Measurement of ambient aerosols by single particle mass spectrometry in the Yangtze River Delta, China: Seasonal variations, mixing state and meteorological effects

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ABSTRACT

Continuous measurements of ambient aerosols were performed with a single-particle aerosol mass spectrometer in Nanjing during all four seasons of 2015. Ambient particles were clustered into 11 classes, which included elemental carbon (EC) mainly with sulfate (EC-S); EC with nitrate and sulfate (EC-SN); EC with obvious organic signals (ECOC); organic carbon (OC); biomass/biofuel burning particles (Biomass); Ammonium; particles with obvious Na, K (NaK) and sulfate (NaK-S), NaK with nitrate and sulfate (NaK-SN); iron-containing particles (Fe-rich); miscellaneous metal-containing particles (MiscsMetals) and Dust. Seasonal local sources, dominated air masses and distinct atmospheric processes all affected the concentrations of various particles and caused different diurnal changes. EC-SN during summer slowly increased in the afternoon and NaK-SN had a peak at noon during winter. Differences in size distribution of each particle type between seasons were discussed. All types of particles showed unimodal number size distributions, their peak radius ranked as follows: fall < spring < summer ≤ winter. OC during fall had higher number fractions of between 0.2 and 0.5 μm (> 20%) as a result from the decrease in temperature and increase in relative humidity (RH). The distributions of ECOC varied with seasons and were obviously influenced by EC and OC particles. Mixing states showed seasonal variations. In general, the fractions of particles mixed with secondary species were the highest/lowest in winter/fall. The effects of meteorological conditions on particles were investigated. With the increase of RH, the fractions of EC increased, and most particles mixed with more NH4+ and less C2H3O+. Characteristics of precipitation, such as duration and total rainfall amount, influenced particles. Enhanced secondary organic/inorganic species were found in particles during long/short-term precipitation with intensities < 1 mm. Less NH4+, C2H3O+ and HSO4− were found during precipitation compared with non-precipitation days.

1. Introduction

Atmospheric visibility, air quality, public health and global climate are closely related to the characteristics of aerosol particles, and thus, relevant studies are appearing worldwide (Bäumer et al., 2008; Langridge et al., 2012; Lohmann and Feichter, 2005; Poschl, 2005; Tang, 2010). The Yangtze River Delta (YRD) is the largest estuary delta and one of the most developed and densely populated regions; rapid industrialization and urbanization has resulted in numerous pollutants in the air, which has facilitated serious air pollution (Fu et al., 2014; Wang et al., 2014). Nanjing is one of the largest cities in the YRD, which is also a comprehensive industrial base in eastern China. Due to various sources and meteorological conditions, the particle matter (PM) level in Nanjing still is high and haze pollution appears frequently, especially during winter (Fu et al., 2013; Kang et al., 2013; Li et al., 2015). Considering that meteorological conditions differ dramatically between seasons, the seasonal variations in the chemical components, size distributions and mixing states of aerosol particles are notable and worth investigation.

The most intuitive, seasonality of ambient chemical components was varied. Results in urban Nanjing showed a high secondary organic carbon/organic carbon (SOC/OC) ratio during summer, which was attributed to stronger oxidation, and the OC and elemental carbon (EC) had the highest levels during winter due to the stable weather (Li et al., 2015). As shown in the research of Zhuang et al. (2014), concentrations of black carbon aerosol (BC) in urban Nanjing were high in spring and autumn and low in summer. Observations at the four sites in the YRD region exhibited clear seasonal trends in the concentrations of fine
particles and ambient trace metals, which showed higher concentrations during winter and lower concentrations during summer (Ming et al., 2017).

Numerous previous studies also showed that the number size distributions of aerosols exhibited distinct seasonal variations and were significantly affected by meteorological factors (Zhang et al., 2013; Zhu et al., 2013). Zhu et al. (2013) presented the variations in number concentrations of particles in different size ranges in Nanjing, particles in the nuclei mode and accumulation mode had the lowest and the highest concentrations in autumn, respectively because of accumulation processes in the persistent air pollution. Yu et al. (2011) observed bimodal logarithm normal structures of aerosol volume size distributions during long-term measurement in the YRD; the fine modes had a larger peak radius in summer, whereas the coarse modes had a larger peak radius in winter.

Mixing states could influence optical properties, hygroscopicity and atmospheric lifetime of aerosols (Cahil et al., 2012), thus complicate their impact on visibility. Wang et al. (2015) observed enhanced sulfate and nitrate in carbonaceous particles during haze days in Nanjing. Due to the energy structures of the YRD, particles from local sources mixed with more chloride and nitrate, while others from long-range transportation mixed with more sulfate (Hu et al., 2018). Also the authors suggested aerosols mixed with more organics and nitrate in short-term rainfall which were different from that in long-term rainfall. Compared with rainy spring in Guangzhou, enhanced sulfate and oxidized organics were found in carbon-containing particles during the fall (Zhang et al., 2013). Wintertime submicron aerosols in Beijing showed more enhanced organics and chloride than aerosols in summer (Sun et al., 2013).

