Particle Growth and Variation of Cloud Condensation Nucleus Activity on Polluted Days with New Particle Formation: A Case Study for Regional Air Pollution in the PRD Region, China

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ABSTRACT

New particle formation (NPF) events on polluted days at a regional supersite in the Pearl River Delta (PRD) region and its impact on the abundance and properties of cloud condensation nuclei (CCN) were investigated. Nucleation and subsequent significant growth of nanoparticles on a regional scale was observed and representative events on 2 and 6 October 2013 were chosen in this study. The measurements showed that the primary components of the particles were sulfate, ammonium, and organics as they were added continuously to secondary aerosol mass and that particles show inversion from growth to shrink if the particles comprise primarily of organics due to evaporation of semi-volatile species under favorable meteorological conditions. The effective hygroscopicity parameter $\kappa$ of fine particles on 2 October composed of sulfate, nitrate and ammonium ($\kappa = 0.26$–$0.42$) was larger than that of fine particles on 6 October containing more organics ($\kappa = 0.19$–$0.36$). Particles in the nucleation mode were observed to grow rapidly to the CCN sizes and dominate the CCN number concentrations at a water vapor supersaturation (S) over 0.46%. At an S range of 0.26–0.86%, the CCN number concentrations reached maximum values of $(1.3$–$2.6) \times 10^4$ cm$^{-3}$ after the NPF event on 2 October. The sulfate component in the particles was found to increase significantly, about 50% higher than that before NPF. Results from events on 6 October showed a significant increase of the organic component and the CCN number concentrations after the NPF event were comparable or slightly lower than those before the event. Nevertheless, the average CCN number concentrations scaled with EC mass concentration with S over 0.46% in the daytime of 2 and 6 October were significantly higher than those on a non-NPF event day.

Keywords: New particle formation; Secondary aerosol formation; Particle growth; Cloud condensation nucleus activity.

INTRODUCTION

Pollution events with high aerosol mass concentrations occur frequently in the Pearl River Delta (PRD) region, especially during autumn and winter seasons (Zhang et al., 2008; Yue et al., 2015). The annual average PM$_{2.5}$ concentrations in this region were 42 and 47 µg m$^{-3}$ in 2013 and 2014, both of which significantly violated the National Ambient Air Quality Standards of China (NAAQS, GB3095-2012, 35 µg m$^{-3}$). Hence a priority should be given to reduce air pollution, especially the PM$_{2.5}$ concentrations in this region.

The PRD region is separated from the west and north by mountains and adjacent to the South China Sea in the east and south. The level of particulate pollution mainly depends on meteorological conditions, pollutant emissions in urban areas as well as point and diffusion sources of particles and precursor gases in this region and neighboring cities. The meteorological patterns for the four seasons are distinct, among which autumn is characterized by intense solar radiation, high temperature (T), low relative humidity (RH) and little precipitation (Yue et al., 2015). In autumn, these meteorological conditions favor frequent formation of the complex air pollution with high PM$_{2.5}$ mass concentration and O$_3$ concentration. Moreover, new particle formation (NPF) events were also observed in autumn even under high aerosol mass loading.

Nanoparticles formed by nucleation and subsequent growth are important sources of ambient aerosols, leading to increases of aerosol number and mass concentrations.
They can modify aerosol optical properties (direct climate effects; Bäumer et al., 2008; Cheng et al., 2008, 2009) and contribute significantly to cloud condensation nuclei (CCN) to influence cloud formation, i.e., the microphysics of clouds and precipitation (indirect climate effects; Pirjola et al., 2004; Reutter et al., 2009). Simultaneous measurement of NPF and CCN number concentrations showed that NPF leads to CCN number concentration enhancement by 1–3 times (Kuwata et al., 2008) and the growing mode particles contributed over 80% to the CCN number concentrations on a NPF day in the North Plain of China (Wiedensohler et al., 2009). According to the simulation results, it was reported that NPF events in the urban area can increase the CCN number concentrations by twice to 9 times (Kuang et al., 2009), and those in the coastal area enhance them by 3–10 times (O'Dowd, 2001). In addition, the performance of climate models simulating the CCN number distribution over the world became better after introducing NPF events to the models, but the influence was diverse according to different nucleation mechanisms (Pierce and Adams, 2009). The hygroscopic properties of atmospheric aerosol particles are vital for a proper description of these effects, since they describe how the particles interact with water vapor both at sub and supersaturated conditions (e.g., McFiggans et al., 2006; Eichler et al., 2008). They are thus of major importance in describing the life cycle of the aerosol and the related direct and indirect effects on climate. The hygroscopic properties can be measured in great details using Hygroscopic Tandem Differential Mobility Analyzers instruments (Swietlicki et al., 2008). The effective hygroscopicity parameter (κ) which approximately describes the influence of chemical composition on the cloud condensation nucleus activity of aerosol particles is mainly estimated based on observational data or simulated with atmospheric chemistry models (Pringle et al., 2010). However, so far only one single study (Peng et al., 2014) has reported the contributions of NPF to CCN formation in the PRD region. In addition, the study did not take the aerosol chemical compositions into account. A detailed study about the effect of NPF on cloud condensation nucleus activity in the PRD region could be an important complement to modeling of cloud formation and cloud microphysical properties.

