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Chemical composition of size-segregated aerosols in Lhasa city, Tibetan Plateau

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ABSTRACT

To reveal the chemical characteristics of size-segregated aerosols in the high-altitude city of Tibetan Plateau, eight-size aerosol samples were collected in Lhasa from March 2013 to February 2014. The annual mean of online $PM_{2.5}$ was 25.0 ± 16.0 μg m^{-3}, which was much lower than Asian cities but similar with some European cities. The annual mean concentrations of organic carbon (OC, 7.92 μg m^{-3} in $PM_{2.1}$ and 12.66 μg m^{-3} in $PM_{9.0}$) and elemental carbon (EC, 1.00 μg m^{-3} in $PM_{2.1}$ and 1.21 μg m^{-3} in $PM_{9.0}$) in Lhasa aerosols were considerably lower than those heavily polluted cities such as Beijing and Xi'an, China and Kathmandu, Nepal. Sulfate, NO_3^-, NH_4^+ and Ca^{2+} were 0.75 ± 0.31, 0.82 ± 0.35, 0.38 ± 0.34 and 0.57 ± 0.29 μg m^{-3} in fine particles while in coarse particles they were 0.57 ± 0.37, 0.73 ± 0.23, 0.07 ± 0.03 and 2.52 ± 1.37 μg m^{-3}, respectively. Secondary water-soluble ions composed 35.8% of the total ionic components in fine particles according to the established electro-neutrality, while in coarse particles they took up only 9.3%. Ca^{2+} (40.6%) was the major component of the coarse particles. For seasonality, the concentrations of OC, EC, SO_4^{2-}, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and Na^+ presented higher values during late autumn and winter but were relatively lower in spring and summer. Nevertheless, NO_3^- was considerably higher in summer and autumn, presumably due to increased tourist-vehicle emissions. During winter and spring, $[Ca^{2+}]/[NO_3^- + SO_4^{2-}]$ ratios in coarse particles showed higher values of 7.31 and 6.17, respectively, emphasizing the dust influence. $[NO_3^-]/[SO_4^{2-}]$ ratios in fine particles during spring, summer and autumn exceeding 1 indicated that the currently predominant vehicle exhaust makes a greater contribution to the aerosols. While more stationary sources such as coal and biomass burning existed in winter since the $[NO_3^-]/[SO_4^{2-}]$ ratio was less than 1. Different sources and formation processes lead to a bimodal size distribution (0–0.65 μm in fine particles and 4.7–9.0 μm in coarse particles) for all of the compounds except Na^+.

1. Introduction

Atmospheric aerosols have significant effects on global climate change, air quality deterioration, visibility reduction and human health, which are highly dependent on their composition, concentration and size distribution (Chow et al., 2008; Ramanathan et al., 2001; Seinfeld and Pandis, 2012). The aerosol sizes ranging from several nanometers to hundreds of micrometers are essential for chemical processes, optical properties and sources (Calvo et al., 2013; Chow et al., 2008). Acting as cloud condensation nuclei or ice nuclei, the aerosols in different sizes can also alter the cloud-precipitation properties (Seinfeld and Pandis, 2012).

Different chemical constituents of the aerosols can influence the climate and environment greatly. For example, element carbon (EC, also referred to as black carbon or soot) has a strong light-absorption per unit mass. Therefore it plays a key role in warming the top of the atmosphere, cooling the ground surface and accelerating glacier melting (Bond et al., 2013; Guo et al., 2016; Huang et al., 2011; Wang et al., 2013b; Xu et al., 2009). Organic carbon (OC) can not only scatter light but also absorb light for solar radiation from visible to UV wavelengths (e.g., brown carbon) (Andreae and Gelencser, 2006; Bahadur et al., 2012). In addition to carbonaceous materials, inorganic species comprise 20–60% of the aerosol mass, which are predominantly in the forms of sulfate, ammonium, nitrate and other basic ions (Kong et al.,

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2014; Li et al., 2012; Xu et al., 2014). Sulfate and mineral dust are highly reflective to light, thereby causing a net cooling effect (Wang et al., 2010). In addition to the various climate effects, different chemical components of aerosols also have distinct impacts on visibility. For example, Gao et al. (2015) reported that organic matter, ammonium sulfate ($(NH_4)_2SO_4$) and EC were the most important components causing visibility impairment, which were prevailing and present in the droplet (0.56–1.8 μm) and condensation (0.1–0.56 μm) size ranges.

Located in the inland Tibetan Plateau (TP), Lhasa is one of the highest cities in the world. The atmospheric environment in Lhasa is unique because of the special climate regime (e.g., strong solar radiation) and different energy consumption structures. Therefore, the chemical and physical properties of aerosols in Lhasa may differ from other cities in China. The emissions from the substantial religious activities (e.g., the burning of juniper) may also exert an influence on the air quality (Gong et al., 2011; Huang et al., 2013). Consequently, the aerosols in Lhasa are attracting special concerns related to scientific research and public attention. For example, Cong et al. (2011) reported the trace element concentrations and Pb isotopic characteristics of Lhasa PM_{10} samples. Recently, Bu Duo et al. (2015) characterized 408 aerosol particles in Lhasa using transmission electron microscopy combined with energy-dispersive X-ray spectra (TEM-EDX). They proposed that the major elements like Si, Al and Ca in aerosols were mainly from crustal materials; while soot was predominately emitted from local anthropogenic sources such as firework combustion and biomass burning. Nevertheless, a comprehensive study on the atmospheric aerosols of Lhasa city is still unavailable.

