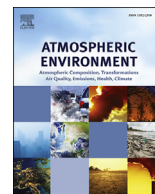




Contents lists available at ScienceDirect

## Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

# Observations of biomass burning tracers in PM<sub>2.5</sub> at two megacities in North China during 2014 APEC summit



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## H I G H L I G H T S

- LG/MN and K<sup>+</sup>/LG ratios varied significantly during APEC.
- Biomass burning aerosol decreased dramatically during APEC, but increased to higher level after APEC.
- Applying biomass burning control measures can effectively reduce PM<sub>2.5</sub>.
- Open biomass and residential burning both need to be controlled.

## A R T I C L E I N F O

### Article history:

Received 11 February 2017

Received in revised form

29 July 2017

Accepted 3 September 2017

Available online 5 September 2017

### Keywords:

Atmospheric aerosols

Fine particulate matter

Biomass burning sources

Emission controls

Source-apportionment analysis

## A B S T R A C T

To evaluate the effectiveness of biomass burning control measures on PM<sub>2.5</sub> reduction, day- and nighttime PM<sub>2.5</sub> samples were collected at two urban sites in North China, one in Beijing (BJ) and the other in Shijiazhuang (SJZ), during the 2014 Asia-Pacific Economic Cooperation (APEC) summit. Typical biomass burning aerosol tracers including levoglucosan (LG), Mannosan (MN), and water-soluble potassium (K<sup>+</sup>), together with other water-soluble ions and carbonaceous species were determined. The levels of biomass burning tracers dropped dramatically during the APEC period when open biomass burning activities were well controlled in North China, yet they increased sharply to even higher levels during the post-APEC period. Distinct linear regression relationships between LG and MN were found with lower LG/MN ratios from periods with much reduced open biomass burning activities. This was likely resulted from the reduced open crop residues burning and increased residential wood burning emissions, as was also supported by the simultaneous decrease in K<sup>+</sup>/LG ratio. The positive matrix factorization and air quality model simulation analyses suggested that PM<sub>2.5</sub> concentration produced from biomass burning sources was reduced by 22% at BJ and 46% at SJZ during the APEC period compared to pre-APEC period, although they increased to higher levels after APEC mainly due to increased residential biomass burning emissions in winter heating season. Biomass burning was also found to be the most important contributor to carbonaceous species that might cause significant light extinction in this region. This study not only suggested implementing biomass burning controls measures were helpful to reduce PM<sub>2.5</sub> in North China, but also pointed out both open crop residues burning and indoor biomass burning activities could make substantial contributions to PM<sub>2.5</sub> and its major components in urban areas in North China.

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## 1. Introduction

Biomass burning releases tremendous amounts of particles and gases into the atmosphere and has exerted significant impacts on

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global climate, regional air quality and human health (Andreae and Merlet, 2001). Aerosols emanated from biomass burning consist of complex mixtures of inorganic and organic compounds, of which most are water soluble and can modify aerosol hygroscopic properties and influence cloud formations (Prenni et al., 2012). Biomass burning is likely the largest contributor of black carbon and an important source of brown carbon on global scale; these compounds can effectively absorb solar radiations and thus affect visibility and climate (Andreae and Gelencsér, 2006; Bond et al., 2004).

Anhydrosugars, such as levoglucosan (LG) and mannosan (MN), are the thermal decomposition products of cellulose and hemicellulose containing materials (Simoneit, 2002). LG is generated from the glucose units of cellulose and hemicellulose when undergoing pyrolysis processes, while MN evolves in a similar way but from the mannose units of hemicellulose (Otto et al., 2006). They are emitted in considerable amounts during biomass burning processes and have not been found in other types of combustion (Simoneit, 2002), rendering them as good molecular tracers for biomass burning. Although LG is subject to degradation in the atmosphere when exposed to strong oxidants such as hydroxyl radical, as recently demonstrated in laboratory studies (Hennigan et al., 2010; Hoffmann et al., 2010), it is still a reliable biomass burning tracer for conservatively estimating biomass burning contributions to ambient aerosols (Ho et al., 2014; Zhang et al., 2013b, 2010a, 2010b). Furthermore, the relative abundances of individual anhydrosugars are suggested to be indicators for specific types of biomass burning aerosols, as various biomass materials contain different amounts of cellulose and hemicellulose. For example, the LG-to-MN ratio was proposed to identify the softwood burning aerosols from those derived from the burning of hardwood and crop residues (Engling et al., 2009; Schmidl et al., 2008). Water-soluble potassium ( $K^+$ ) is also regarded as a reliable tracer for biomass burning (Duan et al., 2004), although other additional sources such as mineral dust, sea salt and meat cooking could also produce  $K^+$  (Schauer et al., 2002). However,  $K^+$  in fine particle is typically well correlated with LG, suggesting biomass burning as its major source (Zhang et al., 2015).