In this study, a regional supersite (Guangdong Atmospheric Supersite) in the PRD region was implemented to monitor air quality and characterize the complex air pollution. NPF events (Here we follow the definition that one burst was counted as a new particle formation event if the duration time was longer than 2.5 h and the maximum number concentration of 3–10 nm particles was larger than 10^6 cm⁻³) were observed more frequently in autumn than in other seasons. Two events were included in the case study to investigate the physical and chemical properties of newly-formed particles. The contributions of secondary particles to the total aerosol mass concentrations during the growth process were also investigated. The aerosol effective hygroscopicity parameter κ was derived from the measured compositions of fine particles, allowing the assessment of the cloud condensation nucleus activity in the PRD region in autumn during polluted days with NPF events.

**METHODOLOGY**

**Experiment**

The Guangdong Atmospheric Supersite is located in Taoyuan, Guangdong Province, China (112.929°E, 22.728°N; altitude 60 m), about 80 km southwest to Guangzhou city, 50 km southwest and 30 km northeast to Foshan and Jiangmen urban area, respectively. It is heavily influenced by the intense emissions of air pollutants from Guangzhou and Foshan area in spring, autumn and winter (Zhong et al., 2013; Peng et al., 2014).

Particle number size distributions, mass concentrations of PM_{2.5}, their chemical compositions (organic carbon (OC), elemental carbon (EC), and water soluble ions), trace gas pollutants (i.e., O₃, HNO₃, NH₃, SO₂, NO₂, and CO), and meteorological parameters were measured on-line at the supersite.

Particle number size distributions from 3 to 1000 nm (mobility diameter) were measured by scanning mobility particle sizers (SMPS, TSI model 3936N76 and 3936L75, TSI Inc., St. Paul, MN, USA) every 5 minutes. The SMPS consists of two sizers in different size ranges: (1) SMPS3936N76 for 3–60 nm with a short differential mobility analyzer (TSI model 3085) coupled to an Ultrafine Condensational Particle Counter (UCPC, TSI model 3776) and (2) SMPS3936L75 for 60–1000 nm with a long differential mobility analyzer (TSI model 3081) and a Condensational Particle Counter (CPC, TSI model 3775). The system was kept dry with silica gel in the sample lines. Size-dependent diffusion losses within the inlet were corrected with empirical particle loss corrections, as given by Willeke and Baron (1993). The particle surface area concentrations were calculated by integrating the particle number size distributions with an assumption of spherical particles.

The water-soluble inorganic ions (i.e., SO₄^{2-}, NO₃⁻, Cl⁻, NH₄⁺ and Na⁺) in PM_{2.5} and trace gases (i.e., SO₂, HNO₃ and NH₃) were detected by a Gas and Aerosol Collector-Ion Chromatography (GAC-IC) system (a custom instrument bought from Peking University). The GAC-IC system was described in details in Dong et al. (2012). Continuous sampling of both gas- and aerosol-phase pollutants is implemented through a set of dull-polished wet annular denuder with a steam jet aerosol collector. The inorganic gaseous and particulate species were detected by two separate ion chromatographers (ICS-90, Dionex, USA) alternately (Yue et al., 2015). The time resolution was 30 minutes and hourly averaged data was considered for analysis.

The OC and EC in PM_{2.5} particles were measured with an in-situ semi-continuous OC and EC analyzer (Model RT-4, Sunset Laboratory Inc, Beaverton, Oregon, USA). Ambient air was first sampled into a PM_{2.5} cyclone inlet with a flow rate of 8 L min⁻¹ and then passed through a carbon impregnated multichannel parallel-plate diffusion denuder. The denuder removed gas-phase organic compounds to avoid adsorption on the quartz filter and hence a positive bias introduced in the measured OC concentrations. We chose one hour cycle during which samples were collected for 40 minutes and analyzed immediately in the remaining 20 minutes for a better time resolution. The mass concentration
of particulate organic matter (POM) was estimated to be 1.6 times of the OC concentration (Hu et al., 2013). PM$_{2.5}$ mass concentration was measured by a tapered element oscillating microbalance (Model TEOM 1405), NO$_2$ by a trace level NO/NO$_2$/NO$_x$ analyzer (Model 42iTL), O$_3$ by a UV spectrophotometry O$_3$ analyzer (Model 49i), and CO by a trace level CO analyzer (Model 48iTLE). These instruments were manufactured by the Thermo Fisher Scientific, USA. UVA was detected by a multiband ultraviolet radiation meter (Model UV-S-A-T/UV-S-B-T, Kipp&Zonen B.V., Holland). Visibility was measured by a Belfort Model 6000 instrument (USA), and the other meteorological parameters including T, RH, precipitation, wind speed (WS), wind direction (WD) were recorded by a portable weather station (Model WXT520, Vaisala, Finland).

