Nighttime particle growth observed during spring in New Delhi: Evidences for the aqueous phase oxidation of SO2

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1. Introduction

Study of atmospheric aerosols is important because of their effects on climate, air quality and human health. These effects vary with the region and meteorological condition, and are directly linked to the atmospheric processes related to the formation and growth of aerosols. Therefore, particle formation and growth studies in typical environmental conditions are of great interest. However, these processes are poorly studied especially in Southeast Asian urban environment, where the meteorological conditions and emission sources are different from urban environment of subtropical and temperate zones on the globe. Also such gaps of understanding in aerosol formation and growth are widening the uncertainties in the current global climate models for the prediction of future climate (Sherwood et al., 2013; IPCC 5th Assessment Report, Climate Change, 2013).

Atmospheric aerosol growth (growth due to various physical processes, such as coagulation and condensation) (Sarangi et al., 2015; Leppä et al., 2011; Seinfeld and Pandis, 2006) is a critical atmospheric...
In general, particles are formed by gas to particle conversion (including condensation of gas on to the pre-existing particle) and are termed as secondary aerosols. Secondary aerosols can be considered as climatically relevant if they survive with the ability to grow up once they are formed. This phenomenon depends on the particle formation rate, concentration of condensable vapors, and composition of particles. Particle growth rates, derived from the atmospheric size distribution measurement reveals information on the concentrations and properties of the condensing vapors. Several aerosol studies revealed that condensable organic species rather than inorganic species are the major source for the growth of aerosol (Riihimäki et al., 2011; Patoulias et al., 2015). In terms of the composition of particles, organic aerosols (OA) represent a substantial fraction (20–90%) of total submicron aerosol mass (Murphy et al., 2006; Zhang et al., 2007). Biomass burning is the major source for atmospheric OA, with contributions from both anthropogenic (biofuel burning, agriculture waste burning, crop residue burning, etc.) as well as natural sources such as wildfires. Aerosols produced from biomass burning have been estimated to account for 90% of all the primary organic carbon emitted globally from combustion sources (Ito and Penner, 2005). Also, the emission of gases further contributes to the particle growth and secondary aerosol distributions.

Current understanding on the growth of aerosols is hampered by high uncertainties because this is not rigorously tested through experiments. Several methods have been developed for determining aerosol growth rates from atmospheric observations. They are derived through complex mathematical equations, which involve particle number size distribution measurements. In ambient atmospheric aerosols, growth is primarily due to coagulation (Sarangi et al., 2015) and condensation of (condensable) vapors such as sulfuric acid and organics (water soluble organic carbon (WSOC), volatile organic compounds (VOCs), etc.) (Seinfeld and Pandis, 2006). It is generally believed that nucleation and subsequent growth of aerosols is initiated by sulfuric acid (H₂SO₄) (Weber et al., 1999; Hallquist et al., 2009) because of its low vapor pressure (e.g., < 0.001 Torr at 300 K for pure H₂SO₄) (Ayers et al., 1980). But this process can be explained in daytime because it needs sunlight to trigger the chemical reaction (Finlayson-Pitts and Pitts, 1999; Seinfeld and Pandis, 2006). Aerosol nucleation and growth events have been observed under a wide range of atmospheric conditions (Kulmala et al., 2000, 2004; Hermann et al., 2003; Lee et al., 2003; McMurry and Eisele, 2005), but discussions on nighttime growth have typically been neglected in spite of scattered evidences of their existence (Man et al., 2015; Wang et al., 2016; Salimi et al., 2017).

In this study, based on the particle size distribution measurements, atmospheric gas composition and the chemical composition of PM₁ samples, we discuss for the first time nighttime aerosol growth during spring in New Delhi. The objective was to understand the conditions responsible for the observed growth of fine particles in an urban atmosphere, and to investigate the candidate chemical species and the involved chemistry for the particle growth events. Our result suggests that nighttime oxidation of SO₂ by NOₓ under high RH condition on fine particles with NH₃ neutralization is an important pathway for the observed nighttime particle growth.

2. Methodology

2.1. Aerosol sampling

The measurements were conducted at CSIR-National Physical Laboratory (NPL, http://www.nplindia.org/), New Delhi during spring (March and April 2013; and April 2014). The sampling site (28°38′N, 77°10′E and ~751 feet asl) is surrounded by flora, residential accommodation, and roadway traffic and agriculture sites. Therefore, it is considered as representative site of mixed source influence, such as biomass burning, traffic emission, biogenic emission, etc. (Fig. 1). The measurement system was placed in a room and aerosols were aspirated (at a flow rate 16.7 L min⁻¹) at the rooftop of the laboratory (~15 m above the ground) through two cyclone inlets. One of the cyclones with cut-off size 1 μm is connected to a filter holder by a copper tubing (internal diameter 6 mm and length ~4 m) to collect PM₁ samples (47 mm, Pallflex® air monitoring quartz filters) and the other one with

Fig. 1. Satellite view (google map) of the sampling site and surroundings.
cut-off size 2.5 μm is connected to scanning mobility particle sizer (SMPS) by the identical copper tubing as shown in Fig. 2. In this study, we used copper tube for sampling purpose because it can reduce the particle losses due to negligible electrostatic effect, and can easily fold to any angle of interest as per the sampling need.

This SMPS comprises with an electrostatic classifier (TSI model 3080 with built-in Kr-85 neutralizer), differential mobility analyzer (DMA, TSI model 3 081 or 3 085) and a condensation particle counter (CPC, TSI model 3778). Before introducing aerosol stream to SMPS, aerosols were dried after being passed through two silica gel diffusion dryers (TSI model 3 062) connected in series. Diffusion dryer includes a removable extractor for collecting large water droplets. Desiccant (silica beads) surrounding the aerosol flow path removes excess moisture by diffusion capture. Because aerosol never comes in contact with the desiccant, we assumed that there is no or minimal particle loss. Then aerosol stream was reached to the inlet impactor (nozzle size 0.045 cm) of SMPS (tube length ~2 m) with a sample flow rate of 0.3 L min⁻¹. The sheath flow rate of SMPS was maintained at 3 L min⁻¹. The measured range of particle size was between 4 and 158 nm using nano-DMA and 14–661 nm using long-DMA with 64 channels/decades.

