Individual Particle Analysis of Atmospheric Aerosols at Nam Co, Tibetan Plateau

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**ABSTRACT**

Twelve filter samples were sampled monthly during a continuous 1-year campaign at a remote site, Nam Co in central Tibetan Plateau. The total aerosol concentrations ranged from 0.48 $\mu$g/m$^3$ to 36.11 $\mu$g/m$^3$ with the annual average of 6.74 $\mu$g/m$^3$, reflecting a typical background level. The composition and morphology of atmospheric aerosols with size ranging from 0.5 to 10 $\mu$m were investigated using a scanning electron microscope coupled with energy dispersive X-ray analysis. Then aerosol particles were classified into 7 groups: soot, tar ball, aluminosilicates/quartz, calcium sulfate, Ca/Mg carbonate, Fe/Ti oxide, and biological particle. Aerosol optical properties from the sun photometer and the results obtained by SEM-EDX could support and verify each other, providing complementary information on aerosol characteristics at Nam Co. Two distinct types of air masses arriving at Nam Co correspond to different aerosol constituent, showing that the summer monsoon circulation may bring considerable pollution from South Asia, while the westerly flow dominated in winter is relative clean.

**Keywords:** Aerosols; SEM-EDX; Nam Co; Tibetan Plateau.

**INTRODUCTION**

The Tibetan Plateau (TP) is the highest and most extensive plateau on Earth. As a unique geomorphic unit, the TP plays a key role in the Asian monsoon system and it greatly influences the climate of Asia. The atmosphere over TP remains pristine due to the sparse human population and minimal industrial activities (Wang et al., 2006).

Recently, climate change has become a crucial issue receiving tremendous attention worldwide (IPCC, 2007; Li et al., 2007). Especially, the TP has been regarded as a sensitive region to global climate change owing to its special landform, ecosystem, and monsoon circulation. For example, over TP, the climate changes have proximately caused a rise in temperature of up to 0.3°C a decade, which is approximately three times the global warming rate (Qiu, 2008). Therefore, an essential question now arises, i.e. what are the regional and global teleconnections and responses of TP climate to changes in external forcing (e.g. aerosols and greenhouse gases)? In this context, increasing attention has been devoted to the study of aerosol effects on regional climate change such as the slowing down of South Asian Monsoon system and the retreat of mountain glaciers (Jin, 2006; Lau et al., 2006; Ramanathan et al., 2007; Xia et al., 2008). However large uncertainties still exist in the climate modeling and assessments due to the lack of comprehensive knowledge of aerosol properties over TP, especially considering the spatial and temporal variations of aerosols.

The majority of pervious studies from TP focused on bulk aerosol composition (Liu et al., 1997; Wen et al., 2001; Zhang et al., 2001; Cong et al., 2007). While little is known about the characteristics of individual aerosol particles, although those information are of crucial importance for understanding their source and formation, as well as assessing their scattering and absorption capabilities. Aerosols consist of many different types of particles (e.g. sea salt, mineral dust, fly ash and biogenic particles). The aerosol optical properties depend on which type they are. For example, the sulfate aerosols are considered to result in a negative radiative forcing that leads to a cooling of the Earth surface. By contrast, soot, or black carbon is an effective absorber of solar radiation and therefore has a warming effect (Mogo et al., 2005).

In this study, as a part of comprehensive characterization of atmospheric aerosols in central TP, the aerosols from Nam Co were analyzed at the individual particle level using scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX). Our intention is to illustrate the range of diversity of aerosol particles in central TP and to provide the insight of aerosol properties for better assessments of aerosol radiative forcing.

**METHODOLOGY**

**Study Site and Sampling Description**

Nam Co is the largest lake in Tibet as well as the highest great lake in the world. On account of the harsh climate, the local population in the Nam Co region is about one thousand. The surrounding areas are covered by grassland with Kobresi pygmee as the predominant vegetation form, which are widely distributed on the alpine meadow/peat soil. Therefore there is scarcely atmospheric pollutant emission in the vicinity. In 2005, Nam Co Monitoring and Research Station for Multispheric Interactions (N30°46.44′, E90°59.31′, 4730 m a.s.l.) was established.

