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Chemical characteristics and light-absorbing property of watersoluble organic carbon in Beijing: Biomass burning contributions

Caiqing Yan ^a, Mei Zheng ^{a, *}, Amy P. Sullivan ^b, Carme Bosch ^c, Yury Desyaterik ^b, August Andersson ^c, Xiaoying Li ^a, Xiaoshuang Guo ^a, Tian Zhou ^a, Örjan Gustafsson ^c, Jeffrey L. Collett Jr. ^b

^a State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China

^b Department of Atmospheric Science, Colorado State University, Fort Collins, CO, 80523, USA

^c Department of Environmental Science and Analytical Chemistry (ACES) and the Bolin Centre for Climate Research, Stockholm University, 10691, Stockholm, Sweden

HIGHLIGHTS

- High and relatively stable levoglucosan concentrations were found in Beijing in winter.
- Light absorption from biomass burning to WSOC was evaluated in Beijing.

• Light absorption (300-400 nm) by WSOC relative to EC was ~40% (winter) and ~25% (summer).

• Residential biomass burning is non-negligible source to fine PM in Beijing winter.

A R T I C L E I N F O

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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 $2.5 \,\mu\text{m}$) 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 ± 145 ng m⁻³) in winter. Ratios of levoglucosan/mannosan (L/M) and levoglucosan/galacosan (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 ± 0.16 m² g⁻¹ in winter and 0.73 ± 0.15 m² g⁻¹ in summer. Biomass burning derived WSOC accounted for 23 \pm 7% and 16 \pm 7% of total WSOC mass, and contributed to 17 \pm 4% and 19 \pm 5% 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.

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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

* Corresponding author. *E-mail address:* mzheng@pku.edu.cn (M. Zheng). with large emissions of gases (including greenhouse gases like CH₄ and CO₂) 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). Watersoluble 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 and Bond, 2010; Hecobian et al., 2010; Kirchstetter and Novakov, 2004; Kirillova et al., 2013, 2014a, 2014b; Lukács 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, 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, or 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 on 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 h. 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. (2013b). 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 μ m.

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 highvolume sample was extracted in 10 mL of deionized water (DI water, >18 M Ω) in a Nalgene amber HDPE bottle with ultrasonication 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 from source testing also followed the above water-soluble organics analysis procedure. Ambient particles collected on Teflon filters were also 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, m² g⁻¹) at 365 nm was calculated based on equation (1):

$$\mathsf{MAE}_{\lambda} = \frac{Abs_{\lambda}}{[WSOC]} = \frac{(ATN_{\lambda} - ATN_{700}) \times \frac{V_{w}}{V_{a} \times l} \times \ln(10)}{[WSOC]}$$
(1)

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