Cloud Condensation Nucleus Activity Evaluation
CCN number concentrations ($N_{CCN}$) at certain water supersaturations can be evaluated by integrating the measured aerosol size distribution above the critical dry particle diameter for CCN activation that corresponds to the values of the aerosol effective hygroscopicity parameter $\kappa$ and water supersaturations based on $\kappa$-Köhler theory (Petters and Kreidenweis, 2007; Rose et al., 2008; Yue et al., 2011). $N_{CCN}$ and $\kappa$ are important indicators for cloud condensation nucleus activity. The $\kappa$ values used in this study were obtained from the particle chemical compositions and their volume fractions.

$$\kappa = \sum_i \varepsilon_i \kappa_i \tag{1}$$

where $\varepsilon_i$ is the volume fraction of the chemical compounds in the particles and $\kappa_i$ is the $\kappa$ of individual chemical composition (Table 1). Eq. (1) was first introduced by Petters and Kreidenweis (2007) and was used for several field campaigns from pristine rain forest to polluted megacity areas (e.g., Gunthe et al., 2009; Rose et al., 2010).

The measured aerosol chemical compositions, including EC, POM, SO$_4^{2-}$, NO$_3^-$, Cl$^-$, NH$_4^+$, Na$^+$, and other species were categorized into four types: (1) secondary and biomass-burning organic aerosols, (2) sulfate and nitrate, (3) sodium chloride and marine aerosols, (4) insoluble compounds. Their average volume fractions were estimated according to the measured mass fractions, assuming that the volume change of mixing is negligible (Table 1). On average, continental and marine aerosols tend to fall into relatively narrow ranges of effective hygroscopicity (continental $\kappa = 0.3 \pm 0.1$; marine $\kappa = 0.7 \pm 0.2$) (Andreae and Rosenfeld, 2008; Rose et al., 2008).

RESULTS AND DISCUSSION

New Particle Formation and Rapid Particle Growth
Time series of PM$_{2.5}$ mass concentration and O$_3$ concentration from 2 to 18 October in 2013 are shown in Fig. 1. Typically, when air pollutants were accumulated, the mass concentration of PM$_{2.5}$ and the daily maximum O$_3$ concentration began to increase in the first few days (i.e., 10$^{-2}$ to 10$^{-5}$ in Fig. 1) and then they began to decrease when the removal of air pollutants was dominant over their production in the next few days (i.e., 10$^{-6}$ to 10$^{-9}$ in Fig. 1). The whole cycle typically lasted about 10 days. During the first half cycle, daily average PM$_{2.5}$ mass concentrations were in the range of 50.5–106.1 µg m$^{-3}$ and the daily maximum O$_3$ hourly concentrations varied from 159.1 to 302.3 µg m$^{-3}$. Fig. 1

<table>
<thead>
<tr>
<th>Species</th>
<th>$\kappa$</th>
<th>Data source</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>secondary and biomass-burning organic aerosols</td>
<td>0.1</td>
<td>OC $\times$ 1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>sulfate and nitrate</td>
<td>0.6</td>
<td>SO$_4^{2-}$ + NO$_3^-$ + NH$_4^+$</td>
<td>1.7</td>
</tr>
<tr>
<td>sodium chloride and marine aerosols</td>
<td>1</td>
<td>Na$^+$ + Cl$^-$</td>
<td>2.2</td>
</tr>
<tr>
<td>insoluble compounds</td>
<td>0</td>
<td>EC</td>
<td>1.0</td>
</tr>
<tr>
<td>Others*</td>
<td></td>
<td>Others$^*$</td>
<td>2.0</td>
</tr>
</tbody>
</table>

* Others = PM$_{2.5}$ – OC $\times$ 1.6 – (SO$_4^{2-}$ + NO$_3^-$ + NH$_4^+$) – (Na$^+$ + Cl$^-$) – EC.

Fig. 1. Time series of the PM$_{2.5}$ and O$_3$ mass concentration from 1 to 18 October. The marked periods indicate the time of NPF events on 2 and 6 October.
also showed that daily average PM$_{2.5}$ mass concentrations exceeded the standard (GB3095-2012, 75 µg m$^{-3}$) by the NAAQS for 12 (out of 19) days, while the daily maximum O$_3$ hourly concentrations violated the standard (GB3095-2012, 200 µg m$^{-3}$) by the NAAQS for 11 (out of 19) days. On more than 50% of the days shown in Fig. 1, both PM$_{2.5}$ and O$_3$ exceeded their respective standards, demonstrating high levels of the complex air pollution in this region.

