



Chemical composition and mass size distribution of PM₁ at an elevated site in central east China

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Abstract. Size-resolved aerosol chemical compositions were measured continuously for 1.5 years from June 2010 to January 2012 with an aerosol mass spectrometer (AMS) to characterize the mass and size distributions (MSDs) of major chemical components in submicron particles (approximately PM₁) at Mountain Tai (Mt. Tai), an elevated site in central east China. The annual mean mass concentrations of organic, sulfate, nitrate, ammonium, and chloride were 11.2, 9.2, 7.2, 5.8, and 0.95 $\mu\text{g m}^{-3}$, respectively, which are much higher than those at most mountain sites in the USA and Europe, but lower than those at the nearby surface rural sites in China. A clear seasonality was observed for all major components throughout the study, with low concentration in fall and high in summer, and is believed to be caused by seasonal variations in planetary boundary layer (PBL) height, near surface pollutant concentrations and regional transport processes. Air masses were classified into categories impacted by PBL, lower free troposphere (LFT), new particle formation (NPF), in-cloud processes, and polluted aerosols. Organics dominated the PM₁ mass during the NPF episodes, while sulfate contributed most to PM₁ in cloud events. The average MSDs of particles between 30 and 1000 nm during the entire study for organics, sulfate, nitrate, and ammonium were approximately log-normal with mass median diameters (MMDs) of 539, 585, 542, and 545 nm, respectively. These values are slightly larger than those observed at ground sites within the North China Plain (NCP), likely due to the relative aged and well-mixed aerosol masses at Mt. Tai. There were no obvious differences in MMDs during the PBL, LFT, in-cloud and polluted episodes, but smaller MMDs, espe-

cially for organics, were observed during the NPF events. During the PBL, NPF, and polluted episodes, organics accounted for major proportions at smaller modes, and reached 70 % at 100–200 nm particles in the polluted events. In cloud episodes, inorganics contributed 70 % to the whole size range dominated by sulfate, which contributed 40 % to small particles (100–200 nm), while organics occupied 20 %, indicating that sulfate is a critical chemical component in cloud formation. Seven clusters of air masses were classified based on 72 h back-trajectory analysis. The majority of the regionally dispersed aerosols were found to be contributed from short distance mixed aerosols, mostly originated from the south with organics and sulfate as major components. Air masses from long range transport always brought clean and dry aerosols which resulted in low concentrations at Mt. Tai. AMS-PMF (positive matrix factorization) was employed to resolve the subtype of organics. Oxygenic organics aerosols (OAs) occupied 49, 56, 51, and 41 % of OAs in the four seasons respectively, demonstrating that most OA were oxidized in summer due to strong photochemical reactions. Biomass burning OAs (BBOAs) accounted for 34 % of OA in summer, mainly from field burning of agriculture residues, and coal combustion OAs (CCOAs) accounted for 22 % of OA in winter from heating.

1 Introduction

Atmospheric aerosol particles, especially the fine particles that have relatively long atmospheric residence times, not only damage human health (Ramgolam et al., 2009) but also: (1) affect the earth's radiative balance by scattering and absorbing solar radiation, and (2) indirectly influence the earth's radiative balance, cloud albedo, and precipitation by serving as nuclei for cloud droplets (Charlson et al., 1992; Solomon et al., 2007; Twomey, 1974; Albrecht, 1989). Despite the growing recognition of their importance for human health and earth systems, the uncertainties of magnitudes of these effects are still large (Solomon et al., 2007). In fact, the influence of regionally dispersed fine aerosols on weather–climate becomes more important than the immediate influence of local specific sources and of coarser particles, whose chemical composition and size distribution are two critical parameters. The size distributions of the principal fine particle constituents also have important impacts on visibility (Watson, 2002), aerosol radiative properties, and aerosol-nucleating ability (Boucher et al., 2013). The mass–size distributions (MSDs) of chemical components of fresh and aged aerosol are also critical for improving the simulation and validation of the aerosol size distributions and their optical properties (Zhou et al., 2012). Differing from conditions at ground level, the atmosphere in mountainous areas tends to have lower temperature, higher relative humidity (RH), and more intense solar radiation (Decesari et al., 2005; Li et al., 2011; Seinfeld et al., 2004). Tropospheric aerosols over mountains are most often derived from long-range transport, and therefore samples from high elevations are often representative of regional- to large-scale atmospheric conditions (Li et al., 2011; Wang et al., 2011).

As to the global scale, tropospheric aerosols are highly variable in time and space, and the aerosol chemical components over China are found to be much higher than those in most areas of the world, except for urban areas in South Asia (Zhou et al., 2012). The sampling site in this study, Mountain Tai (Mt. Tai), is located in central east China (CEC) with a peak elevation of ~ 1500 m a.s.l. As the tropospheric aerosols over mountains are most often representative of regional- to large-scale mixed origins (Li et al., 2011; Wang et al., 2011), Mt. Tai is optimal for investigating the regionally dispersed pollution. The second feature of Mt. Tai is the high frequency with which clouds envelop the mountain peaks, and it provides a region where the interaction of aerosols with clouds can be studied over extended periods of time. Although some recent studies have investigated particulate concentrations at Mt. Tai, they have been limited to the measurement of organic molecular compositions (Fu et al., 2008), gas-phase total peroxides (Ren et al., 2009), the role of biogenic volatile organic compounds (Fu et al., 2010), the impact of open crop residual burning on O₃, CO, black carbon (BC or so-called EC), and organic carbon (OC) (Yamaji et al., 2010), EC–OC and inorganic ions in PM₁₀ dur-

ing spring (Wang et al., 2011), and individual particle analysis (Li et al., 2011). These works were limited to one or two seasons with daily sampling resolutions. No systematic measurements with high time resolution of chemical components' MSDs in fine aerosol particles, covering four seasons, have yet been reported. It is essential to accurately and objectively assess the characterization of various chemical components and their size distribution of fine aerosols in high atmospheric levels in CEC.