According to the records of automatic weather station (AWS), the annual average of temperature at Nam Co is 0°C with a large seasonal and daily variability. The surface weather conditions of each sampling day are tabulated in Table 1. Generally, there are four distinct seasons, winter (December to February), spring...
and accounts for about 70% of annual precipitation (You et al., 2003; Cao et al., 2007). The morphology of this kind of carbonaceous particle varied from short chains to complex clusters, which depend on fuels, burning conditions and atmospheric processing. At Nam Co, all soot particles present in the atmosphere were classified into 7 groups (Table 2). The size of particle morphology, size (equivalent projected area diameter) and elemental composition. Number of particles analyzed per sample was similar to other studies where authors used manual mode (Mogo et al., 2005). The EDX spectrum was obtained by the irradiation of electron beams at the center of individual particles with accelerating voltage 10 kV and a counting time 60-100 s. The intensities of the characteristic X-ray lines were converted to the corresponding elemental concentration by the standardless ZAF correction method.

The optical properties of aerosol such as aerosol optical depth (AOD) and Angstrom parameters (a) were measured by CIMEL Sun photometer following the procedure of ANRONET (http://aeronet.gsfc.nasa.gov/). The sun photometer makes direct solar radiation measurements with a 1.28 full field of view every 15 min at 340, 380, 440, 500, 675, 870, 940, and 1020 nm. These direct solar extinction measurements are used to compute AOD at each wavelength. The instrument calibration and derivation of AOD and a are discussed in detail by Holben et al. (2001).

**RESULTS AND DISCUSSION**

**Aerosol Mass Concentration**

The mass concentration of aerosol is a key criteria for the assessment of air quality. The range of TSP concentrations measured at Nam Co was 0.48–36.11 μg/m³ with the annual average of 6.74 μg/m³, reflecting a typical background level. These values are generally comparable to those observed at other remote sites (Zhang et al., 2008). For example, Mazzera et al. (2001) reported the average PM_{10} mass concentration at McMurdo (Hut Point), Antarctic during 1995/96 and 1996/97 austral summers was 3.4 μg/m³ with the maximum of 7.5 μg/m³. In our previous work, TSP concentrations at an extremely high elevation site (6520 m) on Mt. Qomolangma ranged from 2.02 μg/m³ to 6.34 μg/m³ (Cong et al., 2009). Fig. 1 shows the temporal variation of TSP concentration at Nam Co. The most striking is that TSP values in spring (especially April and May) are significantly higher than other seasons. In spring, the snow layer covering on TP begins to melt, and more ground surface is exposed to the air accompanied more windy days (Table 1), resulting in considerable amount of dust emitted into the atmosphere.

**Major Aerosol Particle Types**

On the base of the morphology and chemical composition determined by SEM-EDX, totally 1800 particles on 12 filters were classified into 7 groups (Table 2). The size of particle analyzed in this study ranges from 0.5 to 10 μm. Then their characteristics and possible sources were discussed.

**Soot**

Soot, also known as black carbon, is clearly distinguishable from other aerosol types due to its unique morphology (aggregates of 20-50 nm spherules, Fig. 2(a)). Soot, as an important particle pollutant in air, is primarily emitted from biomass burning and incomplete fossil fuel combustion (Li et al., 2003; Posfai et al., 2003; Cao et al., 2007). The morphology of this kind of carbonaceous particle varied from short chains to complex clusters, which depend on fuels, burning conditions and atmospheric processing. At Nam Co, all soot particles present in fine mode (< 2.5 μm, Table 3). The elemental composition of soot was predominantly carbon with minor sulfur.
Fig. 1. Temporal variation of total suspended particle concentrations, aerosol optical depth (AOD) and Angstrom parameter.

Table 2. Description of the 7 aerosol groups used in the data analysis and the major selection criteria.

