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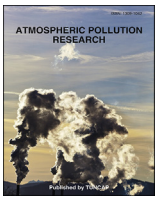

Original article

Characteristics of individual particles in a severe short-period haze episode induced by biomass burning in Beijing

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ABSTRACT

Atmospheric particles were investigated from a haze episode in autumn 2012 in Beijing that was caused by transported pollutants emitted from biomass burning during the crop harvest season in the North China Plain. Four samples from haze and one sample from clean atmosphere were collected in sequence by a multiple-stage cascade impactor. Based on morphology and elemental compositions, the particles were classified into five types: accumulation-mode secondary particles with and without coating, naked and core–shell soot, and other particles. The ratios of accumulation-mode secondary particles to soot containing particles were 4.0, 2.3, 1.7, 1.8, and 5.5, i.e., secondary particles in haze were proportionally less abundant than those in clean air, which was caused by the different dominant secondary formation mechanisms during hazy and clean periods. Meanwhile, the ratios of particles with coating to those without coating were 0.5, 1.0, 0.7, 0.6, and 0.2, implying that the particles in haze were likely more hygroscopic than those in clean air. In haze, the size distributions of particles were multi-modal, with main modes of approximately 0.55–0.85 μm, suggesting that the particles were from multiple sources due to the transported biomass burning plumes mixed with urban air. The size distribution was unimodal in clean air, and the mode was approximately 0.35 μm, with a mean equivalent diameter of 0.45 μm. The core–shell ratio distribution for soot particles collected in haze induced by biomass-burning aerosols was quite different from those in clean air, and soot particles were more aged in haze samples.

1. Introduction

Biomass burning is one of the most important atmospheric emissions throughout the world (Langmann et al., 2009). The emitted gaseous (SO_2, CO and NO_x, etc.), particulate (e.g., carbonaceous aerosols and potassium), and secondary pollutants from biomass burning significantly influence local and regional air quality, chemical processes, and even climate change (Keywood et al., 2013; Wang et al., 2015; Yan et al., 2015), as well as human health (Lighty et al., 2000). Particles emitted from biomass burning are important constituents of regional haze (Li et al., 2003). Combined with local pollutants in large cities, biomass smoke even affects weather patterns (Ding et al., 2013).

Emissions from biomass burning contain high concentrations of potassium, carbonaceous materials, and sulfate, nitrate, and ammonium, which are strongly hygroscopic (Adachi and Buseck, 2008). With high relative humidity (RH) during haze, these water-soluble particles grow quickly. The hygroscopicity of particles influences their optical properties, causing degradation of visibility and affecting their cloud-nucleating ability (Li et al., 2003; Zhang et al., 2008). Under certain situations, emissions may accumulate to become serious pollution and lead to regional pollution by long-range transport through atmospheric turbulence (de Gouw et al., 2004; Wang et al., 2011). The observation and modeling results indicate that pollutants from biomass burning can move

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across continents and that the Antarctic and Tibetan Plateau have already been influenced (Hu et al., 2013; Zhu et al., 2016).

In recent years, studies on biomass burning have mainly focused on monitoring through remote sensing, ground-based data synthesis, estimation of emission amounts, and emission inventory construction (e.g., Andreae and Merlet, 2001; Cao et al., 2005). Pósfai et al. (2003) found that transmission electron microscopy (TEM) is extremely powerful for characterizing biomass plumes and haze particles and provides information on particle agglomeration, coatings, and possible atmospheric reactions, although it has limitations (e.g., poor statistics due to intensive labor and particle vaporization under the electron beam in the vacuum). Li et al. (2016) concluded that single particle analysis, particularly TEM, is a suitable approach to characterize the size, morphology, and mixing states of soot particles in urban atmospheres. A few studies have characterized individual particles emitted from or influenced by biomass burning during strong haze events (e.g., Li et al., 2003, 2010; Pósfai et al., 2003). However, more details regarding the physical and chemical properties of these particles are required to better understand their impact on the environment and climate.

Globally, agricultural biomass burning constitutes almost 20% of total biomass burning emissions (Levine, 1990). The yield of agricultural straw in China is approximately 6×10^8 t a^{-1}. Although the government has banned the burning of straw repeatedly, straw is still burned randomly in fields (Li et al., 2014a). The particulate matter from open burning of straw was about 110.7 million tons in 2000 in China (Cao et al., 2005). Because key crops are mainly harvested in the summer and autumn, air pollution caused by biomass burning occurs seasonally.

As a megacity, Beijing is far from the large agriculture planting regions. However, Beijing has frequently encountered serious haze caused by biomass burning in nearby provinces, such as Shandong, Hebei, Henan, and even Anhui (Li et al., 2010; Wang et al., 2007). So far, information on the haze in Beijing induced by biomass burning plumes from nearby areas, especially accounting for the variation of meteorological condition, is minimal.

