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Characteristics of water soluble ionic species in fine particles from a high altitude site on the northern boundary of Tibetan Plateau: Mixture of mineral dust and anthropogenic aerosol

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ABSTRACT

A year-long field study on the seasonal characteristics of fine particulate matter ($PM_{2.5}$) was conducted at the Qilian Shan Station of Glaciology and Ecologic Environment (QSS), a remote site on the northeast edge of the Tibetan Plateau. The $PM_{2.5}$ samples were collected weekly using a low volume (16.7 L/min) sampler, and then analyzed by ion chromatography for the water soluble ionic species (WSIs). The annual average mass loading of $PM_{2.5}$, retrieved from co-located measurement on aerosol size distribution, was 9.5 ± 5.4 μg m^{-3} with WSIs accounting for $39 \pm 2\%$. The WSIs were dominated by SO_4^{2-} (39%), CO_3^{2-} (19%), Ca^{2+} (16%), NO_3^- (10%), and NH_4^+ (6%), suggesting important contributions from both anthropogenic aerosol and mineral dust. The mass loading of total WSIs showed a seasonal variation with higher concentrations in spring (6.3 μg m^{-3}) and summer (5.1 μg m^{-3}) and lower concentrations in winter (2.2 μg m^{-3}) and fall (1.7 μg m^{-3}). A linear regression of ammonium versus sulfate by equivalent concentration showed a slope of 0.51, suggesting an excess of acids. The excess sulfuric and nitric acids likely reacted with mineral dust, as evidenced by the tight correlation between $[Ca^{2+} + NH_4^+]$ and $[SO_4^{2-} + NO_3^-]$. The oxidation ratios of nitrogen and sulfur estimated based on the datasets of SO_2 and NO_2 from the closest air quality station at Jiayuguan (~150 km from sampling site) showed that the gas-particle partitioning of nitrogen on dust was more efficient than that of sulfur. The size distribution of SO_4^{2-} showed a dominant accumulation mode, with a mode diameter (D_p) ranging from 0.18 to 0.56 μm. In comparison, NO_3^- and Ca^{2+} showed a prominent coarse mode with D_p ranging from 1 to 10 μm. The results of air mass trajectory cluster and potential source contribution function analysis demonstrated that the source regions of the mineral dust were located in the arid areas of northwest China while the anthropogenic aerosol was likely from urban areas in the low elevation areas to the east of QSS. The effects of meteorological parameters on the particle mass loading were also evaluated.

1. Introduction

Atmospheric chemistry can influence the physicochemical properties of aerosol and its behavior through heterogeneous and homogeneous processes. Generally, the water soluble aerosol species, including inorganic and organic components that account for 18–45% of the fine particulate mass (Wang et al., 2003), govern the chemical and optical properties of aerosols by affecting their hygroscopicity (Gysel et al., 2004). The water soluble inorganic fraction generally contributes to a large portion of the water soluble species and has been studied extensively using ion chromatography to understand the physical and chemical characteristics, sources, behaviors and formation mechanisms of aerosols (e.g., Wang et al., 2005). For example, aerosol samples collected downstream from arid and semi-arid regions are commonly found to be a

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mixture of dust species (e.g., Ca^{2+}, Mg^{2+}) and secondary aerosol species (SO_4^{2-}, NO_3^-, and NH_4^+) due to either uptake of anthropogenic aerosols or heterogeneous chemical reactions on dust particles (Usher et al., 2003, and references therein). This phenomenon has been commonly observed in East Asia due to the frequent dust storms and intense anthropogenic pollutions in this region (Seinfeld et al., 2004). In addition, the size distributions of water soluble ions (WSIs) can provide information on the sources and formation pathways of specific compounds (Yao et al., 2003). For example, nitrate has been found in the accumulation mode where it was associated with ammonium, as well as in the coarse mode where it can be produced by the uptake of nitric acid on dust particles (Zhang et al., 2000).