<table>
<thead>
<tr>
<th>Particle group</th>
<th>Elemental associations</th>
<th>Typical morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>soot</td>
<td>Abundant C, often with minor S</td>
<td>Chain aggregations of carbonaceous spherules</td>
</tr>
<tr>
<td>tar ball</td>
<td>Abundant C</td>
<td>Individual carbonaceous spherules</td>
</tr>
<tr>
<td>aluminosilicates/Quartz</td>
<td>Al + Si&gt;60%, with minor Na, Mg, K, Ca, or Fe</td>
<td>Irregular shape</td>
</tr>
<tr>
<td>calcium sulfate</td>
<td>Ca&gt;30% and S&gt;30%</td>
<td>Irregular shape</td>
</tr>
<tr>
<td>Ca/Mg carbonate</td>
<td>Ca&gt;60% or (Ca + Mg)&gt;60%</td>
<td>Irregular shape</td>
</tr>
<tr>
<td>Fe/Ti oxide</td>
<td>Fe&gt;70% or Ti&gt;70%</td>
<td>Irregular shape</td>
</tr>
<tr>
<td>biological particle</td>
<td>Abundant C with minor elements (Ca, Na, Mg, P or K)</td>
<td>Variable morphology</td>
</tr>
</tbody>
</table>

**Tar ball**

Tar ball is a distinct carbonaceous particle type from soot (Fig. 2(b)). It is spherical, amorphous, and typically not aggregated with other particles (Posfai et al., 2004). The composition of the tar ball observed in our study was dominant by C and O. The size of tar ball generally ranged from 200 to 600 nm (Table 3). Tar ball is produced from biomass and biofuel burning. The further investigation shows tar ball can scatter and absorb light efficiently and then may play an important role in climate forcing (Hand et al., 2005).

**Aluminosilicates/Quartz**

The aluminosilicates are characterized by high contents of Si and Al with varying Na, K, Fe, S and/or Ca. Particles containing predominant silicon are classified as quartz. Most particles in this group showed irregular shapes (Fig. 2(c)). From mineralogy, aluminosilicates are mainly made up of kaolinite, illinite, montmorillonite and feldspars, which are typical terrigenous minerals (Shao et al., 2007). Aluminosilicates and silicates account for more than 25% of the mineral species. The major types of chemical compounds in the earth’s crust consist approximately 75% of silicates and aluminosilicates in terms of weight (van Malderen et al., 1996). Therefore, the most evident sources for this particle type would be soil related.

**Calcium Sulfate**

Particles composed of high and approximately equal abundance of Ca and S fall into this group. In this study, calcium sulfates mostly have columnar appearance (Fig. 2(d)). Gypsum originates generally from diverse sources (Zhang and Iwasaka, 1999). The
Note: * means the background signal from Au/Pd coating.

**Fig. 2.** Typical morphology and EDX spectra of seven particle groups.
primary source is crustal material because gypsum is a typical mineral in the earth crust (Hoornaert et al., 1996). The other source is conversion of calcite to gypsum by chemical reactions with sulfuric acid or ammonium sulfate during transport (Liu et al., 2005).

**Ca/Mg Carbonate**
This type of aerosol is characterized by high relative X-ray intensities for Ca and/or Mg (Fig. 2(e)). The size of Ca/Mg carbonate particle varied, ranging from 0.5 to 10 μm (Table 3). According to the irregular shape and coarse grain size, those Ca/Mg carbonate particles were assumed to be soil-related. Carbonate minerals including calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) are common constituent of soils, and often observed in the individual aerosol particle analysis (Shao et al., 2008).

**Fe/Ti Oxide**
Particles abundant in Fe or Ti element are classified into this group (Fig. 2(f)). Fe or Ti oxide particles have natural and anthropogenic origins. However, those metal oxide particles emitted from metallurgic industry usually present as spherical shape. In our study, according to their irregular morphology, Fe and Ti oxides from crustal materials (hematite, magnetite, goethite, rutile, etc) were most likely.

