Observations of New Particle Formation, Subsequent Growth and Shrinkage during Summertime in Beijing

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ABSTRACT

Size-resolved aerosol number concentrations (10 nm–10 µm in diameter) were measured at an urban site in Beijing during summertime of 2008. Case studies of new particle formation (NPF) are presented in this work. The measured mean particle formation rate was 2.37 cm\textsuperscript{–3} s\textsuperscript{–1}, which varied from 1.5 to 3.8 cm\textsuperscript{–3} s\textsuperscript{–1}, with growth rates ranging from 3.2 to 10.6 nm h\textsuperscript{–1}. NPF was observed under low number concentration of preexisting particles as well as under relatively high number concentration of preexisting particles. It was found that condensation contributed mainly and preferentially to particles growth, however, coagulation would contribute a lot when formation rate of new particles was sufficiently high. The variation of concentration of nucleation mode particles was found to be coincident with sulfur dioxide, indicating that NPF could occur under relatively high number concentration of preexisting particles if sufficient concentration of gas-phase H\textsubscript{2}SO\textsubscript{4} existed in the atmosphere. Grown particles were also observed to shrink from 61.1 nm to 15.4 nm at a shrinkage rate of 16.6 nm h\textsuperscript{–1}, accompanied by a reduction of the particle number concentration. The shrinkage rate was higher than those reported in recent studies, probably due to particle shrinkage occurred during summertime in Beijing with higher temperature and lower RH compared to those observed in other regions, thus enhanced particle shrinkage.

Keywords: Particle formation; Growth; Particle shrinkage; Beijing.

INTRODUCTION

New particle formation events have been observed in many different atmospheric environments, including rural, coastal, boreal forest, and urban areas over the past decade (Kulmala et al., 2004). NPF usually occurs during daytime, when the preexisting particle concentration is low, and under sunny and dry conditions (Birmili and Wiedensohler, 2000; Dunn et al., 2004; Stanier et al., 2004; Laaksonen et al., 2005). It usually takes several hours or 1 to 2 days for newly formed particles to grow to > 100 nm (Kulmala et al., 2004a). Nucleated particles grow in size by condensation of low-volatile vapors, intramodal coagulation of nucleation mode particles, and extramodal coagulation of nucleation mode particles with preexisting particles (Stolzenburg et al., 2005). Coagulation directly reduces the aerosol number concentration without increasing the mass concentration, although condensation does not directly alter the number concentration. Through intramodal and extramodal coagulation, the modal size of nucleation mode particles would increase, thus the growth of newly formed particles would be enhanced (Stolzenburg et al., 2005; Anttila et al., 2010).

Particle shrinkage refers to the growth reversal of particles, which may be attributed to many possible reasons, including evaporation of water and/or of volatile/semi-volatile species from grown nucleated particles (Zhang et al., 2004). The occurrence of particle shrinkage has been reported in São Paulo (Backman et al., 2012), central Taiwan (Young et al., 2013), and Hong Kong (Yao et al., 2010). Particle shrinkage of preexisting Aitken mode particles and newly formed particles has also been reported in a recent study (Cusack et al., 2013). The areas where particle shrinkage has been observed are mainly subtropical regions; however, we have found that particle shrinkage also occurs in an urban area in a temperate region.

As one of the biggest cities of China, Beijing has been experiencing severe haze pollution, and fine particles become the chief pollutant. The enormously efficient aerosol nucleation and growth over an extended period yields a high mass concentration, creating an essential factor for haze formation (Guo et al., 2014). During the summertime...
of 2008, when the Olympic Games were being held in Beijing, the air quality was significantly improved due to the drastic emission control measures and favorable weather conditions (Gao et al., 2011; Guo et al., 2013). NPF events during that period in Beijing were observed by several studies for investigating secondary aerosol formation, sulfuric acid promoting NPF, as well as the role of low-volatility organic vapors in NPF (Yue et al., 2010; Wang et al., 2011; Zhang et al., 2011; Gao et al., 2012; Wang et al., 2015). Characteristics of aerosol size distribution and NPF in absence of emission control measures in the summertime of 2006 in Beijing had been studied (Yue et al., 2009).

In order to identify and understand the characteristics of NPF during the special period, particle number size distribution (PNSD) from 10 nm to 10 µm were measured from July 19 to September 7, 2008 at an urban site in Beijing. Case studies of new particle formation, subsequent growth under different number concentration of preexisting particles as well as particle shrinkage were presented. By analyzing the evolution of geometric mean diameter, condensation sink and coagulation sink, different potential mechanisms of particle growth were investigated. Comparisons of particle size distributions as well as the growth rate between 2008 and 2006 were discussed to identify the effect of temporary emission control policies. The new particle formation rate, growth rate, condensation sink, coagulation sink, and shrinkage rate were calculated according to the particle number size distributions. The meteorological conditions and concentration of gaseous pollutants were studied to identify the inherent link with NPF.