The evident seasonal activities could lead to substantial changes in ambient aerosols. Using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) in Nanjing, Zhang et al. (2015) suggested that high PM pollution appeared during harvest seasons (summer and autumn). Observation focused on biomass burning in Nanjing also showed high levels of BC (Zhuang et al., 2014) and close link between OC and estimated K* (Li et al., 2015). Moreover, fireworks burning was identified to be an important source of polycyclic aromatic hydrocarbons in Nanjing during the Chinese Spring Festival with reduced traffic, industrial and construction activities (Kong et al., 2015). In addition, coal combustion was the largest primary source during the heating season in Beijing (Sun et al., 2013).

Meteorological conditions such as the origin of air masses, temperature, relative humidity (RH), precipitation, turbulent mixing, wind speeds and direction are mainly reflected in the formation, diffusion/accumulation and deposition processes of aerosols. All of the referenced researches above have more or less mentioned the impacts of meteorological conditions on ambient particles. Here are more examples, freshly pure BC particles were observed to age rapidly from photochemical processes (Ma et al., 2017). Particles mixed with substantial sulfate and OC during afternoon were results from photochemical reactions, meantime, nitrate was correlated well with aerosols during the night because of heterogeneous hydrolysis of N2O5, low temperature and high RH (Zhang et al., 2017). Liang et al. (2017) pointed that stable conditions are essential for the variations of aerosol chemical components, and the aqueous-phase reaction is important for the formation of PM2.5 at high RH (Zhang et al., 2018).

Above all, it is obvious that most studies have concentrated on summer and winter, and thus, there has been a lack of comprehensive research on seasonal contrasts, as well as carbonaceous particles (which basically referred to EC and OC) have been the main focus, which does not represent all air conditions. Moreover, mixing states have been discussed in many special conditions, such as polluted periods and rainfall processes. Although seasonal differences also exist in mixed states, there are fewer relevant reports. Relevant seasonal studies also were limited by instruments. Traditional observations could not provide real-time single particle results, which prevented us from detailed learning about the interactions between various particles, as well as the dependence of aerosols on meteorological conditions. Furthermore, accurate observations would provide new insights into the atmospheric processes experienced by particles after emission and their seasonal differences. Although considering the results from Xu et al. (2017) and Sultana et al. (2017), there are some issues need to be fixed and we will explore those in depth in the following work.

The observation site is surrounded by commercial areas, residential areas and industrial; thus, the sampled particles were influenced by numerous sources. We conducted continuous measurements of ambient aerosols using real-time single particle aerosol mass spectrometer (SPAMS), and comprehensively analyzed seasonal variations in single particles in this paper. Furthermore, we discussed the correlations between ambient particles and meteorological conditions with the sincere hope these results would provide a more scientific basis for understanding the atmospheric processes of aerosols and air pollution mitigation.

2. Experimental methods

2.1. Sampling

Single particle measurements were obtained over nearly a year in 2015 using SPAMS (Guangzhou Hexin Analytical Instrument Co., Ltd., China); winter (between 1 and 31 January 2015), spring (from 29 March to 20 April 2015), summer (from 16 June to 15 July 2015) and fall (between 1 and 31 October 2015) periods were chosen to investigate the characteristics of particles during different seasons. Influenced by Changjiang-Huaihe Meiyu, the total rainfall duration (amount) during summer in Nanjing was 166-h (489.6 mm), which was 3.0 (15.6), 2.7 (5.4) and 3.3 (5.8) times larger than that during winter, spring and fall, respectively.

The observation site is located on the top of the meteorological building, which is approximately 40 m from the ground and 62 m above sea level, on the campus of Nanjing University of Information Science and Technology (NUIST, 32.21°N, 118.72°E). Within 1 km of the eastern observation site, there are some iron and steel plants and coproduction plants. The Nanjing Chemical Industry Park and Yangzi Petrochemical are located to the north of the site. In addition, to the west of the site were villages and agricultural fields, which included agricultural product factories, ecological parks and vineyards. Additionally, there are many roads around the observation point, such as Jiangbei Avenue Expressway in the east and G40 Hushan Expressway in the west.

2.2. Instruments and data analysis

The d4,4 (vacuum aerodynamic diameter) and chemical components of single particles were analyzed using SPAMS, which has been described in detail in previous studies (e.g., Li et al. (2011)). Briefly, aerosol particles are introduced into SPAMS using an aerodynamic lens, and then those particles are detected and aerodynamically sized by two continuous wave 532-nm green lasers. The particle chemical composition is subsequently detected through a desorption/ionization process using a pulsed laser (266 nm), and then, mass to charge ratios (m/z) for individual ions are analyzed. Particle size and mass calibrations for this instrument were carried out using standard polystyrene latex particles (PSL) and metallic solution.