**Biological Particle**
Biological particles are recognized from their characteristic morphology (Fig 2(g)) with the size larger than 5 μm. Usually, such type particles have minor amounts of elements (Na, Mg, K, Ca, and P) which are essential tracers present in plants. Such biological particles were attributed to the likely occurrence of pollen, spores, bacteria, algae, parotozoa, fungi, fragments of leaves, as well as the excrements and fragments of insect.

**Seasonality of Number Abundances for Particle Groups**
The relative abundances of each particle group in different size fractions are shown in Fig. 3. According to the definition of different season, the samples used for spring, summer, autumn and winter are 3, 3, 4 and 2, respectively. Clearly,

<table>
<thead>
<tr>
<th>Seasons diameter (μm)</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5-1</td>
<td>1-2.5</td>
<td>2.5-10</td>
<td>0.5-1</td>
<td>1-2.5</td>
</tr>
<tr>
<td>soot</td>
<td>31</td>
<td>42</td>
<td>0</td>
<td>36</td>
</tr>
<tr>
<td>tar ball</td>
<td>29</td>
<td>0</td>
<td>0</td>
<td>162</td>
</tr>
<tr>
<td>aluminosilicates/quartz</td>
<td>36</td>
<td>156</td>
<td>174</td>
<td>30</td>
</tr>
<tr>
<td>calcium sulfate</td>
<td>6</td>
<td>18</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Ca/Mg carbonate</td>
<td>0</td>
<td>18</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Fe/Ti oxide</td>
<td>0</td>
<td>24</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>biological particle</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Sum</td>
<td>102</td>
<td>258</td>
<td>228</td>
<td>246</td>
</tr>
</tbody>
</table>

Note: the ultra-fine particles with diameter less than 0.5 μm are not analyzed.

**Table 3. Size-resolved number of aerosol particles in different groups**
aluminosilicates was predominant in all seasons, indicating the crustal sources were always the most important contributor. In the previous study, the elemental composition of aerosols in Nam Co also mainly consisted of Si, Ca, Fe, Al and K which originated from crust material (Cong et al., 2007). For summer, the most remarkable characteristic was the significant increase of soot and tar ball’s relative abundances (the sum up to 46%). The autumn took the second place in terms of soot and tar ball content, while the winter and spring exhibited the lowest. The seasonal variations of soot and tar ball content suggested the Nam Co area possibly received more anthropogenic influence in summer than other seasons. Moreover, the biological particles in the summer and autumn (6-8%) were slightly more than winter and spring, reflecting the increased contribution of vegetation on the land surface. While the number abundances of other aerosol type (i.e. calcium sulfate, Ca/Mg carbonate and Fe/Ti-rich particle) generally kept constant through the whole year. Furthermore, considering the large amount of soot and tar ball particles in summer, which could lead to considerable local climatic warming, more attention should be devoted to their potential contribution to the glacier retreat in Nam Co region.

Comparison with Sun Photometer Measurements

Aerosol optical depth and Angstrom parameter retrieved from the sun photometer (CIMEL 318) are shown in Fig. 1. The mean value of AOD for the whole year (0.05 at 500 nm) is comparable to other background sites such as Mauna Loa (Holben et al., 2001). Very low aerosol optical values in Nam Co were consistent with the result of mass concentration of TSP. Actually, AOD and mass concentration revealed the clear atmospheric environment (low loading of aerosols, Fig. 1) of Nam Co from different aspects.

The seasonal variation of the monthly average AOD showed maximum values in the spring (April and May) and remained high values in summer monsoon season (June, July, August). This seasonal peak in spring was thought to be substantial dust particles. The high values of AOD in summer were possibly caused by the enhanced anthropogenic emissions. The high aerosol loading in spring accompanied with low α indicated that dust dominated the aerosol regime associated with loose ground surface and subsequent more soil dust in the atmosphere. In contrast, high AOD associated with high α in summer could be attributed to larger proportion of fine anthropogenic aerosols. The SEM-EDX results showed the dominant aerosol particles were aluminosilicates in all seasons, which are typical crustal minerals and mainly exist in coarse mode (Table 3). Especially in spring, the relative number concentration of aluminosilicates was about 61%. While in summer, the percentage of aluminosilicates decreased to 29% with increased amount of soot and tar ball (19% and 27%). Soot and tar ball are produced mainly from anthropogenic activities like fossil fuel and biomass burning and usually present in fine mode. Therefore, the result of aerosol optical properties and SEM-EDX support and verify each other, providing a reliable understanding of aerosol characteristics at Nam Co.

