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Size-resolved carbonaceous components and water-soluble ions measurements of ambient aerosol in Beijing

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ABSTRACT

A MOUDI-120 sampler was used in Beijing to collect multi-stage samples in the summer and winter of 2013 to 2015. Thirty-three sample sets were collected during the daytime, nighttime, and different pollution levels. The actual relative humidity in the impactors was calculated for the first time. The carbonaceous components (organic and elemental carbon, OC and EC, respectively) and water-soluble inorganic ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) were analyzed in each sample. The characteristics of the mass concentration distribution and charge balance were discussed. On the basis of relative humidity in the impactors, aerosols less than 1.0 μm were sampled under relatively dry conditions in most cases. The concentration levels for the chemical species were higher in the winter than in the summer. Three modes (condensation mode, droplet mode, and coarse mode) could be identified from the distributions of NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, K^+, OC and EC. The distribution characteristics for the pollution dissipation process were different from the pollution accumulation process. NO_3^- and NO_2^- contributed most of the negative electric charges in the stage below 0.1 μm. In the condensation mode, the cations were dominated by NH_4^+, which was sufficient to balance the anions. In the droplet mode of the heavily polluted samples, the ammonium was not sufficient to balance the anions. In the coarse mode, the positive electric charges were primarily composed of metal cations. The analyzed anions were not sufficient to neutralize the measured cations.

Introduction

Size distribution is probably the most fundamental parameter for aerosol particles. The size distribution covers several orders of magnitude, from nanoscale to dozens of micrometers. Four modes of different size classes (nucleation mode, Aitken mode, accumulation mode, and coarse mode) have often been used when discussing aerosol number concentrations (Wu et al., 2008). Generally, particles in different modes have different sources or specific formation processes; thus, each chemical component has its typical size distribution. The new particle formation processes generally occur in the nucleation mode. New particles could grow into the Aitken mode by condensation and coagulation (Wu et al., 2007). Most of the particles in the Aitken mode arise from primary emissions of fossil fuel combustion. Aitken mode particles could also grow into the accumulation mode,

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which often consists of two sub-modes, the condensation mode and the droplet mode (John, 2011). The accumulation mode contains most of the mass and surface area of $PM_{2.5}$. The particles originating from anthropogenic sources, such as sulfates, nitrates, organics, ammonium, and black carbon, are primarily distributed in this mode. Because they cover the visible wavelengths, accumulation mode particles cause the majority of light extinction. In addition, the strong hygroscopicity of this mode further enhances visibility impairment (Yan et al., 2008; Garland et al., 2009; Ma et al., 2011). The coarse mode particles generally arise from crustal materials. Size-resolved chemical compositions, especially those of the carbonaceous components and water-soluble ions, provide important information for studying the formation mechanism, the light extinction effect, the radiation force, and the human health effects of atmospheric aerosols.

Size spectrometers based on electrical mobility, optical, or aerodynamic methods are commonly used to study the detailed aerosol number concentration distributions. The surface area concentration and mass concentration can also be calculated *via* the number concentration. An aerosol mass spectrometer is typically used for real-time analysis of chemical compositions. However this instrument is expensive and requires a great deal of labor. Generally, only the thermally unstable chemical species can be accurately measured by a mass spectrometer. Therefore, cascade impactors have also been widely used for size-resolved chemical composition analysis. The formerly used cascade impactors, such as the Andersen sampler, do not have the ability to differentiate submicron particles. However, the sulfates, nitrates, organics, ammonium, and black carbon are primarily distributed in submicron range. The size distribution data obtained by the Andersen sampler are not detailed enough for studying secondary formation, light extinction, or radiation force of aerosols. The latest model, the MOUDI-12X, has more than ten stages and could achieve the minimum cut point of 10 nm. The quality assurance or quality control (QA/QC) is important for effectively detecting different compositions from the filters because the amount of aerosol captured by the cascade impactors is quite low.