Before these measurements, DMAs were calibrated with 60 and 100 nm standard polystyrene latex (PSL) particles (Sarangi et al., 2016). We have also checked the calibration of CPC counts based on a gravimetric approach (Aggarwal et al., 2013a). We followed quality assurance and international agreement on particle number size distribution measurement as described in ACTRIS and GAW (Wiedensohler et al., 2012, 2018). The residence time of particles inside the tube before entering to SMPS was calculated to be ~12.2 s (residence time of particles between D and F points is ~0.8 s and between F and G points is ~11.4 s, Fig. 2). Whereas, total scan time for sample analysis in SMPS was 135 s (i.e., 120 s up scan time + 15 s retrace time), which is fairly high, i.e., ~10 times higher than that of total residence time of the particle in sampling line. Therefore, we assumed that the residence time did not considerably affect the growth of particles.

Parallel to SMPS measurements, PM₁ samples (n = 56) were collected for every 3 h during daytime (i.e., between 06:00–18:00 h local time (LT)) and night time for every 6 h (18:00–06:00 h). In this paper the concentration reported for chemical species is not calculated directly from mass concentration. Blank samples (n = 4) were also collected during the spring season 2013 and 2014. The filter samples were placed in a clean glass jar (pre-combusted) individually with Teflon lined screw cap, and stored at below 0 °C prior to analysis.

2.2. Chemical analysis (PM₁ samples)

For the determination of water-soluble organic carbon (WSOC), 3.14 cm² disc of each filter sample was extracted with Milli-Q water (>18 MΩ cm, 15 ml) in a glass bottle using an ultrasonic bath for 30 min. Particles in the extracts were removed using a disc filter (Milllex-GV, Millipore, 0.22 μm). A 2 M HCl solution (0.1 ml) was added to 5 ml of water extracts. After purging for 10 min with ultrapure air (80 ml min⁻¹), 100 μl of solution was injected into a TOC analyzer (Model TOC-Vcsh, Shimadzu, Kyoto, Japan). An analytical error (repeatability) was estimated to be within 6% by the duplicate analysis. In this study, we did not perform the positive and negative artifact measurement during sampling. However, we assumed the positive artifacts would be ~0.5 μg C m⁻² in particular organic carbon under similar condition of sampling (using bare quartz filter) performed elsewhere (Subramanian et al., 2004).

For the measurement of inorganic ions, 3.14 cm² disc of filter sample was extracted with Milli-Q water (10 ml) in a polyethylene bottle using an ultrasonic bath for 30 min. The water extracts were filtered using a disc filter. The major ions (i.e., SO₄²⁻, PO₄³⁻, NO₃⁻, NO₂⁻, CI⁻, NH₄⁺, K⁺, Ca²⁺, Mg²⁺, and Na⁺) were determined using a Metrohm-761 Ion Chromatograph (IC) coupled with an auto sampler (Aggarwal et al., 2013b). The analytical errors (repeatability) were estimated to be 4% based on the duplicate analysis.

2.3. Trace gas and meteorological data

Hourly meteorological data (temperature, relative humidity, wind speed and direction) were obtained from the NPL meteorological station situated about 100 m distance from the sampling location) and concentration of atmospheric gases, i.e. SO₂, CO, O₃ and NO₂ for the study period are obtained from a Continuous Ambient Air Quality Monitoring Station (CAQMS) of Central Pollution Control Board (CPCB), Shadipur located within 3 km radius from the measurement site (http://www.cpcb.gov.in/CAAQMS/mapPage/frmindiamap.aspx).

2.4. Air mass backward trajectories

To characterize the air masses encountered at New Delhi, 5 days backward trajectory analysis was performed for each sampling period using the HYSPLIT4 model (http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory, Silver Spring, Maryland, United States). These trajectories were calculated for air masses ending at the
site (with sampling ending time) at 500 m height using the model vertical velocity and reanalysis data. The flow pattern was updated every 24 h (Fig. 3).

2.5. Particle growth event and growth rate calculation

Based on the temporal variations of particle count mean diameter (CMD), the ascending trend of the particle count mean diameter (CMD) which sustains more than 3 h (this time limit is an assumption and has been proposed to study the growth trend) is considered as growth events whereas rest of the trends are considered as non-growth events (Sarangi et al., 2015). Particle growth rates were represented by the observed growth of the particles from nucleation/Aitken to accumulation size ranges. Count mean diameters (Hinds, 1999) for each size distribution were calculated to examine particle growth processes (Dal Maso et al., 2005; Leppä et al., 2011). The observed growth rate (GR) of the ambient particle was calculated by fitting the CMD of particles over a period of time 't' during the growth events.

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

(1)

$$CMD = (d_i) = \sum_{i=1}^{105} N_i \times d_{pi}$$

(2)

$$N = \sum_{i=1}^{105} N_i$$

(3)

where $d_i$ is the count mean diameter of the particles, $d_{pi}$ is the particle diameter of size bin $i$, and $N_i$ is the particle number concentration in size bin $i$ over a size range 4–158 nm using nano-DMA and 14–661 nm using long-DMA.

3. Results and discussion

3.1. Particle size distribution

Particle size distributions measured during the study period showed daytime bimodal distribution and nighttime unimodal distribution (Fig. 4). Daytime particle size distribution (PSD) shows bimodal because of photochemistry (responsible for formation of condensable vapor). Photochemistry is playing a crucial role here thereby resulting in secondary formation due to nucleation of condensable vapor responsible for first mode, whereas the second mode is due to preexisting aerosol. Nighttime shows single mode distribution representing the preexisting particle and secondary formation is negligible due to absence of photochemistry. The count mean diameter (CMD) of the particles observed mostly existed between nucleation ($\leq 25$ nm) and accumulation mode ($\geq 100$ nm). The nucleation ($\leq 25$ nm), Aitken (25–100 nm) and accumulation mode ($\geq 100$ nm) size protocol followed according to Dal Maso et al. (2005). Particle growth events (shifting of CMD towards higher size) were frequently observed during the study period and the growth trends were similar to those observed...
in a number of other investigations (Kulmala et al., 2004). It is further observed that the particles nucleation events and subsequent growth were initiated in daytime, and growths were continuous and prominent during nighttime.