This paper presents a data set covering 1.5 years of measurement of the mass concentrations and size distributions of selected chemical components in PM₁. The purpose is to assess the regionally representative concentration levels of different aerosol chemical components, and to obtain the seasonal variations. In terms of the high altitude of the site, making it prone to be influenced by planetary boundary layer (PBL), lower free troposphere (LFT), and cloud events, through the identification of relative fresh (associated with new particle formation events) and polluted aerosols, and aerosols in the PBL, LFT, and cloud, the MSDs of organics, sulfate, nitrate, and ammonium (OSNAC) under different conditions were estimated to better characterize the aerosol chemical compositions of well-mixed aerosols and also for model verification. As the site is often influenced by regional-scale transported pollutants, the chemical and size properties of PM₁ from different air masses are also discussed. Finally, the secondary organics aerosol (SOA) and primary OA (POA) fractions are subtyped by using a positive matrix factorization (PMF) method, and the mass loading level and contribution of different types of organics are presented and discussed.

2 Experimental procedure

2.1 Description of study

As part of the aerosol–cloud interaction study, supported by the National Key Project of Basic Research, the aerosol chemical composition analyses were conducted at the summit of Mt. Tai (36.251° N, 117.101° E), located in Shandong Province of China with the highest elevation (1534 m a.s.l.) in CEC and located along the pathway of Asian continental outflow. Tai'an is the nearest small city, 15 km away in the south with $\sim 500\,000$ population while Jinan, the capital city of Shandong Province (population: 2.1 million) is 60 km away in the north. Because the elevation of Mt. Tai station is close to the top of the planetary boundary layer, and the sampled aerosols are representative of the region rather than the immediate locality, it is a suitable site for investigating the regionally dispersed aerosol pollution over the heavily polluted CEC.

From June 2010 to January 2012, an aerosol mass spectrometer (Q-AMS, Aerodyne Research, Inc., Boston, MA, USA) was used to measure the mass concentrations

(30 nm–1 μm) of OSNAC in mass spectrometry (MS) mode with 5 min time resolution (Jayne et al., 2000; Zhang et al., 2011). The sampling periods for the AMS study were 24 June–15 August, 22 September–11 October in 2010, 26 March–20 April, 5–30 June, 22 October–1 December in 2011, and 22 December 2011–13 January 2012. As a result of interruptions due to calibration, instrument failures, and local burning events, only 123 days of valid data were obtained. From July to December in 2010, a scanning mobility particle sizer (SMPS) (TSI 3936, TSI, Inc., St Paul, MN, USA) was also used to monitor the number size distribution of aerosols over a size range of 10–680 nm at a time resolution of 5 min (2.5 min per scan, two scans) (Zhang et al., 2011). From 25 December 2010 until the end of the study, a tandem differential mobility particle sizer (TDMPS, IFT, Leibniz Institute for Tropospheric Research, Germany) and an aerodynamic particle sizer (APS, model 3321, TSI, Inc.) were used instead of the SMPS for particle number size distribution (PNSD) measurements. Together these two instruments covered particles from 3 nm to 2.5 μm in diameter. To correct the concentrations for bounce at the vaporizer and the partial transmission of particles by the lens, a fixed particle-collection efficiency factor of 0.5 was used, which was obtained in studies conducted in Beijing (Sun et al., 2010; Zhang et al., 2011, 2012d), and a comparison of results presented below indicates that a reasonable correction was conducted.

Detection limits (DLs) for the AMS mass concentration were evaluated based on the mass spectra of particle-free ambient air, that is, air filtered with a HEPA filter. The DLs were defined as three times the standard deviation of each species signal in the particle-free air. During this study, the DLs for sulfate, nitrate, ammonium, organics, and chloride for the 5 min averaged data were 0.03, 0.017, 0.063, 0.101, and 0.01 μg m⁻³, respectively (Zhang et al., 2011).

The room temperature was controlled at 25 ± 3 °C, 40–60 % for RH and atmospheric air was sampled through a PM₁₀ impactor, which was followed by a PM_{2.5} cyclone (the flow rate was 16.7 L min⁻¹) and dried to RH < 30 % with the use of an automatic aerosol dryer unit (Tuch et al., 2009).

2.2 Quality assurance of the data

To validate the assumed collection efficiency and demonstrate the data quality of our measurements, a plot of the NR-PM₁ mass concentration from the AMS against the reconstructed mass obtained with the SMPS/TDMPS is shown in Fig. 1. Here, the SMPS/TDMPS dry mass concentrations were obtained by converting the measured SMPS/TDMPS number distributions to volume distributions which were then integrated into total volume and multiplied with the aerosol density, and then SMPS/TDMPS mass was calculated. The aerosol density used in SMPS/TDMPS mass calculations was assumed to be that of the average composition of (NH₄)₂SO₄, NH₄NO₃ and organics, whose densities are 1.77, 1.72, and 1.3 g cm⁻³, respectively. As noted

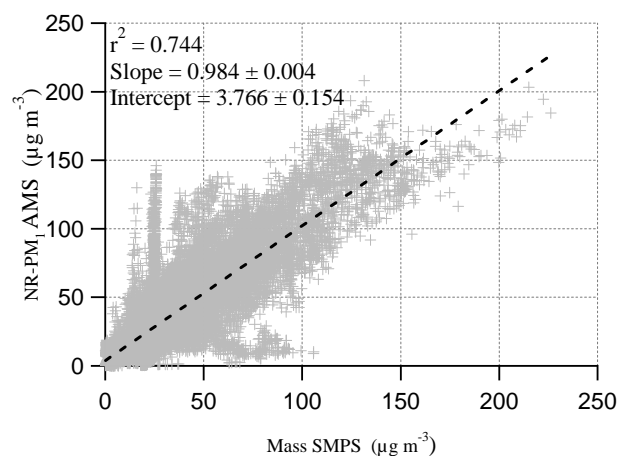


Figure 1. Correlation between AMS and (reconstructed) SMPS mass concentrations.

above, fixed collection efficiency (CE) of 0.5 was assumed for the entire study, which generally yielded a good correlation between the AMS and reconstructed SMPS/TDMPS mass data. The coefficient of determination (r^2) of AMS mass vs. SMPS/TDMPS mass was 0.744 with a slope of 0.984, demonstrating a good level of agreement in the masses obtained by the two methods.

