Insights into Chemical Coupling among Acidic Gases, Ammonia and Secondary Inorganic Aerosols

Sailesh N. Behera, Raghu Betha, Rajasekhar Balasubramanian*

Department of Civil and Environmental Engineering, National University of Singapore, 117576, Singapore

ABSTRACT

This study has investigated the chemical association among acidic gases, ammonia and secondary inorganic aerosols based on hourly measurements in a tropical urban atmosphere. The 24 hr average concentrations of SO$_2$, NH$_3$, HONO, HNO$_3$ and HCl were 21.77, 2.47, 1.73, 3.00 and 0.08 $\mu$g/m$^3$, respectively while those of SO$_4^{2-}$, NO$_3^-$, Cl$^-$, Na$^+$, K$^+$, NH$_4^+$, Ca$^{2+}$ and Mg$^{2+}$ in PM$_{2.5}$ were 4.41, 1.29, 0.28, 0.30, 0.32, 1.76, 0.14 and 0.07 $\mu$g/m$^3$, respectively. The results of this study for SO$_2$, NH$_3$, HONO, HCl, SO$_4^{2-}$ and Cl$^-$ showed significant diurnal variations, whereas there was a lack of significant diurnal variations for HNO$_3$, NO$_3^-$, Na$^+$, NH$_4^+$, Ca$^{2+}$ and Mg$^{2+}$. Analysis of the charge balance of ionic species indicated that sufficient NH$_3$ was present most of the time to neutralize both H$_2$SO$_4$ and HNO$_3$ to form (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. The conversion of SO$_2$ into SO$_4^{2-}$ and HNO$_3$ into NO$_3^-$ was observed to be sensitive to changes in temperature and relative humidity, respectively. The study area experienced ambient relative humidity, which was higher than the estimated deliquesce relative humidity of NH$_4$NO$_3$ most of the time during the measurement period. As a result, the NH$_4$NO$_3$ formation was thermodynamically favorable during both daytime and nighttime. However, NH$_4$Cl formation was not favored under ammonia-poor conditions. It was observed that biomass burning could trigger nitrate and chloride formation in the ambient air.

Keywords: Secondary inorganic aerosol; Acid gases; Gas-to-particle conversion; Diurnal variation; Semi-volatile particulates; Ammonia.

INTRODUCTION

Fine particulate matter (PM$_{2.5}$) plays a significant role in atmospheric visibility reduction through the formation of haze, human health effects and climate change from the regional to global scale (Charlson and Heintzenberg, 1995; Vedal, 1997; IPCC, 2007). A significant portion of PM$_{2.5}$ is formed in the atmosphere through chemical transformations of precursor gases such as nitrogen oxides (NO$_x$), sulfur dioxide (SO$_2$), and ammonia (NH$_3$). This gas-to-particle conversion occurs either by condensation, which adds mass onto pre-existing aerosols, or by direct nucleation of these precursor gases (Baek and Aneja, 2004; Song et al., 2006). The major inorganic compounds formed through the gas-to-particle formation process are ammonium bisulfate (NH$_4$HSO$_4$), ammonium sulfate (NH$_4$)$_2$SO$_4$, ammonium nitrate (NH$_4$NO$_3$) and ammonia chloride (NH$_4$Cl). NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$ are non-volatile in nature whereas NH$_4$NO$_3$ and NH$_4$Cl are semi-volatile. These secondary inorganic aerosols (SIA) are formed by reactions involving the only alkaline gas in the atmosphere, NH$_3$, with sulfuric acid (H$_2$SO$_4$), nitric acid (HNO$_3$) and hydrochloric acid (HCl) (Lin and Cheng, 2007; Aneja et al., 2009; Behera and Sharma, 2011). SIA, represented by ionic species of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and Cl$^-$, can account for 20–48% of the mass of PM$_{2.5}$ (Balasubramanian et al., 2003; Lin and Cheng, 2007; Weijers et al., 2011).