METHODOLOGY

Observation Site

The observation site was located in north center of Beijing, in the middle of the 4th ring road and the 5th ring road, 500 meters away from the main Olympic stadium. Our measurement was done on the roof of the office building of the Institute of Remote Sensing and Digital Earth (40.00°N, 116.38°E, 20 m ASL). The site was more than 1000m away from three major roads with heavy traffic, and there was no major industry nearby; therefore, it could be a representative urban background site of Beijing.

Instrumentation

The particle number size distribution from 10 nm to 10 µm was measured by using a wide-range particle spectrometer (WPS340 Model 1000XP, MSP Corporation, USA) (Liu et al., 2010). The WPS system consists of a differential mobility analyzer (DMA) connected to a condensation particle counter (CPC), which measures the 10–500-nm particle size distribution, and to a laser particle spectrometer (LPS), which measures the 350 nm–10-µm particle size distribution.

The mass concentration of PM$_{2.5}$ and PM$_{10}$ was continuously monitored by Tapered Element Oscillating Microbalance (TEOM) with a detection limit of 2.0 µg m$^{-3}$. To obtain the equivalent Black Carbon (BC) concentration, an aethalometer was used. It measures the light attenuation by the aerosol particles (deposited on a filter) at 7 wavelengths (from 370 to 950 nm), and the 880 nm channel was utilized to estimate aerosol equivalent BC concentration. Gaseous pollutants concentration (O$_3$, NO$_2$, SO$_2$) were measured and then inversed by the open path differential optical absorption spectroscopy (OP-DOAS) technique (Qin et al., 2009) with an optical path of 456 m. Meteorological data such as temperature, relative humidity, wind direction and wind speed were recorded by automatic weather station.

Data Analysis

Classification Scheme

Identification of NPF events was made visually based on the temporal evolution of PNSD according to a set of distinct features proposed by Dal Maso et al. (2005). Once a NPF event starts, the number concentration of nucleation mode particles increase rapidly. The small particles grow to Aitken mode size range by condensing vapors and coagulating with other particles. However, the number concentration of nucleation mode particles decreased simultaneously. This can be illustrated in the contour plot of PNSD time series as a “banana-like” shape (Kulmala et al., 2012), usually starting from 9 or 10 am.

Particle Formation Rate and Growth Rate

Definition of NPF Episode

We define the start time of NPF event ($t_{\text{START}}$) as the moment when a new mode appears in nucleation mode, and the end time ($t_{\text{END}}$) is the moment when the geometric mean diameter (GMD) of newly formed particles moves out of the nucleation mode size range. $t_{\text{END}} - t_{\text{START}}$ represents the duration of NPF process.

Growth Rate

The growth rate (GR) is defined as the temporal change of the GMD during NPF episode.

$$GR = \frac{\Delta D_m}{\Delta t}$$

where $D_m$ represents the GMD of newly formed particles. The typical PNSD ranging from 10 nm–10 µm can be fitted by 2–4 log-normal modes. GMD is the median diameter in log-normal distribution, indicating that the majority of the particles sizing close to GMD. By fitting log-normal distribution functions of the PNSD at each time bin, the temporal variation of GMD can be obtained; GR can be estimated by fitting the temporal variation of GMD using a first-order polynomial.

Formation Rate

The particle formation rate (FR) (Dal Maso et al., 2005) is used to evaluate the NPF intensity denoted by $J_{\text{Nuc}}$

$$J_{\text{Nuc}} = \frac{dN_{\text{Nuc}}}{dt} + F_{\text{coag,Nuc}} + F_{\text{growth,Nuc}}$$

where $dN_{\text{Nuc}}/dt$ is the temporal variation of nucleation mode particles number concentration. The $F_{\text{coag,Nuc}}$ is the coagulation...
loss
\[ F_{\text{coag}, \text{Nuc}} = \text{CoagS}_{\text{Nuc}} \cdot N_{\text{Nuc}} \] (3)

where CoagS_{\text{Nuc}} is the mean coagulation sink of nucleation mode particles by choosing the log-normal fitted GMD as the reference size. \( F_{\text{growth}, \text{Nuc}} \) is the flux of particles growing out of the nucleation mode size range. Here, we only take the number concentration of particles with diameter of 25 nm (upper diameter of nucleation mode size range) into consideration
\[ F_{\text{growth}, \text{Nuc}} = \frac{\text{GR}}{\Delta D_p} \cdot N_{25} \] (4)

Several studies have reported measured formation rate by using instruments with a minimum detection size of as low as 3 nm. However, it should be noted that the minimum detection size of WPS was 10 nm; therefore, the formation rate would be underestimated compared to those measurements of aerosol number size distributions down to 3 nm.