Fig. 5a describes the particle size distributions measured for the period March 18–21, 2013. It is important to mention that a segment (spanning over 15 h) of data was absent due to technical reasons (e.g., instrument maintenance). Fig. 5b presents a unique particle size distribution, which is measured during April 22–25, 2013. The distribution is unique because all the measurement days showed similar trend of particle size distributions. Further, nighttime particle growths are prominent, clearly distinct and sustained for the longer period. Similar size distributions were observed during the same month in 2014 using both long-DMA and nano-DMA as shown in Fig. 5c and d. The average particle number concentration over the size range 4–661 nm using both nano- and long-DMA was found to range between $0.72 \times 10^4$ and $1.42 \times 10^4$ cm$^{-3}$ as shown in Table 1. It is important to note that nano-DMA was used to catch both nucleation (observation of nucleation...
mode below 25 nm size range) and growth events but this study is limited to particle growth only. Most of the sampling period experienced particle size distribution during daytime showed bimodal size distribution (between 09:00 LT and 18:00 LT), where the first mode peak was observed between 14 and 60 nm and the second peak was above 60 nm. It is also observed that the nighttime particle size distribution has unimodal distribution sustained till next day morning (09:00 LT). Daytime particle number concentrations in the nucleation range (< N52) are about a factor of 2 higher than that of nighttime, indicating new particle formation in the presence of sunlight (Kiendler-Scharr et al., 2009). Nighttime particle number concentrations also experienced the shifting of mode peak diameters towards larger size. Before proceeding for further analysis of the observed growth events, it is important to understand the limitations of a single sampling location. The important assumption in using this approach is that the air mass in which the aerosol is being sampled is relatively homogeneous over large spatial scales (McMurry and Wilson, 1983; Juozaitis et al., 1996). Most particle growth events observed at a stationary location showed sustained growth over several hours, which implies that the particles grow over large spatial scale by condensation and/or coagulation also occurs throughout the air masses, otherwise there would be no pattern in the observations. At the site, the prevailing winds bring air parcels that may be more affected by anthropogenic as the day proceeds. Under these conditions, it is likely that the emissions from the regional sources (Fig. 1) and the subsequent post physico-chemical processing of such emissions may influence the observed growth events at the nighttime. Furthermore, aerosol growths are more prominent where meteorological parameters and nighttime gas precursors are supposed to have considerable contributions. The following analysis characterizes the daily conditions under which growth events do and do not occur, with an eye towards understanding the trace gas concentrations and meteorological conditions which are linked to growth of particles.

3.2. Growth rate

Growth rate (GR) of particles can be calculated from the measured size distribution data using Eq. (1). We determined the growth rate based on the SMPS data measured on typical nighttime growth events, i.e., March 2013, April 2013 and April 2014. Fig. 6 shows the plot between count mean diameter (CMD, nm) of particle size distribution plotted against the local time (hour) during the growth events. The growth rates for different time periods of these events were determined by fitting (fitting over size distributions is unimodal) of the data of a particular time segment for which an abrupt change in CMD was observed. The slope of the regression fit of the data (trend line) gives the growth rate (nm h⁻¹) during the growth events. The average growth rate from the regression line was calculated as 5.64 ± 3.03 nm h⁻¹ for the whole period of study.

The present experimental system does not allow for the detection of particles in the smaller mode (size < 25 nm) except April 05–09, 2014 where nano-DMA was used, hence we do not have enough data to explain the particle nucleation that has occurred during the measurement period. However, we can study the events where particle growth was observed. The rate at which particles grow depends upon the amount of vapor available for condensation, and intra-modal coagulation between particles (Sarangi et al., 2015). Particle growth due to coagulation and condensation is characterized from the temporal trend of measured particle size and number concentrations (Seinfeld and Pandis, 2006). If particle size increases with decrease in number concentration then it is considered as coagulation growth. Whereas if number concentrations do not show much change with respect to increase in particle size then it is considered as condensation growth. Condensation is generally considered to be the primary mechanism responsible for the growth of the nuclei mode particles (Zhang et al., 2004; Kulmala et al., 2004). Previous investigators have found that it can take from 2.5 to 7 h from the time when 3 nm sized particles are first detected to grow to a size distribution with a 20 nm number mode peak (Weber et al., 1997; Kulmala et al., 1998, 2004). In our observation, we found that a particle of CMD 19.4 nm can grow up to 56.5 nm and the maximum time taken for this is about 20 h and 3 min. It was also observed that at slightly higher CMD (49.4–90.4 nm) the time taken was more than 3 h (Table 2). It has been observed that faster time taken for the growth of particles in an urban area from the size range 3–10 nm to 18–33 nm was approximately 1 h (Zhang et al., 2004). Also, the growth duration had no specific magnitude with respect to size of the particles. Therefore, growth duration depends on the prevailing atmospheric conditions where growth events are observed. In order to investigate the relationship between the occurrence of growth events and other variables measured at the site, it is important to understand the growth events with respect to the influence of both meteorological parameters and trace gas species, and also the particle chemical constituents.

3.3. Meteorological parameters

Hourly variation in temperature, relative humidity (RH), net radiation, wind speed, and directions are shown in Figs. 7 and 8. Hourly averages were performed on a subset of the data during which the SMPS system was operational, i.e. during March 18–21, 2013, April 22–25, 2013, and April 01–09, 2014. This time period was essentially spring, i.e., transition from winter to summer where the weather transition is characterized by warm days, cold nights and dry ambiance. The diurnal variations in wind speed (WS) and wind direction (WD) are shown in Fig. 8, which clearly indicates the low diurnal up- downslope flow pattern that is prevalent throughout in the Delhi region. In general, between 05:00 and 18:00 LT, the wind speed gradually increases and decreases then onwards. In addition, cloudy sky is less observed because of transition from winter to summer. Plenty of bright sunlight is also observed during spring which ensures that most of the days experience similar level of radiation intensity (Fig. 7a) that gradually varies seasonally with the sun angle.

3.4. Trace gas composition

The diurnal variation in ozone concentration shows a morning dip in concentration after sunrise followed by an increase to an afternoon maximum (Fig. 9). This pattern is typically observed at this location during the measurement season. Kurpius et al. (2002) reported that the morning decrease in ozone concentration was attributed to increase of stomatal activity at sunrise, taking up ozone when the air is relatively stable with little vertical or horizontal mixing. However, recent ozone flux measurements indicate significant ozone loss within the canopy due to gas-phase chemical reaction (Kurpius and Goldstein, 2003). This conclusion has been recently strengthened by VOC measurements that showed a correlation between highly reactive, light dependent terpene compounds which are emitted upon sunrise and the observed decrease in ozone concentration, suggesting that some of the morning decrease in ozone is likely due to chemical reactions with terpenes in the canopy (Lee et al., 2005). As vertical mixing increases, the ozone concentration rebounds (Fig. 9). The afternoon increase is possibly because of the formation of ozone when nitrogen oxides and hydrocarbons emitted from vehicles and industrial units are combined with oxygen in the presence of sunlight (TERI-Toyota Asian Ozone project, 2011). In the late afternoon, the decreasing trend of ozone concentration is possibly due to the retardation of photochemical oxidation as the net radiation decreases (Reeves et al., 2010).