The secondary gaseous pollutants such as nitrous acid (HONO), HNO$_3$ and H$_2$SO$_4$ are produced from natural and manmade emissions of primary gas phase pollutants, NO$_x$ and SO$_2$, through photochemical reactions (Derwent et al., 2010). HCl, a precursor responsible for SIA formation, is mainly emitted by biomass burning, coal combustion and waste combustion (Bari et al., 2003). The affinity of H$_2$SO$_4$ for NH$_3$ is much larger than that of HNO$_3$ and HCl for NH$_3$. As a result, the available ambient NH$_3$ is first taken up by H$_2$SO$_4$ to form (NH$_4$)$_2$SO$_4$ or NH$_4$HSO$_4$ (Ianniello et al., 2011). The excess available NH$_3$ may react with HNO$_3$ and HCl to form NH$_4$NO$_3$ and NH$_4$Cl. Because of the semi-volatile nature of NH$_4$NO$_3$ and NH$_4$Cl and particulate ammonium salts, the formation mechanisms are rather complex (Trebs et al., 2004; Finlayson-Pitts and Pitts, 2006).
A number of studies (e.g., Nakajima et al., 1999; Muraleedharan et al., 2000) on atmospheric aerosol composition in tropical urban environments situated in Southeast Asia (SEA) have been reported, but most of these studies were focused on measuring specific aerosol components in biomass burning impacted air masses over a limited period of time. Some recent studies (e.g., Balasubramanian et al., 2003; Abas et al., 2004; Balasubramanian and Qian, 2004; See et al., 2006; See et al., 2007; Hyer and Chew, 2010) have investigated the status of air quality in SEA, notably Singapore and Malaysia, in detail. However, these studies did not fully address the chemical coupling among SIA and their corresponding precursor gases, which is important from both scientific and regulatory perspectives. In the past, several studies dealing with simultaneous measurements of SIA and the precursor gases have been reported from other regions of the World including Europe, U.S.A., China, and India (e.g., Bari et al., 2003; Pavlovic et al., 2006; Hu et al., 2008; Wu et al., 2009; Behera and Sharma, 2010; Ianniello et al., 2011; Gómez-González et al., 2012). However, the climatic conditions of SEA are quite different from those in other regions of the world, and characterized by high temperature and humidity throughout the year. Therefore, the chemistry behind the formation of SIA in tropical countries in SEA is expected to be different from what has been reported in other studies. To verify this hypothesis, systematic measurements of ionic species of PM$_{2.5}$ and the precursor gases on the time resolution of 1 hr are needed. Previous measurements of gaseous and particulate species on a daily (24 hr) basis, or 12 hr basis elsewhere (e.g., Bari et al., 2003; Pavlovic et al., 2006; Hu et al., 2008; Wu et al., 2009; Behera and Sharma, 2010; Ianniello et al., 2011; Gómez-González et al., 2012) could not explain the formation of SIA convincingly during different hours of the day. Moreover, there are concerns over the measurements of semi-volatile particulates due to artifact effects.

The novelty of the work addressed in the present study is that we provide deep insights into the formation of SIA based on hourly observations of acidic gases, ammonia and particulate-phase water soluble inorganic ions in a tropical environment in Southeast Asia for the first time. These hourly concurrent measurements eliminated the artifact effects associated with integrated measurements of semi-volatile particles. In this study, we used an online analyzer of model ADI 2080 (Monitoring of AeRosols and Gases, MARGA, Applikon Analytical B. V. Corp., Netherlands) with a PM$_{2.5}$ inlet to measure the mass concentrations of major water-soluble aerosol inorganic ions, ammonia and acidic gases at the time resolution of 1 hr from 14 September through 8 November, 2011. This time period represents the dry season in Southeast Asia during which time, biomass burning-impacted air masses are usually advected from Indonesia over the region, causing smoke haze episodes, under the influence of the Southwest monsoon (Balasubramanian et al., 2003; See et al., 2007). The specific objectives of the study were as follows: (1) simultaneous measurements of gaseous species (SO$_2$, NH$_3$, HONO, HNO$_3$ and HCl) and water soluble inorganic components of PM$_{2.5}$ (Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, NH$_4^+$, NO$_3^-$, SO$_4^{2−}$ and Cl$^-$); (2) investigation of their temporal as well as diurnal trends during the measurement period; (3) examination of the relationship between meteorology and chemical equilibrium involved in the formation of semi-volatile aerosol components (NH$_4$NO$_3$ and NH$_4$Cl).

**MATERIALS AND METHODS**

**The Study Area**

The study area, Singapore (Fig. 1.), is located at the southern tip of the Malayan Peninsula, between latitudes 1°09’N and 1°29’N and longitudes 103°36’E and 104°25’E, and measures 42 km from east to west and 23 km from north to south (Balasubramanian et al., 2003). The measurement of air quality and meteorology parameters was conducted on an hourly basis for two months at the Atmospheric Research Station (67 m above the sea level and about 1 km from the open sea), National University of Singapore. The details of the characteristics of the sampling site and study area are described in Balasubramanian et al. (2003). This is to be noted that the study area reported in the earlier study of Balasubramanian et al. (2003) is the same as the one used in the present study.