Condensation Sink (CS) and Coagulation Sink (CoagS)

Condensation Sink

CS represents the ability of pre-existing particles to remove condensable vapors from the atmosphere. Because elevated per-existing particles can scavenge freshly nucleated particles and condensable vapors, large CS exerts adverse effect on NPF. Assuming sulfuric acid as the condensable species, the CS can be calculated as follows:
\[ \text{CS} = 2 \pi D_p \int_0^\infty D_p \beta_{\text{D}}(D_p) n_p(D_p) dD_p \] (5)

where \( D_p \) is the diffusion coefficient of the condensing vapor, for simplicity, sulfuric acid is assumed to be the dominant specie, \( \beta_{\text{D}}(D_p) \) is the size dependent transitional correction factor (Fuchs and Sutugin, 1971), \( n_p(D_p) \) is the particle number concentration of size \( D_p \). Particles between 10 nm and 10 µm are used to calculate CS. Taking the hygroscopic growth effect into consideration, the real CS of ambient particles may be higher than the calculated values.

Coagulation Sink

CoagS_{\text{Dp}} describes the speed of formed nano-particle removed in coagulation process (Kulmala et al., 2001). Nanoparticles can grow to Aitken mode or even accumulation mode and coagulate with large particles. Coagulation directly reduces particle number concentration without changing the mass concentration. The coagulation sink of size \( D_p \) can be determined according to the following equation:
\[ \text{CoagS}_{\text{Dp}} = \int_{D_p'} \int_{D_p} K(D_p, D_p') n_n(D_p') dD_p' = \sum_{D_p'=D_p}^{D_p_{\text{max}}} K(D_p, D_p') n_n(D_p') \] (6)

where \( K(D_p, D_p') \) is coagulation coefficient between particles of size \( D_p \) and \( D_p' \). Extramodal coagulation was taken into consideration to evaluate the effect on particles growth rate.

RESULTS AND DISCUSSION

Overview

Owing to the emission control measures, the concentration of atmospheric particles measured in summertime of 2008 had experienced a significant decrease compared to that of 2006 (Yue et al., 2009). The measured total particle number was \((6.4 \pm 2.9) \times 10^7 \text{cm}^{-3}\), lower than that in summertime of 2006, \((1.8 \pm 0.8) \times 10^4 \text{cm}^{-3}\), although there could be a underestimation due to the limitation of minimum detection size of WPS. The total aerosol volume concentration was \(59.4 \pm 55.9 \mu m^3 \text{cm}^{-3}\), ~40% lower than that of 2006, \(83.5 \pm 59.7 \mu m^3 \text{cm}^{-3}\). Although it was sometimes overcast and rainy during the observation period, 8 episodes of NPF events were observed over the 50 sampling days. Table 1 provides a summary of the date and time of NPF events, meteorological and NPF related parameters. For the 8 NPF events, the measured mean particle formation rate was 2.37 cm\(^3\) s\(^{-1}\), which varied from 1.5 to 3.8 cm\(^3\) s\(^{-1}\); this was within the range summarized by Kulmala et al. (2004) from various studies in the boundary layer. However, it was much

<table>
<thead>
<tr>
<th>Date</th>
<th>Start time</th>
<th>End time</th>
<th>RH</th>
<th>Temp</th>
<th>N_{nuc,max}</th>
<th>CS</th>
<th>J_{nuc}</th>
<th>GR</th>
</tr>
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<tbody>
<tr>
<td>2008/8/1</td>
<td>9:40</td>
<td>11:50</td>
<td>55%</td>
<td>30</td>
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<td>3.76</td>
<td>8.54</td>
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<tr>
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<td>11:30</td>
<td>62%</td>
<td>31</td>
<td>7493</td>
<td>0.014</td>
<td>3.40</td>
<td>10.64</td>
</tr>
<tr>
<td>2008/8/15</td>
<td>9:40</td>
<td>12:20</td>
<td>50%</td>
<td>31</td>
<td>5116</td>
<td>0.019</td>
<td>1.52</td>
<td>4.61</td>
</tr>
<tr>
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<td>11:10</td>
<td>47%</td>
<td>31</td>
<td>5350</td>
<td>0.02</td>
<td>1.67</td>
<td>7.56</td>
</tr>
<tr>
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<td>10:00</td>
<td>11:10</td>
<td>59%</td>
<td>29</td>
<td>4813</td>
<td>0.019</td>
<td>1.74</td>
<td>9.16</td>
</tr>
<tr>
<td>2008/8/23</td>
<td>10:00</td>
<td>12:00</td>
<td>45%</td>
<td>34</td>
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<td>2.16</td>
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<td>11:30</td>
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<td>2.06</td>
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</tr>
<tr>
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<td>11:40</td>
<td>45%</td>
<td>29</td>
<td>11171</td>
<td>0.025</td>
<td>2.65</td>
<td>4.43</td>
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</table>

\(^a\)NPF events occurring date, event start and end time, average relative humidity (RH, %) and temperature (Temp, °C) during NPF episode, maximum concentration of nucleation mode particles (N_{nuc,max}, cm\(^{-3}\)), condensation sink (CS, s\(^{-1}\)), formation rate (J_{nuc}, cm\(^3\) s\(^{-1}\)), and growth rate (GR, nm h\(^{-1}\)).

