Chemical characteristics of submicron particles at the central Tibet Plateau: influence of long-range transport insights from aerosol mass spectrometry

Jianzhong Xu\(^1\), Qi Zhang\(^2\), Jinsen Shi\(^3\), Xinlei Ge\(^4\), Conghui Xie\(^1\), Junfeng Wang\(^4\), Shichang Kang\(^1\), Ruxiong Zhang\(^5\), Yuhang Wang\(^5\)

\(^1\)State Key Laboratory of Cryospheric Sciences, Northwest Institute of Eco-Environment and Resource, CAS, Lanzhou 730000, China
\(^2\)Department of Environmental Toxicology, University of California, Davis, CA 95616, USA
\(^3\)Key Laboratory for Semi-Arid Climate Change of the Ministry of Education, College of Atmospheric Sciences, Lanzhou University, Lanzhou 730000, China
\(^4\)Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China
\(^5\)School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA

Abstract

Recent studies have revealed a significant influx of air pollution from south Asia to Himalayas and Tibet Plateau (TP) during pre-monsoon period. In order to characterize the chemical composition, sources, and transport mechanism processes of polluted air mass in this pristine area, we performed a field study during June 2015 by deploying a suite of online instruments including an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-AMS) and a multi-angle absorption photometer (MAAP) at Nam Co Station (90°57′E, 30°46′N, 4730m a.s.l) at the central of the TP. The measurements were made at a time period when the transition from pre-monsoon to monsoon occurred. The average ambient mass concentration of submicron particulate matter (PM\(_1\)) over the whole campaign period was \(\sim 2.0 \mu g \text{ m}^{-3}\), with organics accounting for \(\sim 46\%\), followed by sulfate \(\sim 41\%\), black carbon \(\sim 9\%\), ammonium \(\sim 8\%\), and nitrate \(\sim 3\%). This mass loading and composition were comparable with most of AMS results in remote sites worldwide. Air pollution episodes were observed during the pre-monsoon period, whereas persistently low aerosol concentrations were observed during the monsoon period. However, the chemical composition of aerosol during the air pollution episodes in the pre-monsoon season was on a case-by-case basis, depending on the prevailing meteorological conditions and air mass transport routes. Most of the chemical species exhibited significant diurnal variations with higher values occurring during afternoon and lower values during early morning. Organic aerosol (OA) was more
1. Introduction

The Tibet Plateau (TP) and Himalayas is a vast and elevated highland in Central Asia that extends over the area of 27-45°N, 70-105°E with a mean elevation of more than 4000 m above sea level (a.s.l.). It is a sparsely populated area with minimal local pollution. The TP is an ideal area for observations of free tropospheric air masses and pollutants transported from polluted areas surrounding the TP after long-range transport distances. Determination of the chemical characteristics of aerosol particles in TP is important for assessment of assessments of their influences on atmospheric chemistry and climate (Li et al., 2016), which are so far poorly understood due to harsh conditions and logistic limitations.

Over recent decades, an increasing number of field studies have been conducted in these regions to characterize aerosol physical and chemical features from mountain observatories, e.g., the Nepal Climate Observatory-Pyramid (5079 m), which set up for long-term monitoring and synchronous observation (Bonasoni et al., 2010; Liu et al., 2017). There are significant seasonal variations in aerosol mass loading in the southern TP and Himalayas. Higher aerosol concentration was often found during pre-monsoon due to less precipitation and favorable atmospheric circulation (Bonasoni et al., 2010; Marinoni et al., 2010; Marinoni et al., 2013; Zhao et al., 2013). For example, the concentration of carbonaceous species at the Qomolangma (Mt. Everest) Station (4276 m a.s.l.), northern Himalayas during pre-monsoon was found to be 3 – 5 times higher than that during the monsoon periods (Cong et al., 2015). Since this seasonal variation of aerosol loading is consistent at both the southern and northern Himalayas (Xu et al., 2014), polluted air mass was thought to be able to across the Himalayas, a condition which is also supported by model results (Lu et al., 2012; Lüthi et al., 2015; Zhang et al., 2015). During monsoon period, ambient aerosol mainly originated from marine area, which had an lead to aerosol chemical differences between pre-monsoon and monsoon. The distinct seasonal variation of aerosol loading is mainly attributed to the change of the dominated climatic systems and then weather conditions. During pre-monsoon, the cold and dry southern Westliers dominated the southern TP and Himalayas, while the South Asia Monsoon covers most of South Asia, Himalayas, and the southern TP during summer period.
Most of the studies conducted in these regions focused on some specific species, such as black carbon, which has strong light absorption. Burning of biomass fuels and wildfires in the south Himalaya and South Asia are thought to be important sources for the black carbon (Stone et al., 2010; Engling et al., 2011; Kumar et al., 2011). However, a recent study shows that sources of black carbon in the region of South Asia are highly complex, including emissions from low efficient transport tools and cooking using cow dung and biogas as well (Stockwell et al., 2016). These burning activities also emit other species such as organic and inorganic particulate species and volatile organic compounds, which generate a well-mixed aerosol plume eventually via processes such as coagulation, evaporation, oxidation, and condensation. Fang et al. (2015) recently suspected that biogenic aerosol could also be an important contribution for aerosol in the TP during summer. However, these mixed plumes have been rarely, if ever, characterized by comprehensive field measurements.

Filter-based sampling method with a low time resolution (days) were widely adopt in these remote regions due to logistical difficulties with deployment of real-time instruments. The low time resolution made the understanding of chemical processes of aerosol during transport challenging. Secondary species such as sulfate and water soluble organic carbon (WSOC) are normally the dominated species in aerosol. For example, WSOC accounted for about 60% of OC and the ratio between OC and EC could be up to 10 (Zhao et al., 2013; Cong et al., 2015), suggesting a dominant contribution of secondary organic aerosol (SOA) to carbonaceous aerosol loading in the TP. The ambient conditions at high elevation regions are characterized by higher solar radiation and concentrations of oxidants such as OH radicals and O₃, which therefore high dominant. High-time resolution measurement is thus necessary in these regions this region for detecting short-term events and the evolution of pollution events pollutants. In addition, the high time resolution data are useful for constraining atmospheric chemical transport models.