2.3 Data separation of PBL, LFT, and NPF in cloud, polluted, and different air masses

Characterization of air masses sampled at the site from either PBL or LFT is important to the subsequent analysis of the chemical data. In this study, the criteria developed by Gallagher et al. (2011) were used to differentiate the data influenced by the PBL vs. the LFT. Data during night time (00:00–06:00) were considered to have been influenced by the LFT. The day time between 8:00 and 20:00 with enhanced water vapor and high aerosol concentration at the mountain top was considered to be a signal of PBL influence on the mountain. The new particle formation (NPF) events were identified based on the evolution of the size distributions and particle number concentrations following Kulmala's definitions (Kulmala et al., 2004). The in-cloud events were picked up based on the meteorological data when the relative humidity was in the range 95–100 % with no rain event. The polluted episodes were the periods with high mass concentration and high number concentration for accumulation mode particles.

To characterize the long-range transport pathways, 72 h back trajectories were computed every 6 h (00:00, 6:00, 12:00, and 18:00 UTC) using the HYSPLIT-4.8 (Hybrid Single Particle Lagrangian Integrated Trajectories) model of the National Oceanic and Atmospheric Administration, USA (NOAA) (<http://ready.arl.noaa.gov/HYSPLIT.php>). The resolution of the terrain data in the HYSPLIT model is 1° × 1°,

thus the real height of the mountain site has been smoothed. Therefore, 1500 m above the model ground level was chosen as trajectory start height, which is about 840 hPa in the model and is a little lower than the pressure of the measurement site (845 hPa). TrajStat (Wang et al., 2009), a program using trajectory statistical analysis data to identify potential source pathways and locations from long-term air pollution measurements, was used to construct clusters from the air-mass trajectories for long-range transport pathways study. The Global Data Assimilation System (GDAS) meteorological data archives of the Air Resource Laboratory, NOAA, were used as the input.

3 Results and discussion

3.1 Mass concentration of chemical components

The annual mean mass concentrations of OSNAC in PM₁ were 11.2, 9.2, 7.2, 5.8, and 0.95 $\mu\text{g m}^{-3}$, respectively, totalling $\sim 34.3 \mu\text{g m}^{-3}$. This PM₁ concentration is roughly half of the ground-based values at urban Beijing (~ 500 km northwest of Mt. Tai) ($\sim 76 \mu\text{g m}^{-3}$) (Zhang et al., 2012d), lower than that in suburban Gucheng station ($\sim 52 \mu\text{g m}^{-3}$), $\sim 38\%$ of the suburban Tianjin level (~ 80 km southeast from Beijing), and lower than that at several urban/rural sites in the Pearl River Delta in China (Xiao et al., 2011). It is higher than that in several European cities ($10\text{--}30 \mu\text{g m}^{-3}$) (Lanz et al., 2007) and some field studies conducted at various ground sites in urban areas, downwind of urban areas, and rural/remote locations in the mid-latitudes of the Northern Hemisphere (Zhang et al., 2007), comparable to that of Mexico City (Volkamer et al., 2006). The mass concentrations of chemical components in PM₁ at Mt. Tai are about a factor of 2–3 lower (for organics and sulfate), and slightly lower (for nitrate, ammonium, and chloride) than those at the near surface rural areas of China (Zhou et al., 2012). The mass loading of Mt. Tai is much higher than that at other elevated sites such as Whistler Mountain (Sun et al., 2009), Mt. Jungfrauoch (Cozic et al., 2008), and a Himalayan station in Nepal (Decesari et al., 2010). The chemical components of PM₁ in spring for this study are about 45% of the previous research results during March–April 2009 from filter results in PM₁₀ (Wang et al., 2011) of a study carried out at the same site. But they are larger than at high-altitude sites in Europe, Japan, India, and the USA in TSP, PM₁₀, or PM_{2.5} (Table 1).

Seasonally, the average concentrations of PM₁ in spring, summer, fall, and winter were 30, 55, 18, and 37 $\mu\text{g m}^{-3}$ respectively, which is similar to previous research for PM_{2.5} (Zhou et al., 2009) at Mt. Tai (Table 1), but somewhat different from typical seasonal patterns of winter minimum and summer maximum at Mt. Jungfrauoch (Cozic et al., 2008). For Mt. Tai, in summer, plenty of volatile organic compounds (VOCs), gas-phase pollutants, active photochemistry, and stagnant meteorological conditions on regional scale re-

sulted in the high concentration of chemical species within the boundary layer. With enhanced thermally driven convection, the vertical transport of ground pollutants influences the site markedly. The minimum concentrations in fall would be related to the weak vertical mixing, reduced emission from ground, and active horizontal regional transport from clean places. In winter, although the site was more easily influenced by LFT for weak vertical transport, the pollutants from coal combustion for heating would increase the mass concentration of near surface aerosols and cause relative high concentration at the Mt. Tai through vertical convection.

3.2 Relatively aged chemical components with summer maximum found at the elevated site

Figure 2 summarizes the average MSDs of organics, sulfate, nitrate, and ammonium on an annual and seasonal basis. The MSDs of these four chemical species in particles with diameters between 30 and 1000 nm were found to be approximately lognormal. The annual mass median diameters (MMDs) for bulk organics, sulfate, nitrate, and ammonium in the entire observational period were quite similar: 538, 585, 540, and 541 nm, respectively. The standard deviations (σ_g) of the fitted MSDs were generally less than 2, showing that accumulation mode particles significantly impact the MSDs for each chemical component.

Seasonally, maximum MMDs for almost all chemical components were found in summer and fall, and minimum MMDs in spring. During summer half year, high temperature, high relative humidity, and strong radiation enhanced oxidation reactions; under the stagnant meteorological condition, the aerosol will stay longer at the atmosphere, and the aged pollutants are prone to be transported to the site via the vertical convection process, which results in more aged aerosols. In the winter, organics and nitrate display smaller MMDs than sulfate, indicating that the organics and nitrate are fresher than sulfate. The local emissions from coal combustion and traffic are the main sources contributing to organics and nitrate, and the aged sulfate is from the regional transport. In addition, the smallest MMDs were found in spring, which was due to the transport of relatively fresh aerosols from the north. Consequently, relatively larger MMDs were also found at this high elevated site than at several ground sites in the North China Plain (NCP), including the suburban Gucheng station, suburban Tianjin (Zhang, 2011), and urban Beijing (Zhang et al., 2012d), showing the relative aged and regionally dispersed fine aerosols received compared with those from ground-based measurement.

Table 1. The concentration of main aerosol chemical species at Mt. Tai compared to other mountain stations, SOC represents secondary organic carbon. Data are provided in $\mu\text{g m}^{-3}$.