\(^b\)The minimum detection size of WPS was 10 nm; therefore, the N_{nuc,max} and J_{nuc} would be underestimated compared to those measurement of aerosol number size distributions down to 3 nm.
higher than that observed in clean environments, such as in Hyytiälä (0.9 cm$^{-3}$ s$^{-1}$ on average) (Dal Maso et al., 2005), and similar with that in urban sites, such as Helsinki (2.4 cm$^{-3}$ s$^{-1}$ on average) (Hussein et al., 2008). Because vehicle and plant emissions had been strictly controlled by the government, the air quality was greatly improved during the Olympic Games period, and the particle formation rate was much less than that observed in 2004 (3.3–84.1 cm$^{-3}$ s$^{-1}$) (Wu et al., 2007). The growth rate ranged from 3.2–10.6 nm h$^{-1}$, which was higher than that in Hyytiälä (3.8 nm h$^{-1}$ on average) (Dal Maso et al., 2005) and Helsinki (3.0 nm h$^{-1}$ on average) (Hussein et al., 2008). It was also a little higher than that of 2006 (1.2 to 5.6 nm h$^{-1}$) (Yue et al., 2009), probably indicating that the clean atmospheric condition may favor the growth of newly formed particles.

Case Studies of NPF and Growth

In the atmosphere, a main sink of newly formed nucleation mode particles is coagulational scavenging into preexisting particles (Kerminen et al., 2001). Smaller particles are depleted more rapidly than larger ones because of their higher diffusivities (Stolzenburg et al., 2005). Coagulation between nucleation mode particles and larger preexisting particles decreases the particle number concentration of nucleation mode, thus results in an apparent growth of the mean modal size of the nucleation mode particles (Stolzenburg et al., 2005; Leppä et al., 2011). Preexisting particles promote nucleation mode particles growth, however, they may prevent new particle formation by quickly depleting nucleated particles when the concentration of preexisting particles is relatively high. In addition, preexisting particles provide a significant sink for condensable vapors in atmosphere which contribute to condensational growth of newly formed particles. Characteristics of NPF vary with concentration of preexisting particles, as discussed in detail in the following sections.

NPF Events under Low Number Concentration of Preexisting Particles

Fig. 1 presents NPF events occurred on August 1 and 31 under low number concentration of preexisting particles. The air mass that came from the northwest was clean and had very low concentration pollutants, as shown in Fig. 1(c). During most of these two days, the BC mass concentration was lower than 1 µg m$^{-3}$; the SO$_2$ and NO$_2$ concentrations were also quite low during the NPF episode. The primary emission indicators were very low; therefore, the high concentration of particles shown in the contour plot consisted mainly of secondary particles rather than primary particles. The average particle concentrations before NPF episode of the two days were about 4000 cm$^{-3}$ and 3000 cm$^{-3}$, respectively. Given the very low concentration of preexisting particles, the calculated CS was lower than 0.02 in the morning and reached a minimum value close to 0.015 before the NPF episode which would favor the occurrence of NPF in Beijing, as pointed out by Wu et al. (2007).

Newly formed particles contributed little to the mass concentration and surface area concentration before growing to larger ones. The measured growth rate of nucleation mode particles from 10 nm to 25 nm was about 8.54 nm h$^{-1}$ on August 1, more than twice of that on August 31 (3.21 nm h$^{-1}$). The mechanism of particle growth on August 1 may differ from that on August 31. By investigating the temporal evolution of the total particle number concentration, different results were found for these two days. On August 1, the total particle number concentration experienced a sharply decrease after the NPF episode, while the decrease in total particle number concentration was less pronounced on August 31. The decrease rate of the total particle number concentration were 53.5 cm$^{-3}$ min$^{-1}$ and 16.4 cm$^{-3}$ min$^{-1}$, respectively. As condensational growth does not change the particle number concentration at all, the sharply decrease of total particle number concentration may be contributed by coagulation among particles. Although atmospheric dilution may play an important role, it is assumed that this would be equally important in these two days.

