosol in Ulaanbaatar. The negative offset (–6.88 μg m^{-3}; Fig. 8a) during the winter was due to an excess of K^+. In winter, additional coal and wood are used for heating and cooking in most traditional Ulaanbaatar houses (Batmunkh et al., 2013). Soil particles present on the surface of coal and wood are unavoidably burned with the biomass. Furthermore, the lignite coal commonly used for domestic purposes has a high ash content (Batmunkh et al., 2013). Biomass and coal are burned in traditional stoves with no pollution control devices (Batmunkh et al., 2013), so soil and ash particles are entrained in convective processes and suspended in the atmosphere together with smoke particles (Nirmalkar et al., 2019). The excess K^+ during winter may thus be due to the mixing of BB and coal-burning particles with soil and ash particles.

3.3 Tracing the source of BB aerosol

OC is a major contributor to $PM_{2.5}$ during spring and winter in Ulaanbaatar, with PCA indicating that BB is the major source of OC in both seasons. To quantify the OC_{BB}, it is necessary to identify the BB fuel type. Several investigators used levoglucosan/mannosan and levoglucosan/K^+ ratios to identify BB fuel types (Puxbaum et al., 2007; Cheng et al., 2013; Jung et al., 2014; Chen et al., 2018; Thepnuan et al., 2019).

The levoglucosan/mannosan ratio is source-specific and may be used to identify BB fuel types due to the unique cellulose and hemicellulose compositions of different biomass fuels (Zhang et al., 2007; Cheng et al., 2013). A previous study suggested that

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

the levoglucosan/mannosan ratio is strongly dependent on wood type, rather than on the site where the wood is grown (Cheng et al., 2013). Therefore, the levoglucosan/mannosan ratio was used to trace the type of wood burnt during winter and spring for indoor heating and cooking purposes. Previous studies have used levoglucosan/mannosan ratios to investigate the BB fuel types (Cheng et al., 2013; Jung et al., 2014). However, the levoglucosan/mannosan ratio cannot distinguish between emissions from crop residuals (rice straw, wheat straw, and corn straw) and hardwood due to the overlap of ratios between these fuel types (Cheng et al., 2013). However, levoglucosan/K^+ ratio can distinguish between the two groups (Jung et al., 2014, Chen et al., 2018). Both levoglucosan/mannosan and levoglucosan/K^+ ratios are therefore useful in distinguishing various types of fuel (Cheng et al., 2013; Puxbaum et al., 2007).

A levoglucosan/mannosan–levoglucosan/K^+ scatter plot based on results of the present and previous studies is shown in Fig. 9, using data from Schauer et al. (2001), Fine et al. (2001, 2002, 2004a, b), and Engling et al. (2006) for hardwood grown in the USA; Schauer et al. (2001), Hays et al. (2002), Fine et al. (2001, 2002, 2004a, b), and Engling et al. (2006) for US softwood; Schmidl et al. (2008), Bari et al. (2009) and Goncalves et al. (2010) for hardwood grown in Europe; Iinuma et al. (2007), Schmidl et al. (2008), and Goncalves et al. (2010) for European softwood; Engling et al. (2006) and Sullivan et al. (2008) for needles and duff found in the USA; 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 average levoglucosan/mannosan ratio was 3.6 ± 0.2 (range: 3.4 − 4.1) in winter and 4.1 ± 1.0 (2.12 − 7.05) in spring, whereas the levoglucosan/K^+ ratio was 8.9 ± 1.8 (5.5 − 12.4) in winter and 4.2 ± 2.1 (0.58 – 7.49) in spring at the study site (Fig. 9), within

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

the ranges reported for softwood burning sources (2.5 − 6.7 and 4.6 − 261, respectively) (Fine et al., 2001; Schauer et al., 2001; Fine et al., 2002, 2004a, b; Hays et al., 2002; Engling et al., 2006; Iinuma et al., 2007; Schmidl et al., 2008; Goncalves et al., 2010; Cheng et al., 2013). During winter and spring, the levoglucosan/K^+ and levoglucosan/mannosan ratios thus appear in the softwood region (Fig. 9) for most of the Ulaanbaatar ambient $PM_{2.5}$ samples analyzed in this study. Interestingly, levoglucosan/mannosan ratios were similar in winter and spring, whereas the levoglucosan/K^+ ratio was significantly lower in spring. The most likely cause of the similarity in levoglucosan/mannosan ratios is the use of similar types of domestic biofuels (i.e., softwood; Fine et al., 2001, 2002; Cheng et al., 2013) all year around in Ulaanbaatar (Batmunkh et al., 2013). Low levoglucosan/K^+ ratios have been reported in aerosols from crop-residue burning in China (Cheng et al., 2013) and South Korea (Jung et al., 2014), and are likely due to the application of potassium fertilizers causing elevated K^+ levels in the residues (Thepnuan et al., 2019). However, in Ulaanbaatar the lower levoglucosan/K^+ ratios are due mainly to higher concentrations of levoglucosan in winter than spring with K^+ concentrations being similar in both seasons (Fig. 9). Therefore, softwood burning seems to be the major source of BB aerosol in Ulaanbaatar during both winter and spring, consistent with previously reported softwood-burning emissions from fireplaces of northern and southern regions of the USA (Fine et al., 2001, 2002), from household combustion in Zhengzhou, China (Chen et al., 2018), and from stove wood combustion in the mid-European region (Austria; Schmidl et al., 2008).

3.4 Optimization of OC/levoglucosan ratio for estimating OC_{BB} emission

OC_{BB} was estimated by multiplying OC/levoglucosan ratio and levoglucosan

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

concentration. Previous studies have used the OC/levoglucosan ratio obtained from sources of BB aerosol to estimate OC_{BB}. A ratio of 7.35 reported for burning of four types of US hardwood (Fine et al., 2002) was used for estimating OC_{BB} at four background sites in Europe (Puxbaum et al., 2007). Later, mean value of 11.2 of OC/levoglucosan ratio derived from ratios ranged between 4.5 – 24.6 was used for estimating OC_{BB} in the UK (Harrison et al., 2012). However, such estimates may not be accurate as the OC/levoglucosan ratio is highly variable in BB emissions. For example, the average OC/levoglucosan ratio from softwood burning (23.8) is much higher than that of hardwood burning (7.35) (Fine et al., 2002; Schmidl et al., 2008), differences are more than ten-fold among studies of softwood-burning OC/levoglucosan ratios (Fine et al., 2002; Hays et al., 2002; Engling et al., 2006; Iinuma et al., 2007; Goncalves et al., 2010).

Combustion conditions may also significantly influence OC/levoglucosan ratios. For example, the OC/levoglucosan ratio varied by a factor of about seven between burning the same wood (Loblolly pine) in a fireplace (27.6; Fine et al., 2002) and in a stove (3.4; Fine et al., 2004b). The OC/levoglucosan ratio is also quite variable with a mean of 10.1 ± 7.97 in published data for softwood burning (range 1.90–27.6; Fig. 10). It is therefore necessary to optimize the OC/levoglucosan ratio for use in estimating OC_{BB}. The large variations in OC/levoglucosan ratios among emissions from different fuel types present a major challenge, with the effects of burning conditions making it difficult to obtain the most appropriate ratio for BB emissions at a given site.