Location	Height (m)	Period	Size range	Organics	OC	EC	SOC	Sulfate	Nitrate	Ammonium	Reference
Mt. Tai, China	1534	Annual (2011)	PM ₁	11.2				9.2	7.2	5.8	This study
		Spring (2011)		8.6				7.3	8.8	5.6	
		Summer (2010, 2011)		16.4				20.1	8.3	11.0	
		Fall (2010, 2011)		5.7				5.7	3.8	2.9	
		Winter (2011)		11.6				8.7	9.6	6.8	Wang et al. (2011)
		Mar–Apr 2009	PM ₁₀		13.0	3.3	7.9	16.0	20.0	12.0	
		From south			12.0	2.7		21.0	23.0	16.0	
		From north			13.0	2.8		14.0	18.0	10.0	
		Spring 2007	PM _{2.5}					12.8	5.8	5.6	
		Summer 2007						22.9	4.0	8.0	
Mt. Hua, China	2060	Mar–Apr 2009	PM ₁₀		5.9	1.4	2.1	13.0	5.0	2.5	Wang et al. (2011)
Mt. Waliguan, China	3816	Oct–1994	TSP					0.2	0.2	0.3	Yang et al. (1996)
Zhuzhang, China	3583	Jul 2004–Mar 2005	PM ₁₀		3.1			1.6	0.5	0.2	Zhou et al. (2012)
Mt. Yulong, China	3100	Jan–Feb 2010	TSP					1.8	0.6	0.4	Zhang et al. (2012b)
Lhasa, China	3363	Annual 2006	PM ₁₀		21.0	3.7					Zhang et al. (2008)
Mt. Whistler, Canada	2182	Spring 2006	PM ₁	1.1				0.6		0.2	Sun et al. (2009)
Mt. Jungfrauoch, Switzerland	3580	Jul–Aug 2005	TSP	1.7				0.1	0.1	0.04	Henning et al. (2003)
		Jul–Aug 2005	PM ₁	1.3				0.6	0.1	0.3	Cozic et al. (2008)
NCO-P, Nepal	5079	Apr 2006–May 2008	PM ₁₀		1.5	0.2		0.7	0.3	0.2	Decesari et al. (2010)
			PM ₁								
Mt. Fuji, Japan	3776	Jun 2001–Aug 2002	TSP					1.2	0.1	0.3	Suzuki et al. (2008)
Mt. Abu, India	1680	Annual 2008	TSP		3.7	0.5	1.2	2.9	0.6	0.4	Rastogi and Sarin (2005); Ram et al. (2008)
		Mar 2007–Feb 2008	PM _{2.5}					3.9	0.3	1.2	Kumar and Sarin (2010)
		Mar 2007–Feb 2008	PM _{2.5–10}					0.5	1.1		
		Jan–Dec 2005	PM ₁₀					2.5	1.0	0.1	Chatterjee et al. (2010)
		Jan–Dec 2005	PM _{2.5}					3.8	3.3	0.9	
Manora Peak, India	1950	Winter 2004	TSP		8.7	1.1	2.3	2.6	0.5		Rengarajan et al. (2007)
Yosemite NP, USA	1603	Jun–Sep 2002	PILS method					1.0	0.3	0.4	Lee et al. (2008)
San Gorgonio, USA	1705	Apr–2003						0.6	3.2	0.9	
		Jul 2003						1.3	1.3	1.0	

3.3 PBL, LFT, and NPF events and in-cloud and polluted episodes

3.3.1 Mass concentration of chemical components for different episodes

In order to further explore the controlling factors on aerosols at this site, episodes influenced by PBL, LFT, and NPF, enveloped by cloud (in-cloud), and polluted episodes were classified following methods mentioned in Sect. 2.3 throughout the entire study. Overall, the site was influenced by PBL and LFT at same frequency in spring and winter, while it was influenced more by PBL than by LFT in summer and fall. Cloud and polluted episodes occurred more frequently in summer and fall, and NPF events were observed mostly in spring.

Figure 3 shows the average mass concentration of PM₁ during these episodes. It is shown that the highest, $66 \mu\text{g m}^{-3}$, was from the polluted episode, and lowest was during NPF events from a large contribution of ultrafine particles. The mass loading during PBL influence was slightly higher than that during LFT ($42 \mu\text{g m}^{-3}$) and in cloud ($40 \mu\text{g m}^{-3}$). This LFT mass level is about 2–10 times higher than that monitored during night time at Mt. Jungfrauoch (Cozic et al., 2008), NCO-P (Decesari et al., 2010) and Murodo (Kido et al., 2001). The relatively high concentration at the free troposphere of Mt. Tai indicated that although the boundary layer descended lower than the site, almost 80 % of pollu-

tants transported by the vertical convections stayed at low free troposphere or residual layer, and the pollutants from the ground have impacted the air quality of the mountain site seriously.

The proportions of OSNAC in different episodes for PM₁ are presented in Fig. 3 by pie charts, which show that organics and sulfate contribute distinctly to in-cloud and NPF events. During the new particle formation events, the percentage of organics and sulfate was 37 and 22, respectively. Conversely, sulfate dominated the aerosols with 38 %, and organics contributed less with 24 % in cloud episodes. The higher measured sulfate mass concentrations in the cloud residuals were also observed at the top of East Peak mountain in Cape San Juan (Allan et al., 2008). Most sulfate aerosols in the atmosphere are secondary sulfate formed by the oxidation of gaseous precursors (SO₂), followed by particle formation through nucleation and condensation processes. There are several pathways for sulfate formation such as liquid-phase reactions inside cloud droplets or oxidation of SO₂ with OH via gaseous phase reactions (Calvo et al., 2012). As the saturation vapor of sulfuric acid is very low, it is not found in the gaseous phase in the troposphere but rather condenses rapidly to form droplets of a sulfuric acid solution. Under normal atmospheric conditions, these particles are partially or totally neutralized by ammonia (NH₃) and in the process, depending on relative humidity, they may become solids (Wang et al., 2008). In this case, ammonium sulfate is more stable in the atmosphere. Once there is sufficient