To figure out the contribution of condensation and coagulation to particle growth, the evolution of GMD of nucleation mode particles fitted with log-normal function vs. CS and CoagS was presented as shown in Fig. 2. The consumption of condensable vapors for condensational growth of nucleation mode particles (e.g., gaseous sulfuric acid and other organic vapors) would increase as particles growing to larger sizes, thus CS (for simplicity only gaseous sulfuric acid was taken into consideration) would increase with the increase of GMD. Meanwhile, as the modal size of nucleation mode particles grows into a larger size, the residence time of nucleation mode particles in atmosphere would be extended before being scavenged by coagulation with other particles, thus resulted in a decrease of CoagS of nucleation mode particles. By comparing the evolution of GMD and CS as well as CoagS, a very good agreement ($R^2$ = 0.96) of GMD and CS and a considerable agreement ($R^2$ = 0.84) of GMD and CoagS were found on August 31, as shown in Fig. 2(a2) and Fig. 2(b2), indicating that condensation should be the dominant way for nucleation mode particles growth in this day. For August 1, the situation was quite different. As shown in Fig. 1(a1) and Fig. 1(b1), the correlation between GMD and CS could be divided into two stages. In the first stage (represented by blue dots), CS correlates well with GMD with $R^2$ of 0.98, indicating condensational growth contributes most to the increase of GMD at this stage. However, in the second stage (represented by purple dots), CS decreases as GMD gets larger, indicating that the consumption of condensable vapor which was supposed to increase at that time decreases a lot. However, with lower condensation of condensable vapor, the growth of nucleation mode particles would probably rely on coagulation. As shown in Fig. 1(b1), the CoagS decrease first and later increase with the increase of GMD. It should be mentioned that CoagS of nucleation mode particles was calculated by choosing the log-normal fitted GMD as the reference size, thus CoagS should decrease when the GMD getting larger, as mentioned before. The reasonable explain to such an increase of CoagS with the increase of GMD should be intensive coagulation among high concentration of particles produced by nucleation which leads to a modal size increase. The net formation rate of the nucleation
mode particles $dN_{\text{Nuc}}/dt$ on August 1 was higher than that on August 31, which were 2.45 cm$^{-3}$ s$^{-1}$ and 1.44 cm$^{-3}$ s$^{-1}$, respectively. As limited to the instrument, the formation rate of new particles should be underestimated. It seems that condensational growth comes before coagulational growth, which was also proposed by Kulmala et al. (2004b). The newly formed particles quickly grow to larger sizes by condensation of vapors, however the concentration of condensable vapors would be reduced if large amounts of particles are produced by nucleation continuously, then those newly formed particles turn to coagulate with others, thereby shifting the modal size to larger particles and contributing to apparent growth of the nucleation mode.

It seems that if the correlation between GMD and CS agreed well with that between GMD and CoagS, condensational growth dominated the particle growth. We have summarized the correlation between GMD and CS as well as CoagS of other NPF events in Table 2. It was found that for most NPF events, condensational growth contributes largely to particle growth, while the contribution of coagulational growth could be considerable especially when the total particle number concentration experienced a sharply decrease after the NPF event. However, on August 22, the correlation between GMD and CS ($R^2 = 0.96$) didn’t agree with that between GMD and CoagS ($R^2 = 0.46$) at all. The reason is that we have only taken GMD smaller than 25 nm into consideration. After extending GMD to 50 nm, it was found that the situation was just like that of August 1, indicating that coagulational growth contributed to the growth of particles when they grew to ~50 nm at this time.

A large number of Aitken mode particles emerged at about 20:00 LT on August 1, coinciding with an elevation of BC and NO$_2$ concentrations, as shown in Fig. 1(a). The concentrations of BC, NO$_2$, and PM$_{10}$ at that time were significantly higher than the daily average. There was no change of wind direction or increase of wind speed at the
Fig. 2. The Evolution of GMD of nucleation mode particles (fitted with log-normal function) vs. CS (a1, a2) and CoagS (coagulation sink of nucleation mode particles by choosing the log-normal fitted GMD as the reference size) (b1, b2) of Aug. 1st and Aug. 31th. The black line represents linear fit.

Table 2. Correlation of GMD of nucleation mode particles vs. CS and CoagS and the decrease rate of total particle concentration for NPF events.

