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Quantitative determination of the biomass-burning contribution to atmospheric carbonaceous aerosols in Daejeon, Korea, during the rice-harvest period

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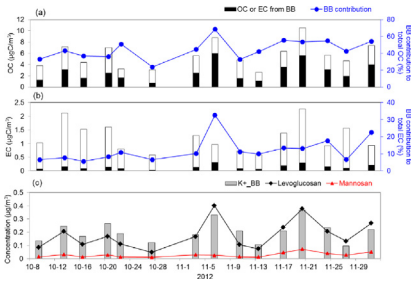
HIGHLIGHTS

- K^+ alone is not suitable as a biomass burning trace in Daejeon during fall.
- BB aerosols were mainly emitted from burnings of crop residue, grass, and leaves.
- 45 ± 12% of OC was emitted from BB burning.
- 12 ± 7.3% of EC was emitted from BB burning.

GRAPHICAL ABSTRACT



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ABSTRACT

To investigate the impact of biomass-burning emissions on atmospheric carbonaceous aerosols, the biomass burning tracers; levoglucosan, mannonsan, galactosan, and K^+ were measured at a suburban site in Daejeon, Korea, during the rice-harvest period, during the fall, 2012. The emissions of K^+ from biomass burning (K^+_{BB}) were estimated by subtracting sea-salt K^+ and soil K^+ concentrations from measured K^+ concentrations. Regression analysis of levoglucosan and K^+_{BB} reveals that K^+_{BB} alone is not suitable as a biomass-burning tracer in the Daejeon atmosphere, especially when the biomass-burning contribution is low. Levoglucosan to K^+_{BB} ratios during the study period ranged from 0.40 to 1.39, with an average of 0.89 ± 0.30, whereas levoglucosan to mannosan ratios ranged from 4.61 to 15.45, with an average of 6.70 ± 2.69. The ratios of levoglucosan to mannosan, K^+, organic carbon (OC), and elemental carbon (EC) show that biomass-burning aerosols in the Daejeon atmosphere during the rice-harvest period are emitted mainly from crop residue, grass, and leaf burnings. The contributions of biomass-burning emissions to OC and EC concentrations were 45% ± 12% and 12% ± 7.3%, respectively, indicating that a large fraction of OC was emitted from biomass burning.

1. Introduction

Biomass burning, which includes wildfires, prescribed burnings, agricultural waste burnings, and domestic biofuel combustion, emits large masses of trace gases and particulate matter to the troposphere (Andreae and Merlet, 2001; Schmidl et al., 2011; Zhang et al., 2013a). Aerosols from biomass burning can act as cloud

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condensation nuclei (Crutzen and Andreae, 1990; Novakov and Corrigan, 1996; Petters et al., 2009; Rose et al., 2010), causing strong radiative forcing (Penner et al., 1992; Hobbs et al., 1997; Wang et al., 2007). A global inventory of carbonaceous aerosols (Bond et al., 2004) suggests that biomass burning is the largest source of organic (OC) and elemental carbon (EC) in the atmosphere, and Streets et al. (2003a) report that biomass burning is the second largest source of OC and EC emissions in Asia. However, despite their potentially large contribution to air pollution in Asian cities (Oanh et al., 2006), biomass-burning emissions are often overlooked in air quality management practices, mainly due to a lack of reliable information on their sources and magnitudes.

There are two types of biomass burning in East Asia: agricultural residue burning after the barley and wheat harvest (between late spring and early summer), and agricultural residue burning after the rice harvest (in the fall) (Ryu et al., 2004; Tao et al., 2013; Zhang et al., 2013b). Post-harvest crop residue burning in open spaces or as biofuel in home stoves is an important source of biomass burning in East Asia (Streets et al., 2003b; Ryu et al., 2006), but information on the nature and abundance of biomass-burning aerosols in East Asia is limited.

In June 2006, an intensive field campaign (MTX2006) was conducted in central East China during a period of intensive wheat-straw burning (Kanaya et al., 2013). Sharp increases in biomass-burning tracers, such as levoglucosan and its isomers and OC, were observed during this period (Fu et al., 2008). However, there has been no systematic investigation of the impacts of agricultural practices on ambient particulate matter (PM) levels in this region, and a quantitative estimate is needed to understand the possible impacts of PM on air quality and climate change in East Asia.

In East Asia, outflows of pollutants from the Asian continent are a complex mixture of inorganic species, organic compounds, black carbon, minerals, and water, all emitted from various sources (Seinfeld et al., 2004). Areas downwind of the prevailing westerly flow across the Asian continent are frequently influenced by the long-range transport of these aerosols (Jung and Kim, 2011). Thus, it is important to characterize the source contributions of aerosols in Asia and downwind areas.