Therefore, for the first time, we have used an optimized OC/levoglucosan ratio to estimate precise concentration of OC_{BB} for the Ulaanbaatar study site. First, candidate OC_{BB} in this study was estimated from OC/levoglucosan ratios for softwood burning in the previous chamber experiment (Cheng et al., 2013 and papers cite therein) and

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

levoglucosan concentration in this site. Second, $OC_{non\text{-}BB}$ concentration was calculated by subtracting OC_{BB} from corresponding total OC. If calculated $OC_{non\text{-}BB}$ doesn't contain OC emitted from biomass burning, both regression slope and R^2 between $OC_{non\text{-}BB}$ versus levoglucosan will be closed to zero. As shown in Fig. 11a and 11b, the lowest R^2 and regression slope were observed when OC/levoglucosan ratios of 27.6 and 18.0 in winter and spring, respectively. Thus, the optimized OC/levoglucosan ratios for our site were determined to 27.6 and 18.0 in winter and spring, respectively.

The OC_{BB} concentrations at the Ulaanbaatar study site were calculated from the optimized OC/levoglucosan ratios and levoglucosan concentrations. The OC_{BB} concentration was estimated to be 33.1 ± 11.9 μg C m^{-3} (range 16.0−58.5 μg C m^{-3}) and 5.64 ± 3.29 μg C m^{-3} (range 0.57−13.1 μg C m^{-3}), accounting for 68% and 63% of the total OC in winter and spring, respectively (Fig. 12). The average of previously published OC/levoglucosan ratios, 10.1 ± 7.9 (range 1.90 − 27.6), gives an estimated OC_{BB} concentration of 12.1 ± 4.4 μg C m^{-3} (range 5.9−21.4 μg C m^{-3}) and 3.2 ± 1.8 μg C m^{-3} (0.32−7.34 μg C m^{-3}) in winter and spring, respectively. There values are 2.7 (winter) and 1.8 (spring) times lower than values estimated using our optimized OC/levoglucosan ratio. Our estimated contribution of OC_{BB} was higher than that in Daejeon, South Korea (24%–68% of total OC, mean 45% ± 12%; Jung et al., 2014) and Beijing, China (50% of total OC; Cheng et al., 2013), where aerosols are produced mainly by the burning of crop residues. The contribution of OC_{BB} to total OC is 57% and 31% during heating (average temperature 0.6°C) and non-heating (average temperature 14°C) seasons in Krynica Zdroj, Poland, significantly lower than that of Ulaanbaatar during both winter (average temperature –21°C) and spring (average temperature 6°C). Such high concentrations of OC_{BB} in Ulaanbaatar and Krynica Zdroj are likely to be due to intense wood burning for

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

heating during winter.

3.5 Tracing sources of $OC_{non\text{-}BB}$

A substantial contribution of $OC_{non\text{-}BB}$ to total OC was found during winter (31% ± 13%) and spring (37% ± 20%; Fig. 12), with the similarity between seasons indicating that $OC_{non\text{-}BB}$ originated mainly from local background sources. There is strong correlation between $OC_{non\text{-}BB}$ and SO_4^{2-}, NH_4^+, and K^+ in winter and $OC_{non\text{-}BB}$ and NO_3^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, and EC in spring (Table 4). Residential combustion of coal emits significant amounts of OC, EC, and inorganic species (SO_4^{2-} and metals) due to incomplete combustion and lack of pollution control devices (Garcia et al., 1992; Li et al., 2016; Watson et al., 2001a, b). Garcia et al. (1992) studied emissions of volatile organic compounds from coal burning and vehicle engines. In Ulaanbaatar, the use of coal for cooking and heating, and emissions from old vehicles are reported as major sources of OC (Batmunkh et al., 2013). The three thermal power plants in Ulaanbaatar are point sources for emissions of carbonaceous aerosol (Batmunkh et al., 2013), burning ~5 million tons of coal per year (Batmunkh et al., 2013). High concentrations of anions (SO_4^{2-} and NO_3^-) and cations (NH_4^+ and Na^+) are reported in China (Zhou et al., 2003), the USA (Caiazzo et al., 2013), Brazil (Flues et al., 2002), India (Guttikunda et al., 2014), Korea (Park et al., 2015), and Spain (Alastuey et al., 1999) near coal-fired thermal power plants. Emissions of volatile organic compounds from vegetation have also been observed in previous studies (Fehsenfeld et al., 1992; Shao et al., 2001; Acton et al., 2016). The correlations of $OC_{non\text{-}BB}$ with ions and EC are thus likely due to volatile organic compounds emitted from coal-burning and vehicles, and vegetative emissions.

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

4. Conclusion

BB was identified as a major source of $PM_{2.5}$ in Ulaanbaatar, Mongolia, during the winter and spring of 2017, based on PCA. OC was the major component of $PM_{2.5}$ during the entire sampling period, winter and spring. For determination of OC_{BB}, the fuel type must be identified and levoglucosan/mannosan and levoglucosan/K^+ ratios obtained from previous studies and our on-site measurements were used for this purpose.

Softwood burning was identified as a major source of OC_{BB}. However, OC/levoglucosan ratios from softwood burning are highly variable, and an optimum ratio was derived by regression analysis between daily concentrations of $OC_{non\text{-}BB}$ and levoglucosan, yielding values of 27.6 and 18.0 for winter and spring, respectively. The application of these ratios indicates that 68% and 63% of OC originated from BB during winter and spring, respectively, which is about double that estimated using average values of previous studies. The atmospheric concentration of OC_{BB} was higher in winter than spring due mainly to additional BB for heating and cooking. BB aerosols in Ulaanbaatar originate mainly from local softwood burning. The approach developed here may be applied elsewhere for screening region-specific OC/levoglucosan ratios for estimating atmospheric appropriate concentrations of OC_{BB}, aiding the establishment of BB control measures.

Author contribution

Jinsang Jung and Batmunkh Tsatsral designed the study and carried out the field work. Jinsang Jung performed chemical analyses and quality-control measures. Jayant Nirmalkar wrote the manuscript under the guidance of Jinsang Jung. All authors

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

commented on and discussed the manuscript.

Competing interests

The authors declare that they have no conflict of interests.

Acknowledgments

This work was funded by a grant (19011057) from the Korea Research Institute of Standards and Science (KRISS) under the Basic R&D Project of Quantification of local and long-range transported pollutants during a severe haze episode over the Korean Peninsula. The authors gratefully acknowledge the NOAA Air Resources Laboratory for the provision of the HYSPLIT transport and dispersion model and access to the READY website (http://www.arl.noaa.gov/ready.html) and the Fire Information for Resource Management System (FIRMS) of the National Aeronautics and Space Administration (NASA), United States (https://firms.modaps.eosdis.nasa.gov/alerts/) used in this study.

Data availability

The data used in this study are available from the corresponding author upon request (jsjung@kriss.re.kr).

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

References

Achad, M., Caumo, S., de Castro Vasconcellos, P., Bajano, H., Gómez, D., and Smichowski, P.: Chemical markers of biomass burning: Determination of levoglucosan, and potassium in size-classified atmospheric aerosols collected in Buenos Aires, Argentina by different analytical techniques, Microchemical J., 139, 181−187, https://doi.org/10.1016/j.microc.2018.02.016, 2018.

Acton, W. J. F., Schallhart, S., Langford, B., Valach, A., Rantala, P., Fares, S., and Carriero, G.: Canopy−scale flux measurements and bottom-up emission estimates of volatile organic compounds from a mixed oak and hornbeam forest in northern Italy, Atmos. Chem. Phys., 16, 7149−7170, https://doi.org/10.5194/acp-16-7149-2016, 2016.