According to the National Environmental Agency (NEA), the main sources of air pollution in Singapore are from the burning of fossil fuel for heat generation in industries, electricity generation and transportation (http://app2.nea.gov.sg/psi_faqairquality.aspx). The other important source is trans-boundary air pollution, which includes the transport of air pollutants from biomass fires in the region (e.g., Indonesia, Malaysia and Brunei). The past biomass burning (smoke haze) episodes occurred largely within the period of May to October due to uncontrolled forest fires in the region, and the prevailing Southwest Monsoon winds blew the smoke from fires in Indonesia to Singapore (Balasubramanian et al., 2003; See et al., 2006).

The NEA has been implementing all possible control options to reduce emissions of air pollutants from vehicular and industrial sources in order to improve the air quality status in Singapore. However, the pollution status in Singapore is still under scrutiny because of the concerns over the ambient PM$_{2.5}$ levels not meeting the goals of World Health Organization. For example, Fig. 2 shows the trends of annual averages of ambient level of PM$_{2.5}$ concentration from year 2005 through 2011.

**Sampling and Chemical Analysis**

The duration of measurements of both ambient aerosol and gaseous species was from 0:00 to 23:00 for each day on a time resolution of 1 hr from 14 September through 8 November, 2011. For the purpose of data interpretation, we classified the time as 7:00 to 19:00 for daytime and 19:00 to 7:00 for nighttime based on the timings of sunrise and sunset during this period (http://www.timeanddate.com/). A model ADI 2080 online analyzer (MARGA, Applikon Analytical B. V. Corp., Netherlands) with a PM$_{2.5}$ inlet was used to measure the mass concentrations of gases and particulate species at the time resolution of 1 hr. The MARGA system was set to draw ambient air into the
Fig. 1. Map showing study area Singapore and its neighboring regions in the Southeast Asia and location of Atmospheric Research Centre at NUS, Singapore. The maps are retrieved from HYPSLIT model and Google map.

Fig. 2. Trends of annual average of ambient concentration of PM$_{2.5}$ in Singapore. (Adapted from EPD Annual Report, 2011).

sampling box at a flow rate of 1 m$^3$/h through an inlet, and exhibited a particle collection efficiency of 99.7%. The gaseous species were captured in the liquid film (0.0035% H$_2$O$_2$) formed by one Wet Rotating Denuder (WRD). Fine particles in the residual airflow went through the supersaturated steam (0.0035% H$_2$O$_2$, 120–140°C) erupted out from one Steam Jet Aerosol collector (SJAC), and were pooled into its collector. MARGA utilized a WRD to collect acidic gases and NH$_3$ by diffusion into an aqueous film. The aqueous solutions from the WRD and SJAC were subsequently analyzed by an online ion chromatograph (IC) for water-soluble anions and cations.
MARGA has the capability of measuring the hourly average concentrations of NH$_4^+$, Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$, HCl, HONO, SO$_2$, HNO$_3$, NH$_3$ in the atmosphere with the detection limits for all the components were 0.1 µg/m$^3$ or better, except for K$^+$ (0.16 µg/m$^3$), Mg$^{2+}$ (0.12 µg/m$^3$) and Ca$^{2+}$ (0.21 µg/m$^3$) as reported by Makkonen et al. (2012). During the measurement period, MARGA was calibrated using the internal standard solution (LiBr) every week to verify accurate detecting limits and to ensure data quality. Field blanks were used and suitable corrections made as recommended by Makkonen et al. (2012). A total of 1038 number valid hourly observations were made for each chemical species over a period of 45 days for further interpretation. During the measurement period, meteorological parameters (temperature, relative humidity and rainfall) were recorded using the Solus meteorological system (Texas Electronics) installed on the roof of the research station with a time resolution of 1 hr. A Data acquisition system for measuring concentrations of gases, aerosols and meteorology was housed in a thermally controlled laboratory room.