Fig. 9 further shows the diurnal pattern of black carbon (BC) concentrations. BC serves as an excellent tracer for anthropogenic sources of aerosol since it is emitted from the combustion activities, and undergoes limited chemical transformation in the atmosphere (Hansen and Rose, 1985; Fierce et al., 2015). Interestingly, BC concentration shows a reverse trend in comparison to ozone. There is an elevation of
BC between 02:00–06:00 LT and then a sharp decrease and further increase around 19:00 LT onwards. This is possibly due to the contribution of biomass burning in nighttime and diesel engine trucks that are allowed to enter into the city at nighttime (22:00 to 07:00 LT of next day). In addition to biomass burning, atmospheric boundary layer fumigation effect is one of the prominent reasons responsible for the nighttime and early morning peak of BC (Ramachandran and Rajesh, 2007). Biomass and other burnings have been reported to be generally intensified in winter and spring in nighttime (Kumar et al., 2015, Miyazaki et al., 2009).

Fig. 10 shows the diurnal variation of gas concentrations of SO$_2$ and NO$_2$ observed during the study period where NO$_2$ concentration was significantly high in comparison to SO$_2$. In Fig. 10a, for the period March 18–21, 2013, the average concentrations of SO$_2$ and NO$_2$ were found to be 8.63 ± 2.9 and 56.1 ± 14 µg m$^{-3}$ (average over 24 h) with elevated concentrations of 9.9 ± 2 and 61.6 ± 12 µg m$^{-3}$ (average over 12 h) at night in comparison to 7.53 ± 3.2 and 49.3 ± 11.6 µg m$^{-3}$ (average over 12 h) during the day, respectively. Similar trend was observed for the period April 22–25, 2013 with average concentrations of SO$_2$ and NO$_2$ observed to be 7.38 ± 5.5 and 68 ± 29.5 µg m$^{-3}$, where nighttime SO$_2$ and NO$_2$ concentrations were elevated at 10.1 ± 6 and 83 ± 21 µg m$^{-3}$ in comparison to daytime 4.9 ± 6 and 48.2 ± 26 µg m$^{-3}$ (Fig. 10b), respectively. Further, similar trend was also observed for NO$_2$ during the period April 02–09, 2014 with average of 20.6 ± 9 µg m$^{-3}$ and nighttime concentrations were peaked at 24.5 ± 7 µg m$^{-3}$ compared to daytime 16.4 ± 9 µg m$^{-3}$ but the trend is slightly opposite with respect to SO$_2$ with average 8.6 ± 1 µg m$^{-3}$ where daytime SO$_2$ concentrations is
9.1 ± 1.2 μg m$^{-3}$ as compared to night, i.e. 8 ± 0.6 μg m$^{-3}$ (Fig. 10c). These results show that nighttime SO$_2$ and NO$_2$ concentrations were repeatedly high during the sampling period. The possible sources of SO$_2$ and NO$_2$ at the site are combustion activities such as vehicular and biomass burning emissions. Apart from this NO$_2$ has a negative correlation with O$_3$ ($r = -0.67, -0.94$ and $-0.88$ for the period March 18–21, 2013, April 22–25, 2013, and April 02–09, 2014, respectively), which suggested that possibly most of the NO$_2$ is formed in the atmosphere from oxidation of NO by consuming O$_3$ (Albaigés et al., 2013).

During the observation periods of March 2013, April 2013 and April 2014, a unique particle size distribution pattern (experienced during the measurement period, i.e. clearly distinctive with daytime bimodal and nighttime unimodal) was observed for three consecutive nights, i.e. April 22–25, 2013, where nighttime particle growth was prominent (Fig. 5b). Apart from this, a uniform elevation/depression of meteorological and trace gas data was noticed for the same period. Therefore, we have taken this period as an example to better understand the gas and particle chemistry responsible for the growth of particles. Table 3 presents different variables (averaged over 3 h duration) calculated for different time windows, an average calculated during the daytime (12:00 to 15:00 LT) as non-growth event and an average calculated from 00:00 to 03:00 LT for nighttime as growth event. This time period was selected because at the site, daytime activities (i.e. sunlight and anthropogenic activity) are at the peak and nighttime activities are at the minimum, respectively. Standard deviations are also reported in the table to provide a measure of the range of values observed for each quantity.

### Table 2: Particles CMD (d$_c$), average number concentration and duration of particle growth events.

<table>
<thead>
<tr>
<th>Date</th>
<th>Initial d$_c$ (time) in nm</th>
<th>Maximum d$_c$ (time) in nm</th>
<th>Initial N (particles cm$^{-3}$) at initial size</th>
<th>N (particles cm$^{-3}$) at Maximum size</th>
<th>Duration of particle growth (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>March 18, 2013</td>
<td>50.4 (16:15)</td>
<td>81.06 (23:56)</td>
<td>13337</td>
<td>10193</td>
<td>7:41</td>
</tr>
<tr>
<td>March 19, 2013</td>
<td>68.1 (21:11)</td>
<td>107.2 (05:02*)</td>
<td>18078</td>
<td>11628</td>
<td>7:51</td>
</tr>
<tr>
<td>March 20, 2013</td>
<td>58.2 (17:04)</td>
<td>85.03 (21:32)</td>
<td>12875</td>
<td>23042</td>
<td>4:28</td>
</tr>
<tr>
<td>March 21, 2013</td>
<td>49.4 (00:00)</td>
<td>90.4 (03:25*)</td>
<td>5561</td>
<td>7852</td>
<td>3:25</td>
</tr>
<tr>
<td>April 22, 2013</td>
<td>35.7 (16:42)</td>
<td>93.5 (03:12*)</td>
<td>19523</td>
<td>10350</td>
<td>10:30</td>
</tr>
<tr>
<td>April 23, 2013</td>
<td>70.7 (20:56)</td>
<td>126.8 (05:07*)</td>
<td>24070</td>
<td>9463</td>
<td>8:11</td>
</tr>
<tr>
<td>April 24, 2013</td>
<td>57.8 (16:01)</td>
<td>135 (04:40*)</td>
<td>9841</td>
<td>9971</td>
<td>12:59</td>
</tr>
<tr>
<td>April 1, 2014</td>
<td>35.7 (14:27)</td>
<td>89.7 (00:43)</td>
<td>9555</td>
<td>7176</td>
<td>10:16</td>
</tr>
<tr>
<td>April 2, 2014</td>
<td>57.1 (22:11)</td>
<td>113.4 (06:37*)</td>
<td>8109</td>
<td>4462</td>
<td>8:26</td>
</tr>
<tr>
<td>April 3, 2014</td>
<td>49.7 (18:08)</td>
<td>77.6 (04:29*)</td>
<td>5367</td>
<td>3814</td>
<td>10:21</td>
</tr>
<tr>
<td>April 4, 2014</td>
<td>40.4 (14:27)</td>
<td>94.6 (04:11*)</td>
<td>7585</td>
<td>3242</td>
<td>13:44</td>
</tr>
<tr>
<td>April 5, 2014</td>
<td>28.6 (15:27)</td>
<td>55.8 (06:36*)</td>
<td>7377</td>
<td>11011</td>
<td>9:09</td>
</tr>
<tr>
<td>April 6, 2014</td>
<td>22.6 (11:49)</td>
<td>57.1 (23:04)</td>
<td>15194</td>
<td>11055</td>
<td>11:15</td>
</tr>
<tr>
<td>April 7, 2014</td>
<td>18.8 (12:34)</td>
<td>55.7 (01:15*)</td>
<td>19589</td>
<td>6441</td>
<td>12:41</td>
</tr>
<tr>
<td>April 8, 2014</td>
<td>19.4 (09:59)</td>
<td>56.5 (06:21*)</td>
<td>20347</td>
<td>6032</td>
<td>08:20</td>
</tr>
</tbody>
</table>