Alastuey, A., Querol, X., Chaves, A., Ruiz, C. R., Carratala, A., and Lopez−Soler, A.: Bulk deposition in a rural area located around a large coal-fired power station, northeast Spain, Environ. Pollut., 106(3), 359−367, https://doi.org/10.1016/S0269-7491(99)00103-7, 1999.

Bari, M. A., Baumbach, G., Kuch, B., and Scheffknecht, G.: Wood smoke as a sourceof particle-phase organic compounds in residential areas, Atmos. Environ., 43, 4722−4732, https://doi.org/10.1016/j.atmosenv.2008.09.006, 2009.

Batmunkh, T., Kim, Y. J., Jung, J. S., Park, K., and Tumendemberel, B.: Chemical characteristics of fine particulate matters measured during severe winter haze events in Ulaanbaatar, Mongolia, J. Air & Waste Manag. Assoc., 63, 659−670, https://doi.org/10.1080/10962247.2013.776997, 2013.

Caiazzo, F., Ashok, A., Waitz, I. A., Yim, S. H., and Barrett, S. R.: Air pollution and early deaths in the United States. Part I: Quantifying the impact of major sectors in 2005, Atmos. Environ., 79, 198−208, https://doi.org/10.1016/j.atmosenv.2013.05.081, 2013.

Cao, J. J., Wu, F., Chow, J. C., Lee, S. C., Li, Y., Chen, S. W., An, Z. S., Fung, K. K., Watson, J. G., Zhu, C. S., and Liu, S. X.: Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China, Atmos. Chem. Phys., 5, 3127−3137, https://doi.org/10.5194/acp-5-3127-2005, 2005.

Chantara, S., Thepnuan, D., Wiriya, W., Prawan, S., and Tsai, Y. I.: Emissions of pollutant gases, fine particulate matters and their significant tracers from biomass burning in

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

an open-system combustion chamber, Chemosphere, 224, 407−416, 2019.

Chen, H., Yin, S., Li, X., Wang, J., and Zhang, R.: Analyses of biomass burning contribution to aerosol in Zhengzhou during wheat harvest season in 2015, Atmos. Res., 207, 62−73, https://doi.org/10.1016/j.atmosres.2018.02.025, 2018.

Cheng, Y., Engling, G., He, K.-B., Duan, F.-K., Ma, Y.-L., Du, Z.-Y., Liu, J.-M., Zheng, M., and Weber, R. J.: Biomass burning contribution to Beijing aerosol, Atmos. Chem. Phys., 13, 7765−7781, https://doi.org/10.5194/acp-13-7765-2013, 2013.

Claeys, M., Kourtchev, I., Pashynska, V., Vas, G., Vermeylen, R., Wang, W., Cafmeyer, J., Chi, X., Artaxo, P., Andreae, M. O., and Maenhaut, W.: Polar organic marker compounds in atmospheric aerosols during the LBA-SMOCC 2002 biomass burning experiment in Rondônia, Brazil: sources and source processes, time series, diel variations and size distributions, Atmos. Chem. Phys., 10, 9319−9331, https://doi.org/10.5194/acp-10-9319-2010, 2010.

Duan, F., Liu, X., Yu, T., Cachier, H.: Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing, Atmos. Environ. 38, 1275−1282, https://doi.org/10.1016/j.atmosenv.2003.11.037, 2004

Engling, G., Carrico, C. M., Kreidenweis, S. M., Collett Jr., J. L., Day, D. E., Malm, W. C., Lincoln, L., Hao, W. M., Iinuma, Y., and Herrmann, H.: Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection, Atmos. Environ., 40, 299−311, https://doi.org/10.1016/j.atmosenv.2005.12.069, 2006.

Engling, G., Lee, J. J., Tsai, Y. W., Lung, S. C. C., Chou, C. C. K., Chan, C. Y.: Size resolved anhydrosugar composition in smoke aerosol from controlled field burning of rice straw, Aerosol Sci. Technol., 43, 662−672, https://doi.org/10.1080/0278682090282511, 2009.

Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A. B., Hewitt, C. N., Lamb, B., Liu, S., Trainer, M., Westberg, H., and Zimmerman, P.: Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, Global Biogeochem. Cy., 6, 389−430, https://doi.org/10.1029/92GB02125, 1992.

Feng, Y., Chen, Y., Guo, H., Zhi, G., Xiong, S., Li, J., Sheng, G., and Fu, J.: Characteristics of organic and elemental carbon in $PM_{2.5}$ samples in Shanghai, China. Atmos. Res., 92, 434−442, https://doi.org/10.1016/j.atmosres.2009.01.003, 2009.

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Fine, P. M., Cass, G. R., and Simoneit, B. R. T.: Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States, Environ. Sci. Technol., 35, 2665−2675, https://doi.org/10.1021/es001466k, 2001.

Fine, P. M., Cass, G. R., and Simoneit, B. R. T.: Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States, Environ. Sci. Technol., 36, 1442−1451, https://doi.org/10.1021/es0108988, 2002.

Fine, P. M., Cass, G. R., and Simoneit, B. R. T.: Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the midwestern and western United States, Environ. Engin. Sci., 21, 387−409, https://doi.org/10.1089/109287504323067021, 2004a.

Fine, P. M., Cass, G. R., and Simoneit, B. R. T.: Chemical characterization of fine particle emissions from the wood stove combustion of prevalent United States tree species, Environ. Engin. Sci., 21, 705−721, https://doi.org/10.1089/ees.2004, 21.705, 2004b.

Flues, M., Hama, P., Lemes, M. J. L., Dantas, E. S. K., and Fornaro, A.: Evaluation of the rainwater acidity of a rural region due to a coal-fired power plant in Brazil, Atmos. Environ., 36, 2397−2404, https://doi.org/10.1016/S1352-2310(01)00563-5, 2002.

Fu, P. Q., Kawamura, K., Chen, J., Li, J., Sun, Y. L., Liu, Y., Tachibana, E., Aggarwal, S. G., Okuzawa, K., Tanimoto, H., and Kanaya, Y.: Diurnal variations of organic molecular tracers and stable carbon isotopic composition in atmospheric aerosols over Mt. Tai in the North China Plain: an influence of biomass burning, Atmos. Chem. Phys., 12, 8359−8375, doi:10.5194/acp-12-8359-2012, 2012.

Garcia, J., Beyne-Masclet, S., Mouvier, G., and Masclet, P.: Emissions of volatile organic compounds by coal-fired power stations. Atmos. Environ. Part A. General Topics, 26, 1589−1597, https://doi.org/10.1016/0960-1686(92)90059-T, 1992.

Gonçalves, C., Alves, C., Evtyugina, M., Mirante, F., Pio, C., Caseiro, A., Schmidl, C., Bauer, H., and Carvalho, F.: Characterisation of PM_{10} emissions from wood stove combustion of common woods grown in Portugal, Atmos. Environ., 44, 4474−4480, https://doi.org/10.1016/j.atmosenv.2010.07.026, 2010.

Gu, J., Bai, Z., Li, W., Wu, L., Liu, A., Dong, H., and Xie, Y.: Chemical composition of $PM_{2.5}$ during winter in Tianjin, China, Particuology, 9, 215−221,

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

https://doi.org/10.1016/j.partic.2011.03.001, 2011.

Guttikunda, S. K., and Jawahar, P.: Atmospheric emissions and pollution from the coal−fired thermal power plants in India. Atmos. Environ., 92, 449−460, https://doi.org/10.1016/j.atmosenv.2014.04.057, 2014.