**Non-Sea-Salt Components in PM$_{2.5}$**

As the sampling site is located near to the sea surface (about 1000 m away from sea), we attempted to estimate aerosol components which are free from the sea salt influence. The concentrations of non-sea-salt sulfate (nss-SO$_4^{2-}$), non-sea-salt K$^+$ (nss-K$^+$) and non-sea-salt Ca$^{2+}$ (nss-Ca$^{2+}$) were estimated by the following equations and by assuming that the chemical composition of sea-salt particles is the same as that of seawater, and that the soluble Na$^+$ in particulate samples comes solely from sea salts (Kennis, 1994; Balasubramanian et al., 2003):

\[
nss\text{-SO}_4^{2-} = [\text{SO}_4^{2-}] - 0.2516 \times [\text{Na}^+] \tag{1}
\]

\[
nss\text{-K}^+ = [\text{K}^+] - 0.037 \times [\text{Na}^+] \tag{2}
\]

\[
nss\text{-Ca}^{2+} = [\text{Ca}^{2+}] - 0.0385 \times [\text{Na}^+] \tag{3}
\]

**RESULTS AND DISCUSSIONS**

**Overall Results**

Table 1 provides a statistical summary of the measured 24 hr mean concentrations of gaseous pollutants and particulate inorganic ions in PM$_{2.5}$. It should be noted that in this paper, all reported (as presented in Table 1) and interpreted values (in the section on ‘Results and Discussions’) for the levels of SO$_4^{2-}$, K$^+$ and Ca$^{2+}$ represent non-sea-salt components. Overall, 24 hr mean concentrations of total (non-sea-salt and sea-salt) SO$_4^{2-}$, K$^+$ and Ca$^{2+}$ were observed as 4.48 ± 1.76 µg/m$^3$, 0.31 ± 0.14 µg/m$^3$, and 0.14 ± 0.04 µg/m$^3$, respectively. The measured mean concentrations of acid gases, inorganic ions and meteorological parameters (temperature and relative humidity) are compared to those from other urban areas of the world in Tables 2 and 3. The overall meteorology of Singapore is characterized by higher humidity than that in other cities of the world (Tables 2 and 3). The role of the prevailing humid conditions in the chemistry of SIA formation is examined in a subsequent section. The overall level of SO$_2$ in Singapore is not significantly different from what was reported from other cities of the World. The NH$_3$ concentration is comparable to that from Nara, Japan (Matsumoto and Okita, 1998), but is otherwise lower than those from other areas of the World. The ambient concentrations of HONO and HNO$_3$ are comparable to those from New York and Taiwan (Bari et al., 2003; Lin et al., 2006) while the level of HCl in Singapore is less than those from other areas of the world (Table 2).

Similar comparisons are made for major PM$_{2.5}$ chemical components in Singapore with those from other cities of the world (Table 3). In general, the measured mean concentrations from this study are comparable to those from New York and Milan (Qin et al., 2006; Lonati et al., 2008). From Table 2, it has been observed that two conditions of ammonia availability prevail in the ambient air: (i) ammonia-poor conditions (molar ratio of (NH$_4^+$/SO$_4^{2-}$) < 2.0) and (ii) ammonia-rich conditions (molar ratio of (NH$_4^+$/SO$_4^{2-}$) ≥ 2.0). This study had experienced a molar ratio of NH$_4^+$/SO$_4^{2-}$ as 2.2, which indicated the atmosphere

<table>
<thead>
<tr>
<th>Species</th>
<th>N</th>
<th>Mean</th>
<th>S.D.</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>45</td>
<td>21.77</td>
<td>15.41</td>
<td>2.39</td>
<td>78.62</td>
<td>18.18</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>45</td>
<td>2.47</td>
<td>2.32</td>
<td>0.53</td>
<td>12.71</td>
<td>1.77</td>
</tr>
<tr>
<td>HONO</td>
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<td>0.89</td>
<td>0.46</td>
<td>4.91</td>
<td>1.69</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>45</td>
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<td>1.52</td>
<td>0.67</td>
<td>6.80</td>
<td>3.03</td>
</tr>
<tr>
<td>HCl</td>
<td>44</td>
<td>0.08</td>
<td>0.08</td>
<td>0.03</td>
<td>0.57</td>
<td>0.06</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>45</td>
<td>4.41</td>
<td>1.76</td>
<td>1.25</td>
<td>8.00</td>
<td>4.63</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>45</td>
<td>1.29</td>
<td>0.30</td>
<td>0.88</td>
<td>2.03</td>
<td>1.25</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>45</td>
<td>0.28</td>
<td>0.19</td>
<td>0.07</td>
<td>1.02</td>
<td>0.24</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>45</td>
<td>0.30</td>
<td>0.10</td>
<td>0.17</td>
<td>0.61</td>
<td>0.28</td>
</tr>
<tr>
<td>K$^+$</td>
<td>45</td>
<td>0.32</td>
<td>0.14</td>
<td>0.16</td>
<td>0.71</td>
<td>0.30</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>45</td>
<td>1.76</td>
<td>0.71</td>
<td>0.52</td>
<td>3.77</td>
<td>1.53</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>45</td>
<td>0.14</td>
<td>0.05</td>
<td>0.02</td>
<td>0.26</td>
<td>0.14</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>45</td>
<td>0.07</td>
<td>0.02</td>
<td>0.04</td>
<td>0.13</td>
<td>0.06</td>
</tr>
</tbody>
</table>