*a Denotes the time of next day.
Averages for the day- and nighttime were examined because the observed growth events were initiated in the noon around 12:00 LT but the growth was more pronounced at around midnight onwards suggesting that nighttime atmospheric conditions are more favorable for the growth of particles. The averages of particle CMD, gas concentrations and meteorological parameters were calculated during the day (midday; peak hour) and night (midnight), when the majority of the observed particle growth had occurred. This may reveal insights into variables affecting the growth process. Table 3 shows the measures of anthropogenic pollution, represented by black carbon (BC) and CO which tend to be low in daytime and high during night. BC and CO are short-lived climate forcing agents, and they are mostly produced from Industrial and residential mobile resources, biomass burning, incomplete combustion of fossil- and bio-fuels used for energy (Bond et al., 2004). High concentrations of BC and CO during nighttime showed that anthropogenic sources/activities have the influence on the nighttime particle growth in New Delhi. The concentrations of SO2, NO2 and RH value were significantly high during nighttime as compared to daytime (as discussed above). To further investigate the components responsible for aerosol growth, chemical composition study of PM1 was also carried out.

3.5. Chemical composition of PM1 samples

To better understand the role of chemical composition on the growth of aerosol, we determined chemical components (i.e., NH4+, SO42−, Na+, K+, PO43−, NO2− + NO3−, and WSOC) in PM1 samples (Fig. 11), which were sampled in parallel to SMPS measurements. Ions such as NH4+ (9.4 ± 3.2 μg m−3), SO42− (2.03 ± 0.7 μg m−3), Na+ (1.29 ± 1.7 μg m−3), K+ (1.06 ± 0.4 μg m−3), PO43− (0.84 ± 1.1 μg m−3) and NO2− + NO3− (0.59 ± 0.36 μg m−3) have significant contributions in PM1 during the whole duration of sampling (2013 and 2014). On average, WSOC concentrations were found to be 9.4 ± 5, 16.2 ± 14.7 and 13.7 ± 7.2 μg m−3 for the periods March 18–21, 2013, April 22–25, 2013 and April 01–09, 2014, respectively.

Table 3

<table>
<thead>
<tr>
<th>Event</th>
<th>Daytime (12:00-15:00)/Nighttime (00:00-03:00)</th>
<th>Time: 3h average</th>
<th>SO2 in μg m−3</th>
<th>NO2 in μg m−3</th>
<th>Black carbon in μg m−3</th>
<th>CO in ppm</th>
<th>O3 in μg m−3</th>
<th>NC×104 in Particles cm−3</th>
<th>RH in %</th>
<th>T in deg C</th>
<th>Wind velocity in m sec−1</th>
</tr>
</thead>
<tbody>
<tr>
<td>April 22, 2013 (Day)</td>
<td>39.52 ± 4.62</td>
<td>20.9 ± 2.03</td>
<td>2.52 ± 0.28</td>
<td>0.96 ± 0.14</td>
<td>81.7 ± 4.8</td>
<td>1.9 ± 0.37</td>
<td>37.03 ± 4.77</td>
<td>28.34 ± 1.23</td>
<td>2.59 ± 0.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 22, 2013 (Night)</td>
<td>89.82 ± 4.38</td>
<td>76 ± 7.4</td>
<td>3.6 ± 0.95</td>
<td>4.74 ± 0.57</td>
<td>7.4 ± 1.4</td>
<td>1.26 ± 0.4</td>
<td>49.01 ± 1.56</td>
<td>25.75 ± 0.55</td>
<td>0.69 ± 0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 23, 2013 (Day)</td>
<td>64.32 ± 4.42</td>
<td>24.3 ± 4.9</td>
<td>2.3 ± 0.22</td>
<td>3.29 ± 0.06</td>
<td>4.10 ± 0.2</td>
<td>16.5 ± 0.5</td>
<td>27.29 ± 1.31</td>
<td>23.90 ± 0.48</td>
<td>4.5 ± 0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 23, 2013 (Night)</td>
<td>26.97 ± 4.42</td>
<td>22.7 ± 4.8</td>
<td>2.49 ± 0.05</td>
<td>4.63 ± 0.05</td>
<td>8.7 ± 0.4</td>
<td>10.4 ± 0.4</td>
<td>20.32 ± 0.61</td>
<td>25.14 ± 0.46</td>
<td>6.8 ± 0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 24, 2013 (Day)</td>
<td>57.87 ± 7.18</td>
<td>40.6 ± 12</td>
<td>2.49 ± 0.05</td>
<td>3.67 ± 0.16</td>
<td>1.03 ± 0.05</td>
<td>1.35 ± 0.28</td>
<td>20.53 ± 0.83</td>
<td>34.74 ± 0.46</td>
<td>1.68 ± 0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 24, 2013 (Night)</td>
<td>114.7 ± 6.51</td>
<td>103 ± 11</td>
<td>28 ± 7.3</td>
<td>7.88 ± 1.33</td>
<td>26.3 ± 0.45</td>
<td>12.9 ± 17.8</td>
<td>32.13 ± 0.26</td>
<td>29.4 ± 0.35</td>
<td>0.70 ± 0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>April 25, 2013 (Day)</td>
<td>58.35 ± 5.07</td>
<td>40.6 ± 12</td>
<td>2.49 ± 0.05</td>
<td>3.67 ± 0.16</td>
<td>1.32 ± 0.05</td>
<td>6.8 ± 1.2</td>
<td>19.36 ± 1.54</td>
<td>35.4 ± 0.62</td>
<td>1.00 ± 0.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 10. Diurnal patterns of sulfur dioxide and nitrogen dioxide concentration observed during the period (a) March 18–21, 2013 (b) April 22–25, 2013, and (c) April 02–09, 2014.
Ammonium ion during the study period was found as one of the most abundant species in PM$_1$ and was maximized up to 14.2 µg m$^{-3}$. The next dominant ion was sulfate with maximum concentration up to 3.03 µg m$^{-3}$.