Harrison, R. M., Beddows, D. C. S., Hu, L., and Yin, J.: Comparison of methods for evaluation of wood smoke and estimation of UK ambient concentrations, Atmos. Chem. Phys., 12, 8271−8283, doi:10.5194/acp−12−8271−2012, 2012.

Hays, M. D., Geron, C. D., Linna, K. J., Smith, N. D., and Schauer, J. J.: Speciation of gasphase and fine particle emissions from burning of foliar fuels, Environ. Sci. Technol., 36, 2281−2295, https://doi.org/10.1021/es0111683, 2002.

Huang, X., Liu, Z., Zhang, J., Wen, T., Ji, D., Wang, Y.: Seasonal variation and secondary formation of size-segregated aerosol water-soluble inorganic ions during pollution episodes in Beijing, Atmos. Res., 168, 70−79, https://doi.org/10.1016/j.atmosres.2015.08.021, 2016.

Iinuma, Y., Brüggemann, E., Gnauk, T., Müller, K., Andreae, M. O., Helas, G., Parmar, R., and Herrmann, H.: Source characterization of biomass burning particles: the combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat, J Geophys. Res., 112, D08209. http://dx.doi.org/10.1029/2006JD007120, 2007.

Ji, D., Zhang, J., He, J., Wang, X., Pang, B., Liu, Z., Wang, L., and Wang, Y.: Characteristics of atmospheric organic and elemental carbon aerosols in urban Beijing, China. Atmos. Environ., 125, 293−306, https://doi.org/10.1016/j.atmosenv.2015.11.020, 2016.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., and Aiken, A. C.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525−1529, doi:10.1126/science.1180353, 2009.

Jung, J., Lee, H., Kim, Y. J., Liu, X., Zhang, Y., Hu, M., and Sugimoto, N.: Optical properties of atmospheric aerosols obtained by in situ and remote measurements during 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006). J. Geophys. Res.: Atmos., 114(D2), https://doi.org/10.1029/2008JD010337, 2009.

Jung, J., Lee, S., Kim, H., Kim, D., Lee, H., and Oh, S.: Quantitative determination of the

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

biomass-burning contribution to atmospheric carbonaceous aerosols in Daejeon, Korea, during the rice-harvest period, Atmos. Environ., 89, 642−650, https://doi.org/10.1016/j.atmosenv.2014.03.010, 2014.

Jung, J., Tsatsral, B., Kim, Y. J., and Kawamura, K.: Organic and inorganic aerosol compositions in Ulaanbaatar, Mongolia, during the cold winter of 2007 to 2008: dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls, J Geophys. Res.: Atmos., 115(D22), https://doi.org/10.1029/2010JD014339, 2010.

Khan, M. F., Shirasuna, Y., Hirano, K., and Masunaga, S.: Characterization of $PM_{2.5}$, $PM_{2.5–10}$ and $PM_{>10}$ in ambient air, Yokohama, Japan, Atmos. Res., 96, 159-172, https://doi.org/10.1016/j.atmosres.2009.12.009, 2010.

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

Li, Q., Jiang, J., Zhang, Q., Zhou, W., Cai, S., Duan, L., Ge, S., and Hao, J.: Influences of coal size, volatile matter content, and additive on primary particulate matter emissions from household stove combustion. Fuel, 182, 780-787, https://doi.org/10.1016/j.fuel.2016.06.059, 2016.

Liang, L., Engling, G., Du, Z., Cheng, Y., Duan, F., Liu, X., and He, K.: Seasonal variations and source estimation of saccharides in atmospheric particulate matter in Beijing, China, Chemosphere, 150, 365−377, https://doi.org/10.1016/j.chemosphere.2016.02.002, 2016.

Lin, Y.-C., Hsu, S.-C., Lin, C.-Y., Lin, S.-H., Huang, Y.-T., Chang, Y., and Zhang, Y.-L.: Enhancements of airborne particulate arsenic over the subtropical free troposphere: impact of southern Asian biomass burning, Atmos. Chem. Phys., 18, 13865-13879, https://doi.org/10.5194/acp-18-13865−2018, 2018.

Louie, P. K., Watson, J. G., Chow, J. C., Chen, A., Sin, D. W. and Lau, A. K.: Seasonal characteristics and regional transport of $PM_{2.5}$ in Hong Kong, Atmos. Environ., 39, 1695−1710, https://doi.org/10.1016/j.atmosenv.2004.11.017, 2005.

Maenhaut, W., Nava, S., Lucarelli, F., Wang, W., Chi, X., and Kulmala, M.: Chemical composition, impact from biomass burning, and mass closure for $PM_{2.5}$ and PM_{10} aerosols at Hyytiälä, Finland, in summer 2007, X-Ray Spectrometry, 40, 168−171, https://doi.org/10.1002/xrs.1302, 2011.

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Nirmalkar, J., Deshmukh, D. K., Deb, M. K., Tsai, Y. I., and Pervez, S.: Characteristics of aerosol during major biomass burning events over eastern central India in winter: A tracer-based approach, Atmos. Pollut. Res., 10, 817−826, https://doi.org/10.1016/j.apr.2018.12.010, 2019.

Nirmalkar, J., Deshmukh, D. K., Deb, M. K., Tsai, Y. I., and Sopajaree, K.: Mass loading and episodic variation of molecular markers in $PM_{2.5}$ aerosols over a rural area in eastern central India, Atmos. Environ., 117, 41–50, https://doi.org/10.1016/j.atmosenv.2015.07.003, 2015.

Oanh, N. T. K., Ly, B. T., Tipayarom, D., Manandhar, B. R., Prapat, P., Simpson, C.D., and Liu, L.J.S.: Characterization of particulate matter emission from open burning of rice straw, Atmos. Environ., 45, 493−502, https://doi.org/10.1016/j.atmosenv.2010.09.023, 2011.

Panda, S., Sharma, S. K., Mahapatra, P. S., Panda, U., Rath, S., Mahapatra, M., Mandal, T. K., and Das, T.: Organic and elemental carbon variation in $PM_{2.5}$ over megacity Delhi and Bhubaneswar, a semi-urban coastal site in India, Nat. Hazards, 80, 1709−1728, https://doi.org/10.1007/s11069-015-2049-3, 2016.

Park, S. M., Seo, B. K., Lee, G., Kahng, S. H., and Jang, Y.: Chemical composition of water-soluble inorganic species in precipitation at Shihwa Basin, Korea, Atmosphere, 6, 732−750, https://doi.org/10.3390/atmos6060732, 2015.

Pio, C. A., Legrand, M., Alves, C. A., Oliveira, T., Afonso, J., Caseiro, A., Puxbaum, H., Sanchez−Ochoa, A. and Gelencser, A.: Chemical composition of atmospheric aerosols during the 2003 summer intense forest fire period, Atmos. Environ., 42, 7530−7543, https://doi.org/10.1016/j.atmosenv.2008.05.032, 2008.

Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencser, A., Legrand, M., Preunkert, S., and Pio, C.: Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background, J. Geophys. Res.: Atmos., 16, 112(D23), https://doi.org/10.1029/2006JD008114, 2007.

Reche, C., Viana, M., Amato, F., Alastuey, A., Moreno, T., Hillamo, R., Teinila, K., Saarnio, K., Seco, R., Penuelas, J., and Mohr, C.: Biomass burning contributions to urban aerosols in a coastal Mediterranean City, Sci. Tot. Environ., 427, 175−190, https://doi.org/10.1016/j.scitotenv.2012.04.012, 2012.