The size distribution and chemical composition of particles were analyzed by YAADA software (www.yaada.org), which is used for processing the single particle mass spectral data with a MATLAB-based software toolkit. Single particle mass spectra were grouped using an adaptive resonance theory neural network, ART-2a (Song et al., 1999). During all seasons, the most abundant (96%) particles with doa of 0.2–2.0 μm were analyzed. We used a learning rate of 0.05, vigilance factor of 0.7, and 19 iterations in this experiment for ART-2a. Further
manual classification was used to refine the aerosols into 11 chemical classes based on mass spectral similarity (Table 1).

Meanwhile, the hourly meteorological parameters (wind speeds and direction, temperature, RH and precipitation) used in this observation were obtained from the China Meteorological Administration observing, and training and practice base (Nanjing) located on the campus of NUIST (http://web.nuist.edu.cn/gcjd/).

3. Results and discussion

3.1. Seasonality of ambient particles

A total of 3,553,798, 1,394,227, 1,156,629 and 4,277,879 particles with positive and negative mass spectra were collected during winter, spring, summer and fall, respectively, and accounted for 89.9%, 98.1%, 87.7% and 87.8% of the hit particles (the number of particle sizes). According to the characteristics of the mass spectrum of every single particle, 11 types of particles were classified, including EC particles mainly with sulfate signals (EC-S), EC particles with nitrate and sulfate signals (EC-SN), EC particles with obvious organic signals (ECOC), OC, biomass/biofuel burning particles (Biomass), Ammonium, particles with obvious Na, K (NaK-S), NaK-S with nitrate and sulfate signals (NaK-SN), iron-containing particles (Fe-rich), miscellaneous metal-containing particles (MiscMetals) and Dust. EC-S and EC-SN particles were collectively referred to as EC-type. NaK-S and NaK-SN particles were collectively referred to as NaK-type. Detailed classifications and characteristics of mass spectra can be found in the supplementary materials.

As shown in Table 1, during winter, spring and fall, the five top ranked particle classes were EC-SN, OC, Biomass, NaK-S and Fe-rich, and their total seasonal fractions were 82.8%, 92.5% and 88.1%, respectively, which represented all ambient conditions. The five top ranked particle classes during summer were EC-SN (38.1%), NaK-SN (22.9%), Fe-rich (13.2%), Biomass (9.0%) and EC-S (5.6%), and their total fractions were 88.8%.

The fraction of EC-S during summer increased sharply, which was 6.2, 3.3 and 1.8 times larger than those during winter, spring and fall, respectively. The significant contributions from western sources during summer may be one of the reasons (Fig. 7). The number fraction of ECOC was the highest in winter (6.2%), followed by fall (1.8%) and was lower than 1% during spring and summer. OC had the same change as ECOC, its number fractions were 12.6% (winter), 9.2% (fall) and ≤ 3% (spring and summer). The worse diffusion due to low wind speeds (both averaged 1.7 m s⁻¹) could cause more various gas precursors (mainly volatile organic compounds) to oxidize near the observation site and/or lead to further growth of OC by mixing with each other as well as with inorganic aerosols (Jimenez et al., 2009). In addition, the lowest average temperatures during winter (5.0 °C) induced the gas-phase conversion of semi-volatile species (Qin and Prather, 2006). Generally, ECOC were directly from primary combustion or the coagulation of elemental particles with volatile organics in the atmosphere (Li et al., 2014). Because of higher OC during winter and fall, higher ECOC could be formed. Due to the inconsistencies between fire points and wind directions during summer and fall (Fig. S2), the fractions of Biomass were < 10% and smaller than those winter and spring (12.9% and 14.2%, respectively). Influenced by local sources (Fig. 7) and long-range transported masses (Fig. 6), Fe-rich played an important role during all four seasons, but the fraction was the highest in summer, which was 1.7–1.8 times larger than during the other seasons. Fig. 6–7 and more discussions could be seen in the Section 3.5.1.

Table 1

<table>
<thead>
<tr>
<th>Single particles classes</th>
<th>Number count</th>
<th>Number fractiona (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Winter</td>
<td>Spring</td>
</tr>
<tr>
<td>EC-S</td>
<td>33,159</td>
<td>17,858</td>
</tr>
<tr>
<td>EC-SN</td>
<td>723,385</td>
<td>510,862</td>
</tr>
<tr>
<td>ECOC</td>
<td>217,416</td>
<td>9979</td>
</tr>
<tr>
<td>OC</td>
<td>443,119</td>
<td>37,442</td>
</tr>
<tr>
<td>Biomass</td>
<td>455,121</td>
<td>194,734</td>
</tr>
<tr>
<td>Ammonium</td>
<td>172,074</td>
<td>11,498</td>
</tr>
<tr>
<td>NaK-S</td>
<td>19,275</td>
<td>6614</td>
</tr>
<tr>
<td>NaK-SN</td>
<td>1,026,628</td>
<td>420,281</td>
</tr>
<tr>
<td>Fe-rich</td>
<td>272,504</td>
<td>107,920</td>
</tr>
<tr>
<td>MiscMetals</td>
<td>85,843</td>
<td>35,416</td>
</tr>
<tr>
<td>Dust</td>
<td>76,289</td>
<td>22,403</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>20.5</td>
<td>37.2</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>0.7</td>
</tr>
</tbody>
</table>

a Number fraction was calculated through dividing the number count of each particle classes by the total particle count.