As discussed earlier, we have classified the temporal variation of CMD into two segments, one which has successive ascending trend is known as growth event period and the other one is non-growth event period. Further, it is important to mention that PM$_1$ sampling is done for every 3 h interval in daytime and 6 h interval in nighttime during the period of March and April 2013. Therefore, it is possible to classify the component concentrations based on the growth events and non-growth events and draw the correlations between chemical constituents in PM$_1$ samples and the trace gases monitored during the study period.

Most of the ions showed elevated concentrations during the growth events (Fig. 12). For example, during the growth events (March and April 2013) the concentrations of NH$_4^+$, K$^+$, NO$_2^+$ + NO$_3^-$ and SO$_4^{2-}$ were on average 11.6 ± 3.7, 1.35 ± 0.28, 0.57 ± 0.29 and 2.56 ± 0.66 µg m$^{-3}$, respectively, compared to non-growth events periods i.e., 9.54 ± 3.6, 0.59 ± 0.07, 0.44 ± 0.03 and 2.25 ± 0.35 µg m$^{-3}$, respectively. Similar observations were noticed during the study period of April 2014 where growth events were mostly influenced with elevated concentrations of NH$_4^+$ (8.6 ± 7.3 µg m$^{-3}$), K$^+$ (1.38 ± 1.49 µg m$^{-3}$) and SO$_4^{2-}$ (1.54 ± 1.21 µg m$^{-3}$) compared to that of non-growth events 5.69 ± 0.32, 1.12 ± 0.81 and 1.03 ± 0.82 µg m$^{-3}$, respectively. The concentration of Na$^+$ in PM$_1$ was considerably high during April 2014 and was elevated during growth event with an average 4.5 ± 6.4 µg m$^{-3}$ compared to that of non-growth event, i.e., 1.94 ± 2.98 µg m$^{-3}$. The possible source for Na$^+$ is biomass burning (Hudson et al., 2004), and other burning practices, such as waste burning (Kumar et al., 2015). These chemical components are also chemical tracers that help to identify the potential sources of aerosols. For example, K$^+$ is known as potential tracers for biomass burning aerosols (Simoneit et al., 1999) whereas SO$_4^{2-}$ is a marker for anthropogenic sources (Aggarwal and Kawamura, 2013). NH$_4^+$ has numerous sources, e.g., agriculture, volatilization of animal waste, synthetic fertilizers, biomass burning (including forest fires), losses from soils under vegetation, emissions from human excreta and fossil fuel combustion (Olivier et al., 1990; Zhang, 2008; Aneja et al., 2012). For this site, during growth events NH$_4^+$ is believed to be coming from biomass burning sources as indicated by strong correlation between NH$_4^+$ and K$^+$ ($r = 0.85$). PO$_4^{3-}$ is believed to largely originate from multiple sources such as mineral dust, biomass burning, and fuel emissions (Adams et al., 1999; Anderson et al., 2010). Most of the phosphate is enriched in mineral dust. We obtained phosphate in fine mode aerosols, hence dust contribution or soil contribution for PO$_4^{3-}$ should be negligible. The possible sources for PO$_4^{3-}$ in Delhi are biomass burning and waste burning (Anderson et al., 2010; Kumar et al., 2015).

During the growth events of March 18–21, 2013, WSO$_C$ concentration was on average 13.3 ± 3.6 µg m$^{-3}$ compared to non-growth event, i.e., 6.83 ± 6.5 µg m$^{-3}$. Similar observation was found during April 22–25, 2013 where WSO$_C$ concentration was 19.5 ± 4 µg m$^{-3}$ compared to non-growth event, i.e., 12.4 ± 2.3 µg m$^{-3}$. During the study period of April 2014, the concentration of WSO$_C$ showed a reverse trend in comparison to the past observations, which was found to be 10.85 ± 2.18 µg m$^{-3}$ during growth events compared to non-growth events (13.02 ± 2.18 µg m$^{-3}$). This reverse trend possibly depends on the prevailing atmospheric conditions and also restricts any direct relation of WSO$_C$ with the growth events (April 2014) compared to earlier events (March and April 2013). At the site, WSO$_C$ constitute as one of the major components (among other measured components) during the whole study period (Fig. 12).

As discussed, most of the growth events were influenced by elevated WSO$_C$ concentration. Therefore it is important to better understand the sources of WSO$_C$. It has been suggested that WSO$_C$ in atmospheric particles may come from a wide range of primary and secondary sources (e.g., Debesari et al., 2007; de Gouw et al., 2008, Aggarwal and Kawamura, 2013). A few initial studies with direct measurement of the natural abundance of radiocarbon content of WSO$_C$ appears promising to constrain the sources of this large aerosol carbon fraction. Short-term radiocarbon-based studies of WSO$_C$ in North America and Europe suggest an overwhelming contribution of modern carbon sources to WSO$_C$ in both rural and urban environments (Szidat et al., 2004; Weber...
et al., 2007; Wozniak et al., 2008). Recent year-round 14C-WSOC campaigns at two regional background sites constrained a 20% fossil contribution in South Asia (Kirillova et al., 2013). It is also evident that biomass burning is predominantly the largest source of WSOC (e.g., Hoff er et al., 2006; Asa-Awuku et al., 2008). In this study during the growth events, WSOC showed good correlations with particles CMD \( r = 0.32 \), NO2 \( r = 0.39 \) and CO \( r = 0.40 \), which suggest that fossil fuel combustion (vehicular emission) could be the major source for WSOC (Kirillova et al., 2013)( Table 4) at the site. It is also an important contributor to particle growth (secondary WSOC).