A growing number of studies have focused on the apportionment of biomass-burning emissions to ambient aerosols over the Asian continent (Duan et al., 2004; Cao et al., 2005; Zheng et al., 2005; Zhang et al., 2008; Cheng et al., 2013). For example, using regression analyses on OC and K^+, Duan et al. (2004) estimated that ~46%–70% of OC originated from post-harvest wheat residue burning in a mountainous area near Beijing, China, between May and July 1998 (Duan et al., 2004). Using the levoglucosan to OC ratio, Zhang et al. (2008) estimated the contribution of biomass burning to carbonaceous aerosols in the Beijing area to be 18%–38% of the $PM_{2.5}$ (PM with an aerodynamic diameter less than 2.5 μm) OC and 14%–32% of the PM_{10} (PM with an aerodynamic diameter less than 10 μm) OC. Further, positive matrix factorization (PMF) showed that ~50% of OC and EC in the Beijing atmosphere during 2011–2012 originated from biomass burning (Cheng et al., 2013). Zheng et al. (2005) used a chemical mass balance (CMB) receptor model in combination with particle-phase organic compounds as fitting tracers to show that the contribution of biomass-burning aerosols to the $PM_{2.5}$ mass was ~12% at five urban and rural sites in Beijing during the fall of 2000. The contribution of biomass-burning aerosols to the $PM_{2.5}$ mass was estimated to be ~11%–16% at urban and rural sites in Beijing during the fall of 2006 using the PMF method (Wang et al., 2008).

To quantitatively determine the impact of biomass-burning emissions to ambient aerosols, it is essential to correctly identify biomass-burning tracers. Common biomass-burning tracers include three isomeric anhydrous sugars: levoglucosan (1,6-anhydro-ß-D-glucopyranose), mannosan, and galactosan, as well as K^+ (Andreae and Merlet, 2001; Simoneit, 2002). These isomeric anhydrous sugars are formed during pyrolysis of cellulose and hemicellulose, and are not emitted from burning other materials, such as fossil fuels (Simoneit et al., 1999; Caseiro et al., 2009; Elias et al., 2001). However, because K^+ can also be emitted from sea salt and soil (Pio et al., 2008), caution is required when using K^+ as a biomass-burning tracer.

Recent laboratory chamber experiments have shown that levoglucosan to mannosan ratios and levoglucosan to mannosan (or K^+) ratios can be used as indicators of specific biomass-burning types (Schmidl et al., 2008a,b; Cheng et al., 2013). Several studies have also used levoglucosan to OC ratios as well as levoglucosan to PM ratios to estimate the contribution of biomass-burning emissions to ambient aerosols (Fine et al., 2002; Puxbaum et al., 2007; Schmidl et al., 2008a). Large differences in levoglucosan to OC ratios, as well as levoglucosan to PM ratios, have been observed for different types of biomass burning (Sullivan et al., 2008; Gonçalves et al., 2010; Harrison et al., 2012). If biomass-burning types are not correctly identified, this type of estimations based on ratios are problematic as levoglucosan to OC ratios as well as levoglucosan to PM ratios have been shown to be strongly dependent on biomass-burning types.

In this study, we quantified four biomass-burning tracers; levoglucosan, mannosan, galactosan, and K^+, in aerosols collected in Daejeon, Korea, during the rice-harvest period and evaluated these tracers using regression analysis. Biomass-burning emission sources were also determined using levoglucosan to K^+ ratios and levoglucosan to mannosan ratios. Finally, we quantified the contribution of biomass-burning emissions to OC and EC concentrations using the identified biomass types and levoglucosan to OC and EC ratios.

2. Experimental methods

2.1. Atmospheric aerosol sampling and sample preparation

Integrated PM_{10} sampling was carried out for three days at a suburban site (36°23′19″ N, 127°22′21″ E) in Daejeon, Korea, from 8 October to 3 December 2012. The PM_{10} aerosol samples were collected on pre-baked quartz fiber filters (20 × 25 cm, Pall-Life Sciences, Ann Arbor, MI, USA) using a high volume air sampler (PM10HVPLUS, Tisch Environment Inc., Cleves, OH, USA) at a flow rate of 67.8 $m^3\ h^{-1}$ on the rooftop of a chemistry building (~15 m above the ground) at the Korea Research Institute of Standards and Science (KRISS). Before and after sampling, filter samples were stored in zip-lock plastic bags (3M, SCC1500) and wrapped with aluminum foil at −20 °C. A total of 15 filter samples were collected in this study, and additional field blank filters were collected before and after the sampling period. Hourly carbon monoxide (CO) concentrations were obtained from the Korean National Observatory located ~1.8 km south of the sampling site (http://www.airkorea.or.kr/airkorea/eng/index.jsp).

Ultrapure water used in this study was prepared using a Labpure S1 filter with a UV lamp, with resistivity and TOC values of 18.2 MΩ cm^{-1} and 1 ppb, respectively (ELGA, PureLab Ultra). To measure carbohydrates and water-soluble K^+, an aliquot (2.01 cm^2) of each filter sample was extracted with 10 mL of the ultrapure water under ultrasonication (for 30 min) and then passed through a disk filter (Millipore, Millex-GV, 0.45 μm). Water extracts were stored in a refrigerator at 4 °C before analysis.

2.2. Analysis of saccharidic tracers emitted from biomass burning

Levoglucosan, mannosan, and galactosan were determined by an improved high-performance anion-exchange chromatography