3.2. Seasonal differences in diurnal variations

Ammonium counted the most during winter (4.9%, Table 1) due to the prevailing west wind over agricultural lands (Fig. 1). The time series of Biomass during winter showed biomass burning processes frequently and dramatically influenced ambient particles. During spring, more Biomass particles were brought to the sampling site after 4/11. The fractions of EC-type particles during summer were occasionally < 1% because of stronger precipitation with intensities larger than 10 mm. And western sources caused regular variations in EC-S, its fraction clearly increased from 10:00 to approximately 20:00 on 7/1, 7/2, 7/13, 7/14. During fall, it was evident that carbonaceous particles increased, since the wind directions turned east, and thus, those particles correlated with eastern sources such as traffic and industrial emissions. Generally, the particle counts of Na-K collected by SPAMS were usually lower than 2000 during fall, but there was a period of rapid increase (between 13:00–20:00 on 10/2, which can be seen in Fig. 1) when the counts were higher than 5000, and even above 10,000. In addition, Biomass, NaK-S, Fe-rich and MiscMetals all increased. During this specific period, a fire point occurred on the west side of Nanjing within a short distance, and the increased wind speeds of the prevailing west wind (from 0.7 m s⁻¹ to 3.1 m s⁻¹) brought more fire point-related particles, which means higher levels of NaK-type could be caused by these combustion emissions (More discussions on this part in the Supplemental material).

As shown in Fig. 2, except for EC-S and NaK-S, other particle types tended to decrease after 06:00, likely due to convective process, which became intense since sunrise and helped particles diffuse. The intensity of nitrate in negative mass spectra is used for identifying the age of particles in single-particle mass spectrometry analyses (Moffet et al., 2008), the aged particles mixed with more nitrate. EC-S and NaK-S with lower nitrate indicated that they were probably freshly emitted and were not significantly affected by the atmospheric processes. Those two types tended to increase between 06:00–09:00 as results from increased human activities. Compared with other seasons, EC-S during winter was
not associated with prominent sources (Fig. 7) and the diurnal variation was gentle. However, EC-S showed a unimodal diurnal profile during spring, which peaked at 16:00, and had bimodal distributions during summer and fall with the first peak at 14:00 and the second one at 18:00. During summer and fall, major sources of EC-S were similar, and the average temperatures were 24.4 °C and 18.4 °C, respectively, which were higher than that of winter and spring, stronger convection in the boundary layer occurred in the afternoon and caused transient decreases in EC-S.

Except for summer, EC-SN had the same diurnal variations with higher counts at night. The diurnal changes in EC-SN and wind speeds were the opposite during winter, spring and fall, and the correlation coefficient (R) were −0.7, −0.8 and −0.9, respectively. Low wind speeds lasting for a long time at night were unfavorable for diffusion and helped the nitrate accumulate in the EC-type. Unlike other seasons, sources close to the sampling site contributed prominently to EC-SN during summer, and the stronger solar radiation in the afternoon helped photochemical reactions, which led to the increase of gaseous nitric acid in the atmosphere (Wang et al., 2009), and the adsorption by EC-type caused the increase in the afternoon. Affected by the sources (Fig. 7) and heights of boundary layers, diurnal variations in Fe-rich, Dust and EC-SN were similar.
NaK-SN and Biomass in winter were both influenced by the same source located in the west-northwest (Fig. 7), their diurnal variations were similar (R = 0.7), and they both peaked at noon. NaK-SN particles were negatively correlated with wind speeds (R = −0.7) during spring and summer. During fall, NaK-S and NaK-SN were significantly affected by the combustion processes and their diurnal variations were consistent, both changed along with the wind speeds (R = 0.97 and 0.63, respectively), which indicated that stronger winds in fall brought more NaK-type particles to the sampling site.