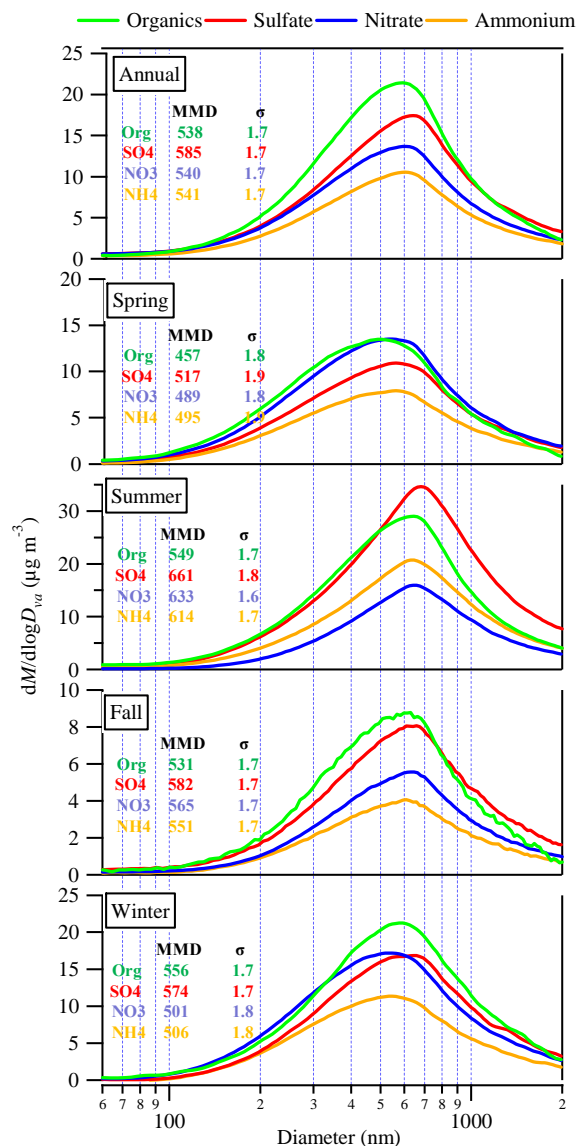


Figure 2. Mass size distributions of chemical species on annual and seasonal scales.

supply of water vapor, it is possible that some of the mass could have been added in the cloud through aqueous processes, and the sulfate-dominant particles were more easily activated as cloud condensation nuclei (CCN). With the polluted background and limitation of water vapor, still some interstitial aerosol remained in the cloud and was measured by the AMS. The higher contribution of organics in NPF events indicates its significant role for the particle formation and growth process. The importance of organics by the atmospheric new particle formation was emphasized in several researchers (Kulmala et al., 2013). A similar phenomenon was observed and discussed in more detail in a ground site study in Beijing (Zhang et al., 2011). In terms of nitrate, ammonium, and chloride, no dramatic variations in their pro-

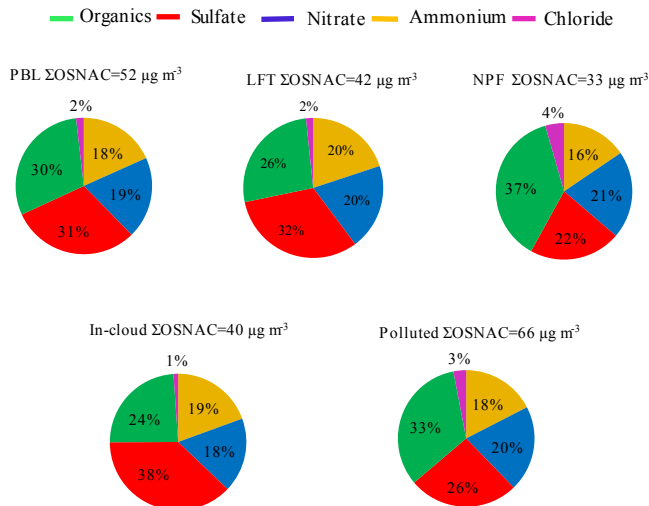


Figure 3. Mass concentrations of chemical components in different episodes.

portions of PM₁ were observed in these episodes, indicating their minor roles.

3.3.2 Mass size distributions of chemical components during different episodes

The MSDs of PM₁ (Σ OSNA) and chemical species, and their proportions at different size ranges during PBL, LFT, and NPF events, and in-cloud and polluted episodes are plotted in Figs. 4 and 5. In total, the MSDs of PM₁ for these episodes displayed accumulation mode with 600–700 nm MMD, except smaller MMD (550 nm) with wider size distribution for NPF. The standard deviation of the fitted MSD for NPF ($\sigma = 2.1$) was larger than in other episodes ($\sigma = 1.7 - 1.8$) for the impact of small particles. The same MSDs for other events were found, indicating they may originate from similar sources or from the evolution process again.

Since NPF events are the significant sources of the aerosols, the links between MSDs of NPF events and polluted episodes can be employed to investigate the evolution of particles. Statistical results from all the NPF events and polluted episodes showed comparatively small MMDs (~ 373 – 459 nm) for organics during NPF events at Mt. Tai and larger MMDs (~ 473 – 792 nm) during polluted episodes. The nitrate and ammonium also displayed relatively smaller MMDs during NPF than during polluted episodes. No obvious differences of sulfate MMDs between NPF events and polluted episodes were found, meaning that sulfate was more aged than organics, nitrate, and ammonium in NPF events. This phenomenon suggests that sulfate may originate from regional polluted area, and organics, nitrate, and ammonium from local sources. In this paper, the ratio of the value of MMD between the polluted episodes and NPF events is defined as an increasing factor. The organics' increasing factors

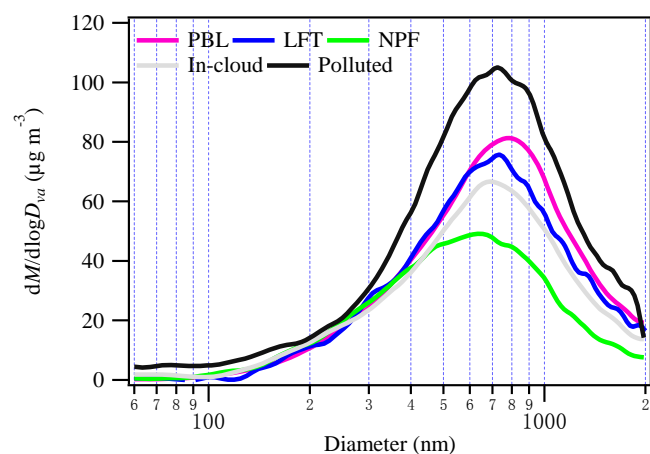


Figure 4. The MSDs of PM₁ in different episodes.

in MMDs between NPF events and polluted episodes are larger than for an urban ground site in Beijing (~38–61%), a suburban site in Wuqing (~27–32%), and a rural site in Gucheng (8–42%). The increasing factors for sulfate, nitrate, and ammonium in Beijing were all lower than that at Mt. Tai. The increasing factors of MMD from NPF events to polluted episodes at Mt. Tai are smaller than those in less polluted areas. At a regional site in Pittsburgh, USA, the increasing factors for organics, sulfate, nitrate, and ammonium from a nucleation event to polluted air were 165, 200, 29, and 160%, respectively. These data suggest that the background level of aerosol would influence the evolution of MMDs, and the MMDs to a certain degree, i.e., the pollution level and particle aging.