The aerodyne aerosol mass spectrometer (AMS) has been widely used to study the chemical composition of non-refractory submicron particle (e.g., Xu et al., 2014b; Xu et al., 2016). There are two merits of the AMS including its high time resolution and bulk measurement. The high time resolution is usually minute in minutes which has advanced our understanding of fundamental chemical composition processes of fine aerosols at different regions of the world (Canagaratna et al., 2007). The bulk measurements makeable the observation to obtain material information of various aerosol in one time, chemical species simultaneously. The organic aerosol, which is often the most important component of aerosol, can be further analyzed for their mass spectra to determine the average elemental ratios and by positive matrix factorization (PMF) analysis to determine the sources and atmospheric processes of aerosol (Ulbrich et al., 2009; Zhang et al., 2011). The atomic elemental ratios of oxygen and hydrogen within carbon (O/C and H/C) calculated from the OA mass spectra can provide information about the sources and evolution
processes of OA in the atmosphere (Aiken et al., 2008; Heald et al., 2010; Kroll et al., 2011; Ng et al., 2011). They also often closely correlate with key OA properties such as hygroscopicity, material density, and phase separation (Jimenez et al., 2009; Bertram et al., 2011). In addition, due to high sensitivity and low detection limits, AMS has been successfully deployed at many remote sites with low aerosol mass loading such as Antarctica (Schmale et al., 2013; Giordano et al., 2017). However, there are not AMS measurement in the TP and Himalayas so far.

The study here presents an analysis of comprehensive results from measurements using an AMS acquired at the central part of the TP during the transitional season period from pre-monsoon to monsoon. The study was designed to characterize aerosol chemical composition, temporal variations, transport processes, and emission sources. During the campaign, besides the AMS, multiple other real-time instruments were also deployed.

2. Methodology

2.1 Site description

The field study was conducted between May 31 and July 1, 2015 at a high altitude observatory, i.e., Nam Co Station for Multisphere Observation and Research, Chinese Academy of Sciences (Nam Co station, 90°57′E, 30°46′N 4730m a.s.l.), at the central part of the TP (Figure 1). The Nam Co station is located nearby Nam Co lake (Figure 1b), the second largest inland lake in the TP (area: 1920 km²) which is located at the northern border of Nyainqentanglha Mountains. The melted glacier from Nyainqentanglha Mountains supply water to the lake each year during warm seasons. The Nam Co station and its surrounding is a pristine region except for a small county for local people that is about 10 km west of the station. In the past several years, tourism for this beautiful lake has grown grown. A highway (Tibet Highway) for tourists was built about 45 km south of the station. The capital city (Lhasa) of the Tibet Autonomous Region is about 100 km southeast of the station with an average elevation of 3600 m a.s.l. between which is Nyainqentanglha Mountains (higher than 6000 m a.s.l) (Figure 1c). The closest town, Danxiong, is along alongside the famous highway, Qinghai-Tibet Highway, and about 70 km east of the station with an average elevation of 4200 m a.s.l. Overall, the station is surrounded by the mountains in the south and east, and the lake at the west. The ecology of surrounding area is semi-arid type land dominated by alpine meadow and barren areas. The precipitation is mainly occurred during summer monsoon period. The cooking and heating at the station is maintained supplied by the power and natural gas.

2.2 Instrument setup

The study was conducted at the observatory field of the station using a customer-made trailer with inlet stepped out of the top with the height of ~5m above ground. All the instruments were arranged inside the trailer where the air temperature was controlled at ~20°C by two conditions. Figure 1 shows the setup of the instruments. The total 4 air conditioners. The inlet was maintained by a vacuum pump with a flowrate of...
10 mL/min, following by a high-resolution time-of-flight aerosol mass spectrometer (HR-AMS, Aerodyne Research Inc., Billerica, MA, USA), a custom-made scanning mobility particle sizer (SMPS), a soot particle Aerodyne mass spectrometer (SP-AMS, Aerodyne Research Inc., Billerica, MA, USA), a single-particle intracavity laser-induced incandescence photometer (SP2, DMT, Inc., Boulder, CO, USA), and a seven wavelength Aethalometer (model AE31, Magee Scientific, Berkeley, CA, USA). The total flowrate of the inlet was maintained at ~16 mL/min and a PM$_{2.5}$ cyclone was used in the beginning front of the inlet (model URG-2000-30EH, URG Corp., Chapel Hill, NC, USA) to remove coarse particles. Several additional instruments were also co-located but with their own inlets, such as a Nephelometer (model 3563, TSI, Shoreview, MN, USA), a PM$_{2.5}$ sampler (model PQ200, BGI, USA), and a multi-angle absorption photometer (MAAP, model 5012, Thermo Electron Cooperation, USA). The operations of the instruments used in this study were described below.

2.2.1 HR-AMS

HR-AMS was used to measure the non-refractory PM$_1$ (NR-PM$_1$), which was thermally vaporized at ~600 °C, ionized with a 70eV electron impact and measured using a time-of-flight mass spectrometry. The details of the instrument have been described elsewhere (DeCarlo et al., 2006). For this study, HR-AMS was only operated with V-mode with 5 min resolution due to the low aerosol mass loading. Due to damage/malfunction of the chopper, the size distribution of NR-PM$_1$ was not determined. The HR-AMS was calibrated for ionization efficiency (IE) with the ammonium nitrate following standard procedures (Jayne et al., 2000) at the beginning, in the middle and end of the study. Particulate-free air was sampled twice during the study period to adjust the interaction influences of air on the fragmentation table and determine the detection limits (DLs) of aerosol species. The DLs were calculated as 3 times the standard deviations (3σ) of the measured values during this period-the particle-free sampling periods. The 2.5-min DLs for organic, sulfate, nitrate, ammonium, and chloride were determined at 0.108, 0.014, 0.007, 0.002, 0.010 μg m$^{-3}$, which are comparable to the values reported in previous studies.