This study explored the pollution process and formation mechanism of a severe short-period haze episode in Beijing based on aerosol samples. The samples were collected during a haze episode induced by long-range transported pollutants from biomass burning, as well as in clean air following the haze episode. The aging processes of atmospheric particles under these different meteorological conditions, as well as the differences of the particle properties in biomass burning smokes after transport, were investigated through single particle analysis using TEM.

2. Sample site and instrumentations

2.1. Supersite for the online monitoring of aerosol characteristics

Measurements were conducted at an urban site named the PKU Urban Atmosphere Environment MonitoRing Station (PKUERS). This site is on the sixth floor of an academic building (20 m a.g.l.) on the campus of Peking University (39.99 °N, 116.31 °E), located in the northwestern urban area of Beijing and outside of the fourth ring road. No obvious stationary sources were found nearby the site (Wu et al., 2007). This site works as a supersite for monitoring complex air pollution (Hu et al., 2016). Continuous measurement of $PM_{2.5}$ mass concentration (TEOM 1400a, Thermo Scientific Inc., USA), and the concentrations of gaseous pollutants NO_2/NO (42i-TL, Thermofisher Scientific Inc., USA), O_3 (49i-TL, Thermofisher Scientific Inc., USA), SO_2 (43i-TL, Thermofisher Scientific Inc., USA), and CO (48i-TL, Thermofisher Scientific Inc., USA) were conducted. The meteorological parameters were measured by an automatic meteorological system (Met One Instruments, Inc., USA). Additionally, a multi-angle absorption photometer (MAAP, Thermo Scientific Inc., USA) was used for black carbon (BC) observation.

2.2. Samples of individual particles and TEM analysis

A multiple-stage cascade impactor was used to collect particles on Cu meshes those were coated with carbon-sprayed Formvar film. The 50% cut-off aerodynamic diameter of the sampler was approximately 1.1 μm, 0.2 μm and 0.2 μm for the first, second and third stages, respectively. The flow rate for sampling was 2.2 L min^{-1}. Five sets of samples were collected (see Table 1) on the roof of the building at the observation site. The sampling durations were 20–40 s. After collection, each mesh was preserved in a plastic capsule. The capsules were sealed in a plastic bag with paper-packaged silica gel and were kept at 4°C until analysis. Second and third stage samples were analyzed, focusing on fine particles. All of the times mentioned in this paper, unless otherwise stated, are Beijing standard time (BST), 8 h prior to UTC.

Using a TEM, samples were analyzed at an accelerating voltage of 200 keV. TEM images were randomly selected and photographed from the center to the margin on the mesh. The equivalent diameter and mixing stage of the particles were analyzed in the images. The equivalent diameter was determined by analyzing particles on the images, which is defined as a diameter of a circle that has the same projection area as the measured particle (Niu et al., 2012). Geometrical estimates from two dimensional (2D) electron microscopy images have been widely used to calculate the 3D shapes of particles, including soot particles, even though it is inaccurate (van Poppel et al., 2005; Li et al., 2016). With an assumption that spherical droplets or coated particles on the meshes after impaction are hemi-spherical, with the same volume as that before being captured, their equivalent diameters are approximately 1.3 times greater than their real geometric or volume equivalent (d_{ve}) diameters in the air (Niu et al., 2012; Zhang et al., 2006). During TEM imaging, 2500–3500 × magnification and very low-intensity beams were applied to alleviate the volatilization of particles. The elemental compositions were determined semi-quantitatively using an energy dispersive X-ray spectrometer (EDX) that was assembled with the TEM. EDX spectra were collected for 30 s to minimize radiation exposure and potential beam damage. The number of analyzed particles was 736, 991, 1105, 1057, and 1045 for Samples 1 to 5, respectively. The technical details on particle collection and analysis can be found in previous studies (Niu et al., 2011, 2012).

3. Results

3.1. Weather condition and air pollution

Fig. 1 shows the air pollution and weather conditions during the observation period. The five arrows on the X-axis indicate the individual particle collection periods. On 7 and 8 October, the air was stagnant, the wind speed was low, RH was high, and atmospheric pressure decreased to the lowest level (~1008 hPa). Under such conditions, pollutants cannot diffuse. In the morning of 7 October, winds came from north or northwest and $PM_{2.5}$ was lower than 100 μg m^{-3}. In the afternoon, the wind came from the south and became stronger, and $PM_{2.5}$ accumulated due to the low pressure. The concentrations of SO_2 and CO also rose with $PM_{2.5}$ increasing. The concentration of BC was stable at approximately 5 μg m^{-3} until 18:00 and then increased gradually. From the night of 7 October to the morning of 8 October, $PM_{2.5}$ remained stable (at approximately 120 μg m^{-3}) due to the static atmosphere, as did SO_2, CO and BC. On the afternoon of 8 October, as the wind direction changed to the

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