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 3. C1-C29 organic compounds from fireplace combustion of wood, Environ. Sci. Technol., 35, 1716−1728, https://doi.org/10.1021/es001331e, 2001.

Schmidl, C., Marr, I. L., Caseiro, A., Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A., and Puxbaum, H.: Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions, Atmos. Environ., 42, 126-141, https://doi.org/10.1016/j.atmosenv.2007.09.028, 2008a.

Shao, M., Czapiewski, K. V., Heiden, A. C., Kobel, K., Komenda, M., Koppmann, R., and Wildt, J.: Volatile organic compound emissions from Scots pine: mechanisms and description by algorithms, J. Geophys. Res.: Atmospheres, 106(D17), 20483−20491, 10.1029/2000JD000248, 2001.

Sharma, A., Pareek, V., and Zhang, D.: Biomass pyrolysis—A review of modelling, process parameters and catalytic studies. J. Renew. Sustain. Energy, 50, 1081−1096, https://doi.org/10.1016/j.rser.2015.04.193, 2015.

Sheesley, R. J., Schauer, J. J., Chowdhury, Z., Cass, G. R., and Simoneit, B. R. T.: Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia, J Geophys. Res., 108, 4285, http://dx.doi.org/10.1029/2002JD002981, 2003.

Simoneit, B. R., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and Cass, G. R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, Atmos. Environ., 33, 173−182, https://doi.org/10.1016/S1352-2310(98)00145-9, 1999.

Sullivan, A. P., Guo, H., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., Campos, T., Shah, V., Jaegle, L., Lee, B. H., Lopez-Hilfiker, F. D. and Thornton, J. A.: Biomass Burning Markers and Residential Burning in the WINTER Aircraft Campaign. J Geophys. Res.: Atmos., 124, 1846−1861, https://doi.org/10.1029/2017JD028153, 2019.

Sullivan, A. P., Holden, A. S., Patterson, L. A., McMeeking, G. R., Kreidenweis, S. M., Malm, W. C., Hao, W. M., Wold, C. E., and Collett Jr., J. L.: A method for smoke marker measurements and its potential application for determining the contribution

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

of biomass burning from wildfires and prescribed fires to ambient $PM_{2.5}$ organic carbon, J Geophys. Res., 113, D22302, http:// dx.doi.org/10.1029/2008JD010216, 2008.

Tai, A. P., Mickley, L. J., and Jacob, D. J.: Correlations between fine particulate matter ($PM_{2.5}$) and meteorological variables in the United States: Implications for the sensitivity of $PM_{2.5}$ to climate change, Atmos. Environ., 44, 3976-3984, https://doi.org/10.1016/j.atmosenv.2010.06.060, 2010.

Tao, J., Zhang, L., Ho, K., Zhang, R., Lin, Z., Zhang, Z., Lin, M., Cao, J., Liu, S., and Wang, G.: Impact of $PM_{2.5}$ chemical compositions on aerosol light scattering in Guangzhou—the largest megacity in South China, Atmos. Res., 135, 48−58, https://doi.org/10.1016/j.atmosres.2013.08.015, 2014.

Thepnuan, D., Chantara, S., Lee, C. T., Lin, N. H., and Tsai, Y. I.: Molecular markers for biomass burning associated with the characterization of $PM_{2.5}$ and component sources during dry season haze episodes in Upper South East Asia. Sci. Tot. Environ., 658, 708−722, https://doi.org/10.1016/j.scitotenv.2018.12.201, 2019.

Verma, V., Fang, T., Guo, H., King, L., Bates, J. T., Peltier, R. E., Edgerton, E., Russell, A. G., and Weber, R. J.: Reactive oxygen species associated with water-soluble PM2.5 in the southeastern United States: spatiotemporal trends and source apportionment, Atmos. Chem. Phys., 14, 12915-12930, https://doi.org/10.5194/acp-14-12915-2014, 2014.

Wang, T., Tian, M., Ding, N., Yan, X., Chen, S. J., Mo, Y. Z., Yang, W. Q., Bi, X. H., Wang, X. M., and Mai, B. X.: Semivolatile organic compounds (SOCs) in fine particulate matter ($PM_{2.5}$) during clear, fog, and haze episodes in winter in Beijing, China, Environ. Sci. Tech., 52, 5199−5207, https://doi.org/10.1021/acs.est.7b06650, 2018.

Watson, J. G., Chow, J. C., and Fujita, E. M.: Review of volatile organic compound source apportionment by chemical mass balance, Atmos. Environ., 35, 1567−1584, https://doi.org/10.1016/S1352-2310(00)00461-1, 2001a.

Watson, J. G., Chow, J. C., and Houck, J. E.: $PM_{2.5}$ chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in Northwestern Colorado during 1995, Chemosphere, 43, 1141−1151, https://doi.org/10.1016/S0045-6535(00)00171-5, 2001b.

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Zhang, F., Wang, Z. W., Cheng, H. R., Lv, X. P., Gong, W., Wang, X. M., and Zhang, G.: Seasonal variations and chemical characteristics of $PM_{2.5}$ in Wuhan, central China, Sci. Tot. Environ., 518, 97−105, https://doi.org/10.1016/j.scitotenv.2015.02.054, 2015.

Zhang, Y. X., Min, S., Zhang, Y. H., Zeng, L. M., He, L. Y., Bin, Z. H. U., Wei, Y. J., and Zhu, X. L.: Source profiles of particulate organic matters emitted from cereal straw burnings. J Environ. Sci., 19, 167−175, https://doi.org/10.1016/S1001-0742(07)60027-8, 2007.

Zhou, Y., Levy, J. I., Hammitt, J. K., and Evans, J. S.: Estimating population exposure to power plant emissions using CALPUFF: a case study in Beijing, China, Atmos. Environ., 37, 815−826, https://doi.org/10.1016/S1352-2310(02)00937-8, 2003.

Zhu, C., Kawamura, K., and Kunwar, B.: Effect of biomass burning over the western North Pacific Rim: wintertime maxima of anhydrosugars in ambient aerosols from Okinawa, Atmos. Chem. Phys., 15, 1959−1973, https://doi.org/10.5194/acp-15-1959-2015, 2015.

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

Table 1. Concentrations (μg m^{-3}) of organic carbon, elemental carbon, levoglucosan, mannosan, galactosan, and water-soluble ions in $PM_{2.5}$ samples collected from Ulaanbaatar, Mongolia, during the winter (n = 17) and spring (n = 17) of 2017.