### 3.6. Nighttime aerosols growth chemistry

The condensation growth of aerosol particles generally proceeds through condensation of condensable vapor molecules on their surface. Under the atmospheric condition, the major condensable gases are SO2, NOx, NH3, VOCs, etc. It is evident, based on experimental and model studies, that particle formation in the atmosphere is most likely dominated by ternary nucleation of H2SO4 – H2O – NH3 vapors and subsequent growth by condensation of VOCs (Kulmala et al., 2004). The actual process of different mechanisms of condensable vapor formation that are relevant to aerosol growth under different atmospheric conditions has not been fully understood and quantified yet. Although there are numerous mechanisms proposed for the atmospheric formation of condensable vapor (i.e., through experimentally or model simulation) but studies on nighttime formation of these vapors are seriously lacking. In any case, the growth of aerosol due to condensation exhibits a strong and nonlinear dependence on atmospheric composition and meteorological conditions, and competes with gas–particle partitioning and heterogeneous or multiphase reactions (Laaksonen et al., 2004). In case of sulfuric acid vapor, the daytime sulfate and the subsequent sulfuric acid vapor formation (4)–(8) are mainly through photo oxidation reaction (Finlayson-Pitts and Pitts, 1999; Seinfeld and Pandis, 2006). This is because OH radical is readily produced in the presence of sunlight and strongly influences the oxidation of SO2 to SO4^2-:

\[
\text{O}_3 + \text{light} (\lambda < 340 \text{ nm}) \rightarrow \text{O} (^1\text{D}) + \text{O}_2 \quad (4)
\]
\[
\text{O} (^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad (5)
\]
\[
\text{SO}_2(g) + \text{OH}(g) \rightarrow \text{HSO}_3(g) \quad (6)
\]

(Rate determining steps)

\[
\text{HSO}_3(g) + \text{O}_2(g) \rightarrow \text{SO}_3(g) + \text{HO}_2(g) \quad (7)
\]
\[
\text{SO}_3(g) + \text{H}_2\text{O}(aq) \rightarrow \text{H}_2\text{SO}_4(aq) \rightarrow 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \quad (8)
\]

But nighttime sulfate formation due to photo oxidation is very rare. This is due to absence of light and OH radical. Few studies reported that OH production during nighttime from hydrocarbon ozonolysis reactions with ozone (Paulson et al., 1997; Donahue et al., 1998), and such dark OH chemical sources are rare. Therefore, nighttime formation of sulfate possibly be happened through other reaction route.

As discussed in our study, we observed high nighttime concentrations of SO2, NO2, NH4+ and SO4^2- both in gas phase and PM1 with elevated RH. Our field measurements demonstrate that efficient conversion of SO2 to SO4^2- occurs at high RH and concurrently with elevated concentrations of SO2, NOx, and NH3, implicating aqueous sulfate production from the participation of these species. In this study, we proposed three possible reaction pathways at the experimental site for the formation of nighttime SO4^2- from SO2 in the elevated presence of NH3 (9)–(12), NO2 (13) and (14), and RH (15)–(18).

\[
\text{NH}_3(g) + \text{H}_2\text{O}(aq) \rightarrow \text{NH}_4\text{OH}(aq) \rightarrow \text{NH}_4^+(aq) + \text{OH}^-(aq) \quad (9)
\]
\[
2\text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(aq) + 1/2\text{O}_2(g) \quad (10)
\]
\[
\text{SO}_2(g) + 1/2\text{O}_2(g) \rightarrow \text{SO}_4^{2-}(g) \quad (11)
\]
\[
\text{SO}_3(g) + \text{H}_2\text{O}(aq) \rightarrow \text{H}_2\text{SO}_4(aq) \rightarrow 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \quad (12)
\]

Sulfur dioxide emitted from the combustion of fossil fuels and possible routes undergo oxidation to sulfate in the presence of ammonium ion (Junge and Ryan, 1958). Van den Huvel and Mason (1963) suggested that the rate of production of sulfate was two orders of magnitude higher in the presence of ammonia. Further, we observed high concentration of gaseous NO2 during growth events (nighttime) promotes oxidation of SO2 to SO4^2- (Jaffe and Klein, 1966; Cofer et al., 1980). Therefore, we proposed SO4^2- formation in the presence of

<table>
<thead>
<tr>
<th>Growth Event</th>
<th>Gas component</th>
<th>Particulate component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>O3</td>
</tr>
<tr>
<td>Non-growth event</td>
<td>1</td>
<td>0.37</td>
</tr>
<tr>
<td>O3</td>
<td>0.76</td>
<td>1</td>
</tr>
<tr>
<td>SO2</td>
<td>-0.16</td>
<td>-0.22</td>
</tr>
<tr>
<td>NO2</td>
<td>0.35</td>
<td>-0.24</td>
</tr>
<tr>
<td>RH</td>
<td>-0.14</td>
<td>-0.27</td>
</tr>
<tr>
<td>CMD</td>
<td>0.32</td>
<td>-0.10</td>
</tr>
<tr>
<td>Na^+</td>
<td>-0.18</td>
<td>-0.15</td>
</tr>
<tr>
<td>NH4+</td>
<td>0.19</td>
<td>-0.07</td>
</tr>
<tr>
<td>K^+</td>
<td>0.03</td>
<td>-0.24</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>0.11</td>
<td>0.05</td>
</tr>
<tr>
<td>PO4^{3+}</td>
<td>-0.03</td>
<td>-0.16</td>
</tr>
<tr>
<td>SO4^2-</td>
<td>0.36</td>
<td>0.20</td>
</tr>
<tr>
<td>NO2+NOx</td>
<td>0.10</td>
<td>-0.14</td>
</tr>
<tr>
<td>WSOC</td>
<td>0.40</td>
<td>-0.02</td>
</tr>
</tbody>
</table>
NO₂, and it plays a crucial role in nighttime sulfate formation at the site. The reaction path can be expressed as:

\[
\text{NO}_2(g) + \text{HSO}_3^-(aq) \rightarrow \text{H}^+(aq) + \text{NO}^-(aq) + \text{SO}_4^{2-}(aq) \tag{13}
\]

(Zhang et al., 2015)

\[
\text{SO}_2(g) + 2\text{NO}_2(g) + 2\text{H}_2\text{O}(aq) \rightarrow 4\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2\text{HONO}(g) \tag{14}
\]

(Wang et al., 2016)

This reaction (14) is also supported by Kadowaki (1986), who reported that the conversion of SO₂ to sulfate requires high relative humidity as well as high oxidant concentration, and SO₂ oxidation processes to sulfate mainly occur in aqueous phase. Further, relative humidity can be the driving force (\(r = 0.52\) between RH and \(\text{SO}_4^{2-}\)) for the nighttime formation of sulfate at the site. The aqueous phase oxidation process consists of following steps (Sun et al., 2013; Wang et al., 2014).