NPF events were observed on 2, 3, 6, and 13 October at the supersite, and 2 and 6 October were chosen as representative days in this study because both days followed significant NPF events and accumulation of air pollutants under diverse meteorological condition and with different particle chemical compositions at the supersite. The daily PM$_{2.5}$ mass concentration (71.9 µg m$^{-3}$) met the NAAQS, while the daily maximum O$_3$ hourly concentration (207.2 µg m$^{-3}$) exceeded the NAAQS on 2 October. Both PM$_{2.5}$ (86.8 µg m$^{-3}$) and O$_3$ (237.0 µg m$^{-3}$) violated the corresponding standards on 6 October. In addition, the polluted day without NPF event of 4 October was selected for comparison. On this day, the daily PM$_{2.5}$ mass concentration and maximum O$_3$ hourly concentration were 106.1 µg m$^{-3}$ and 302.3 µg m$^{-3}$, respectively.

Fig. 2 shows the contour plots, along with the meteorological parameters (T, RH, WS, WD) and other important parameters from 2 to 6 October. Fig. 3 shows the peak diameters of the particles and the mass concentrations of PM$_{2.5}$ for 2 and 6 October. The volume concentration ratio of 3–100 nm particles to 3–1000 nm particles showed a clear diurnal variation pattern with a peak at around 14:00 local time (LT), indicating the influence of nucleation and subsequent growth with strong solar radiation. However, NPF events were not observed every day, as most of the nucleated particles might be captured immediately by the preexisting particles if the particle surface area concentrations were high. Moreover, the product of UV × SO$_2$, a proxy for sulphuric acid production, showed a clear diurnal variation with one sharp peak around noon. Their peaks on other days especially on 4 October were lower than those on 2 and 6 October, indicating a weaker source for NPF.

New particle formation events on 2 and 6 October started at about 9:30 am LT and rapid decreases in particle surface area and mass concentrations were observed. It should be noted that nucleation from gas phase and the growth of nuclei start from smaller sizes, for example 1–2 nm. However, the SMPS used at the Guangdong Atmospheric Supersite can only measure particles down to 3 nm in diameter. Therefore, we defined that NPF events on 2 and 6 October started at 9:30 LT, when particles larger than 3 nm were first observed.

The nocturnal inversion layer was developed during nighttime and was broken in the morning. Meanwhile a new boundary layer was formed due to solar heating. A wind speed of about 0.5–4 m s$^{-1}$ was observed to facilitate dispersion and dilution of air pollutants. The RH values were kept low (about 25–40%) and the particle surface area concentrations kept at below 2.0 × 10$^4$ µm$^2$ cm$^{-3}$ during the NPF events on both 2 and 6 October. Distinct characteristics were observed between the two events. A nice “banana-shaped” contour plot was obtained after data inversion of the number size distribution on 2 October. Particles were produced by nucleation, followed by condensational growth with a stable air mass during particle formation and growth. However, the contour plot for 6 October showed a growth-shrink-growth patterns that might be due to change of the air mass or condensational growth, which will be determined in the following discussion.

Growth rates of the particle mode diameter and the PM$_{2.5}$ mass concentration were evaluated. The particle geometric mean diameters were calculated from the size distribution by mode fitting (Wu et al., 2007). A nearly linear increase in the particle peak diameters (the geometric mean diameter of the particle mode with the highest number concentration per logarithmic diameter) with time indicated a constant growth rate from around 9:30 LT to the midnight on 2 October. The particle peak diameter increased from around 6 nm to approximately 100 nm, resulting in a growth rate of about 7 nm h$^{-1}$. Meanwhile, the PM$_{2.5}$ mass concentration increased steadily from 12:00 to 21:00 LT with an average growth rate of about 5 µg m$^{-3}$ h$^{-1}$ and reached to an even higher level than that prior to the event. In contrast to the event on 2 October, the growth rates were 9.5, –4.5, and 13 nm h$^{-1}$ for the “growth-shrink-growth” process on 6 October, corresponding to time periods of 9:30 to 13:00 LT–13:00 to 16:00 LT–16:00 to 20:00 LT, respectively. The average growth rate of PM$_{2.5}$ mass concentrations was as high as about 10 µg m$^{-3}$ h$^{-1}$ from 16:00 to 20:00 LT. The differences of the growth process between the two NPF events were attributed to different mechanisms and different species for the particle growth as well as the distinct meteorological conditions, as will be discussed in the next section.

In the morning of 4 October, higher RH, lower wind speed, and higher PM$_{2.5}$ mass concentration were observed, and most importantly the particle surface area concentration was significantly larger than that on 2 or 6 October. Consequently, no significant burst of nucleation mode particles was observed and the 20–100 nm particle number concentrations remained relatively low. A particle growth process with peak diameters from about 50 nm to about 90 nm was clearly observed in the contour plots, while the PM$_{2.5}$ mass concentrations kept at a constant level until a small increase from about 18:00 to 21:00 LT; and the growth of larger particles was not so clear as those on 2 and 6 October. The volume concentrations of 3–100 nm particles (PV$_{3-100}$) and the ratio of PV$_{3-100}$ to PV$_{3-1000}$ increased in the afternoon; however they were still significantly lower than those in the afternoon on 2 or 6 October. These results suggested that the particle growth in the afternoon of 4 October concentrated more on the ultrafine particles and did not change the PM$_{2.5}$ mass concentration noticeably.