	OC	EC	Levoglucosan	Mannosan	Galactosan	Cl^-	SO_4^{2-}	NO_3^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Temperature (°C)	Wind Speed (m sec^{-1})	RH (%)
Winter																
Mean	49.06	1.71	1.20	0.33	0.24	1.69	9.74	4.17	0.64	6.18	0.13	0.05	0.60	-20.8	1.36	66.1
SD	17.32	0.58	0.43	0.13	0.09	0.76	3.37	1.69	0.44	2.42	0.04	0.02	0.24	4.74	0.73	4.56
Min	24.62	0.79	0.58	0.15	0.10	0.26	2.17	0.76	0.10	3.16	0.08	0.02	0.22	-27.8	0.41	58.5
Max	79.07	3.34	2.12	0.61	0.43	2.89	16.06	7.51	1.34	11.59	0.18	0.08	1.04	-10.5	3.55	72.7
Spring																
Mean	8.50	1.11	0.31	0.08	0.04	0.30	1.90	0.70	0.13	0.74	0.08	0.04	0.93	6.11	2.60	35.1
SD	3.55	0.42	0.18	0.04	0.02	0.11	0.50	0.32	0.04	0.28	0.05	0.02	0.36	6.16	0.79	13.9
Min	2.80	0.60	0.03	0.01	0.00	0.11	1.04	0.10	0.07	0.33	0.02	0.02	0.48	-1.52	1.64	17.8
Max	16.63	2.03	0.73	0.15	0.08	0.51	3.02	1.40	0.21	1.47	0.22	0.08	1.61	15.9	4.56	65.2

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

Table 2. Source identification of chemical species using principal component (PC) analysis and varimax rotation at Ulaanbaatar, Mongolia, during winter of 2017.

Winter	Component			
Chemical species	PC1 (Biomass Burning)	PC2 (Dust)	PC3 (Secondary formation)	PC4 (Vehicular)
Levoglucosan	**0.96**	−0.06	0.24	0.06
Mannosan	**0.95**	−0.08	0.27	0.06
Galactosan	**0.95**	−0.07	0.28	0.04
Cl^-	0.19	**0.94**	−0.05	−0.07
SO_4^{2-}	0.43	0.01	**0.88**	0.09
NO_3^-	0.28	0.20	**0.87**	0.20
Na^+	−0.27	**0.87**	−0.33	−0.17
NH_4^+	0.48	−0.12	**0.86**	0.07
K^+	**0.70**	0.11	**0.61**	0.25
Mg_2^+	−0.15	**0.90**	0.25	0.26
Ca_2^+	−0.12	**0.92**	0.19	0.24
OC	**0.82**	−0.17	0.47	0.07
EC	0.14	0.14	0.19	**0.95**
Eigenvalues	4.54	3.44	3.30	1.20
% of Variance	34.95	26.49	25.37	9.21
Cumulative %	34.95	61.44	86.81	96.02

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions
Open Access
EGU

Table 3. Source identification of chemical species using PCA and varimax rotation at Ulaanbaatar, Mongolia, during spring of 2017.

Spring	Component		
Chemical species	PC1 (Biomass Burning)	PC2 (Dust and Vehicular)	PC3 (Secondary formation)
Levoglucosan	**0.88**	0.13	0.39
Mannosan	**0.94**	0.00	0.30
Galactosan	**0.95**	−0.11	0.20
Cl^-	**0.81**	0.32	−0.03
SO_4^{2-}	0.18	0.12	**0.93**
NO_3^-	**0.59**	0.54	0.52
Na^+	0.08	**0.91**	−0.09
NH_4^+	0.44	0.05	**0.88**
K^+	0.41	**0.67**	**0.55**
Mg^{2+}	0.05	**0.90**	0.35
Ca^{2+}	0.10	**0.97**	0.15
OC	**0.77**	0.41	0.46
EC	0.10	**0.94**	0.01
Eigenvalues	4.59	4.53	2.87
% of Variance	35.30	34.84	22.04
Cumulative %	35.30	70.14	92.18

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

Table 4. Correlation coefficients (r) from Spearman correlation analysis for $OC_{non\text{-}BB}$ and water-soluble ions during winter and spring of 2017 at Ulaanbaatar, Mongolia.

		Cl^-	SO_4^{2-}	NO_3^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	EC
$OC_{non\text{-}BB}$	Winter	−0.26	0.71**	0.44	−0.58*	0.72**	0.64**	−0.16	−0.16	0.15
	Spring	0.29	0.37	0.59*	0.74**	0.23	0.65**	0.78**	0.77**	0.74**

*Correlation is significant at the .05 level (2-tailed); **Correlation is significant at the .01 level (2-tailed).

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

Figure captions

Fig. 1 Sampling site in Ulaanbataar, Mongolia (https://www.google.com/earth/versions/#earth-pro). ©Google Earth.

Fig. 2 Daily variations in atmospheric concentrations (μg m^{-3}) of chemical species in Ulaanbaatar during winter (a) and spring (b) of 2017.

Fig. 3 Daily atmospheric concentrations of OC (μg C m^{-3}) as a function of wind speed (m s^{-1}) and temperature (°C) during winter (a) and spring (b) of 2017.

Fig. 4 Relationship between $PM_{2.5}$ concentrations of $Ca^{2+}$and EC (μg m^{-3}) and temperature (°C) during spring of 2017.

Fig. 5 (a) Five-day backward air-mass trajectories (https://ready.arl.noaa.gov/HYSPLIT.php) and (b) FIRMS fire counts (https://firms.modaps.eosdis.nasa.gov/alerts/) around Ulaanbaatar during spring of 2017.

Fig. 6 Correlations of $PM_{2.5}$ concentrations (μg m^{-3}) of mannosan and galactosan with levoglucosan during winter (a) and spring (b) of 2017.

Fig. 7 Correlation between $PM_{2.5}$ concentrations of (a) OC (μg C m^{-3}) and levoglucosan (μg m^{-3}) and (b) K^+ and levoglucosan (μg m^{-3}) in during winter and spring of 2017.

Fig. 8 Correlation between $PM_{2.5}$ concentrations of OC (μg C m^{-3}) and K^+ (μg m^{-3}) during winter (a) and spring (b) of 2017.

Fig. 9 Scatter plot of levoglucosan/K^+ versus levoglucosan/mannosan from different types of BB emissions, including those measured in Ulaanbaatar (blue circles and red squares).

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

Fig. 10. Comparison of previously reported OC/levoglucosan ratios for softwood burning.

Fig. 11 Graphical determination of optimized OC/levoglucosan ratios used to estimate $PM_{2.5}$ concentrations of OC_{BB} in Ulaanbaatar in winter (a) and spring (b) of 2017.

Fig. 12 Relative contributions (μg C m^{-3}) of OC_{BB} and $OC_{non\text{-}BB}$ to $PM_{2.5}$ in Ulaanbaatar during winter and spring of 2017.