\[
\text{SO}_2(g) + \text{H}_2\text{O}(aq) \Leftrightarrow \text{SO}_2\text{H}_2\text{O}(aq) \tag{15}
\]

\[
\text{SO}_2\text{H}_2\text{O}(aq) \Leftrightarrow \text{H}^+(aq) + \text{HSO}_3^-(aq) \tag{16}
\]

\[
\text{H}^+(aq) + \text{HSO}_3^-(aq) \Leftrightarrow 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \tag{17}
\]

\[
\text{SO}_3(g) + \text{H}_2\text{O}(aq) \rightarrow 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \tag{18}
\]

These reaction pathways (15)-(18) supported our observation during the period April 22–25, 2013 and of special interest because of unique temporal variation of particles CMD leads to the observation of consecutive nighttime growth events (Table 3). For this period, correlation study of particles CMD is performed between SO₂, NO₂, O₃ and RH during the growth event, where CMD showed strong correlation with SO₂ (i.e., \(r = 0.54, 0.88 \text{ and } 0.89\)) and RH (i.e., \(r = 0.97, 0.94 \text{ and } 0.98\)) for all the successive nights. These correlations indicate the presence of sulfuric acid vapors in nighttime.

Sulfate and hence sulfuric acid vapors that are formed during night can react with ammonia to form secondary ammonium sulfate salt (mostly found during study period) on particle surface at the site. The overall reaction pathway is expressed as (19)

\[
2\text{NH}_3 (g) + \text{SO}_2(aq) + 2\text{NO}_2(g) + 2\text{H}_2\text{O (aq) } \rightarrow 2\text{NH}_4^+(aq) + \text{SO}_4^{2-}(aq) + 2\text{HONO}(g) \tag{19}
\]

(Wang et al., 2016)

It is also important to note that PM₁ samples showed high NH₄⁺ content and presented good correlation with particles CMD (\(r = 0.68\)). Ammonium ion showed good correlation with RH (\(r = 0.41\)) and NO₂ (\(r = 0.62\)) during growth events. Therefore, the presence of ammonium nitrate is observed only during growth events as indicated by a strong correlation coefficient (\(r = 0.82\)) between NH₄⁺ and NO₂⁻ + NO₃⁻, and the possible reaction pathway for the formation of ammonium nitrate could be:

\[
\text{NO}_2(g) + \text{NO}_3(g) \rightarrow \text{N}_2\text{O}_5(g) \tag{20}
\]

(Moons, 2005)

\[
\text{N}_2\text{O}_5(g) + \text{H}_2\text{O}(aq) \rightarrow 2\text{HNO}_3(aq) \tag{21}
\]

(Moons, 2005)

\[
\text{NH}_3(g) + \text{HNO}_3(aq) \rightarrow \text{NH}_4\text{NO}_3(aq) \tag{22}
\]

(Finlayson-Pitts and Pitts, 2006)

Therefore, growth events observed especially at nighttime during spring has significant contributions of inorganic vapors (i.e. ammonium nitrate, ammonium sulfate, and sulfuric acid) compared to organics (WSOC) at the site. Our observation results (especially the aerosol growth chemistry due to inorganic and organic vapors) are comparable to the studies reported elsewhere (Weber et al., 1996; Kulmala et al., 2004; Smith et al., 2005; Kulmala and Kerminen, 2008; Kerminen et al., 2010; Kuang et al., 2010; Sipilä et al., 2010; Kuang et al., 2010, 2010). Based on these findings and data related to both gas and particulate phase, a nighttime chemistry pathway (Fig. 13) is hypothesized to demonstrate the particle growth at the site.

4. Conclusions

Fine particle growth events were observed at a representative site located in the central part of Delhi. This site provides a unique opportunity to investigate nucleation and growth events in an urban environment that is consistently influenced by various emission sources as it is surrounded by flora, residential accommodation/housing, roadway traffic and agriculture. During the measurement period (March, April of 2013 and April of 2014), particle growth events (observed from the size distribution measurement using SMPS) were observed, which were
sustained for a longer time (even $>8$ h during nighttime). The measured particle size distributions showed daytime bimodal and nighttime unimodal distributions. The results indicate that both meteorology and gaseous pollutant concentrations are important for determining periods in which growth events were observed. Growth events were mostly influenced with low wind speed and high relative humidity. Further, growth events were influenced with high concentrations of gaseous $\text{SO}_2$, $\text{NO}_2$ and particulate constituents (e.g., WSO, $\text{NH}_4^+$, $K^+$, $\text{NO}_3^-$ + $\text{SO}_4^{2-}$) in PM$_1$ than the non-growth events.

One of the major findings in this study is the evidence of nighttime $\text{SO}_2^{2+}$ formation through aqueous phase oxidation of $\text{SO}_3$ at the site, and this heterogeneous reaction is mediated by high concentration of $\text{NH}_3$ and $\text{NO}_2$ at elevated RH. For this, we discussed more than three possible reaction pathways for nighttime sulfate formation at the site (comparable to the studies reported elsewhere (Zhang et al., 2015; Wang et al., 2016)). As a consequence, a detailed reaction mechanism for the formation of secondary salts (i.e. $\text{NH}_4\text{NO}_3$, (NH$_3$)$_2\text{SO}_4$) along with the $\text{H}_2\text{SO}_4$ vapors is discussed. These inorganic species coat the particle through condensation and enhance the growth under atmospheric condition. These findings are based on the major chemical constituents present in the PM$_1$ sample and correlation study was performed among the particle CMD, gas pollutant, meteorological parameter and particulate constituents observed during the study period.

Based on these analyses, a nighttime reaction pathway for the formation of inorganic species (i.e., $\text{NH}_4\text{NO}_3$, (NH$_3$)$_2\text{SO}_4$ and $\text{H}_2\text{SO}_4$) is proposed for the site. In this study, we observed significantly high concentration of WSO$_4$ during entire study, but could not see any linear relation with others (i.e., particle CMD, gaseous and particle constituent). Therefore, water soluble inorganic constituents in the atmosphere play a vital role in particle growth than WSO$_4$ and hence promote the growth events at the site. The probable sources responsible for the growth of particle are biomass burning and anthropogenic sources as indicated by high concentrations of $K^+$, $\text{CO}$ and $\text{BC}$ during nighttime growth events. More investigations are needed in the future to better understand the nighttime aerosol growth (in sub-micron size range) chemistry linked to organic and inorganic species in different environments.

Acknowledgements

BS is thankful to Department of Science and Technology, New Delhi for awarding INSPIRE research fellowship (DST/INSPIRE Fellowship/2011/114). We gratefully thank CSIR-NPL for providing the facility for this work. We also acknowledge the financial support from the Japan Society for the Promotion of Science (JSPS) through Grant-in-Aid No. 24221001.

References


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