2.2.2 Other instruments

The Aethalometer was used to measure the equivalent black carbon mass concentration using seven wavelength lights. The data for BC is commonly calculated from measurement at 880 nm using recommended MAC from the manufacture. The instrument was operated at the time resolution of 5 min with a flow rate of 5 L/min, which was calibrated once a week frequency.

PM$_{2.5}$ sampler was operated at the top of the trailer. Filter samples were collected between 2 June and 1 July 2015. Each aerosol sample was collected on a 47 mm quartz filter (Whatman, Maidstone, UK) using the aerosol sampler, with a flow rate of 16.7 L/min (BGI, USA, model PQ 200). The meteorological data was recorded at the tower of the Nam Co station at a height of 20 m above ground.
2.3 Data processing

The HR-ToF-AMS data were processed using the standard software of SQUIRREL (v1.56) and PIKA (v1.15c) written in IGOR (Wavemetrics, Inc., Lake Oswego, OR, USA) ([http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html](http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html)) to determine the mass concentrations of the NR-PM\(_1\), species and the ion-speciated mass spectra of organics, written in IGOR (Wavemetrics, Inc., Lake Oswego, OR, USA). An empirical particle collection efficiency (CE) of 0.5 was used, which has been widely used in field studies employing AMS with a dryer installed in front of the equipment's particle inlet. This CE value was further validated by the consistency and reasonable slope between HR-AMS measured mass concentrations and SMPS-determined particle volumes (section 3.1.2, \(R^2 = 0.9, \text{slope} = 1.48\)). The elemental ratios of OA (O\(_x\)C, H\(_y\)C, and organic matter to carbon (OM\(_x\)OC)) for this study was determined using the “improved-ambient” method (Canagaratna et al., 2015). Default relative ionization efficiency (RIE) values were used for organics (1.4), nitrate (1.1), and chloride (1.3), while an RIE value of 3.8 was determined for ammonium and 1.1 for sulfate based on the calibration for pure NH\(_4\)NO\(_3\) and (NH\(_4\))\(_2\)SO\(_4\), respectively.

The source decomposition/apportionment of organics was analysed/conducted by PMF with the robust engine. First, organic matrix was analysed using the PMF2.exe algorithm in robust mode (Paatero and Tapper, 1994) and explored using the PMF Evaluation Toolkit (PET) (Ulbrich et al., 2009). The PMF solution was evaluated following the procedures outlined in Table 1 of (Zhang et al., 2011) including modification of the error matrix and downweight of low SN ions; Zhang et al. (2011) including modification of the error matrix and downweight of low signal-to-noise ions. Moreover, based on the AMS fragmentation table, some organic ions were not directly measured but scaled to the organic signal at m/z 44, which were downweighted by increasing their errors by a factor of 3. A two-factor solution with fPeak = 0 was chosen in this study, as it is able to reconstruct the total OA mass and temporal profiles very well. The results of three-factor solution with fPeak = 0 are shown in supplementary material (Figure S1), which show splitting in the solutions.

3 Results and discussions

3.1 The meteorological conditions during the study

During the field study, the meteorological conditions were generally cold and windy (Figure 2a and b). The average air temperature was 8.4 ± 3.6 °C with a diurnal hourly average ranging from 4.8 to 12.3 °C; the diurnal average wind speed (WS) ranged from 4.5 to 6.5 m s\(^{-1}\). The dominant wind directions were south and southwest, although they varied during different periods (Figure 2b and S2). The wind direction (WD) had distinct diurnal variation with air mass from south during night to morning and west.
during afternoon. Based on the report of the Climate Diagnostics Bulletin of India (http://imd.gov.in/Climate_Diagnostic_Bulletins/cdbi_apr_2015.pdf), the precipitation from Indian monsoon had covered most part of India on June 12 to June 14, and these days are treated as the onset of India monsoon. Indeed, precipitation was recorded at the Nam Co station on June 13 and lasted for several days (Figure 2a). Based on this weather condition, the period before June 14 was classified as the pre-monsoon period and afterwards as the monsoon period. The RH during the pre-monsoon and monsoon periods were 48.4 ± 19.2% and 58.8 ± 16.5%, respectively. The origins of the air masses were also different during these two periods. Figure 3 shows the air mass from west during pre-monsoon period accounted about 30–40%, while it was only 7% during monsoon period, of which ~80% was from south.

3.2 The temporal variation of chemical species

The average mass concentration of PM$_1$ (NR-PM$_1$ + BC) was 2.0 µg m$^{-3}$ during the whole study period with 68% OA, 15% sulfate, 2% nitrate, 7% ammonium, and 8% BC. The NR-PM$_1$, mass loading (1.84 µg m$^{-3}$) at Nam Co Station was lower than the values observed at some high elevation sites such as Menyuan (10.8 µg m$^{-3}$) (Du et al., 2015), Montsec (4.9 µg m$^{-3}$) (Ripoll et al., 2015), Mt. Cimone (4.5 µg m$^{-3}$) (Rinaldi et al., 2015), Puy de Done (5 – 27 µg m$^{-3}$), and Mt. Bachelor (15.1 µg m$^{-3}$) (Zhou et al., 2017), but higher than those in some other sites, such as sub-Antarctic (0.46 µg m$^{-3}$) (Schmale et al., 2013) and Jungfraujoch (0.55 µg m$^{-3}$) (Fröhlich et al., 2015), similar with that at Mt. Whistler (1.91 µg m$^{-3}$) (Sun et al., 2009) (Table 1 and Figure S3). Although the sampling seasons and elevational altitudes of these sampling sites are different (Table 1), the results of these studies could basically represent the level of pollution at these sites due to their relatively long sampling spans (from one month to ten months). The contribution of OA at these high-elevation sites ranged from 50% – 90%; the highest value was at Mt. Bachelor which was frequently influenced by transported biomass burning plume, while the relative low OA contribution (38%) at sub-Antarctic was due to the dominant source from marine emission containing high sulfate. The mass concentration of PM$_1$, varied dynamically during the study period with distinct difference between pre-monsoon and monsoon periods. The average mass concentrations of PM$_1$ for these two periods were 2.6 and 1.2 µg m$^{-3}$, respectively. For comparison, the concentrations of various species for these two periods were side-by-side displayed in Figure 4a. The ratios between pre-monsoon and monsoon for all the species were higher than 1 with the maxima for ammonium (3.1) and sulfate (2.8), suggesting high efficiency of wet scavenging for ammonium sulfate during monsoon. The contribution of OA was thus slightly higher during the monsoon period than during the pre-monsoon (71% vs. 64% with a mass concentration ratio of 1.9). Apart from the potential scavenging effect, these results could also be influenced by the sources, transport route, and chemical processes during different periods.
Based on the mass concentration and temporal variations of PM$_1$ species and weather conditions, the pre-
monsoon period could be further divided into two periods, i.e., period 1 (P1: May 30 to June 7) and period
2 (P2: June 8 to June 13). The P1 was characterized by a higher sulfate concentration (0.46 vs.
0.41 µg m$^{-3}$) and sunny days, while P2 was characterized by high PM$_1$ concentration (2.9 vs. 2.1 µg
m$^{-3}$, higher, P < 0.005, chi-square test), high nitrate contribution, and wet and cold days (Figure S4). The
air masses for P2 had higher contribution from west and north than those during P1 (Figure 3). Figure 4b
shows the comparisons of mass concentration of different species between these two periods. For chemical
species, from P1 to P2, nitrate and OA increased dramatically by a factor of 1.6 and 2.2, respectively, and
BC and ammonium were also increased, suggesting the influence of transported polluted air mass.
However, sulfate and chloride decreased slightly (the ratios between P1–P2 and P2–P1 were ~0.95). The
variations of sulfate and nitrate during these two periods could be related to the photochemical conditions
and origination of air mass (see section 3.3).