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

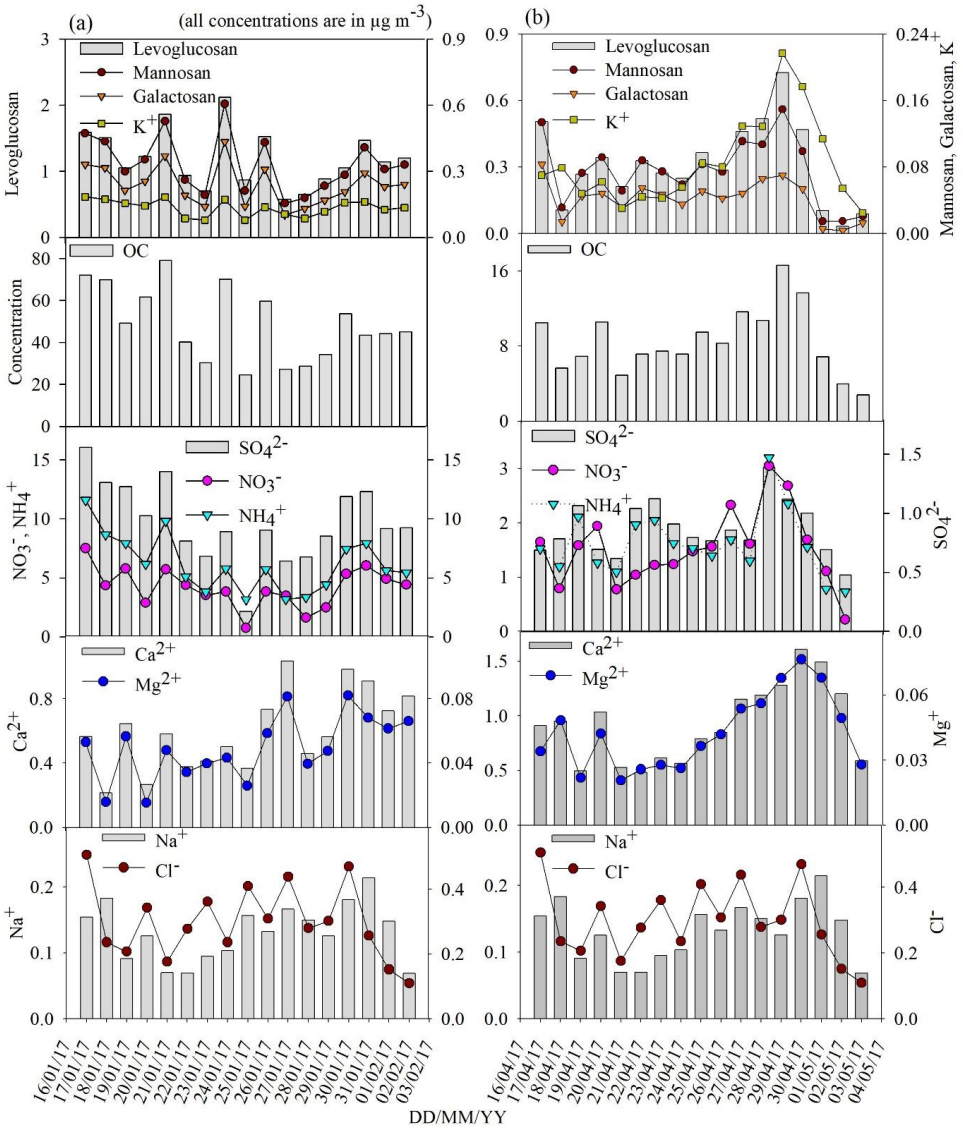
Atmospheric Chemistry and Physics
Discussions