Secondary Aerosol Formation and Growth

Chemical composition of PM$_{2.5}$, size segmented particle number concentrations, and SO$_2$ were shown in Fig. 4. For 2 October (left in Fig. 4), the mass concentrations of SO$_4^{2-}$ and NH$_4^+$ stayed high during the night and started to drop at about 10:00 LT in the morning; their concentrations reached minimum levels at noon and then began to increase steadily, although some fluctuations were observed. Abrupt
Fig. 2. Evolution of the meteorology parameters, particle number size distributions, size resolved particle number, surface area and volume concentrations, the product of UV × SO₂ (a proxy for sulphuric acid production), and the ratios of NO₃⁻/SO₄²⁻ and Km/Ke from 2 to 6 October. N₃–20 (N₂₀–100) means a total number concentration of 3–20 (20–100) nm particles; PS₃–1000 means a total surface area concentration of 3–1000 nm particles; and PV₃–100 (PV₃–1000) indicates a total volume concentration of 3–100 (3–1000) nm particles.
increase of the POM concentration at 17:00 LT was seen and the concentration of NO$_3^-$ began to increase at about 18:00 LT. The mass concentration of Cl$^-$, an important indicator of primary aerosol composition, stayed very low during the whole day. Results from the chemical compositions of PM$_{2.5}$ demonstrated that particle growth was mainly driven by secondary aerosol formation and condensation and that NO$_3^-$ and POM tended to participate in larger particle growth. Sulfate aerosol (SO$_4^{2-}$) was found to be the most abundant species in the PM$_{2.5}$. The contribution of POM was small in the early stage (prior to 17:00) but became increasingly significant in later stage of particle growth. 
The EC component also increased in the late afternoon and at night, but much less pronounced than the secondary aerosol components. The SO$_2$ emission influenced the particle nucleation and subsequent growth and the SO$_2$ concentration showed similar trend to PM$_{2.5}$, staying high during nighttime and early morning. The SO$_2$ concentration mainly showed two peaks. The first one peaked from 8:00 to 10:00 LT just before burst of 3–20 nm particle number concentration, and the other appeared late at night with high 100–1000 nm particle number concentration and PM$_{2.5}$ mass concentration. At 18:00–20:00 LT, the 20–100 nm particle number concentration slightly increased and showed a small peak while the number concentration of 3–20 nm particles kept a decrease trend, suggesting the influence of traffic emission. However, we probably sampled the same regional air mass in our measurements since the “banana-shaped” evolution of the number size distribution indicated continuous growth of particles without further interruption and the ratios of CO/EC and POM/EC kept at similar levels. The PM$_{2.5}$ mass concentration decreased significantly from over 95 µg m$^{-3}$ at night to around 70 µg m$^{-3}$ in the morning when air mass changed. The SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ components accounted for about 41.5% and 36.2% of the PM$_{2.5}$ mass for the whole day and for the time period of 10:00–18:00 LT, both significantly lower than those on 2 October. The corresponding contributions of POM were 22.0% and 26.0%, respectively, higher than those on 2 October. The corresponding contributions of EC were 2.5% and 2.0%, respectively, similar to those on 2 October. The separate contributions of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ to PM$_{2.5}$ during the time period of 10:00–18:00 LT were 37.8%, 3.9% and 17.8%, respectively. The results showed that SO$_4^{2-}$ played a dominant role during the particle growth process.