<table>
<thead>
<tr>
<th>Date</th>
<th>GMD vs. CS</th>
<th>GMD vs. CoagS</th>
<th>Decrease rate of total particle concentration (# cc⁻¹·min⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>8.1</td>
<td>0.77</td>
<td>0.28</td>
<td>53.5</td>
</tr>
<tr>
<td>8.12</td>
<td>0.97</td>
<td>0.98</td>
<td>27.6</td>
</tr>
<tr>
<td>8.16</td>
<td>0.91</td>
<td>0.76</td>
<td>34.1</td>
</tr>
<tr>
<td>8.22</td>
<td>0.96</td>
<td>0.46</td>
<td>63.6</td>
</tr>
<tr>
<td>8.23</td>
<td>0.83</td>
<td>0.97</td>
<td>36.9</td>
</tr>
<tr>
<td>8.31</td>
<td>0.96</td>
<td>0.84</td>
<td>16.4</td>
</tr>
<tr>
<td>9.1</td>
<td>0.91</td>
<td>0.92</td>
<td>35.2</td>
</tr>
</tbody>
</table>
same time, indicating that the high concentration of Aitken mode particles may not come from regional transport. It’s worth mentioning that a parking lot of the Olympic center was located in the east of the observation site. The majority of particle number from vehicle exhaust are in the size range 20–130 nm for diesel engines (Morawska et al., 1998) and the count median diameter (CMD) at 90 m away from a freeway with heavy-duty diesel traffic was reported to be ~60 nm (Zhu et al., 2002). Since the Olympic center was closed to traffic except for special transport vehicles, and the particles emerged at that time were concentrated in the size range of 40–100 nm with a CMD of ~65 nm which was measured ~100 m away of the road to the parking lot, we can infer that the elevated concentration of gaseous pollutants and particulate matter may be induced by the emission from diesel vehicles transporting goods to the Olympic center. This did not last long as the particle number concentration decreased rapidly to an average of about 22:00 LT. Coincidentally, the same thing happened almost at the same time on August 31, with the peak appearing at a later time.

NPF Events under Relatively High Number Concentration of Preexisting Particles

NPF was not supposed to occur under very high number concentration of preexisting particles as gaseous nucleating vapors would be depleted by preexisting particles and newly formed smaller particles would be scavenged significantly even totally by larger particles before reaching detectable sizes (Kermnien et al., 2004; Cheung et al., 2013). This process would be further enhanced with the increase of the concentration of preexisting particles; therefore, NPF would not occur in severely polluted environment. However if sufficient concentrations of precursors to begin NPF are present in the atmosphere, nucleation can occur even under relatively high background levels of pre-existing particles (Fiedler et al., 2005).

Two NPF events occurred on August 23 and September 1, as shown in Fig. 3. The NPF events recorded on these two days were similar to the NPF events recorded in section 3.2.1, albeit with relatively higher concentration of preexisting particles. The average particle concentrations before NPF episode of the two days were about 7000 cm⁻³ and 6500 cm⁻³, respectively. Since there were few primary emissions during the Olympic period in Beijing except for the special transport vehicles which appeared in the night, those preexisting particles were very likely came from the efficient growth of particles in the previous day. The lifetime of those ~100 nm particles was several days in atmosphere while particles sizing in nucleation mode and coarse mode experienced a rather short lifetime due to efficient removal mechanisms, i.e., coagulation and sedimentation. Given the relatively high concentration of preexisting particles, the calculated average CS on the two days was larger than 0.03, and the average surface area concentrations were 207.5 µm² m⁻³ and 144.3 µm² m⁻³, respectively. The total concentration of particles on September 1 was a litter higher than that on August 23 as shown in Fig. 3(b), whereas the surface area concentration on September 1 was quite smaller than that on August 23.

It was mainly because of the mean diameter of preexisting particles on August 23 was larger than that on September 1, which were 90–100 nm and 60–70 nm, respectively, as shown in Fig. 3(a). The larger the particle surface area concentration, the more intensively the particles consumed condensable vapors.

During the NPF events of these two days, the variation of concentration of nucleation mode particles was found to be coincident with SO₂, a significant precursor of gaseous H₂SO₄. Gas-phase H₂SO₄ is known to be an essential factor in NPF and subsequent particle growth (Sipilä et al., 2010), whose major sink is condensation on preexisting aerosols. If the concentration of H₂SO₄ has been consumed in quantity, the NPF events would be interrupted. However, if sufficient concentrations of H₂SO₄ were present in the atmosphere, nucleation could occur even under relatively high concentrations of preexisting particles (Fiedler et al., 2005). The production and concentration of H₂SO₄ depend on the concentration of its precursors, SO₂ and OH (Mikkonen et al., 2011), where the OH concentration is dependent on the photolysis rate of O₃ by solar radiation in the 280–320-nm UVB range. The H₂SO₄ concentration can be estimated by evaluating the variation of SO₂, solar radiation, CS, and RH, where radiation represents the proxy of OH concentration. The SO₂ and OH concentrations are considered as the producers of H₂SO₄ whereas CS and RH are regarded as the consumers. The FR on September 1 (2.16 cm⁻³ s⁻¹) was higher than that on August 23 (2.16 cm⁻³ s⁻¹), where the difference lies mainly in dNₙuc/dt (1.77 cm⁻³ s⁻¹ and 1.11 cm⁻³ s⁻¹, respectively). The average SO₂ concentration on September 1 was higher than that on August 23 during the NPF episode (6.2 ppb and 3.8 ppb, respectively). Given these, combined with the slightly low CS and similar RH, we can infer that the gaseous H₂SO₄ concentration on September 1 may be higher than that on August 23, resulting in the larger FR. The intensity of NPF would be enhanced under a larger FR. Therefore the maximum number concentration of nucleation mode particles on September 1 was much higher than that on August 23, which were 11171 cm⁻³ and 7848 cm⁻³, respectively. The GRs of these two days were 6.29 nm h⁻¹ and 4.43 nm h⁻¹, respectively; similar to that derived by Birmili and Wiedensohler (2000) in a polluted continental boundary layer with particle surface areas between 200 and 300 µm² m⁻² during the nucleation events.