The particles were generally neutralized as illustrated in Figure 5. All these species unexpected present significant diurnal patterns, especially during P2. The diurnal variation of aerosol are usually related to the local source emission (e.g., Xu et al., 2016). The diurnal variation at Nam Co may be related to the diurnal variations of long-range transport air mass, photochemistry, and the variation of plenary boundary layer (PBL) unexpectedly present dramatic diurnal variations, especially during P2. OA, sulfate, ammonium, and BC showed a similar pattern with low values during nighttime to early morning and high values during afternoon. We checked which suggest their common sources or similar transport pathways (Zhang et al., 2001). We checked the diurnal variation of the origination of air masses and found that there were increased air masses from south during nighttime and from west during afternoon (Figure S6), which could be related to the plateau monsoon during summer.

### 3.3 Diurnal variation and chemical process of different species

The diurnal cycles of OA, sulfate, nitrate, ammonium, and BC during different periods are shown
in Figure 5. All these species unexpected present significant diurnal patterns, especially during P2. The
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from west during afternoon (Figure S6), which could be related to the plateau monsoon during summer.
The enhanced air mass from west during afternoon could be more favorable for the transportation of polluted air mass. The enhanced WS during afternoon was also observed with the increase of air temperature (Figure 5). The diurnal variations of chemical species during monsoon period were relatively flat comparing with those during P1 and P2, which may relate with the relatively consistent air mass origination during monsoon. Nitrate presented a significant different diurnal variation with high values during nighttime to early morning and low values during afternoon. These features were highly correlated with that of the RH and air temperature (Figure 5) suggesting the important importance of thermodynamically-driven gas/particle/gas partitioning of ammonium nitrate and heterogeneous production of nitrate due to hydrolysis of N\textsubscript{2}O\textsubscript{5}. In addition, during the early morning time (6:00 – 8:00), there was a peak for most of species, which were accompanied with the lowest air temperature and the highest RH, then the lower plenary boundary layer (PBL) which could concentrate all the polluted air in a smaller space. (Yanai and Li, 1994). Overall, the diurnal variations of aerosol species at Nam Co may be dominated by the variabilities of both long-range transport air mass and local meteorological conditions.

Although in order to further elucidate the diurnal patterns for each species were similar during the three periods, chemical processes and potential sources of the aerosol species, the relationships of chemical species with wind conditions were significant different. Analyzed based on bivariate polar plot analysis (Figure 6). Sulfate and ammonium during During P1, sulfate and ammonium had hotspots from all of the directions across a big wide range of wind speed (0 – 10 m s\textsuperscript{-1}) suggesting the local/regional transport and formation of ammonium/sulfate from different air mass; while OA were concentrated depending to the prevailing wind direction from southeast and northwest suggesting important transport routes for OA from these two directions; winds; nitrate had hotspots at the lowest wind speed was relatively slow (0 – 8 m s\textsuperscript{-1}) only from southwest suggesting the nearby sources and/or local formation; while from southeast/east mainly, BC had hotspots from south, west and northwest at high wind speeds (4 – 12 m s\textsuperscript{-1}) during P1 suggesting long range transport from the concentrated polluted regions in northern India and northwestern India. During P2, all species except nitrate had hotspots from south/southwest at high wind speeds (6 – 14 m s\textsuperscript{-1}) suggesting the different synoptic process comparing with that during P1; Nitrate also had hotspots at a relative low wind speed from southwest during P2. These results suggested that the sources and chemical formation for formations of aerosols during P1 and P2 were similar could be different, albeit the wind conditions were different, diurnal variations of species between these two periods were similar. During monsoon period, all species had more similar distributions of the hotspots and strongly, which could be from northwest and weakly from all directions but relatively weak from southeast.

The significant difference of diurnal variation between sulfate and nitrate suggested the different chemical evolution of these two species. Nitrate and sulfate during three periods all had weak correlations. During P1,
the ratios of sulfate versus nitrate had peaks (> 20) during afternoon time, while during P2, the ratios all kept at low values (< 20) (not shown). In order to further investigate the chemical evolutions of these two species, we selected the high concentration periods based on nitrate concentration (> average + 2σ). Figure 7 showed all periods during the day with high nitrate period. The study and the corresponding meteorological conditions. It is easy to find that most of the high mass loading periods occurred during the nighttime. The wind speed and wind direction were varied dynamically and most of them were from southwest. Higher wind speed from this wind direction could transport more polluted air mass to Nam Co as illustrated from the event 1 (E1) during which all the species (OA, sulfate, ammonium, and BC) except nitrate increased; the weather during this type of event was accompanied with warm and dry air conditions. When the wind direction was from southwest with lower wind speed (E2), the RH increased to higher than 90% accompanying deceased air temperature, and the mass concentrations of nitrate, sulfate and OA increased significantly and BC decreased significantly in contrast to the increase of nitrate being the most significant. The decreased mass concentration of BC indicated no primary aerosol transportation, thus the increased species were mainly secondary formation secondarily formed.

