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Biomass burning emissions contaminate winter snowfalls in urban Beijing: A case study in 2012

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ABSTRACT

Three monosaccharide anhydrides levoglucosan, mannosan and galactosan were detected in winter snowfall samples of 2012 in urban Beijing. Concentrations of three isomers vary from 0.15 to 54.43 ng mL^{-1}, with an average value of 10.49 ng mL^{-1}. Levoglucosan is the most abundant component. Winter snowfalls are contaminated by biomass burning emissions seriously in urban Beijing. The main sources are softwood and crop residue burnings around Beijing from late autumn to early winter, while long–range transport of biomass burning emissions contribute more during the late winter. Concentrations of monosaccharide anhydrides in snowfall samples may be affected by both topography and the meteorological conditions around urban Beijing.

Keywords: *Biomass burning aerosols, levoglucosan, snow chemistry, air pollution, urban Beijing*

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1. Introduction

Air pollution has been a widespread topic in recent years (Akimoto, 2003; Huang et al., 2014). Aerosols and greenhouse gases are the two main air pollutants (Akimoto, 2003). Aerosols can significantly alter the Earth's radiation by scattering and absorbing solar radiation, and impact microphysical characteristics of cloud droplets (Ramanathan et al., 2001; Gyawali et al., 2009). Atmospheric Brown Clouds (ABCs) caused by anthropogenic aerosols in South Asia has been received public attention due to the unclear effects on regional and global climate system and hydrological cycle (Ramanathan et al., 2001; Ramanathan and Crutzen, 2003). Similar phenomena were also observed at densely–populated regions like Central America, Brazil, the Mediterranean and North China in recent years (Ramanathan and Crutzen, 2003; Li et al., 2010).

Biomass burning (BB) emissions contribute to more than half of the carbonaceous aerosols (including both elemental carbon and organic carbon) all over the world (Jacobson et al., 2000; Gyawali et al., 2009). This is more serious in China, e.g. urban Beijing (Li et al., 2010; Cheng et al., 2013). Several studies suggested that air quality in Beijing was impacted significantly by BB emissions all year around, and winter was the most remarkable time (Wang et al., 2006a; Cheng et al., 2013; Yu et al., 2013). Burning of crop residue (include wheat–straw and cornstalk) and firewood were highlighted as two main sources of organic aerosols in urban Beijing from late autumn to winter (Wang et al., 2009; Yu et al., 2013). Aerosol samples collected from urban Beijing showed high concentrations of organic matter during winter time (Wang et al., 2006a; Zhang et al., 2008; Huang et al., 2014). The organic matter in aerosol particles has a complex composition in urban Beijing. More than one hundred kinds of organic compounds were identified in aerosol samples collected from urban Beijing (Wang et al., 2006a; Wang et al., 2006b). Polycyclic aromatic hydrocarbons (PAHs), n–alkanes, fatty acids and alcohols, polyols/poly acids, dicarboxylic acids and saccharides have been considered to be the main organic components (Wang et al., 2006b). Among various kinds of organic compounds, levoglucosan and its isomers showed similar variation patterns to traditional BB tracer K^+ all year around (Cheng et al., 2013). Levoglucosan accounts about 90% of total identified sugars in winter aerosols in urban Beijing (Zhang et al., 2008; Cheng et al., 2013). These studies confirmed that levoglucosan and its isomers could be useful biomarkers for BB studies in urban Beijing.

However, previous studies mainly focused on records of monosaccharide anhydrides (MAs) in aerosols (Wang et al., 2006b; Zhang et al., 2008; Cheng et al., 2013). Considering of their specific sources and characteristics, these MAs can be ideal biomarkers for BB studies in aqueous samples (You et al., 2014). In this study, levoglucosan, mannosan, galactosan were detected simultaneously using Gas Chromatography/Mass Spectrometry (GC/MS) method in winter snowfall samples collected from urban Beijing. The possible impact of BB on snowfall samples in urban Beijing was also analyzed.

2. Experiment and Methods

Snow samples were collected at The Campus of Institute of Psychology, Chinese Academy of Science (40°00'N, 116°22'E). The sampling site is located at central lawn of the campus, and there are no obvious BB sources within 5 km around. Fresh snow was collected in a plastic container with polyethylene (PE) bags when it began to snow. Samples were compacted into pre–cleaned polyethylene terephthalate (PET) bottles within half an hour after snowfall stopped. There were four snow samples collected in total from November 2012 to January 2013 (please see detailed sample information in Table 1). Samples were kept frozen at a temperature of –20 °C before analysis. Samples were dried by freeze–drying for at least 24 h, and then extracted three times using an ultrasonic method for 30 min in a 5 mL mixture of dichloromethane/ methanol=4/1 (v/v). After concentrated and dried completely under high purity N_2, samples were silylated by N–methyl–N–trimethylsi–lyltrifluoroacetamide containing 1% trimethylchloro-silane before GC/MS analysis. Silylated extracts were analyzed using a Trace GC 2000 gas chromatograph connected to a PolarisQ ion trap mass spectrometer. More detailed information about the sample preparation and determination can been found in a previous study (You et al., 2014).