As the MSDs of chemical species were very similar between PBL and LFT, the LFT's MSDs are omitted from Fig. 5. By investigating the MSDs and percentage of chemical species in different size modes, organics and sulfate were found to present different roles, while nitrate and ammonium displayed relatively stable patterns. During PBL, NPF events, and polluted episodes, organics accounted for major proportions at small mode, and organics were about 70% at 100–200 nm particles in polluted episodes. Under episodes influenced by PBL and NPF, half of chemical species were organics for the particles around 100 nm, 20% from sulfate, another 20% from nitrate, and 10% from ammonium. The larger the particle was, the more the sulfate contributed to the particles. In cloud episodes, sulfate contributed most fractions (60%) to the small particles (100–200 nm), and dominated the particles through the whole size range of PM₁. Organics occupied less, with 20%, at small particles. The percentage of organics increased to a maximum at 200–300 nm, and fractions of nitrate and ammonium increased accordingly. In total, more than 70% of inorganics contributed to the PM₁ in-cloud episodes. Due to the hygroscopicity of ammonium sulfate and ammonium nitrate, they were likely

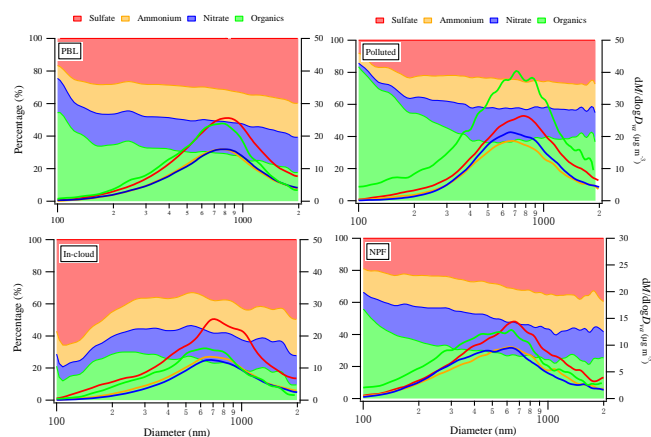


Figure 5. The MSDs and proportions of chemical species in different episodes.

grown by water uptake and partially participated in the cloud formation.

3.4 Transport pathways and associated chemical component changes

Seven main back-trajectory clusters were identified by using TrajStat and the HYSPLIT-4.8 model (Fig. 6). Based on the distances of air masses transported, clusters 1, 2, and 3 were defined as short pathways, cluster 4 and 6 were mediums, and clusters 5 and 7 were considered as long transport pathways. Cluster-1 (~17% of the total) represents the shortest transport pathway, which was from the south. These trajectories passed over Xuzhou in Anhui Province, an area that suffers from serious pollution, mainly due to biomass burning (Wang et al., 2002; Woo et al., 2003; Suthawaree et al., 2010). Tai'an, a prefecture-level city, located on the southern flank of Mt. Tai, is a likely source for pollution when the airflow followed this pathway. Trajectories in Cluster-2 (~16%) started over the Yellow Sea and passed over the eastern side of the Shandong Peninsula. Air masses following this relatively short path would bring both marine aerosol and ground-level air pollutants to Mt. Tai. Cluster-3 (another ~25%) was from the north/northeast of Mt. Tai, starting at Chengde in Hebei Province and then passing over Bohai sea and through Shandong Peninsula. The three short distance clusters account for ~60% of all the air masses, showing that the majority of regionally dispersed aerosols received at Mt. Tai were from short distance mixed aerosols, mostly from its south.

Cluster-4 (~7%) shows the airflow from the north of China to the NCP, including Tianjin and Hebei Province. These trajectories are representative of a regional-scale transport path. Trajectories in Cluster-5 (20%) originate over remote areas in north/northwest China with a transport path above 3000 m. These air masses swept through Hebei province to the site at high wind speed, which has assumed

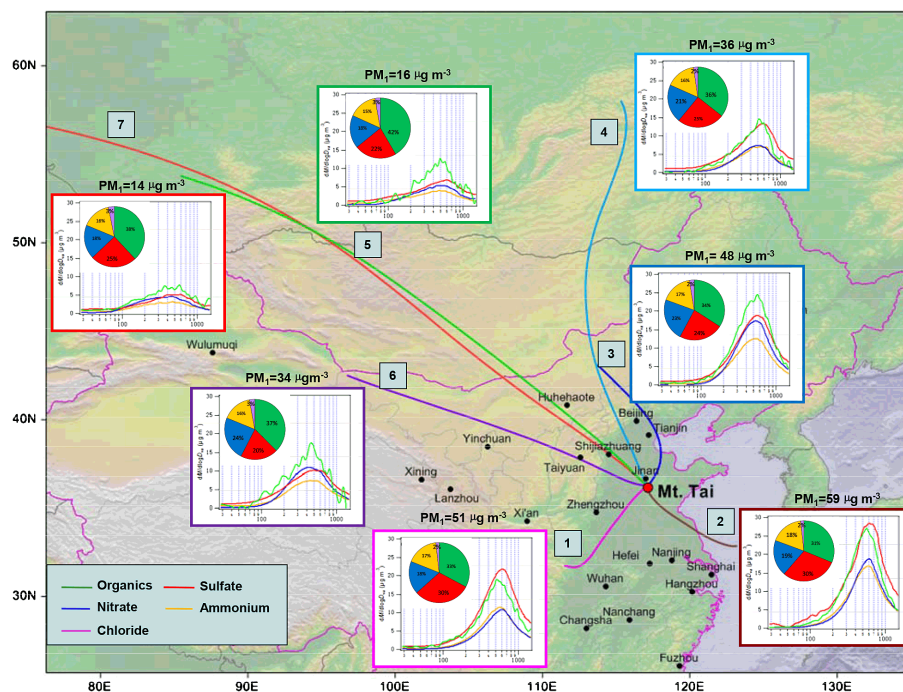


Figure 6. Averaged mass concentrations, mass-size distribution, and percentage of chemical components associated with different air-mass trajectory clusters.

