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Classification and chemical compositions of individual particles at an eastern marginal site of Tibetan Plateau

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Aerosol particles at Shangri-La, an eastern marginal site of Tibetan Plateau, were collected in July and August 2011. Morphologies and elemental compositions of individual particles were investigated through transmission electron microscopy coupled with energy dispersive X-ray spectroscopy. More than 14 elements were detected in the aerosol particles, and S were detected in more than 70% of the 292 analyzed particles. Six morphological types of individual particles were identified: soot, fly ash, complex secondary particles, crustal minerals, organic particles, and metal particles. The aerosol particles mainly comprised mineral particles (36.02%) and complex secondary particles (30.73%), followed by organic particles (17.38%), soot (8.06%), fly ash (6.08%), and metal particles (1.01%). The diameters of fly ash, soot, and metal particles were less than 2 μm. Approximately 81% of the particles were internally or externally mixed with two or more aerosol components from different sources. Soot, fly ash, organic, and fine mineral particles were commonly internally mixed with S-rich particles. Mineral particles tended to commonly associate with visible coatings, probably formed through chemical reactions on the surface of the particles. Back-trajectories revealed that air mass arriving at Shangri-La were transported from Northeast Burma, a region of the Indian subcontinent.

1. Introduction

Atmospheric aerosols are gaining considerable attention because they are crucial in many climate and environmental processes (Buseck et al., 2000). Aerosol particles affect the climate directly by scattering and absorbing solar radiation and indirectly by regionally and globally altering cloud properties and precipitation (Griessbach et al., 2013; Rozanov et al., 2014). Thus, studying the physicochemical characteristics of atmospheric aerosols is essential in understanding the various phenomena that affect the behavior of aerosol particles in the atmosphere (Braziewicz et al., 2004). Understanding the chemical and physical properties of background aerosols facilitate their source determination, thus elucidating the mechanism of the long-range transport of anthropogenic pollutants and validating both regional and global atmospheric models (Fattori et al., 2005; Toscano et al., 2005). In addition, the chemical compositions of aerosols from remote areas are a valuable reference for studying the rapid industrialization-driven evolution of the atmosphere.

The Shangri-La background station is located in the eastern margin of the Tibetan Plateau and the hinterlands of the Hengduan mountain range. The Tibetan Plateau, called the roof of the world, is the highest and most extensive plateau and has an area of 2.5×10^6 km^2 and a mean elevation of >4500 m. In particular, the Tibetan Plateau plays a crucial role in the climatology of and atmospheric circulation in Asia and is regarded a sensitive region for global climate change owing to its special landform, ecosystem, and monsoon circulation (Qiu, 2008). Particularly in summers, as an elevated heat source, the low pressure over the Tibetan Plateau draws moist, warm air from the Indian Ocean to the continent, thus affecting summer monsoon circulation in Asia. The atmosphere of

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the area, particularly the aerosol compositions, has been extensively studied (Cong et al., 2010a; Huang et al., 2010; Ming et al., 2010; Wan et al., 2015; Zhao et al., 2013); the results indicate that its atmospheric environment is affected by long-range transported pollutants, such as heavy metals and black carbon. However, only few studies have focused on individual aerosol particles in the Tibetan Plateau (Cong et al., 2010b; Duo et al., 2015; Hu et al., 2013; Li et al., 2015; Zhang et al., 2001); studies on Shangri-La have focused mainly on gases (Fang et al., 2012; Gao et al., 2013; Ma et al., 2014) and visibility (Yang, 2013).

Transmission electron microscopy is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. Transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (TEM-EDX) has been used to characterize individual particles and obtain detailed information on the morphologies, sizes, elemental compositions, and internal structures of individual aerosol particles. Studying the detailed analysis information of individual aerosol particles is crucial to evaluate their effects on climate and human health both locally and regionally (Lu et al., 2007; Shao et al., 2007). Individual particle optical properties depending on their aging properties or mixing states can be well revealed by laboratory and field measurements and theoretical calculations (Adachi and Buseck, 2010; Moffet and Prather, 2009; Thompson et al., 2012). Individual particle analysis can provide the mixing state of these non-refractory particles and explain heterogeneous reactions on particle surfaces during air pollution episodes (Adachi et al., 2014; Fu et al., 2012; Yang et al., 2012; Zhang et al., 2013). TEM is commonly used to study individual aerosol particles (Li et al., 2010a; Shi et al., 2012; Smith et al., 2012; Pósfai et al., 2013; Ueda et al., 2014; Li et al., 2016).