Many related studies on $PM_{2.5}$ chemical compositions have been performed in Beijing and in the surrounding areas. Research advances have been summarized in another study (Zhao et al., 2013a, 2013b). In comparison, fewer results on multi-stage (≥10 stages) size-resolved chemical compositions for aerosols in this region have been reported (Yao et al., 2003; Hu et al., 2005; Guo et al., 2010; Wang et al., 2013). However, only the distributions of water-soluble ions were discussed in the above studies. The wide-range of size distributions for elemental carbon or black carbon (EC or BC), especially in submicron range aerosols, are very important to mixing state or light extinction studies. However, there are no related results on the distributions of carbonaceous components obtained by the multi-stage cascade impactors in Beijing that have been published. In some studies, the volume fractions of BC were assumed to be the same value in different size bins, because of the lack of BC distribution results (Ma et al., 2011, 2012). The water-soluble organic compounds (WSOCs) comprise a substantial fraction of the organic aerosols and influence the hygroscopic properties of aerosols. Some studies in northern areas of China focused on the size distributions of WSOCs from samples collected by an Andersen sampler (Wang et al., 2011).

Relative humidity is one of the most crucial influencing factors for phases of the aerosol. For example, ammonium nitrate may exist as a solid or as an aqueous solution of NH_4^+ and NO^{3-} depending on the ambient RH (relative humidity). However, the pressure drop in the lower stages of impactors could evidently decrease the inner relative humidity. Thus, it is important to determine the actual relative humidity in each stage to evaluate the influence of hygroscopic growth on the aerosol size distributions. However, nobody has ever done the calculation of relative humidity in the impactors. In some studies, the relative humidity in different stages of the impactors was assumed to be the same as the relative humidity in ambient air when calculating the Stokes diameters in each stage (Liu et al., 2014).

In this study, size-resolved particles were sampled using a MOUDI sampler in the summer and winter, and carbonaceous components as well as water-soluble ions were analyzed. The MOUDI measurement was an important part of one comprehensive aerosol observations. In addition, the $PM_{2.5}$ mass concentration (Metone, 1020), aerosol number concentration distribution (SMPS + APS), absorption coefficient (MAAP 5012), scattering coefficient (M9003), and visibility (Belfort 6000) were synchronously obtained by on-line monitoring. One of the main purposes of these observations is to study the hygroscopic growth and light extinction ability of particles in different size ranges by using these size-resolved chemical composition data. Due to the WSOC accounted for only a small percentage of a hygroscopicity parameter κ in aerosol more than 30 nm, and accounting for even a smaller portion of the total light extinction (Liu et al., 2014), the WSOCs was not analyzed from the filter samples collected in this study. As mentioned above, the variations or differences of size-resolved chemical compositions between seasons and size ranges have not been fully analyzed in Beijing. In this paper, we mainly characterize the size distributions of light extinction species in different seasons or at different pollution levels, calculate the actual relative humidity in the impactors, and study the interrelationships among different compositions. Further analysis related to hygroscopic growth will be provided in other additional papers.

1. Sampling and analysis

All of the equipments were placed on the roof of the Institute of Urban Meteorological in the Haidian district (39.94°N, 116.30°E), approximately 36 m above the ground. A Micro-Orifice Uniform-Deposit Impactor (MOUDI-120) was used for aerosol sampling. The calibrated 50% cut sizes were 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.1, 6.2, 9.9 and 18 μm. The sampling flow was approximately 30 L/min. A TSI-4043 flowmeter was used to adjust the airflow. The MOUDI-120 could monitor the temperature inside of the cabinet and monitor the absolute pressure at the inlet and downstream of stages 6, 7, 8, 9, and 10 of the impactor every minute.

In Beijing, more hazy days appeared in the summer, and more heavy pollution episodes occurred in the winter (Zhao et al., 2011, 2012). Therefore, size-resolved sampling was

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