* the concentrations reported are for non sea salt particles; N for number of valid observations; S.D. for standard deviation; Min for minimum; Max for maximum.
Table 2. Comparison of levels of gaseous species and meteorology with other studies in the world (μg/m³).

<table>
<thead>
<tr>
<th>Location</th>
<th>Gaseous species (μg/m³)</th>
<th>Meteorology</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO₂</td>
<td>NH₃</td>
<td>HONO</td>
<td>HNO₃</td>
</tr>
<tr>
<td>Nara, Japan</td>
<td>4.3</td>
<td>2.4</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>New York, USA</td>
<td>18.7</td>
<td>4.3</td>
<td>2.0</td>
<td>3.6</td>
</tr>
<tr>
<td>Seoul, South Korea</td>
<td>6.6</td>
<td>5.2</td>
<td>7.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Taichung, Taiwan</td>
<td>NA</td>
<td>8.5</td>
<td>1.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Lahore, Pakistan</td>
<td>19.4</td>
<td>50.1</td>
<td>19.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Pearl River Delta, China</td>
<td>55.4</td>
<td>7.3</td>
<td>2.9</td>
<td>6.3</td>
</tr>
<tr>
<td>Beijing, China</td>
<td>14.1</td>
<td>16.6</td>
<td>3.6</td>
<td>1.9</td>
</tr>
<tr>
<td>Kanpur, India</td>
<td>21.7</td>
<td>22.3</td>
<td>NA</td>
<td>7.2</td>
</tr>
<tr>
<td>Singapore</td>
<td>21.8</td>
<td>2.5</td>
<td>1.7</td>
<td>3.0</td>
</tr>
</tbody>
</table>

NA represents “not available”.

Table 3. Comparison of levels of PM$_{2.5}$ characteristics with other studies in the world.

<table>
<thead>
<tr>
<th>Location</th>
<th>Levels of major ions (μg/m³)</th>
<th>Molar ratios of SIA components</th>
<th>Meteorology</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K⁺</td>
<td>NH₄⁺</td>
<td>Cl⁻</td>
<td>NO₃⁻</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>Pearl River Delta, China</td>
<td>NA</td>
<td>9.2</td>
<td>2.4</td>
<td>7.2</td>
<td>24.1</td>
</tr>
<tr>
<td>Guangzhou, China</td>
<td>1.4</td>
<td>7.3</td>
<td>2.4</td>
<td>9.5</td>
<td>21.6</td>
</tr>
<tr>
<td>Seoul, South Korea</td>
<td>0.4</td>
<td>5.3</td>
<td>0.2</td>
<td>7.1</td>
<td>8.1</td>
</tr>
<tr>
<td>Beijing, China</td>
<td>NA</td>
<td>12.5</td>
<td>NA</td>
<td>14.2</td>
<td>20.8</td>
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<tr>
<td>Bangkok, Thailand</td>
<td>NA</td>
<td>1.6</td>
<td>NA</td>
<td>1.2</td>
<td>5.6</td>
</tr>
<tr>
<td>Milan, Italy</td>
<td>NA</td>
<td>3.0</td>
<td>0.3</td>
<td>8.7</td>
<td>4.7</td>
</tr>
<tr>
<td>New York, USA</td>
<td>0.1</td>
<td>1.9</td>
<td>0.1</td>
<td>2.0</td>
<td>4.3</td>
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<tr>
<td>Lahore, Pakistan</td>
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<td>16.1</td>
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<td>19.2</td>
</tr>
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<td>Kanpur, India</td>
<td>2.6</td>
<td>15.7</td>
<td>2.3</td>
<td>19.8</td>
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<tr>
<td>Lanzhou, China</td>
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<tr>
<td>Durg, India</td>
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<td>2.1</td>
<td>3.2</td>
<td>6.8</td>
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<tr>
<td>Nanchang, China</td>
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<td>1.6</td>
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<td>28.9</td>
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<tr>
<td>Goshan, Korea</td>
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<td>0.2</td>
<td>1.2</td>
<td>9.6</td>
</tr>
<tr>
<td>Athens, Greece</td>
<td>0.1</td>
<td>0.9</td>
<td>0.5</td>
<td>4.0</td>
<td>1.2</td>
</tr>
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<td>Singapore</td>
<td>0.3</td>
<td>1.8</td>
<td>0.3</td>
<td>1.3</td>
<td>4.4</td>
</tr>
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</table>