3.3. Seasonal variations in chemically resolved size distribution

As shown in Fig. 3, size distributions of various particle classes shared the same characteristics during different seasons. Submicron EC-type was abundant and linked with fresh vehicle exhausts (Shields et al., 2007); the obvious contributions for EC-S to smaller particles (0.2–0.5 μm) suggested notable impacts of sulfuric acid on the processing of EC (Khalizov et al., 2009; Zhang et al., 2013). Fe-rich increased along with the sizes, and its number fractions for those larger than 0.7 μm varied as follows: summer > spring > fall > winter, which changed along with the total amount of rainfall during each season. Thus, Fe-rich played a more important role for particles (> 0.7 μm) during the rainy seasons. Dust first increased and then deceased across the four seasons, and the valley values were between 0.5 and 0.8 μm. Dahl et al. (2006) found significant submicron particles (< 1 μm) originating from the road-tire interface through a road simulator study, which could be further demonstrated by the source distributions in Fig. 7.

There were also seasonal differences. OC particles had similar trends during winter, spring and summer, which first increased and then decreased, peaked at approximate 0.7 μm and peak fractions were 27.5%, 15.0% and 16.7%, respectively. However, OC during fall had higher number fractions of between 0.2 and 0.5 μm (> 20%), and decreased continually as the sizes increased. Diurnal profiles of OC clearly had higher levels at night and in the early morning, which was shown in Fig. 2. In addition, based on Fig. S3, the decrease in temperature and increase in RH together favored the spikes in OC. Among all four seasons, these specific meteorological characteristics appeared the most frequently at night and in the early morning during fall. More and smaller OC particles formed by gas-particle partitioning of semi-volatile species, which underwent aqueous phase processing at night (Qin and Prather, 2006), and then, they grew into larger particles, which could be detected by SPAMS under high RH (Zhang et al., 2013).

ECOC had distinct size distributions in all four seasons; its fractions in each size range were obvious during winter and increased between 0.2 and 0.7 μm and 1.0–2.0 μm (> 6%). However, ECOC during spring and summer had decreased contributions to particles larger than 0.6/0.7 μm (<1%). During fall, fractions of ECOC decreased as sizes increased and peaked at 0.2–0.3 μm (6.1%). Based on Fig. 3, EC-SN increased, and OC dropped dramatically after 0.7 μm, 0.6 μm, 0.7 μm and 0.5 μm during winter, spring, summer and fall, respectively. Further analysis found that except for the winter, size distributions of EC-SN and OC had negative relationships in all seasons, and the R values were smaller than −0.6. ECOC had negative and positive relationships with EC-SN and OC, respectively, especially in summer and fall. The formation of secondary ECOC normally corresponded to the sink of EC-type and was proportional to the content of organics. During winter, the difference in the number fractions between EC-SN and OC was lower than 10%, which was significantly distinct from other seasons and could not provide sufficient EC-type cores. Thus, more OC condensed on fewer EC-type and led to larger ECOC particles. In short, the fractions of ECOC (secondary) were obviously influenced by the fewer fractions between EC-type and OC particles.

Smaller Biomass particles (between 0.2 and 0.6 μm) during winter had higher fractions (> 55% in each size range) because of the influences of close fire points. Ammonium during winter in each size range had obvious number fractions, which were > 5% after 0.7 μm and changed. NaK-SN particles had unique sources during fall, and its size distributions first peaked at 0.5–0.6 μm (40.9%) and decreased to 1.1–1.2 μm (28.0%). This type of particles gently increased during other seasons which indicated the NaK-SN emitted by combustions mainly contributed in the size range of approximately 0.5–0.6 μm.

From Fig. 4, all types of particles showed unimodal distributions; the peak radius ranked as follows: fall < spring < summer ≤ winter. Because of the meteorological characteristics, more small particles were detected during the fall, especially for ECOC and OC. Also, the specific
Fig. 4. Unscaled SPAMS size spectra for each type of particle during winter, spring, summer and fall.

Fig. 5. Mixing state of secondary markers associated with particle classes, which was indicated by the coloration that represented the number fractions of particle classes that contained the secondary markers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. Clusters of daily 72-hour backward air-mass trajectories reaching the Nanjing site at 500 m a.g.l. and 00:00 (local time) during winter (black), spring (pink), summer (green) and fall (blue). During winter, the northwest air mass (81%) reached the sampling site, travelling over Mongolia and inland China. During spring, there were north and east air masses, which were 55% and 35%, respectively. The northeast air mass during summer reached the site originating from the ocean, and east masses dominated during this season, accounting for 89% in July. During fall, the northwest (34%), southeast (31%, short back-trajectory) and east (34%) air masses originating from the ocean affected the sampling site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
combustion process occurred in early October had an important impact on smaller fire point-related particles, such as EC-S, NaK-S and metal-containing particles. Poor meteorological conditions (low wind speeds, low boundary layer height, low temperature and high RH) led to the largest peak size during winter. The larger peaks during summer were consistent with the results from Yu et al. (2011), which caused by the growth of hygroscopic particles and the highest seasonal water vapor content.