Organic species, however, may play an important role in particle growth on 6 October. The POM mass concentration was much higher than that of NH$_4^+$ concentrations and comparable or even higher than that of SO$_4^{2-}$ concentration. In addition, the average ratio of POM/EC during particle growth period was significantly higher on 6 October than that on 2 October. Under proper meteorological conditions, for example, high wind speed and low RH, some semi-volatile organic species in the particles would evaporate to the gas phase, resulting in the observed particle shrink in the late afternoon. The air mass during NPF event may differ from that in the early morning, as indicated by the ratio of CO/EC that primarily originates from the combustion sources. For example, on 6 October, the CO/EC ratio kept low before 8:00 LT and changed to a higher constant value after 9:00 LT, indicating two different air masses. This change of the air mass can also be clearly seen from the ratios of Cl$^-/EC$ and POM/EC, as well as an abrupt change of meteorological parameters (i.e., wind speed, temperature and RH). Another air mass change probably occurred at around 20:00 LT, imposing obvious effect on the particle number size distributions and chemical compositions. As it was not closely related to the new particle formation-growth-shrink process, such process will not be discussed in detail in this paper). The PM$_{2.5}$ mass concentration decreased significantly from over 95 µg m$^{-3}$ at night to around 70 µg m$^{-3}$ in the morning when air mass changed. The SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ components accounted for about 41.5% and 36.2% of the PM$_{2.5}$ mass for the whole day and for the time period of 10:00–18:00 LT, both significantly lower than those on 2 October. The corresponding contributions of POM were 22.0% and 26.0%, respectively, higher than those on 2 October. The corresponding contributions of EC were 2.5% and 2.0%, respectively, similar to those on 2 October. The separate contributions of SO$_4^{2-}$, NO$_3^-$ and
Fig. 4. Time series of selected parameters on 2 (left), 6 (middle) and 4 (right) October. The particle number concentrations are measured every 5 min and others are hourly averaged values. N_{3-20} (N_{20-100}, N_{100-1000}) means a total number concentration of 3–20 (20–100, 100–1000) nm particles.
NH$_4^+$ to PM$_{2.5}$ during the time period of 10:00–18:00 LT were 23.4%, 2.8% and 10.0%, respectively. The results showed that the contribution of POM increased during the particle growth, while that of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ decreased, implying that the POM played a dominant role in particle growth on 6 October. This might be attributed to the participation of more condensable organic species in the growth because of the change of air masses. Secondary organic matters (SOM) in PM$_{2.5}$ on 6 October were estimated by using the EC-tracer method (Lin et al., 2009). The average SOM concentrations during the growth-shrink-growth process were 11.8 µg m$^{-3}$, 9.4 µg m$^{-3}$, and 11.8 µg m$^{-3}$, respectively. Its contributions in combination with contributions of other major compounds to PM$_{2.5}$ during the growth-shrink-growth process on 6 October were given in Table 2. The average fractions of EC in PM$_{2.5}$ showed an increasing trend during the growth-shrink-growth process, reflecting the important continuous influence of primary emissions. During the growth processes POM contributed the largest part to PM$_{2.5}$, while during the shrink process SO$_4^{2-}$ was the dominant contributor. The average contribution of SOM decreased by 2.6 percentage points during the shrinkage in comparison with the former growth, which was obviously higher than that of POM by 1.7 percentage points during the same process; and it recovered to a similar SOM contribution during the latter growth to that during the former growth. It confirmed the important roles of organic matters essentially of the secondary organic compounds in the particle growth and shrinkage. The fractions of NO$_3^-$ in PM$_{2.5}$ showed a decreasing trend during the growth-shrink-growth process, and the gas-particle partitioning of the HNO$_3$-NH$_3$-NH$_4$NO$_3$ was also probably one of the important reasons for the observed particle shrink. As the most important inorganic cation in PM$_{2.5}$ in the PRD region, the fractions of NH$_4^+$ were less than those of SO$_4^{2-}$ and SOM, but significantly higher than those of NO$_3^-$ and EC.

For 4 October, primary emission was probably a major source of the Aitken mode particle burst and secondary formation of nitrate played an important role in fine particle pollution. The number concentrations of 3–20 nm and 20–100 nm particles were very low and the 100–1000 nm particle number concentrations were comparable or higher than those on 2 and 6 October. The SO$_2$ concentration showed a similar trend except that it had a small peak concuring with a peak of 20–100 nm particle number concentration, suggesting a local emission of those particles. The mass concentration of SO$_4^{2-}$ increased continuously, while NO$_3^-$ and NH$_4^+$ reached minimum values in the daytime (at about 17:00). Fig. 2(g) showed high ratios of both NO$_3^-$/SO$_4^{2-}$ and K$_{no}/K_e$ ($K_m = [NH_3] \times [HNO_3]$ and $K_e$ is defined as the theoretical constant for the equilibrium NH$_3$(g) + HNO$_3$(g) $<=>$ NH$_4$NO$_3$(s,aq)) (Yue et al., 2015), indicating that secondary nitrate contributed to fine particle pollution. The SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, POM and EC components respectively accounted for about 31.8%, 5.7%, 17.1%, 21.4% and 2.0% of the PM$_{2.5}$ mass during the time period of 10:00–18:00 LT.

Sulfur oxidation ratio (SOR = [SO$_4^{2-}$]/[SO$_2$] + [SO$_3$]), ([] denoting molar concentration), nitrogen oxidation ratio (NOR = [NO$_3^-$]/([NO$_3$] + [NO$_2$])), and ammonia transformation ratio (NTR = [NH$_4^+$]/([NH$_4^+$] + [NH$_3$])) were calculated with an hour average to investigate their roles in particle growth/shrink (Fig. 4). On both 2 and 6 October, SOR during NPF events were obviously higher than that prior to the events, in particular, it increased rapidly in the early stage of particle growth. During the particle shrink process, fast decreases of NOR and NTR were observed, while SOR slightly increased. The results confirmed the significant role of SO$_4^{2-}$ in NPF and subsequent particle growth and the gas-particle partitioning of the HNO$_3$-NH$_3$-NH$_4$NO$_3$ being one likely reason for the observed particle shrink. The SOR decreased at night, while the NTR and NOR showed increase trends, as higher RH and lower temperature would favor the NH$_4$NO$_3$ formation through gas-particle conversion (Yue et al., 2015). In general, all SOR, NOR and NTR on 4 October were larger than those on 2 and 6 October. It should be noted that the average NOR was 70% higher on 4 October, implying the importance of nitrate in fine particle pollution on non-NPF event days.