to deliver most of aerosol in the FT. Cluster-6 ($\sim 11\%$) represents regional transport from the west of Mt. Tai. Cluster-7 (4%) represents a group of trajectories from the further northwest with longer distances. The air masses in these four clusters account for another $\sim 40\%$ of all transport, and bring less polluted aerosol from the north. These can also be supported by the sums of the mass concentrations of the OSNAC of 51, 59, and $48\ \mu\text{g m}^{-3}$ for the first three clusters aerosols, and 36, 16, 34, and $14\ \mu\text{g m}^{-3}$ for the rest of the clusters respectively. The mass loadings for Clusters 5 and 7 were the lowest of the seven clusters. Even though they are still much higher than those at Whistler Mt. ($1.2\ \mu\text{g m}^{-3}$), they are close to a similar level to what has been observed in Korea and Japan ($11\text{--}13\ \mu\text{g m}^{-3}$) (Zhang et al., 2007). The MMDs, standard deviations, and mass concentrations of chemical Mass concentrations but no size information for chloride are presented because no mass fragmentation of chloride was selected in time-of-flight (TOF) mode during the study. The relatively smaller MMDs were also found for chemical components associated with long-distance transported aerosols (clusters 4–7), suggesting relatively fresh aerosols, while the larger MMDs for short clusters indicated that the aerosols were more aged.

Organics and sulfate were the two largest fractions, accounting for $\sim 30\%$ each for the ΣOSNAC in the airflow associated with the first three short-distance paths (clusters 1, 2, and 3) from the south (Table 2), demonstrating again more pollutants from Pan-Yangtze river delta area. The ni-

trate was about 20% with mean concentrations of 9.0, 11.2, $10.9\ \mu\text{g m}^{-3}$ for cluster 1, 2, and 3 respectively. The ammonium and chloride were the two smallest fractions with ~ 17 and 2%, respectively. The much higher organics were found for aerosols that traveled a long distance from the north relative to the short-distance moving aerosols from the south. About 40% organics were found in aerosols associated with clusters 4, 5, 6, and 7.

3.5 Composition of OA

To further investigate the secondary OA, AMS-PMF modeling of OA spectra (Aiken et al., 2009; Ulbrich et al., 2009) was used to identify presumptive sources for the OA during each of four seasons at Mt. Tai. Different types of organics were resolved based on specific mass-spectral profiles, and the mass concentrations are presented in Table 3. The mass spectra for hydrocarbon-like OA (HOA) are characterized by hydrocarbon ions of the general form $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$, including C_3H_7^+ (m/z 43), C_4H_7^+ (m/z 55), and C_4H_9^+ (m/z 57). A signal from m/z 60, a tracer ion for biomass burning OAs (BBOAs; Alfarra et al., 2006; Aiken et al., 2009), which can be attributable to primary OA (POA; Jimenez et al., 2009), was resolved in the mass spectra from spring, summer, and fall. In winter, another factor with high m/z 43 and m/z 60 was identified as the coal-combustion OA (CCOA) (Sun et al., 2013). The mass concentration of subtype organics and their percentage in organic matter are presented in Table 3. HOA, BBOA, and CCOA can be

Table 2. MMDs (nm), standard deviations (σ_g), and mass concentration (Mass, $\mu\text{g m}^{-3}$) for chemical components in samples grouped by air-mass trajectory cluster.

Air mass	Organics			Sulfate			Nitrate			Ammonium			Chloride
	MMD	σ_g	Mass	MMD	σ_g	Mass	MMD	σ_g	Mass	MMD	σ_g	mass	Mass
Cluster 1	545	1.7	16.8	570	1.7	15.6	582	1.7	9.0	542	1.7	8.7	0.9
Cluster 2	533	1.6	18.2	584	1.7	17.6	581	1.6	11.2	553	1.7	10.2	1.0
Cluster 3	511	1.7	16.4	528	1.8	11.4	514	1.7	10.9	497	1.8	8.1	1.2
Cluster 4	464	1.7	12.8	517	1.7	9.1	470	1.7	7.4	478	1.7	5.8	0.8
Cluster 5	458	1.6	6.8	515	2.0	3.7	462	2.1	2.9	440	2.0	2.5	0.5
Cluster 6	417	1.8	12.7	464	2.0	6.8	435	1.8	8.0	437	1.9	5.4	1.0
Cluster 7	426	2.0	5.2	459	1.9	3.4	357	2.3	2.5	395	2.2	2.1	0.4

Table 3. Seasonal averaged mass concentrations ($\mu\text{g m}^{-3}$) and standard deviation (in parentheses) of specific types of organic aerosols from positive matrix factorization analysis.

Subtype organics*	Spring	Summer	Fall	Winter
Primary OA				
HOA	2.3 ± 1.2 (27 %)	1.6 ± 1.8 (10 %)	0.60 ± 0.38 (11 %)	5.6 ± 1.6 (37 %)
BBOA	2.1 ± 1.1 (24 %)	5.1 ± 10.7 (34 %)	1.1 ± 0.65 (19 %)	
CCOA			1.1 ± 0.61 (19 %)	3.3 ± 2.2 (22 %)
Secondary OA				
SV-OOA		3.1 ± 4.2 (21 %)		
LV-OOA	4.2 ± 2.3 (49 %)	5.3 ± 6.4 (35 %)	2.9 ± 1.59 (51 %)	6.1 ± 3.56 (41 %)

* HOA = hydrocarbon-like organic aerosol, BBOA = biomass-burning organic aerosol, CCOA = coal combustion organic aerosol, semi-volatile oxidized organic aerosol = SV-OOA, and low-volatility oxidized organic aerosol = LV-OOA.