3.4 The average chemical feature of organic aerosol

The average mass spectrum of OA was shown in Figure 8a. The organic mass was on average composed of 51% oxygen, 44% carbon, and 5% hydrogen with an average nominal formula being \( \text{C}_{13.3} \text{O}_{10.8} \text{N}_{0.06} \). On average, \( \text{C}_{x} \text{H}_{y} \text{O}_{z}^{+} \) (38.1%) and \( \text{C}_{x} \text{H}_{y}^{+} \) (37.3%) ions dominated the total OA following by \( \text{C}_{x} \text{H}_{y} \text{O}_{z}^{+} \) (19.8%), and \( \text{H}_{2} \text{O}_{z}^{+} \) (4.6%). m/z 44 was the base peak in the OA spectrum and mainly composed of \( \text{CO}_{2}^{+} \) (99%). m/z 43 had a significant contribution from both \( \text{C}_{2} \text{H}_{4} \text{O}_{2}^{+} \) (82%) and \( \text{C}_{2} \text{H}_{5}^{+} \) (18%). m/z 55, likely an important primary fragment was consisted of 51% \( \text{C}_{2} \text{H}_{5}^{+} \) and 49% \( \text{C}_{2} \text{H}_{4} \text{O}^{+} \). The OA was highly oxidized with an O/C of 0.88 on average. The OA was more oxidized during pre-monsoon than monsoon with higher \( \text{O} / \text{C} \) ratio (0.909 vs. 0.887) and lower \( \text{H} / \text{C} \) ratio (1.308 vs. 1.271) (Figure 8b). The oxidation states of OA during two pre-monsoon periods were also different. The O/C during P2 (0.98) was higher than P1 (0.90) and the H/C was higher during P1 than P2 (1.130 vs. 1.27). Correspondingly, the OA during P2 was containing higher contribution of \( \text{C}_{2} \text{H}_{4} \text{O}^{+} \) (40.3 vs. 39.1%) and \( \text{C}_{2} \text{H}_{5}^{+} \) (25.2 vs. 23.6%) ions than those during P1 (Figure 8c).

The diurnal variations of both O/C and OM/C ratios presented higher values during late morning to afternoon and lower values during early morning (Figure 9a). H/C presented an opposite trend. These patterns suggested that OA was more oxidized during daytime which could be due to photo oxidation and/or transport of highly oxidized OA during daytime. We examined the variation of elemental ratios at the function of OA mass concentrations, and found that the O/C increased significantly accompanied with the increase of OA mass concentration (Figure 9b). This
relationship could relate with the different influences of wet scavenging on more oxidized and less oxidized OA. In addition, this result likely suggested the importance of transportation on the oxidized OA, during afternoon due to the higher mass concentration occurring frequently on afternoon time. However it was not possible that the polluted air mass arrived at Nam Co within several hours due to the long distance from source regions (more than 1000 km from India). Previous studies have reported the presence of an aerosol layer between 6 – 18 km a.s.l altitude over the Tibet Plateau during summer (Tobo et al., 2007; Vernier et al., 2011). He et al. (2014) examined the vertical profiles of aerosol extinction coefficients measured with a Micro Pulse Lidar at Naqu, about 100 km east of Nam Co Station, and observed a maximum in aerosol extinction coefficient between 18 – 19 km a.s.l during summer 2011. Recently, Gu et al. (2016) examined the chemical aerosol compositions using the global three-dimensional Goddard Earth Observing System chemical transport model (GEOS-Chem) and found elevated aerosol-concentrations of sulfate, nitrate, ammonium, BC, and organic carbon over the TP. Further, observational and modeling studies have also shown that deep convection over the Tibet Plateau TP during daytime which is one of the important routes for tropospheric and stratospheric exchange of aerosols (Cristofanelli et al., 2009; Cristofanelli et al., 2010; Lin et al., 2016). Thus the enhanced aerosol concentrations during afternoon could possibly be attributed to the mixed downward of aerosol layer at 16 – 18 km altitude during the growth of TP boundary layer. This type of transportation could not be captured by the re-analysis of data used in the back-trajectory analysis likely due to the low time and spatial resolution. The need for this hypothesis needs further validation in the future in this region.

3.5 The PMF decomposition apportionment on the OA

The two OA factors determined by PMF have distinctly different mass spectra and diurnal patterns (Figure 10), including a less oxidized OOA (LO-OOA; O/H = 0.49) and a more oxidized OOA (MO-OOA; O/H = 0.96). Both factors appeared to be secondary in nature. Our inability to separate an HOA primary traffic-related OA factor is consistent with the fact that C/HO was a minor peak in the OA spectra (0.6% of the total signal) and the average organic-equivalent concentration of C/HO was only 0.008 μg m⁻³ during this study (Figure 5a). Collier et al. (2015) reported that the average C/HO (fraction of total organic signal accounted for by C/HO) was 8.1% in the mass spectrum of HOA primary OA from vehicle emissions. Based on this relationship, even assuming C/HO was completely contributed by primary OA (POA) from vehicle emissions-derived OA, the average HOA vehicle-OA concentration would be only ~ 0.1 μg m⁻³, or 7% of total OA mass, during this study. Note that in this study, C/HO was fitted well in the PMF analysis with very small residual, indicating that the signal of this ion was properly apportioned between the two OOA factors.