The increasing PM$_{2.5}$ mass concentration during the nighttime was attributed to both decreasing dilution and condensational growth. However, for the present cases, especially on 2 October, increase of the secondary particle mass by condensational growth was more important under stagnant meteorological conditions. As shown in Fig. 2, the particle diameters increased continuously and significantly. Without condensational growth, decreasing dilution cannot lead to this particle diameter growth. To rule out the effect of decreasing dilution at night, the integrated particle number concentrations in the ranges of 20–100 nm and 100–1000 nm were scaled by the EC concentration. As shown in Fig. 5, the scaled number concentration of 20–100 nm particles reached the highest values at around noontime, and decreased rapidly afterward. The scaled 100–1000 nm particle number concentration kept at a quite stable level and slightly increased at night on 2 October, while it increased in the morning and then decreased from late afternoon to midnight.

### Table 2. Comparison on contributions of major chemical compounds in PM$_{2.5}$ during particle growth-shrink-growth process on 6 October.

<table>
<thead>
<tr>
<th>Item</th>
<th>Former Growth (%)</th>
<th>Shrink (%)</th>
<th>Latter Growth (%)</th>
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<tr>
<td>SO$<em>4^{2-}$/PM$</em>{2.5}$</td>
<td>22.3</td>
<td>25.4</td>
<td>21.4</td>
</tr>
<tr>
<td>NH$<em>4^+$/PM$</em>{2.5}$</td>
<td>9.9</td>
<td>10.7</td>
<td>8.5</td>
</tr>
<tr>
<td>NO$<em>3^-$/PM$</em>{2.5}$</td>
<td>3.6</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>POM/PM$_{2.5}$</td>
<td>26.5</td>
<td>24.8</td>
<td>28.8</td>
</tr>
<tr>
<td>SOM/PM$_{2.5}$</td>
<td>17.8</td>
<td>15.2</td>
<td>17.9</td>
</tr>
<tr>
<td>EC/PM$_{2.5}$</td>
<td>1.7</td>
<td>1.9</td>
<td>2.1</td>
</tr>
</tbody>
</table>
with an obviously lower decreasing rate (decreased about 20% in seven hours) than that of 20–100 nm particles (decreased about 80% in seven hours) on 6 October.

Cloud Condensation Nucleus Activity
The hourly κ of fine particles, κ of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ (κ-SNA) and κ of POM (κ-POM) in fine particles from 2 to 6 October was given in Fig. 6(a). In general, κ resembled the variation trend of the total contribution of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ to PM$_{2.5}$ (SNA/PM$_{2.5}$), as κ-SNA contributed over 80% to the κ of fine particles, and the contribution of κ-POM was usually below 20%. The hourly κ on 2 and 6 October was 0.26–0.42 and 0.19–0.36, respectively, with daily average values of 0.35 and 0.27, comparable to that (κ = 0.3) in Guangzhou urban area in summer. The average contributions of κ-SNA on 2 and 6 October were 91.4% and 86.1%, respectively, and those of κ-POM were 7.3% and 11.7%, respectively. As κ-POM increased during the particle growth process on 6 October, κ-SNA and κ decreased significantly. Larger POM and smaller SO$_4^{2-}$ mass fractions in PM$_{2.5}$ were the main causes of the smaller κ on 6 October. The daily average κ on 4 October was 0.35, the same as κ on 2 October, and the contributions of κ-SNA and κ-POM were 92.0% and 6.3%, similar to those on 2 October. The atmospheric conditions during NPF events on 6 October were more favorable for POM especially SOM formation, the ultrafine particles mainly produced by NPF would be also composed of more organic matters than those on 2 October. Consequently, the κ of ultrafine particles on 6 October should be also significantly lower than that on 2 October.

The critical dry particle diameters (D$_{\text{c}}$) for CCN activation that corresponds to κ and certain water supersaturations (S = 0.26%, 0.46%, 0.66%, 0.86%) based on κ-Köhler theory on 2, 4 and 6 October were summarized in Table 3. As the water supersaturation increases, corresponding D$_{\text{c}}$ decreases, meaning that smaller particles can be activated as cloud condensation nuclei under a higher water supersaturation. At a certain water supersaturation, D$_{\text{c}}$ decreases, indicating that smaller particles composed of more water soluble compositions such as more sulfate, nitrate and ammonium on 2 October can readily act as CCN.