3.4. Mixing states during different seasons

The secondary species mixed in particles are helpful for determining...
the various atmospheric chemical processes. Markers $m/z$ 18 ($^{18}$NH$_4^+$), $m/z$ 43 ($^{43}$C$_2$H$_3$O$^+$), $m/z$ 35 ($^{35}$Cl$^-$), $m/z$ 62 ($^{62}$NO$_3^-$) and $m/z$ 97 ($^{97}$HSO$_4^-$) were selected. Fig. 5 exhibited that despite the season, the mixing state exhibited similar traits. Ambient particles were associated with significant secondary species in Nanjing, which were the results of the energy structures in the YRD and was similar to the results from Wang et al. (2003) and Wang et al. (2016). KCl appeared in fresh smoke from biomass burning (Zauscher et al., 2013), and the gas phase HCl, which was derived from coal combustion and incineration of municipal and industrial waste (Graedel and Keene, 1995) (mostly the combustible plastics, polyvinyl chloride particularly), could be partitioned into various particles. The top three ranked particle types, which mixed with more Cl$^-$, were Biomass, MiscMetals and Dust; the first two types indicated the contributions from combustion processes, and the last type suggested the secondary uptake of HCl (Sullivan et al., 2006). Most of the HSO$_4^-$ in OC were found during all seasons, and the
fractions of OC mixed with HSO₄⁻ changed as follows: summer > spring > winter > fall. As reported by previous studies, the acid-catalyzed heterogeneous reaction in the presence of sulfuric acid might be related well with enhanced OC (Jang and Kamens, 2001; Riccobono et al., 2012). Also, the presence of organics in atmospheric water drops could enhance the production of secondary sulfate through aqueous-phase SO₂ oxidation (Blando and Turpin, 2000).

The fractions of particles mixed with NH₄⁺ were the largest during winter and the least during spring, which corresponded with the fraction of Ammonium for each season. In addition, the fractions of C₂H₃O⁺ showed the same changes. Smoke from biomass burning is composed of ~50–60% organic carbon (Reid et al., 2005). Close fire points during winter (Fig. 7) meant higher levels of semi-volatile components, which could partition to the particle phase with the help of lower temperatures, low inversion layers and wind speeds. The Cl⁻ in particles could be replaced by HNO₃ and/or H₂SO₄ through heterogeneous reactions (Moffet et al., 2008). Most particles were linked with clear Cl⁻ and NO₃⁻ during spring, and it was evident that particles during spring had more complex mixing states, and relative fresh and aged types were grouped together. Enhanced Cl⁻ in some Fe-rich and MiscMetals during spring indicated that some of those particles were emitted from waste combustion in residential areas (sources located in the southwest side of sampling site shown in Fig. 7). During spring, high RH favored the condensation of nitrate on particles and accelerated their growth, but those large particles were not removed as effectively as they were during summer due to relatively weaker rainfalls. The fractions of particles mixed with NO₃⁻ changed as follows: spring > winter > summer > fall. In addition, for most particles, the fractions of particles mixed with HSO₄⁻ changed as follows: winter > summer > spring > fall. The relative small wind speeds during winter (the fraction of periods with prevailing calm winds was the highest at 3.8%) caused the worst diffusion air conditions across the four seasons, which further resulted in considerable secondary species mixing into the particles. The least fractions of particles associated with
secondary inorganic species during fall, indicating they were probably freshly emitted and were not significantly affected by the atmospheric processes. Furthermore, seasonal contrasts of peak radii in size spectra were corresponding to the particles mixing states (Fig. 4). C$_2$H$_3$O$^+$ was the most important impacting factor and secondary inorganic species (such as NO$_3^-$ and HSO$_4^-$) were next (this might not be applicable when only discussing particles during rainfall).

### 3.5. Impacts of meteorological conditions on particles

#### 3.5.1. Effects of air masses and wind speed/direction on ambient particles

Numerous papers suggested that long-range transported air masses could influence the major types of particles (Liang et al., 2017; Wang et al., 2018). East air masses with short back-trajectories dominated in the spring and July, as shown in Fig. 1, which accounted for 35% and 89% of the total masses, respectively. Sources of EC-type included fossil fuels for transportation (Zhang et al., 2013), solid fuels for industrial, waste incineration (Moffet et al., 2008), residential uses, and open burning of biomass (Bond et al., 2013). Approximately 500 m east of

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**Fig. 10.** The hourly counts of various particles in each type of RH during winter. (For spring, summer and fall, see Fig. S5.)

**Fig. 11.** Number fractions and hourly count distributions of various particles during different precipitation types.
the sampling site is Ningliu Road and the Jiangbei Expressway, as well as iron and steel industries. The fractions of EC-SN were the largest in spring and summer, which were 37.2% and 38.1%, respectively. The lack of eastern air masses may be one of the reasons why the fraction of EC-SN was the smallest (20.5%) during winter. The NaK-type has been found in industrial processes, sea salt, soil dust and combustions (Moffet et al., 2008). NaK-SN contributed the most during winter and fall with 29.1% and 34.9%, respectively. The northwest air masses were important during winter and fall, accounting 81% and 34% of the total number of air masses, respectively; these air masses travelled over Mongolia and some inland provinces of China (e.g., Inner Mongolia Autonomous Region, some industrial provinces (Shanxi and Anhui)), which caused particles detected at the sampling site to be in

**Fig. 12. Mixing state of particles and species during each type of precipitation.**

Combined with wind speeds and direction, source distributions of each particle type were illustrated in Fig. 7. Due to the lack of source profiles, this analysis could not link particles with specific sources, but it might still be indicative.