The mass spectra of MO-OOA and LO-OOA were characterized by high peaks at m/z 44 (mostly CO₂⁻) and LO-OOA had a relative large peak at m/z 43 (mostly C₂H₅O⁻) as well (Figure 10a). The contributions
of the C$_{11}$H$_{17}$O$_8^+$ ion category in these two mass spectra were 15.1% and 28.6%, respectively, while the contributions of C$_{13}$H$_{15}$O$_{11}^+$ were 37.8% and 41.5%, respectively. The time series of LO-OOA correlated well with C$_{11}$H$_{17}$O$_8^+$ and C$_{13}$H$_{15}$O$_{11}^+$ ions, while MO-OOA correlated well with C$_{11}$H$_{17}$O$_8^+$ ions (Figure S7). In addition, the time series of MO-OOA correlated well with sulfate (R$^2$ = 0.55), BC (R$^2$ = 0.54) and less well with nitrate (R$^2$ = 0.33), while LO-OOA correlated poorly with sulfate, BC and nitrate (Figure 10b and S8).

These results highlight the oxidation degree of MO-OOA and LO-OOA. LO-OOA and MO-OOA accounted for 41% and 59% on average, respectively, of total OA mass during this study (Figure 11a), and their relative contributions varied across the study (Figure 2e). For example, LO-OOA accounted for 41% of the total OA mass during P1 of the pre-monsoon period, 24% during P2, and 67% during the monsoon period (Figure 11b). The diurnal pattern of MO-OOA was characterized by higher concentrations during afternoon similar to those of sulfate and BC. While the diurnal pattern of LO-OOA peaked at early evening time (Figure 10c). The polar plot showed concentrated hotspots to the northwest of the sampling site for MO-OOA, and southeast for LO-OOA (Figure 6), indicating that the sources of these two components were totally different. MO-OOA was likely closely related to long-range transport of air mass from South Asia, while LO-OOA could from relative shorter distance transport such as marine air mass and regional background aerosol during the nighttime. Shen et al. (2015) reported that there were significant aerosol source from biogenic emission during summer near the Nam Co Station. As shown in Figure 12a and b, MO-OOA, which was highly oxidized (O$_{\infty}$/C = 0.96), appeared on the up-left corner of the triangle plot while LO-OOA was in the middle part with an O$_{\infty}$/C ratio of 0.49. The high oxidation degree of MO-OOA was likely related to extensive aging processes occurred during long-range transport. The slope of linear fitting of all the data points in V-K diaphragm is –0.76 suggesting the evolution of OA as carboxylic acid functionalization (Figure 12c).

Biomass burning emission is an important source in South Asia and could be transported to Himalayas and TP during pre-monsoon (Engling et al., 2011; Kumar et al., 2011; Sang et al., 2013; Cong et al., 2015), however there are not evidently significant signals of biomass emitted aerosol in our AMS results such as signals at m/z 60 and 73 in mass spectrum of OA which were found to be associated with levoglucosan formed from the pyrolysis of cellulose (Alfarra et al., 2007). The contribution of f60 (fraction of total organic signal accounted for by m/z 60) for LO-OOA and MO-OOA were 0.2% and 0.3%, respectively, which were similar with the global background level (less than 0.3%) suggested by Cubison et al. (2011). These results suggest that OA, if ever partly originated from biomass burning emission, could have been highly oxidized during transport. This behavior had been observed in a few studies that levoglucosan could be quickly (within a few hours) oxidized after being emitted (Ortega et al., 2013). In addition, Zhou et al. (2017) recently reported the observation of a highly aged BBOA factor with f60 < 0.3% in its mass spectrum, in aged wildfire plumes that had gone through extensive photochemical oxidation.
3.6 Sensitivity of the chemical characteristics transport of PM pollutants to synoptic process

Synoptic process is an important factor determining if the regional emissions can be transported to the TP. It is interesting to know what kind of synoptic process is favorable for transporting the polluted air mass to the Himalayas and the TP. A 3-D Regional chemical transport Model (REAM) coupled with the Weather Research and Forecasting model (WRF) was used to examine the chemical evolution and regional transport of pollutants such as aromatics in this study. REAM has been used in previous studies of the Tibet Plateau, and details about the model can be found in Zhang et al. (2017) and supplementary material. REAM could capture some synoptic processes which cannot be simulated by the normally used reanalysis data due to their low-resolution and the complexity of terrain in the Tibet Plateau. Figure 13 shows the distribution of simulated daily surface wind, 300 hPa geopotential height fields and concentrations of reactive aromatics over the Tibetan Plateau during 30 May – 13 June, 2015. During 30 May to 7 June corresponding to P1 in this study, there was a trough over the north propagated from west to east and this low pressure induced increasingly stronger surface wind from India to the TP, which could lead to transport of polluted air mass as illustrated by the results of model and AMS. The simulated concentration of reactive aromatics showed a peak during this period (Figure S9). During 8-11 June, there was a weak ridge system over the north. Intensified wind from north was observed as illustrated by HYSPLIT results (Figure 5b) and the simulated concentrations of reactive aromatics were sharply decreased (Figure S9). After that, a weak low-pressure trough system was observed again. The increased concentrations of reactive aromatics were also observed accompanying with intensified southern wind. Although these trends were basically consistent with our AMS results, there were also significant differences (Figure S9). The potential reason for this difference was that the weak trough during P2 intensified the wind from west other than south where a lot of biomass burning emission sources were located (Figure 5b). Meanwhile the interaction between cold dry air mass from north and warm-wet air mass from south increased the RH at Nam Co which was very favorable for aqueous formation locate (Figure 5b). Zhang et al., (2017) suggested that a low-cut system from stratosphere could be an important driver for pollution transport into the Tibet Plateau. However, in our study, the trough/ridge system seems to be also an important factor affecting the transport of air pollution from south and west, although this effect tends to be weaker in summer than in the other seasons because the tropopause is higher and stratospheric wave activity is weaker in summer. In our study, the trough/ridge system could be an important factor affecting the transport of air pollution from south and west.