In this study, aerosol particles were collected at the Shangri-La regional atmosphere background station in Tibet during the summer of 2011, and the morphology and elemental compositions of individual aerosol particles were analyzed through TEM-EDX. The possible sources and heterogeneous reactions are discussed.

2. Materials and methods

2.1. Sampling

The Shangri-La regional atmosphere background station is located in the Diqing Tibetan Autonomous Prefecture (Elevation 3580 m; Lin et al., 2009). Here, June–October and November–May are the wet and dry seasons, respectively (Xie and Zhang, 2000). Shangri-La is located northwest of Yunnan Province of China, in the eastern margin of Qinghai-Tibet Plateau and the hinterlands of the Hengduan mountain range.

Aerosol particles were collected on copper TEM grids coated with a carbon film (300-mesh, China) using a KB-2F single-stage cascade impactor with a 0.5-mm-diameter jet nozzle at an air flow rate of 1 L/min. Theoretical collection efficiency calculations for the impactor are well established (Marple et al., 1993). The sampling time varied from 20 to 80 min depending on particle loading, which was estimated from the visibility (Li et al., 2011). The meteorological parameters during the sampling period were automatically recorded using Kestral 4000 (Table 1).

2.2. Experimental

TEM: Aerosol samples were analyzed using TEM-EDX at the China University of Petroleum. Samples were placed in an F20 FETEM (with an attached PV9000 spectrometer), and the spectral acquisition time was 30 s. The elemental composition of the samples was determined through EDX at 200 kV. Cu was excluded from the analysis because the TEM grids were composed of Cu. The distribution of aerosol particles on the TEM grids was nonuniform; coarse particles were present near the center, and fine particles were present at the periphery. Therefore, to ensure that the analyzed particles were representative, particles from five areas from the center and periphery of the sampling spot on each grid (Li et al., 2013) were analyzed.

Back-trajectory calculation: The backward trajectories at Shangri-La from July 16, 2011, to August 01, 2011, were simulated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (version 4.8) model. The endpoints were set at 100, 500, and 1000 m above the ground level. Global Data Assimilation System (GDAS) output dataset was used and the vertical motion method in the calculations is the default model selection.

3. Results

3.1. Nature of individual aerosol particles

The aerosol composition at the Shangri-La regional atmosphere background station was complex. More than 14 elements were detected through EDX (Fig. 1). S were detected in more than 70% of the 292 analyzed particles. K in more than 50%, and Ca, Mg, Fe, and Al in more than 25% of the 292 analyzed particles; P, Na, Cl, and heavy metals (e.g., Mn, Ti, and Zn) occurred in less than 20%.

Compared with the brown haze particles around Beijing, in which more than 18 elements were detected and S was present in more than 87% of the analyzed particles (Li and Shao, 2009a), the aerosol particles at Shangri-La were chemically less complex. However, the high frequency of S in the aerosol particles indicated that the particles were affected by human activities.

3.2. Individual particle types

Six types of individual particles, namely soot, fly ash, complex secondary particles, minerals, organic particles, and metal particles, were classified on the basis of their morphologies and elemental compositions (Table 2). "Element-rich" in the sub types means that the analyzed particles are mainly composed of this element occupies the first position in the chemical composition of the analyzed particles.

The morphology of soot particles exhibited individual chains and compact aggregates. The main component was C, which mainly originated from fossil fuel and biomass burning by local residents (Fig. 2a). One soot aggregate may contain ten to hundreds of C spheres, with typical diameters of 10–100 nm and a maximum of 150 nm. The high-resolution TEM image of soot spheres exhibited the discontinuous onion-like structure of a graphitic layer (Li and Shao, 2009a). Soot particles enhance the production of secondary species, such as sulfate and nitrate, on their surface (Wang et al., 2010).

Fly ash has a typical spherical morphology and is generally composed of Si and Al and occasionally contains minor quantities of Na, Mg, S, K, Ca, and Fe (Fig. 2b). They are typical anthropogenic aerosols that originate from coal combustion during heating and industrial activities. Such refractory particles with small sizes (diameter <1 μm) are usually mixed with secondary sulfate particles. The presence of fly ash particles at Shangri-La is attributable to long-distance transportation because no other major anthropogenic sources are in close proximity to the site; the nearest township is approximately 30 km from the station.

The composition of secondary particles is complex. Three types of secondary particles were identified, namely K-rich, S-rich, and $CaSO_4$ particles. Ca-S, K-, and S-rich particles are often referred to as