The Tibetan Plateau (TP) is the highest landmass on Earth, with an average altitude above 4000 m a.s.l. Due to the sparse population and minimal industrial activity, the atmosphere over this region is probably the least affected by human activities of any on the Asian continent. The transport of dust storms over TP has been observed by satellite, and the arid and semi-arid areas on and around TP are thought to be the major origins of aerosols (Huang et al., 2007; Liu et al., 2008). In the past few decades, however, the long-range transport of air pollutants over TP has received increasing attentions due to its significant effects on the radiation budget and glacial melting over this pristine region (Lau et al., 2006). A number of studies have been conducted on TP through collecting reactive trace gases (Bonasoni et al., 2008; Xue et al., 2011), aerosols (Kivekas et al., 2009; Cong et al., 2007; Zhao et al., 2013), snow (Zhang et al., 2012a; Zhang et al., 2012b; Yu et al., 2013), rain water (Liu et al., 2013), and river water (Huang et al., 2008) to evaluate the anthropogenic impact and to identify possible pollution sources. Particulate matter here has been found to be a mixture of dust and sulfate, nitrate, ammonium, and elemental and organic carbon (Rengarajan et al., 2007; Ram et al., 2010; Zhao et al., 2013), and the margin of TP is thought to be more polluted due to its relatively short distance from pollution centers (Yu et al., 2013). For example, the Himalayas, facing south toward south Asia, can encounter the pollution input during the pre-monsoon periods every year (Bonasoni et al., 2010).

Understanding the temporal and spatial distributions as well as the chemical and dynamic processes of air pollutants is important in this area. Although many studies were conducted over TP during the past several decades, most of them focused on the Himalayas (southern TP), and were often conducted for only short periods, so there is limited knowledge of the seasonality of aerosol mass and chemical composition. Only a few long term observations have investigated the seasonal variations (Bonasoni et al., 2010; Dumka et al., 2010; Ram et al., 2010; Hegde and Kawamura, 2012). Compared with the southern TP, relatively fewer stations have been established in northern TP (Fig. S1), restricting the long term studies in this region. Remote mountains in the northern TP are also considered to be the area suffering from the long-range transport of pollutants from industrialized regions in inland China, especially during summer when the heating difference at low and high elevations on the continent create a strong thermal wind circulation (Fu et al., 2012). For example, Kivekas et al. (2009) reported a year-long dataset of particle number concentration from the Mount Waliguan Observatory (WLG) in the northeastern TP, one of the background monitoring stations of the WMO (World Meteorological Organization), and showed an increase of particle numbers during summer. These results, together with our previous study (Xu et al., 2013), suggest that there is a significant influence of long-range transport anthropogenic pollutants on the northern TP. In comparison to WLG, the northwestern TP is close to the arid and semi-arid regions of western China, likely indicating a more important role of the heterogeneous reactions between aerosols and dust.

The Qilian Shan Station of Glaciology and Ecologic Environment (QSS) is located on the north slope of the western Qilian Mountains, north of TP (Fig. 1). This station mainly focuses on research in glaciology, ecology and the atmospheric environment in this remote area. To better understand the aerosol pollution in northern TP, aerosol samples were collected at a one-week interval over a year (July 2010 to July 2011). In our previous study (Xu et al., 2013), we investigated the effect of polluted air during summer and fall based on the size distribution and number concentration of particulate matter, while in the present study, we focus on the chemical compositions of collected fine particulates. The main objectives of this study were to (1) characterize the seasonal variations of $PM_{2.5}$ mass loading, the chemical compositions, and size distributions of WSIs, and (2) evaluate the aerosol sources and chemical processes as well as the factors influencing its transport and accumulation.

2. Sampling and analysis

2.1. Site description and sampling

All samples used in this study were collected from the atmospheric chemistry observatory of QSS (39.50°N, 96.51°E; 4180 m a.s.l.). A detailed description of this site and QSS can be found elsewhere (Xu et al., 2013). Briefly, the sampling site at QSS represents a typical pristine environment on the northern TP and is located near the toe of a group of glaciers. The climate at the QSS is dominated by the East Asian monsoon during summer and the westerlies during winter (Fig. 1), and a transitional state between these two climate systems during fall and spring. The field study was conducted from July 16, 2010 to July 28, 2011. $PM_{2.5}$ samples were collected using a solar-power low-volume (16.7 L/min flow rate) aerosol sampler (PQ200, BGI, USA). All samples were collected on Teflon filters (2-μm pore size, 47-mm diameter, Zeflour™, Pall). The flow rate of aerosol sampler was cyclical (one month) calibrated with a calibrator (TetraCal®, BGI, USA). The flow rate was recorded at 5 min intervals by the online volume flow meter supplied by the instrument and this data was used to calculate the sampling volume; the air temperature and pressure were recorded at 30 min intervals at the meteorological station at QSS, and were used to calculate the air volume under standard conditions (1013 h Pa, 273 K). Forty-six aerosol samples were collected at one-week intervals, and to determine background contamination, 13 field blanks were obtained. For these blanks, a similar preparation and sampling protocol was followed, exposing the sampling materials for the ~5 min duration without pumping the air. Due to the power failure during extremely low air temperature or continuously cloudy conditions, no sample was collected during March 2011. In