N$_{\text{CCN}}$ at certain water supersaturations on 2, 4 and 6 October was evaluated by integrating the measured aerosol size distribution above the corresponding critical dry particle diameters. In order to rule out the dilution or accumulation effect, the integrated CCN number concentrations were scaled by EC mass concentration (N$_{\text{CCN}}$/EC). Fig. 7 illustrated the time series of N$_{\text{CCN}}$ and N$_{\text{CCN}}$/EC. Although the maximum total fine particle number concentration from 3 to 1000 nm on 6 October ($7.7 \times 10^{3} \text{ cm}^{-3}$) was significantly higher than that on 2 October ($5.8 \times 10^{3} \text{ cm}^{-3}$), the CCN number concentrations after 9:00 LT were comparable or even lower on 6 October, especially when scaled with EC under high water supersaturations (e.g., S > 0.66%). This can be explained with the average particle number size distributions from 10:00 to 17:00 LT on 2, and 6 October (Fig. 6(b)). Both average particle number size distributions had very high peaks below 50 nm, while the former were absolutely higher.
than the latter and they were significantly higher than those on 4 October. Compared to 2 October, higher concentrations of growing particles on 6 October were observed in the nucleation mode (3–20 nm), probably due to the shrink process. In the daytime, the maximum total fine particle number concentration from 3 to 1000 nm on 4 October was $3.1 \times 10^4$ cm$^{-3}$, about 40% of that on 6 October and the CCN number concentrations were similar to those on 6 October, but the average $N_{CCN}/EC$ values were much lower. The average $N_{CCN}/EC$ values from 10:00 to 17:00 LT on 2 and 6 October were about 70%, 48%, 15% and 30%, 16%, 13% higher than those on 4 October for a supersaturation of 0.86%, 0.66% and 0.46%, respectively.

$N_{CCN}$ tended to decrease when the NPF event just started, and to increase when significant particle growth was observed. The CCN number concentrations during the NPF event on 2 October reached maximum values of $(1.3–2.6) \times 10^4$ cm$^{-3}$ at a supersaturations of 0.26–0.86%, about 50% higher than those just before NPF, while comparable or slightly lower maximum CCN number concentrations were seen on 6 October. The CCN number concentrations also increased obviously during the particle growth process in the afternoon of 4 October and the peak values were close to those on 6 October. The $N_{CCN}$ peaks at nights were observed at around 20:00LT for the three days. The $N_{CCN}/EC$ ratio showed significant peaks from around noon to 18:00 on both 2 and 6 October and one sharp peak in the afternoon on 4 October, and the ratio remains low at night on all the three days. The results suggested that NPF and subsequent particle growth have dramatic influence on CCN concentrations during daytime.

**CONCLUSION**

This study showed characteristics of new particle formation events in the PRD region under regional complex air pollution in autumn. The observed evolution of particle number size distributions showed particle nucleation and growth on a regional scale. Secondary aerosol mass was produced continuously during the particle growth, and the major components were sulfate, ammonium, and organic matter. When organics played a significant role and the meteorological conditions favored semi-volatile species to evaporate from particles, particle growth can transit to particle shrink.

The effective hygroscopicity parameter $\kappa$ of fine particles with sulfate, nitrate and ammonium as major component on 2 October was about 0.26–0.42, larger than that of fine particles.

**Table 3.** The average critical dry particle diameters on 2 and 6 October at different water supersaturations.

<table>
<thead>
<tr>
<th></th>
<th>S = 0.26%</th>
<th>S = 0.46%</th>
<th>S = 0.66%</th>
<th>S = 0.86%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_\kappa=0.35$ on 2 and 4 October (nm)</td>
<td>87.4</td>
<td>59.8</td>
<td>47.0</td>
<td>39.5</td>
</tr>
<tr>
<td>$D_\kappa=0.27$ on 6 October (nm)</td>
<td>95.3</td>
<td>65.2</td>
<td>51.3</td>
<td>43.0</td>
</tr>
</tbody>
</table>
Fig. 7. Time series of CCN number concentrations ($N_{\text{CCN}}$) at certain water supersaturations ($S$), and corresponding scaled $N_{\text{CCN}}$ on 2 (left), 6 (middle) and 4 (right) October, 2013.
particles composed of more organics ($\kappa = 0.19–0.36$) on 6 October.

The nucleation mode particles grew rapidly to be activated as CCN, and dominated the CCN number concentrations at high water vapor supersaturations (> 0.46%). The CCN number concentrations during the NPF event on 2 October reached maximum values of $(1.3–2.6) \times 10^6 \text{ cm}^{-3}$ at water vapor supersaturations of 0.26–0.86%, about 50% higher than those prior to NPF. The CCN enriched with more water soluble components (i.e., sulfate, nitrate and ammonium) on 2 October. The enhancement of the CCN number concentrations during the NPF event on 6 October was not as significant as those on 2 October and they were comparable or slightly lower than those before NPF. The pronounced increase of organics instead of sulfate and the resultant particle shrink process were the likely causes for this insignificant enhancement. Nevertheless, the average N$_{CCN}/$EC values during NPF events on 2, and 6 October were about 70% (48%, 15%) and 30% (16%, 13%) higher than those on 4 October (a non-NPF event day) for $S = 0.86\%$ (0.66%, 0.46%). In summary, this study concluded that the species participated in NPF and subsequent growth played a critical role in constraining the CCN formation under polluted air pollution environment.

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REFERENCE


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