The main sources of Fe-rich and MiscMetals were corresponding to EC-SN, these were concentrated in the southeast side and apportioned to some plants. Fe-rich, Dust and EC-SN had similar diurnal variations (Fig. 2), their counts increased at 15:00 to some plants. Fe-rich, Dust and EC-SN had similar diurnal variations

**3.5.2. Effects of RH on ambient particles**

Excluding the precipitation, each season was divided into four types based on the RH values, and they were defined as follows: Vis1 (< 1 km), Vis2 (1–5 km), Vis3 (5–10 km) and Vis4 (> 10 km). RH3 appeared a lot during winter and spring, which accounted for 32.4% and 30.3% of the whole, respectively, RH4 occurred frequently during summer and fall, and the fractions were 50.0% and 38.0%, respectively.

The available data for analysis was sufficient during fall and winter, but there was a small difference between the fractions of the four types of RH during winter, and thus, the discussion was mainly focused on this season. From Fig. 8, as the RH increased during winter, the fractions of Vis2 increased, and the fractions of Vis3 and Vis4 decreased. Vis3 was dominant in RH1 and RH2 (73.7% and 53.5%, respectively), Vis2 was dominant in RH3 and RH4 with fractions of 68.8% and 68.6% respectively. Vis1 only appeared in RH4, and its fraction was 3.8%. The correlation between visibility and RH during spring was consistent with that during winter. The fraction of RH1 during summer was < 1%, and the visibility data during fall was seriously lacking, and thus, neither could be used. In general, the higher the RH, the lower the visibility.

The contribution of each particle type to ambient aerosols changed along with the RH. During winter, with the increase of RH, the fractions of EC-type, ECOC, Ammonium and Fe-rich increased, and the fractions of OC, Biomass, NaK-type and Dust decreased. The variations in the main types of particles such as EC-SN, NaK-SN, OC and Fe-rich during spring and fall were basically consistent with those in winter. There was no obvious relationship between the main types of particles and RH during summer.

With the increase in RH, the main types of particles (such as EC-SN and NaK-SN) mixed with more NH4+ and less C2H3O+, the latter of which was consistent with the changes in OC. SOA produced by volatile organic compounds (VOCs) through photochemical reactions, which formed semi-volatile products (Seinfeld and Pandis, 2006), as well as distinct seasonal characteristics, such as unique coal combustions occurring in winter. All types of particles (except OC) mixed with less NO3− with the increase in RH during fall, whereas most particles showed the opposite changes during other seasons. During winter, most particles (except NaK-type) mixed with more HSO4− with an increasing RH when RH < 80%, whereas the trends completely opposite for other seasons.

During winter, all kinds of particles (except Biomass and
Table 2

<table>
<thead>
<tr>
<th>Types of precipitation</th>
<th>Duration (hours)</th>
<th>Total rainfall amount (mm)</th>
<th>Detailed time</th>
<th>Characteristics of rainfall intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>No rain (rain0)</td>
<td>24</td>
<td>0</td>
<td>06/18 00:00–06/18 23:00</td>
<td>No rain 0 00:00–06/21 20:00 0.1 mm</td>
</tr>
<tr>
<td>Light rain (rain2)</td>
<td>25</td>
<td>9.4</td>
<td>10/07 11:00–10/08 11:00</td>
<td>The 91% of hourly precipitations were &lt; 1 mm, the maximum was 1.1 mm</td>
</tr>
<tr>
<td>Moderate rain (rain3)</td>
<td>20</td>
<td>43.1</td>
<td>06/29 08:00–06/29 14:00</td>
<td>The maximum hourly precipitation was 4 mm</td>
</tr>
<tr>
<td>Heavy torrential rain (rain5)</td>
<td>38</td>
<td>169.0</td>
<td>06/16 21:00–06/17 17:00</td>
<td>The hourly precipitation in 06/16 21:00, 06/17 2:00 and 3:00 were &gt; 20 mm, the maximum was 25.4 mm</td>
</tr>
</tbody>
</table>

3.5.3. Influence of different types of precipitation on aerosols

If the interval between two rainfall processes is < 6 h, those two are considered one precipitation event; otherwise, they are considered two separate precipitation events (Huff, 1967). The criteria for different types of precipitation is defined by the Chinese Meteorological Administration (Table 2), and the wind was easterly prevailing when those precipitation events occurred, which eliminated the influences of sources.