Given the importance of aerosols in the climate system (Kang et al., 2010), several studies have been carried out over the TP in terms of the aerosol composition. Nevertheless, those research sites were all located in remote or background areas to obtain a large spatial representative (Cong et al., 2015a; Ma et al., 2003; Wan et al., 2015; Zhao et al., 2013). From this aspect, the aerosol sampling and analysis conducted in TP cities have special significance, especially for size-segregated aerosols. This kind of work could illuminate the characteristics of local emissions inside the TP, which are apparently meaningful for distinguishing the relative contributions from local vs. long-range transport. Recently, substantial evidence has demonstrated that the air pollutants (Atmospheric Brown Clouds) over South Asia could penetrate into the Himalayas and impact the TP (Cong et al., 2015a, 2015b). For the evaluation of their effects by modeling approaches (e.g., RegCM4), the composition profile and loading strength of local emissions are urgently needed.

In this study, we present the results of OC, EC and water-soluble ions (WSIs) in the size-segregated aerosols collected at Lhasa. Our goals are to 1) reveal the composition and size distributions of the aerosols, 2) improve our knowledge on the anthropogenic sources of aerosols over TP cities, and 3) provide an essential database for the regional climate models.

2. Methodology

2.1. Description of research site

Size-segregated aerosol samples were collected at Lhasa Station (29°38′N, 91°38′E, 3640 m a.s.l.) in the campus of the Institute of Tibetan Plateau Research (Lhasa branch). The station is one part of the "Campaign on Atmospheric Aerosol Research" network of China (CARE-China), which is a comprehensive monitoring network with the aim to reveal the spatiotemporal variations of aerosols across China (Xin et al., 2015). The city of Lhasa is located in a narrow west–east valley in the southern part of the TP (Fig. S1). Our sampling site is close to Jinzhu road, one of the busiest roads in the city. There is a large coal-fired power and cement factory approximately 10 km to the west of the sampling site. In addition, Lhasa is a famous tourist–historic city and leads to significant seasonal variation in traffic and religious activities (Cong et al., 2011; Huang et al., 2013). The climate of Lhasa is characterized by a wet summer monsoon season and a dry non-monsoon season. During the monsoon season (July through September), low pressure over the TP attracts warm air masses from the Indian Ocean into the plateau. While in other seasons (non-monsoon), the large-scale atmospheric circulation patterns over the TP are mainly dominated by westerlies (Guo et al., 2015).

2.2. Sampling

From March 2013 to February 2014, size-segregated aerosol samples were collected every two weeks at Lhasa Station using the ambient 8-stage (non-viable) cascade impactor sampler (BGI, USA, flow rate: 22.82 L min^{-1} at standard condition). The equivalent aerodynamic cut-off diameter (Dp) of each stage is 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8, and 9.0 μm, respectively. Since our sampler did not have a 2.5 μm cutting point, the diameter of 2.1 μm was defined as the cutting point to split the fine and coarse particles in this study. Therefore, the coarse mode particle range corresponded to stages 5–8 (Dp = 2.1–9.0 μm) and the fine mode particle range corresponded to stages 1–4 (Dp = 0–2.1 μm). $PM_{9.0}$ corresponded to stages 1–8 (Dp = 0–9.0 μm).

The sampler was installed on the rooftop of the tallest building (20 m above ground level) in the Lhasa branch campus, and the sampling duration of each set sample was 72 h. Aerosol samples were collected on 81 mm quartz fiber filters (Munktell T293, Sweden), which were pre-combusted at 800 °C for 5 h. The filters were weighed before and after sampling by a microbalance with sensitivity ±0.01 mg. Filters were conditioned in a dryer (temperature: 25 ± 3 C; relative humidity: 10 ± 2%) for 72 h before each weighing. Field blanks were collected before sampling by mounting filters onto the filter holder for 10 min without air flowing. Subsequently, the samples and blank filters were placed in plastic Petri dishes, which were thoroughly cleaned previously along with the filter holder, and preserved in frozen condition with temperature under −20 °C prior to analysis. Eventually, 234 size-segregated samples (i.e. 26 sets) were successfully obtained.

In addition, $PM_{2.5}$ mass concentration was measured simultaneously by a tapered-element oscillating microbalance (R&P TEOM 1400, USA). Surface gas precursors were also observed with instruments from Thermo-Fisher Scientific, USA, including O_3 (a UV photometric analyzer, model 49i), SO_2 (a pulsed-fluorescence analyzer, model 43i) and NO/NO_2/NOx (a chemiluminescence analyzer, model 42i). The precisions, accuracies and the calibration protocols used for the monitoring instruments have been well described elsewhere (Ji et al., 2008). High resolution (5-min average) data sets from March 2013 to February 2014 were obtained and 1-h average data were presented after strict quality control. No data were available on several days because of instrument malfunctions.

2.3. OC and EC analyses

OC and EC in the size-segregated samples were analyzed using the thermal/optical carbon aerosol analyzer (DRI Model 2001A, Desert Research Institute, USA) with the thermal/optical reflectance (TOR) method, following the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol (Chow et al., 2007). Briefly, the OC and EC were measured by progressively heating a punch area of 0.5 cm^2 from the quartz fiber filters. Each filter was put in a quartz boat inside the analyzer. The OC fractions were determined by heating at 140 °C (OC1), 280 °C (OC2), 480 °C (OC3) and 580 °C (OC4) in a pure He atmosphere; subsequently, EC fractions were measured at 580 °C (EC1), 740 °C (EC2) and 840 °C (EC3) in an oxidizing atmosphere of 2% O_2 and 98% He. The involved carbon is oxidized to CO_2 and then reduced to CH_4 for detection by a flame ionization detector. The residence time of each heating step was defined by the flattening of the carbon signal. The pyrolyzed organic carbon (OPC) was monitored when the reflected laser signal returned to its initial value after O_2 was introduced to the