3.7 Atmospheric implications

Our results have several potential implications to the atmospheric studies in the TP and Himalayas. Firstly, it is useful for the accurate estimation of the radiative forcing of aerosols in this region and validation of
current model simulation results based on our observed chemical composition and mass loadings of fine aerosols. Ji et al. (2015) estimate the radiative forcing from aerosols over the TP and Himalayas at the surface level using a regional climate model (RegCM4.3); for carbonaceous aerosols, there are several literatures that tested the model results, but all other species were referred to data available in the published inventory with a coarse spatial resolution. Secondly, our findings are implicate to the estimation of aerosol deposition on the glacier of this region and evaluation of subsequent impacts on the melting of snow/ice (Yasunari et al., 2010). Thirdly, highly-time resolved aerosol data is very scarce in this remote plateau, thus our data are valuable to validate modeling results regarding the transport of polluted air mass as demonstrated in section 3.6. At last, the transport mechanism of aerosol to the inland of TP is less understood so far. Hindman and Upadhyay (2002) suggested that the vertical lifting due to convection and subsequent horizontal mountain-valley wind could lead to the transport of aerosol from Nepal to Tibet. Dumka et al. (2010) also highlighted the important role of mountain-valley wind in the aerosol transport in the central Himalayas. The dynamic variations of aerosol chemical species measured here, are likely helpful to elucidate the transport mechanism of polluted air mass. Nevertheless, this scientific issue required further detailed investigations in the future.

4. Conclusion

The average PM$_1$ loading measured at Nam Co during June 2015 was 2.0 µg m$^{-3}$ with organics accounting for 68%, followed by sulfate (15%), black carbon (8%), ammonium (7%), and nitrate (2%). This mass concentration was comparable to some AMS observations from mountain-top sites. The mass concentration of PM$_1$ varied during different weather conditions with higher concentration during pre-monsoon and lower concentration during monsoon. The pre-monsoon period could also be divided into two periods (P1 and P2) based on meteorological conditions and aerosol chemical composition. During P1, PM$_1$ was characterized with high contribution from OA and sulfate, while increased contribution of nitrate was observed during P2 with wet and cold weather conditions. All PM$_1$ species had clear diurnal variations with OA, sulfate, BC, and ammonium peaking during afternoon due to photochemical production of these species coupled with transport of polluted air mass. Nitrate, however, peaked during the nighttime and early morning, which was related to the high RH condition and low air temperature. The formation of nitrate was highly correlated with transport of air masses from southwest under very low wind speeds, while the mass concentrations of sulfate, OA, and BC were highly correlated with air masses from northwest and southeast under higher wind speed conditions. OA was overall highly oxidized during the entire study with higher O/C ratios during the pre-monsoon period. Based on PMF analysis, the OA was found to be composed of a LO-OOA and a MO-OOA. LO-OOA was mainly associated with air masses originated from south, while MO-OOA was mainly from northwest. MO-OOA dominated OA during the pre-monsoon period, while LO-OOA dominated during the monsoon period. The transport mechanism of polluted air plume was further investigated using the REAM chemical model coupled with the WRF model. The
polluted air plume was found to be more easily transported to the TP and Himalayas during low pressure trough weather.

Acknowledgements

Thanks for the logistical supports of Nam Co Station for Multisphere Observation and Research, Chinese Academy of Sciences. This research was supported by grants from the Key Laboratory of Cryospheric Sciences Scientific Research Foundation (SKLCS-ZZ-2017-01), the National Natural Science Foundation of China (41771079, 41330526), the National Natural Science Foundation of China Science Fund for Creative Research Groups (41421061), the Key Laboratory of Cryospheric Sciences Scientific Research Foundation (SKLCS-ZZ-2017-01), the US National Science Foundation, and the Chinese Academy of Sciences Hundred Talents Program.
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Table 1. Summary of AMS measurement at mountain sites around the world. The mass concentration was for NR-PM₁.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Instruments</th>
<th>Lat.</th>
<th>Long.</th>
<th>Elev.</th>
<th>Date</th>
<th>Mass Conc.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nam Co</td>
<td>HR-AMS</td>
<td>30.77°N</td>
<td>90.9°E</td>
<td>4730</td>
<td>Jun-15 5 September – 15 October, 2013</td>
<td>1.84</td>
<td>Du et al. (2015)</td>
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<tr>
<td>Montsec</td>
<td>ACSM</td>
<td>42.05°N</td>
<td>0.73°E</td>
<td>1570</td>
<td>27 July 2012 - 2 October 2013</td>
<td>4.9</td>
<td>Fröhlich et al. (2015)</td>
</tr>
<tr>
<td>Jungfraujoch</td>
<td>ToF-ACSM</td>
<td>46.55°N</td>
<td>07.98°E</td>
<td>3580</td>
<td>2008 Autumn: 7.82, Winter: 5.58, Summer: 27.594</td>
<td>0.55</td>
<td>Fröhlich et al. (2015)</td>
</tr>
<tr>
<td>Mt. Cimone</td>
<td>HR-AMS</td>
<td>44.18°N</td>
<td>10.7°E</td>
<td>2165</td>
<td>June - July 2012</td>
<td>4.5</td>
<td>Rinaldi et al. (2015)</td>
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<tr>
<td>Mt. Whistler</td>
<td>HR-AMS</td>
<td>50.01°N</td>
<td>122.95°E</td>
<td>2182</td>
<td>Apr - May 2006</td>
<td>1.91</td>
<td>Sun et al. (2009)</td>
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<tr>
<td>Puy de Done</td>
<td>cToF-AMS</td>
<td>45.77°N</td>
<td>2.95°E</td>
<td>1465</td>
<td>Sep 2008 - June 2010</td>
<td>2008 Autumn: 7.82, Winter: 5.58, Summer: 27.594</td>
<td>15.1</td>
</tr>
<tr>
<td>Mt. Bachelor</td>
<td>HR-AMS</td>
<td>43.98°S</td>
<td>121.69W</td>
<td>2800</td>
<td>25 July - 25 August, 2013</td>
<td>2009 Autumn: 7.82, Winter: 5.58, Summer: 27.594</td>
<td>0.46</td>
</tr>
<tr>
<td>Sub-Antartic Bird Island</td>
<td>HR-AMS</td>
<td>54.00°S</td>
<td>38.00°W</td>
<td>ND</td>
<td>November and December, 2010</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Location map for (a) the Tibetan Plateau and (b) Nam Co Station colored by the altitude. (c) The elevation profile of altitude from coastal area to Nam Co Station (vertical dash line). The red arrow in the map represent the possible wind direction.
Figure 2. The combo plot of the data of the Nam Co study including (a) the meteorological conditions (T: air temperature; RH: relative humidity; Precip.: precipitation), (b) the variation of WS (wind speed) colored by WD (wind direction), (c) the temporal variation of mass concentration of PM$_1$ species and the average contribution each species (pie chart), (d) the mass contribution of each PM$_1$ species and the total mass
concentration of PM$_1$, and (e) the mass contribution of PMF results (section 3.5). Three periods based on the meteorological conditions were marked.
Figure 3. Air mass trajectory statistics for (a) P1, (b) P2, and (c) monsoon period. The classes of trajectories are colored by pressure. Fire spot observed by MODIS and average wind rose plot during each period are also shown.
Figure 4. The comparisons of PM$_1$ species of the mass concentration (left axis) and the ratio between them (right axis) between (a) pre-monsoon and monsoon and (b) P1 and P2.
Figure 5. Diurnal variations of each species and weather conditions (RH: relative humidity; Tem: air temperature; and WS: wind speed) during three periods of the study. Note that the signals of sulfate, ammonium, and BC are increased by a factor for comparison.
Figure 6. Bivariate polar plots that illustrate the variations of the concentrations (colored) of each species as a function of wind speed (m s\(^{-1}\)) and wind direction during different periods of the study.
Figure 7. The high aerosol loading periods based on nitrate (> average + 2σ) accompanying with meteorological data.
Figure 8. (a) The average mass spectrum of organic aerosol, (b) the average ratios of $H/C$ and $O/C$ during different periods, and (c) the average contribution of six ion categories during different periods.
Figure 9. (a) Diurnal variations of elemental ratios and (b) the variations of elemental ratios as the function of mass concentration of organic aerosol.
Figure 10. PMF results of (a) the mass spectra, (b) the temporal variation and (c) diurnal variations of two factors. The temporal and diurnal variations of sulfate and nitrate are also shown for comparisons.
Figure 11. (a) The average mass contributions of two factors (a) during the study, (b) during the different periods, and (c) the diurnal mass contribution of two factor (left axis) accompanying with the total organics (right axis).
Figure 12. Scatter plots of (a) $f_{44}$ vs. $f_{43}$, (b) $f_{\text{CO}_2^+}$ vs. $f_{\text{C}_2\text{H}_3\text{O}^+}$, and (c) $\text{H}_2\text{C}$ vs. $\text{O}_2\text{C}$ for the OA. The corresponding values of the OOAs identified in this study are also shown.
Figure 13. Daily distribution of WRF-simulated surface wind and REAM-simulated concentrations of reactive aromatics over the Tibet Plateau during 30 May to 13 June, 2015.
Supplementary of:

Chemical characteristics of submicron-particle at the central Tibet Plateau: influence of long-range transport insights from aerosol mass spectrometry

Jianzhong Xu¹, Qi Zhang², Jinsen Shi³, Xinlei Ge⁴, Conghui Xie¹, Junfeng Wang⁴, Shichang Kang¹, Ruxiong Zhang⁵, Yuhang Wang⁵

¹State Key Laboratory of Cryospheric Sciences, Northwest Institute of Eco-Environment and Resources, CAS, Lanzhou 730000, China
²Department of Environmental Toxicology, University of California, Davis, CA 95616, USA
³Key Laboratory for Semi-Arid Climate Change of the Ministry of Education, College of Atmospheric Sciences, Lanzhou University, Lanzhou 730000, China
⁴Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China
⁵School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA
Model description

The 3-D Regional chEmical trAnsport Model (REAM) has a horizontal resolution of 36 km. REAM features 30 vertical layers in the troposphere and 5 vertical layers in the stratosphere, with a model top at 10 hpa. Meteorological fields in REAM are from Weather Research and Forecast model (WRF) assimilations, and are updated every 5 minutes for convective transport related inputs and every 30 minutes for the others. The WRF model is constrained by National Centers for Environmental Prediction Climate Forecast System Reanalysis (NCEP CFSR, Saha et al., 2010) 6-hourly products. The initial and boundary conditions for chemical tracers in REAM are obtained from GEOS-Chem global simulations with a resolution of $2^\circ \times 2.5^\circ$ (Bey et al., 2001). REAM expands GEOS-Chem standard chemical mechanism (v9-02) with aromatic chemistry (Liu et al., 2010, 2012), including benzene and other reactive aromatics as chemical tracers (toluene, ethyl-benzene, and m/p/o-xylene). REAM implements the Intercontinental Chemical Transport Experiment-Phase B (INTEX-B) anthropogenic emissions inventory for South Asia (Zhang et al., 2009; Li et al., 2014) and a mosaic Asian anthropogenic emissions inventory (MIX, Li et al., 2015) for other regions in the model domain. For further model descriptions and evaluations, we refer readers to Zhang et al. (2017).
Figure S1 Three factor solutions.
Figure S2. The wind dataset during field study. The red marker along the wind represent the high nitrate periods.
Figure S3. The field studies conducted at high elevation sites using AMS. The mass concentration of NR-PM$_1$ and the mass contribution of each species (pie chart) are including in each site.
Figure S4. The comparisons of meteorological conditions between (a) pre-monsoon and monsoon and (b) P1 and P2.
Figure S5. Scatter plots of (a) predicted ammonium (\(\text{NH}_4^+\_\text{predicted}\)) calculated from the stoichiometry of sulfate, nitrate, and chloride vs. measured ammonium (\(\text{NH}_4^+\_\text{measured}\)), (b) \(\text{NH}_3^+\) vs. \(\text{NH}_2^+\), (c) \(\text{NH}^+\) vs. \(\text{NH}_2^+\), and (d) \(\text{NO}^+\) vs. \(\text{NO}_2^+\).
Figure S6. The diurnal contribution of two class air trajectories arrived at Nam Co during sampling period.
Figure S7. The correlation coefficient of time series between OOA factor and ions.
Figure S8. Scatter plots between BC and OOA factors.
Figure S9. The mass concentration of (a) AMS results and (b) REAM-simulated reactive aromatics and the averaged wind data.
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