Fig. 1

https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics
Discussions

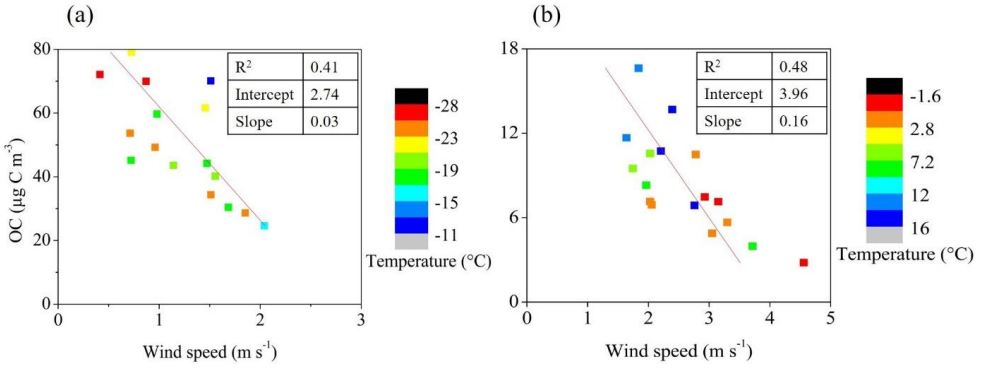
Fig. 2



https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions
Open Access

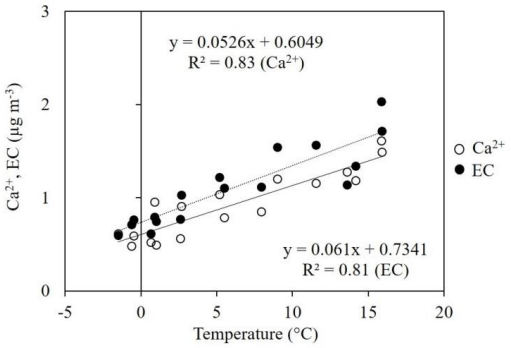
Fig. 3



https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics
Discussions

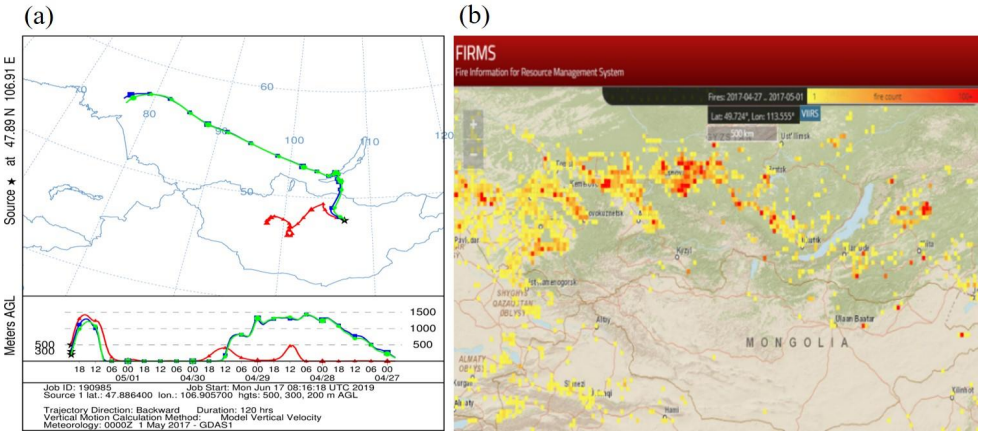
Fig. 4



https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions
Open Access

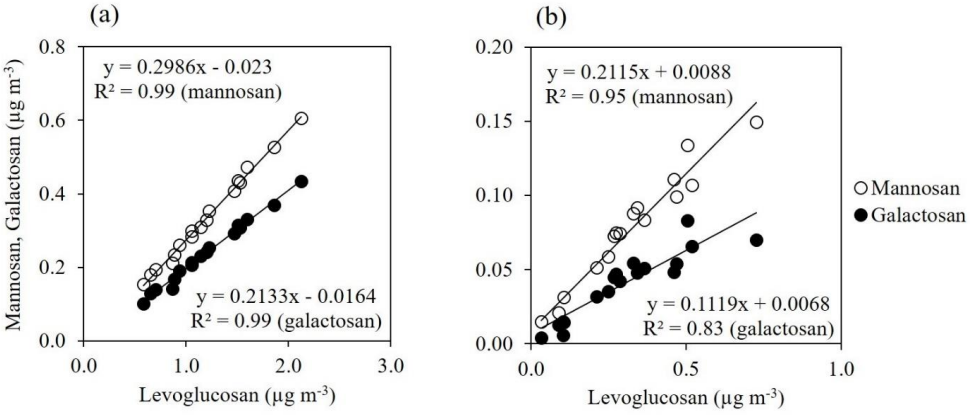
Fig. 5



https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions
Open Access
EGU

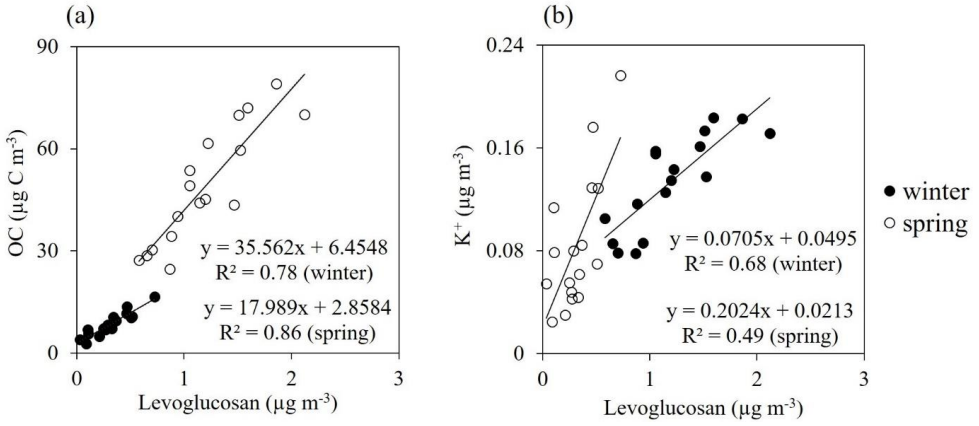
Fig. 6



https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics
Discussions

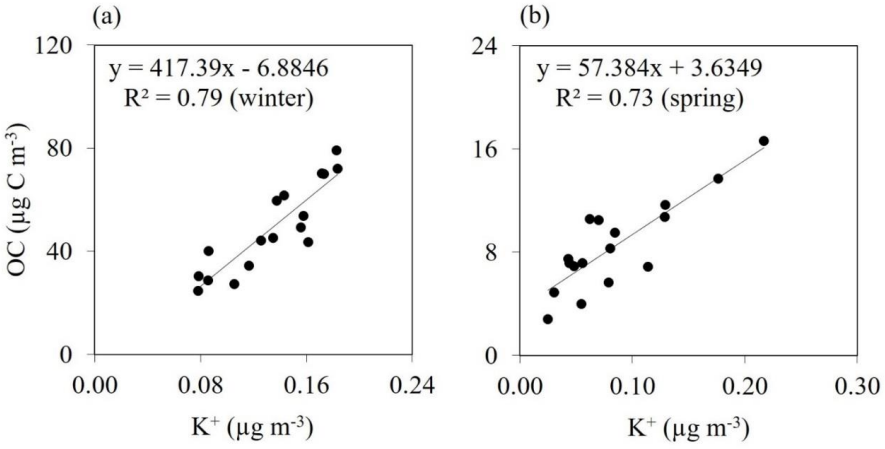
Fig. 7



https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions
Open Access
EGU

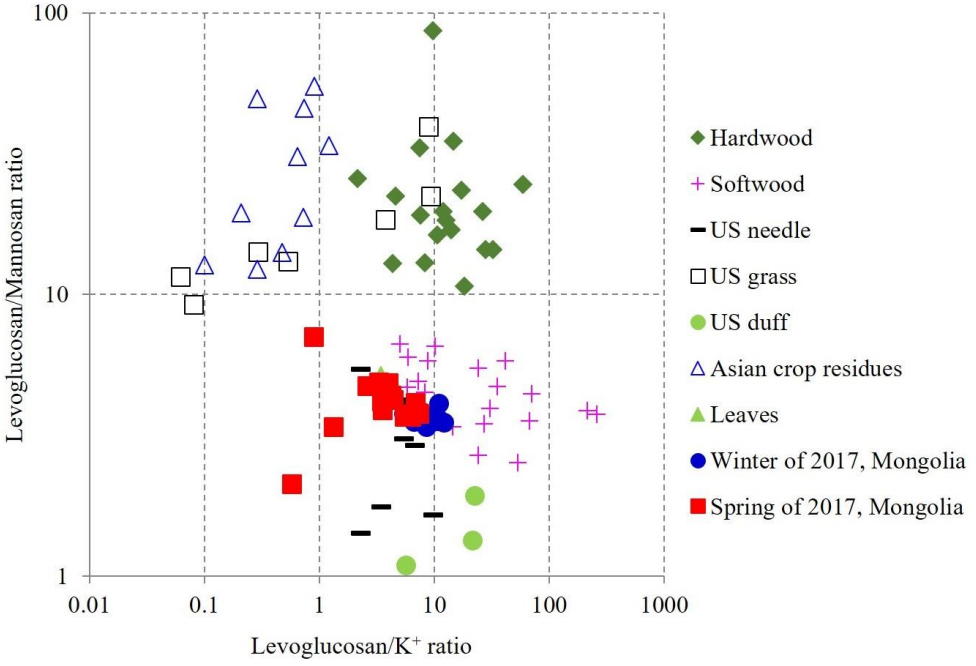
Fig. 8



https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

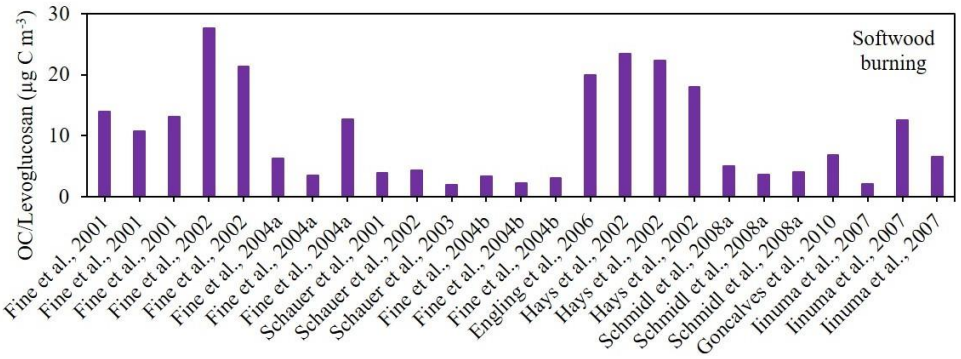
Fig. 9



https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

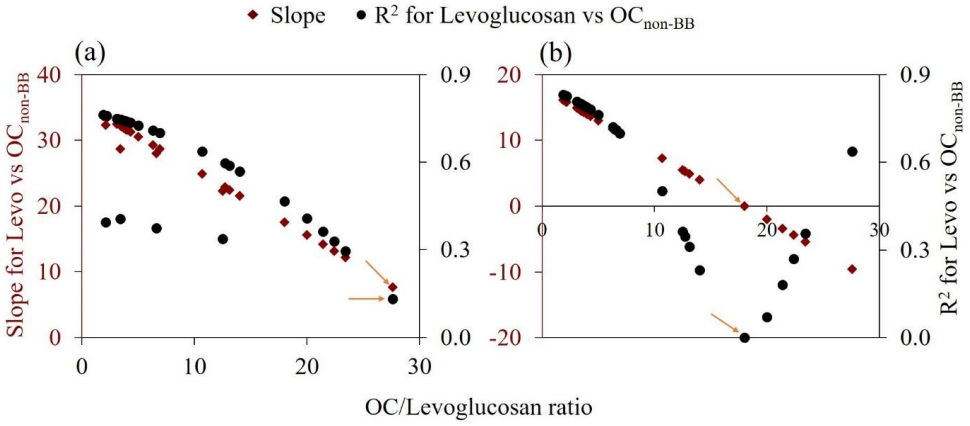
Fig. 10



https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

Fig. 11



https://doi.org/10.5194/acp-2019-831
Preprint. Discussion started: 27 September 2019

Atmospheric Chemistry and Physics Discussions

Fig. 12