China is currently suffering serious  $PM_{2.5}$  pollution and severe haze events, especially in the Beijing-Tianjian-Hebei (BTH) region in North China (Huang et al., 2014; Tao et al., 2017). According to the annual report released by the Minister of Environmental Protection of China, up to 88.8% or 143 cities failed to meet the ambient  $PM_{2.5}$  standard ( $35 \mu g m^{-3}$  annually) in China for the year of 2014. Among the ten worst performing cities, eight were located in the BTH region with the annually  $PM_{2.5}$  concentration registered as  $93 \mu g m^{-3}$ . North China is one of the major granaries in China since it provides more than 20% of the nation's grain, and thus produces large amounts of crop residues, which are commonly burnt in field during the harvest seasons. Moreover, residential wood and crop residues burning for heating and cooking are common practices in vast rural areas of North China, and contribute significantly to regional pollution events and haze formation. For example, Cheng et al. (2013) showed that about 50% of the OC and EC in Beijing was associated with biomass burning processes. Sun et al. (2016) estimated that around 60% enhancement of absorption in the ultraviolet spectral region at a suburban site of Beijing was due to the organic compounds from biomass burning.

Although biomass burning contributes a significant portion of  $PM_{2.5}$  loading and plays a key role in haze formation in North China, little has been done to control biomass burning emissions. Knowledge is needed on the effectiveness of biomass burning controls on reduction of  $PM_{2.5}$  and its major components. To ensure better air quality at Beijing during the 2014 Asia-Pacific Economic Cooperation (APEC) summit, a series of emission reduction measures were enforced from 1 to 12 November 2014 covering the entire region of North China (Wang et al., 2015). In particular, open

crop residues burning activities were prohibited in the neighboring provinces around Beijing. This provided a good opportunity for gaining knowledge of biomass burning contributions to  $PM_{2.5}$  under various emission scenarios and evaluating the effectiveness of biomass burning control policies. Typical biomass burning tracers (i.e. anhydrosugars and potassium) in  $PM_{2.5}$  and chemically resolved components were then obtained in two megacities in North China covering the periods of pre-, during- and post-APEC summit. Furthermore, the effectiveness of biomass burning control measures on  $PM_{2.5}$  were evaluated through positive matrix factorization (PMF) analysis and air quality model simulation. Knowledge gained from the present study provides the much needed information for making future biomass burning emission control policies in North China and other regions with similar pollution issues.

## 2. Experimental

### 2.1. Sites and sampling

Two urban sites in North China, 280 km apart, were selected for aerosol sampling. The first sampling site was in Beijing located inside the Chinese Research Academy of Environmental Sciences (BJ,  $116^{\circ}24'E$ ,  $40^{\circ}02'N$ ). A four-channel aerosol sampler (RP2300, Thermo Scientific, USA) was set on the roof of an office building (~15 m above ground). This site is surrounded by several traffic roads and many residential/commercial buildings without any obvious industrial or open biomass burning activities.

The second sampling site was in Shijiazhuang located at the four-floor platform (~20 m above ground) of the Shijiazhuang TV tower (SJZ,  $114^{\circ}32'E$ ,  $38^{\circ}02'N$ ). The city neighbors Beijing in the north and lies against continuous Taihang Mountain in the West. It has been experiencing rapid growth and industrialization since the 1950s and has become the capital and the largest city of the Hebei province with a population of more than ten million. Based on the Chinese air quality monitoring network report for 2014, air quality in this city ranked the top three worst cities among 143 major ones in China with  $PM_{2.5}$  as the primary pollutant. This site is situated at the Century Park within the Second Ring Road surrounded by residential and commercial areas. Another four-channel aerosol sampler (TH-16A, Wuhan Tianhong instruments, China) was used at this site.

Day- and nighttime  $PM_{2.5}$  samples were both collected on 47 mm teflon filters (PTFE, Whatman) and 47 mm pre-baked quartz fiber filters (QMA, Whatman). Daytime samples were collected from 0800 to 1900 while the nighttime ones from 2000 to the next day 0700 local time. The samples collected by teflon filters were used for determining  $PM_{2.5}$  mass concentrations and water-soluble ions, while those collected by quartz fiber filters were applied for analyzing carbonaceous species and anhydrosugars. Static field blanks were collected by mounting filters on the samplers for around 11 h without turning the pump on. The collected samples and blanks were stored at  $-20^{\circ}C$  before weighting and chemical analysis.

### 2.2. Weighting and chemical analysis

$PM_{2.5}$  mass concentrations were determined by weighing teflon filters using a Sartorius MC5 electronic microbalance ( $\pm 1 \mu g$ , Sartorius, Germany). Filters were equilibrated for 24 h before weighting under constant conditions (temperature  $23 \pm 1^{\circ}C$ , relative humidity  $40 \pm 5\%$ ) and weighted for at least three times before and after sampling. Differences among replicate weights were less than  $20 \mu g$ . Net mass was obtained by subtracting pre-weight from post-weight (Tao et al., 2016).

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