Back Trajectories Analysis

To analyze the source and transport pathways of the air masses arriving at Nam Co, the back trajectory analysis was done for the period of measurements using the HYSPLIT model, developed by NOAA/ARL (Draxler and Rolph, 2003). In this study, five-day back trajectories were calculated at a height of 500 m above ground level at 08:00 UTC for all sampling days. The trajectories were generated using GDAS (Global Data Assimilation System) reanalysis data.
System) meteorological archive from NCEP (National Center for Environmental Prediction). The error accompanying HYSPLIT-generated trajectories were estimated to be anywhere from 15% to 30% of the travel distance, and uncertainty increases with the distance of transport (Stohl, 1998).

The trajectories (Fig. 4) reveal two different types of air mass arriving at the sampling site. In summer (June, July and August), slow-moving air masses come from Bangladesh and Northeast India at low altitude. In other seasons, most of air masses come from the west with a rapid moving speed. Such two kinds of air mass pathway generally correspond to the summer monsoon and westerly system over TP. Namely, in summer monsoon period, the low pressure over TP induces warm air from the Indian Oceans (especially Bay of Bengal) transport to the hinterland of the plateau. While in other time, the large scale atmospheric circulation patterns over TP were mainly dominated by westerlies.

Previous researches have suggested that the summer monsoon circulation can bring considerable pollution from South Asia. While air masses belonging to westerly flow do not carry large quantities of pollutants because they originate and travel far away from the industrialized and heavily populated regions (Duan et al., 2007). The individual particle analysis in this study provides more data on this assumption. Obviously higher proportions of soot and tar ball, typical indicators of anthropogenic influence, were found in summer. Therefore, it could be deduced that the air mass from South Asia in summer may carry such anthropogenic particles. Atmospheric pollution is serious in South Asia (Salam et al., 2003; Salam et al., 2008). Model simulation has pointed out that those atmospheric pollution from South Asia could be lifted and transported to TP (Li et al., 2005). Our previous analysis on elemental composition of aerosols from Nam Co also suggested that several heavy metals may be transported long distances from South Asia (Cong et al., 2007). On the other hand, the possibility that some pollutants from areas inside the TP also exist. For example, the previous studies concerning emissions in Lhasa have suggested that soot particles generated due to the religious activities in the urban area could be transported out of the city, which may impact the atmospheric mass cycle in wide ranges (Zhang et al., 2001).

**SUMMARY AND CONCLUSIONS**

Aerosols at Nam Co, a remote station in central Tibetan Plateau were characterized at the individual particle level. According to the morphology and chemical composition, aerosol particles could be generally classified into 7 groups: soot, tar ball, aluminosilicates/quartz, calcium sulfate, Ca/Mg carbonate, Fe/Ti oxide, and biological particle.

The seasonal variation of the abundances of the different particle types was further investigated. In all of seasons, the aluminosilicates/quartz was the dominate aerosol type, showing that crustal material was the primary contributor of the aerosols. The relative abundances of soot and tar ball that all occur in fine mode increased significantly in summer, reflecting Nam Co received more influence of anthropogenic activities at that time.

By comparison of SEM-EDX results to aerosol optical properties (such as AOD and Angstrom parameter) obtained by sun photometer, it was clearly demonstrated that the individual particle analysis was meaningful to interpret the temporal variation of aerosol optical properties, providing complementary information on aerosol characteristics at Nam Co.

The backward trajectories reveal two different types of air masses arriving at Nam Co in the whole year. Furthermore, the individual particle analysis result shows that such two types of air masses correspond to different aerosol composition. The summer monsoon circulation may bring considerable pollution from South Asia, while the westerly flow dominated in winter is relative clean. More work is needed to figure out the definite source of those aerosols.

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