Only two NPF events were observed under relatively high concentration of preexisting particles during the campaign. Preexisting particles can scavenge newly formed particles and condensable vapors, thus suppress NPF. That’s probably why the occurrence of NPF events under high number concentration of preexisting particles was much less than events under low number concentration of preexisting particles. However, the efficient growth of particles under this environment together with the preexisting particles would contribute a lot to urban haze. In a few days after the NPF events under high number concentration of preexisting particles, the PM₃₀ gradually rise to a significantly high level. The averaged PM₃₀ of August 24 and September 2 had increased to nearly twice of that of the previous NPF day.
Particle Shrinkage Events

Particle shrinkage always occurs after the nucleation and growth process, the mechanism of particle shrinkage is probably associated to the evaporation of condensed semi-volatile species, especially when the condensation process or the chemical reactions involved in the growth of particles are reversible (Yao et al., 2010; Backman et al., 2012; Young et al., 2013). Thus, particle shrinkage is usually accompanied by a reduction of the total particle concentration (Backman et al., 2012).

Particle shrinkage after NPF and subsequent growth was observed on August 22. A nucleation mode burst occurred at about 10:00 LT, and the concentration of nucleation mode particles increased from ~1E3 cm\(^{-3}\) to a maximum of ~5E3 cm\(^{-3}\), lower than that in other NPF events. The newly formed particles quickly grew from 15 nm to 54.3 nm until 14:00 LT, and remained within the range of 55~60 nm during the period between 14:00 LT and 15:00. However, the GMD started to decrease from 15:00 LT; in less than 3 hours, the GMD decreased from 61.1 to 15.4 nm, with the CS declining from 0.078 to 0.028.

Large temporal variations in the number concentration of particles of Aitken mode and accumulation mode was observed after the NPF process, which probably related to transporting of aerosols. An elevated concentration of SO\(_2\) was observed at LT 14:00, coinciding with a sharp increase of the Aitken mode particle concentration, as well as a slight increase of the accumulation mode particle concentration. The back trajectory from a Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model indicated that the air masses in the lower boundary layer were advected from the south at that time, coupled with the elevated wind speed at near-surface, we can infer that the elevation in particle number concentration may be due to an SO\(_2\) enriched small-
scale air mass with a high concentration of large particles transported from the south. The concentration of SO$_2$ returned to average level once the air mass left, slightly ahead of the shrinkage event. The air mass had brought about 5E3 cm$^{-3}$ Aitken mode particles and 1E3 cm$^{-3}$ accumulation mode particles, which can be easily deduced by the variation in the number concentration, as shown in Fig. 4(b). The transient pollutants transportation resulted in a rapid build-up of surface area concentration of particles as well as PM$_{10}$.

The shrinkage terminated at about 17:45 LT, when the nucleation mode particles concentration had returned to the average level, resulting in a secondary peak of the nucleation mode particle concentration. The first peak was reached at 11:00 LT, with a maximum of 4813 cm$^{-3}$, whereas the second was reached at 16:30 LT, with a maximum of 4740 cm$^{-3}$. Considering that no nucleation occurred in that period, it seemed that nearly all the newly formed particles had shrunk back to small sizes after growing to Aitken mode, creating an “arch-like” shape in the size distribution contour plot (Young et al., 2013). The increase in number concentration of nucleation mode particles could not be induced by plume nucleation which has been reported by several recent studies (Wu et al., 2007) since the number concentration of particles in atmosphere was reducing at that period whereas plume nucleation would rapidly increase the particles number concentration within a very short time. It was more likely that those larger particles had experienced shrinkage in sizes and became smaller particles, as the amount of decease in number concentration of Aitken mode particles was very similar to the increasement of number concentration of nucleation mode particles.

However, at the same time, a considerable part of the Aitken mode particles did not show a shrinkage trend, and the GMD remained nearly unchanged. The concentration of this portion was about 6E3 cm$^{-3}$, which was the minimum Aitken mode particle concentration during the shrinkage period. Recent studies suggested that evaporation of semi-volatile organics may contribute to shrinkage of particles below 40–50 nm and evaporation of ammonium nitrate may contribute to shrinkage of particles larger than 40–50 nm (Man et al., 2015). Organic vapors play a significant role in promoting the growth of freshly formed particles; therefore, the new particles may contain a considerable fraction of organic compounds after growing to Aitken mode size (Smith et al., 2008). However, particles may react with SO$_2$ or gaseous H$_2$SO$_4$ in the atmosphere, which causes them to age and become less volatile. The chemical composition of the unshrinking particles was probably different from that of the shrinking particles. It can be assumed that particles coming from the transportation of air mass had undergone aging in the atmosphere and thus did not shrink during the atmospheric dilution period. Excluding the initial concentration of preexisting Aitken mode particles (about 2E3 cm$^{-3}$), it was likely that almost all the particles brought by the air mass had not undergone the shrinkage process.