Table 1. *Meteorological data in four snowfall events*

	T [a] (°C)	RH [b] (%)	SEW [c] (mm)	WS [d] (m s^{-1})	WD [e]
Nov 4th 2012	2.9	82	48.9	5.2	N [f]
Dec 12th 2012	–2.1	69	0.2	1.6	SWW [g]
Dec 21st 2012	–4.6	71	0.6	0.8	SWW [g]
Jan 20th 2012	–2.5	72	2	0.9	SE [h]

[a] *Temperature,* [b] *Relative humidity,* [c] *Snow equivalent water,* [d] *Wind speed,* [e] *Wind direction,* [f] *North,* [g] *South West West,* [h] *Southeast*

Meteorological data is from the China Meteorological Administration. To identify the BB source regions more clearly, backward trajectories were calculated by HYSPLIT model and MODIS hotspot data (1 km×1 km, AFD, 2013) were used (Justice et al., 2002). Because the lifetime of BB aerosols are usually no more than a week (Ramanathan and Crutzen, 2003), seven days backward air mass trajectories were used in this study. The matrixes (centered with sample site, 0.1°×0.1°, 9 points) instead of single–points were used to identify the potential about BB sources around sampling site in HYSPLIT model. The height of the atmospheric boundary layer (ABL) varied from 300 to 600 m above ground level (AGL) in urban Beijing during winter time (Guinot et al., 2007). The height of 100 m (green line), 500 m (blue line) and 3 000 m (red line) AGL was set to analyze the backward trajectories in ABL, the top of ABL and above ABL, respectively.

3. Results and Discussion

3.1. BB aerosols contaminate winter snowfall samples

Concentrations of three isomers in winter snowfall samples ranged from 0.15 to 54.43 ng mL^{-1}, with an average value of 10.49 ng mL^{-1}. Levoglucosan with an average value of 25.30 ng mL^{-1}, accounts for more than 80% of the total detected MAs. Detailed results can be seen in Table 2. Levoglucosan, mannosan and galactosan can only be generated from the degradation of cellulose and hemicellulose when the burning temperature is higher than 300 °C (Simoneit et al., 1999). Therefore, those three MAs are specific biomarkers for BB aerosols. The existence of those three MAs indicates that winter snowfall samples in urban Beijing are substantially contaminated by BB emissions.

Previous observation and modeling results indicated that wet deposition was the dominant sink for organic matter, especially at middle and low latitude regions (Hu et al., 2013). The following equation is used to transform the concentrations of MAs in snow samples to their related concentrations in the atmosphere (Davidson et al., 1993):

$$C_a = \rho_a \times C_s/\omega \quad (1)$$

where C_a is concentration of species (ng m^{-3}) in the atmosphere, p_a is air density (g m^{-3}) under the standard temperature and pressure (0 °C and 1.01×10^5 Pa, in this study the value of 1 293 g m^{-3} is used), C_s is concentration of MAs (ng g^{-1}, actually equals to ng mL^{-1}) in snow, and ω is the scavenging ratio for specific species by snowfall. The value 125 was recommended as a worldwide mean of ω for both black carbon and organic matter (Jacobson, 2004), and this value is used to estimate the concentrations of MAs approximately in this study.

Concentrations of MAs in the atmosphere estimated by the Equation (1) in four snowfall events are shown in Table 2. Total concentrations of MAs varied from 16.01 to 683.15 ng m^{-3}, with an average of 325.61 ng m^{-3}. Levoglucosan concentrations ranged from 6.86 to 563.07 ng m^{-3}, with an average of 261.65 ng m^{-3}. Results in this study can be comparable to previous aerosol studies in urban Beijing. Concentration of levoglucosan was about 575 ng m^{-3} in $PM_{2.5}$ aerosol samples in winter (Zhang et al., 2008). Concentrations of levoglucosan varied from 60 to 1 940 ng m^{-3}, with a mean value of 590 ng m^{-3}, and concentrations of mannosan varied from 50 to 190 ng m^{-3} in typical winter aerosol samples (Cheng et al., 2013). However, the estimated concentrations of MAs in this study are much higher than previous aerosol studies at other regions in China. Concentrations of levoglucosan in aerosols at Mount Tai during the wheat straw burning period varied from 88 to 1 210 ng m^{-3}, with an average of 403 ng m^{-3} (Fu et al., 2008). Concentrations of levoglucosan in winter aerosols in Guangzhou varied from 57.9 to 269.3 ng m^{-3}, with an average value of 176.6 ng m^{-3} (Ma et al., 2009). The concentrations of levoglucosan at Hong Kong ranged from 26.2 to 133.7 ng m^{-3} (Sang et al., 2011). Those comparable results evidently proved that snowfall samples in urban Beijing were seriously contaminated by BB emissions.

3.2. Identification of BB sources

Previous studies suggested different ratios of MAs (e.g. levoglucosan/mannosan) can be useful to identify the BB sources in urban Beijing (Cheng et al., 2013). Although degradation happens during the transport process, the impact of the degradation on the ratios among MAs has been considered to be limited (Hu et al., 2013). Different snow samples display distinct ratios of levglucosan/ mannosan, indicating that snowfall samples in urban Beijing are contaminated by various sources of BB in winter (Table 2 and Figure 1). The ratio of levoglucosan/mannosan is 10.32 for December 12th and 8.86 for December 21st 2012, respectively. The ratios are consistent with results of aerosol studies in Beijing (levoglucosan/mannosan with an average of 9.01±1.47 for typical winter samples) (Cheng et al., 2013). Snowfall samples on December 12th and December 21st 2012 may be contaminated by mixed aerosols released from softwood and crop residual (Figure 1). Hardwood, grass and leaf burning may also act as non–negligible sources. However, ratios of levoglucosan/mannosan on November 4th 2012 and January 20th 2013 are different from previous aerosol studies, which indicate snowfalls on these two days are contaminated by different BB emission sources. Compared with previous studies (please see detailed data in the Supporting Material, SM), the possible sources are soft wood, needle and duff burning on November 4th 2012 and snowfall on January 20th 2013 may be contaminated by hardwood burning. This classification method may have some uncertainties, because it is based on limited statistical analysis results from previous studies. However, this method can help us to understand the contaminations of snowfall samples caused by BB aerosols at some extent.