3.5.3.1. Duration impacts on aerosols.

The processes of rain1 and rain2 were both light rain, but the duration of rain2 was 6.0 times longer than rain1. Based on Fig. 11, metal-containing particles showed little differences between rain1 and rain2. The fractions of EC-SN and NaK-SN in rain2 were 38.5% and 13.60%, respectively, which were 0.8 times and 0.6 times larger than that in rain1. At the same time, the fractions of ECOC and OC in rain2 were 2.1% and 7.5%, respectively, which were greater than that in rain1 (0.4% and 1.3%, respectively). Most of the particles in rain2 mixed with less NH$_4^+$, NO$_3^-$ and HSO$_4^-$, and more C$_2$H$_3$O+ than rain1. This indicated that for rainfall with compositions in rain4 were significant as the particle size increased. This change showed that higher RH favored the increase of OC (> 0.825 μm). With increased RH, the hourly counts of NaK-SN particles smaller than the peak radius decreased, however, those larger than the peak radius showed the opposite trend, which indicated two different formation mechanisms for NaK-SN. Similar to winter, the particles exhibited unimodal distributions during other seasons, but the relationships between peak radius and RH were not clear. Across all four seasons, the hourly counts of EC-type increased significantly when their size was 0.125–0.175 μm smaller than the peak radius. In addition, Biomass particles always tended to have higher hourly counts at low RH (RH1 > RH2 > RH3 > RH4). Lower RH meant better diffusion conditions, and thus, more Biomass particles could be transported to the sampling site.

3.5.3.2. Impact of total precipitation amount on aerosols.

The chemical compositions in rain4 were significantly distinct from those in other precipitations. Biomass contributed as much as 72.3% to the total particles and Ammonium was not collected. The data in MODIS showed that there were no fire points in Nanjing or the surrounding area during rain4; thus the high Biomass came from the an unidentified occurrence of biomass burning near the sampling site. Except for rain4, EC-SN and NaK-SN were dominant, and compared with rain0 and light rain processes, the fractions of Fe-rich in rain3 and rain5 decreased (respectively 11.0% and 7.6%), which implied the effective removal of these particles by intense precipitation events. The fraction of EC-type and NaK-type particles (29.0% and 29.8%, respectively) in rain5 were lower and higher than that in other periods respectively, which indicated that heavy torrential rains had stronger removal effects on EC-type than NaK-type particles.

As shown in Fig. 12, the NH$_4^+$ and C$_2$H$_3$O+ mixed in most particles changed as follows: rain0 > rain3 > rain5. Compared with rain5,
more NO₃⁻ mixed in ECOC, OC, Biomass, Fe-rich and Dust particles in rain1 (the other types of particles did not change much). Particles grew by absorbing more secondary species, and stronger precipitation made it easier to remove larger particles. Because of that, the number fractions of particles mixed with secondary species decreased. The HSO₄⁻ in EC-SN, NaK-SN, Fe-rich, MiscMetals, and Dust changed as follows: rain3 < rain1 (rain2) < rain5 < rain0 (the other types of particles did not change much), which indicated greater impacts of photo-oxidation processes on the formation of sulfate (Xiao et al., 2009).

Particulate growth during the precipitation events, even were zero for some particles larger than ~1 μm. In general, most particles exhibited unimodal distributions. Affected by the removal of larger particles, compared with rain0, the peak radii of EC-type, Biomass, Ammonium, Fe-rich, MiscMetals and Dust were smaller; however, the peak radii of ECOC, OC and NaK-SN particles were greater or similar, which indicated that precipitation did not effectively remove these three types of particles and even may help them grow.

4. Conclusions

In this study, size-resolved aerosols with dva between 0.2 and 2.0 μm were sampled by SPAMS in Nanjing, and 11 clusters were identified, which included EC-S, EC-SN, ECOC, OC, Biomass, Ammonium, NaK-S, NaK-SN, Fe-rich, MiscMetals and Dust.

Long-range transported air masses, seasonal local sources and atmospheric processes experienced by particles after emission both played important roles in the chemical patterns and diurnal variations of particles. All types of particles showed unimodal distributions, their peak radius ranked as follows: fall < spring < summer < winter. The size distribution of OC during fall was distinguished from it in other seasons and was caused by the decrease in temperature and increase in RH. ECOC had distinct size distributions in all four seasons which determined by the fewer fractions between EC-type and OC particles. Mixing states also changed with the season. Enhanced secondary species during winter were found due to the worst diffusion and seasonal emissions, such as the sulfur-containing coal combustions.

The dependence of meteorological conditions on particles was investigated. With the increase in RH, most particles mixed with more NH₄⁺ and less C₂H₃O⁺. More secondary organic/inorganic species mixed in particles during long-/short-term precipitation with intensities < 1 mm. Enhanced secondary species were found in non-precipitation days.

Acknowledgments

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