The growth rate of newly formed particles on August 22 was 9.16 nm h$^{-1}$, while the shrinkage rate was 16.6 nm h$^{-1}$, as shown in Fig. 4(a). The black dotted line represented the
temporal variation in GMD fitted with log-normal function. The favorable conditions for particle shrinkage remained highly uncertain, recent studies suggested that particle shrinkage was probably attributed to the atmospheric dilution and evaporation processes due to changes in meteorological conditions, mainly an elevation of wind speed and temperature (Cusack et al., 2013; Young et al., 2013). One thing those particle shrinkage events observed in various regions in common was that the events were more likely to occur in the afternoon during the warm season, indicating the intensive solar radiation and meteorological conditions would favor the evaporation of semi-volatile species. The highest temperature and lowest RH during the particle shrinkage period reported by Young (2013) was 34°C and 61%, and the RH during the shrinkage period observed in Hong Kong was 57%–59%, as reported by Yao (2010). However, during the observed shrinkage period in Beijing, the maximum temperature and minimum RH was 35.9°C and 41.5%, respectively. The shrinkage rate was much higher than that observed in Hong Kong (10.7 nm h⁻¹) (Yao et al., 2010), São Paulo (5.2 nm h⁻¹) (Backman et al., 2012) and Taiwan (5.1–7.6 nm h⁻¹) (Young et al., 2013). One plausible reason would be that the particle shrinkage occurred during summertime in a high latitude area with higher temperature and lower RH compared to those observed in other regions, thus enhanced particle shrinkage.

CONCLUSIONS

Aerosol number size distributions were observed at an urban site in Beijing during the 2008 Olympic Games. Owing to the emission control measures, the concentration of atmospheric particles had experienced a significant decrease. 8 NPF and growth events were identified; the measured mean particle formation rate was 2.37 cm⁻³s⁻¹, which varied from 1.5 to 3.8 cm⁻³s⁻¹, and the growth rate ranged from 3.2 to 10.6 nm h⁻¹. Case studies were presented to identify the characteristics of NPF under different atmospheric conditions. NPF was observed under low number concentration of preexisting particles as well as under relatively high number concentration of preexisting particles. Different potential mechanisms of particle growth were found by investigating the correlation between GMD and CS as well as CoagS. It seems that if the correlation between GMD and CS agreed well with that between GMD and CoagS, condensational growth dominated the particle growth. When CS decreases or CoagS increases as GMD gets larger, the contribution of coagulation to particle growth may be considerable especially when the total particle number concentration experienced a sharply decrease after the NPF event. Condensation contributed mainly and preferentially to particles growth, however, coagulation would contribute a lot when formation rate of new particles was sufficiently high. NPF events under relatively high number concentration of preexisting particles occurred less frequently. The variation of concentration of nucleation mode particles was found to be coincident with \( \text{SO}_2 \), indicating that NPF could occur under relatively high concentrations of preexisting particles if sufficient concentration of gas-phase \( \text{H}_2\text{SO}_4 \) existed in the atmosphere. However, the efficient growth of particles under this environment together with the preexisting particles would contribute a lot to urban haze.

Particle shrinkage after NPF and subsequent growth was observed with a shrinkage rate of 16.6 nm h⁻¹. Newly formed particles shrank to nucleation mode size after growing to Aitken mode size, creating a secondary peak in the variation of nucleation mode particle concentration. The burst of nucleation mode particles during that period could not be induced by plume nucleation since the number concentration of particles in atmosphere was reducing at that period whereas plume nucleation would rapidly increase the particles number concentration within a very short time. A considerable part of the Aitken mode particles did not shrink at the same time, which would be attributed to that those particles may come from transport of air masses during which particles underwent aging in the atmosphere and became less volatile. The shrinkage rate was higher than those reported in recent studies, probably due to particle shrinkage occurred during summertime in Beijing with higher temperature and lower RH compared to those observed in other regions, thus enhanced particle shrinkage.

ACKNOWLEDGEMENTS

This work was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB05040402), Key Program of the Chinese Academy of Sciences (KJZD-EW-TZ-G06-01), Natural Science Foundation of China (21476221, 41305021), National Key Foundation for Exploring Scientific Instrument (2012YQ 06014703), and the Foundation of Hefei Physical Science and Technology Center (2012FXCX005).

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Atmos. Environ. 81: 651–659.


Received for review, July 28, 2015
Revised, December 11, 2015
Accepted, December 16, 2015