considered as POA directly emitted into the atmosphere. The POA dominated OA during winter with 59 % of organics, and accounted for 51, 44, and 48 % of OA in spring, summer, and fall, respectively. The same result was reported at a ground site in urban Beijing in winter (Sun et al., 2013). BBOA was derived from the AMS database by the PMF model in spring, summer, and fall. In China, June is the high season for harvest of wheat, and also the period when straw burning takes place intensively in some parts of the country (Qu et al., 2012). A previous study mentioned the field burning of wheat straws in the North China Plain during May–June 2006 in urban areas such as Beijing (Li et al., 2007). Study based on organic molecular compositions of Mt. Tai also identified levoglucosan in summer (Fu et al., 2008). It is deemed that burning of agriculture and crop residues is the main source of BBOA that influenced the site. On the other hand, as a tourist spot, burning of incense is a feature of Mt. Tai. Although some special incense burning events including weekends, holidays, and traditional festivals have been deleted in the data sets, incense burning probably is another BBOA source on Mt. Tai on normal days, which needs further investigation. Assuming the emission from incense burning was constant, more BBOA was measured in summer than spring and fall, which suggests intensive emission from field

burning of agriculture residues in summer. In winter, 37 % of organics was identified as HOA and 22 % as CCOA. Coal combustion in China has been found to emit a large quantity of carbonaceous aerosols, contributing 70 % of total emitted PM_{2.5} (Zhang et al., 2012a). It is widely accepted that HOA is mainly associated with combustion-related emissions, e.g., diesel exhaust (Sun et al., 2013). The relatively high concentration of HOA in winter should result from the low ambient temperature and low atmospheric oxidants, and most fresh traffic exhaust was transported to the site with less oxidation.

At Mt. Tai, one can still find other large fractions of oxygenated organic aerosol (OOA), which is generally considered to be secondary (Herndon et al., 2008; Volkamer et al., 2006), in which two subtypes of OOA can be distinguished by a large fraction of CO₂⁺ (m/z 44) for LV-OOA and by C₃H₇⁺ (m/z 43), CO₂⁺ (m/z 44), C₃H₃O⁺ (m/z 55), and C₃H₅O⁺ (m/z 57) for SV-OOA. LV-OOA is strongly correlated with non-volatile secondary species such as sulfate and has a high O:C, mainly attributable to regional, heavily aged OA; SV-OOA has a higher correlation with semi-volatile species such as ammonium nitrate and ammonium chloride and has a lower O:C, consistent with less photochemically fresh OA (Jimenez et al., 2009). SV-OOA and

LV-OOA together contributed 49, 55, 51, and 41 % from spring to winter. More OOA was observed in summer, which was attributed to the strong photochemical reaction and sufficient oxidization process along with regional dispersal in the CEC. This finding about relative contributions of POA and SOA is similar to a 2 yr filter measurement from 16 sites in various regions of China, which reported that the secondary organic carbon contributed ~ 55 and 60 % for urban and rural aerosols, respectively (Zhang et al., 2012c).

4 Summary

The mass concentrations and size distributions of chemical components in PM₁ were characterized in situ with an AMS at the summit of Mt. Tai (~ 1500 m a.s.l.) from June 2010 to January 2012.

The mass concentration of OSNAC in PM₁ at Mt. Tai is higher than mass concentrations at most mountain sites in the USA and Europe, but comparable with previous research results at Mt. Tai. Seasonally, high concentrations of all chemical components at ~ 1500 m high level were found in summer with a minimum in fall, slightly different from typical seasonal patterns in various aerosol components at ground-based measurement in China ("spring minimum"). This seasonal pattern was controlled by the development of PBL, horizontal transportation, and local emissions.

The MSDs for organics, sulfate, nitrate and ammonium were approximately log-normal, with more than 99 % mass fraction attributable to the particle with diameter larger than 100 nm. Different from the seasonality of mass concentrations, maximum MMDs for almost all chemical components were found in summer and secondary high values in fall with a minimum in spring, indicating that the summer half of the year was more conducive to the formation of aged fine aerosols. Larger MMDs are found at Mt. Tai than in ground sites, showing the relative aged and well-mixed aerosols observed. Smaller MMDs were found for organics of the NPF events compared to the aged episodes with MMDs of ~ 473–792 nm. Compared with MMD of organics between NPF events and polluted episodes at Mt. Tai, small increasing factors have been reported at an urban ground site in Beijing (~ 38–61 %), a suburban site in Wuqing (~ 27–32 %), and a rural site in Gucheng (8–42 %). Larger increasing factors for sulfate, nitrate, and ammonium were found in less polluted sites in Europe and the USA. The MMDs of chemical species could indicate the pollution level and particle aging to a certain degree.

Five kinds of episodes influenced by PBL, LFT, NPF events, and in-cloud and polluted episodes at Mt. Tai were classified. The highest mass concentration was observed during polluted episodes with large MMD and the lowest in NPF events with relatively small MMD. The LFT was 80 % of PBL, indicating that most pollutants in PBL could be transported to the low free troposphere. For chem-

ical species, organics dominated the PBL, NPF events, and polluted episodes and sulfate dominated in-cloud episodes. There were no obvious variations on proportions of nitrate and ammonium in five kinds of episodes. In cloud, inorganics contributed 70 % to the PM₁ at the whole size range, and sulfate dominated with 40 % of the small mode particles, while organics were 20 % of small mode particles. The larger quantities of inorganics in particles make them easier to add into the cloud through water uptake.

The air-mass back trajectories were grouped into seven clusters. Three of the clusters exemplified transport from the north, east, and south of Mt. Tai; two medium length clusters were from the northwest and west of site, and two long-range clusters showed airflow from the northwest of the site. Shorter transport pathways corresponded to higher aerosol mass concentrations. The analysis of transport showed that the air quality at Mt. Tai was impacted by the pollution from the Shandong Peninsula, the NCP, and areas immediately north of Suzhou. The air masses represented by clusters 5 and 7 brought clean, dry air from the northwest, which swept pollution away from the site.

At Mt. Tai, a large fraction (normally half) of total OA can still be attributable to OOA that is considered to be generally secondary. Extra high proportions of SOA found in summer represented the intensive solar radiation and oxidized process. Regionally, heavily aged OA were observed with > 40 % OOA. HOA, BBOA, and CCOA were considered as primary organic matter (POA) directly emitted into the atmosphere, and accounted together for 51, 44, 48, and 59 % of the total measured organics in spring, summer, fall, and winter, respectively. Considerable amounts of BBOA in summer and CCOA in winter were found, with 34 and 22 % of OA respectively.

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