NA represents “not available”.
as ammonia-rich condition. However, the ammonium equivalent concentration is less than the sum of sulfate, nitrate and chloride (Table 3). This might be the reason for lower levels of nitrates in the study area. The existing levels of nitrates may be due to nighttime enhancement of nitrates through heterogeneous hydrolysis of NO2 and HNO3 as has been explained in a recent study by Pathak et al. (2011).

To understand the role of precursor gases (SO2, NH3 and HCl) in the formation of secondary gaseous species (HONO and HNO3) and SIA in PM2.5 (NH4+, NO3–, SO4=, and Cl–), correlation coefficients were estimated between various species using Minitab 15 English (as presented in Table S1). The major observation from this analysis revealed that NH3 showed significant correlations with SO4=, NO3–, and NH4+ (P = 0.36, 0.41, and 0.55 respectively with P < 0.01, 0.01, and 0.001) indicating that formation of secondary inorganic components of PM2.5 is dependent on levels of NH3. Significant correlations between SO2–SO4=, HONO–NO3–, NH3–NH4+, NH4+–SO4=, NH4+–NO3– were observed, suggesting chemical coupling between acidic gases, ammonia and the particulates to form (NH4)2SO4 and NH4NO3 under ammonia-rich conditions.

**Diurnal Variation of Pollutants**

The hourly concentration data of gaseous and particulate species were classified into their daytime and nighttime values on the basis of the timing of sunrise and sunset. To assess the overall difference between daytime and nighttime levels of pollutants, a paired t-test with unequal variance was performed for each gaseous and particulate component using Minitab 15 English. From the results of the t-test, it was observed that SO3, NH3, HONO, HCl, SO4= and Cl– showed significant diurnal variations at 95% confidence level (P < 0.05). However, HNO3, NO3–, Na+, NH4+, Ca2+ and Mg2+ did not show any significant diurnal variations. The overall mean meteorological parameters observed during the measurement period were: (i) temperature: 26.8 ± 3.3°C (daytime) and 25.6 ± 0.9°C (nighttime); (ii) relative humidity: 72.9 ± 5.3% (daytime) and 79.7 ± 3.7% (nighttime); (iii) rainfall: 0.6 ± 0.9 mm (daytime) and 0.5 ± 1.2 mm (nighttime), and (iv) wind direction: 179.6 ± 57.6° (daytime) and 141.7 ± 62.4° (nighttime). These meteorological parameters were evaluated with paired t-test similar to air pollutant species to assess the diurnal variations. It was observed that temperature, relative humidity and rainfall showed significant diurnal variation at 95% confidence level (P < 0.05). The diurnal variations of the average temperature and relative humidity during the measuring period are shown in Fig. S1. Overall, the meteorological conditions in the study area were characterized by high humid conditions in the region.

A significant diurnal variation of NH3 was observed with ‘daytime/nighttime’ = 1.8 and P = 0.01. The reason could be due to large evaporative emissions from several sources during the day time (e.g., NH3 from grass leaves). The maximum NH3 of 4.9 μg/m3 was observed during 10:00 to 11:00 hr, and the minimum of 0.9 μg/m3 was observed from 22:00 to 23:00 hr (Fig. 3(a1)). The maximum observed NH3 levels could possibly be due to more evaporation of NH3 from wet surfaces, such as grass leaves and sewerage systems due to more temperature and with moderate mixing layer during these hours of the day. From Fig. 3(a2), it can be clearly observed that NH4+ did not show any distinct peaks except two smaller peaks at 11:00 and 15:00 hr. These smaller peaks of NH4+ could be attributed to formation of NH4NO3 and (NH4)2SO4 during more traffic emissions for NO3– and more industrial emissions for SO2.

Figs. 3(b1)–(b2) show the diurnal variations of SO2 and SO4= concentrations. Both SO2 and SO4= concentrations were observed to be higher during daytime with ‘daytime/nighttime’ = 2.2, (P < 0.0001) and ‘daytime/nighttime’ = 1.3 (P = 0.006), respectively. The higher levels of SO4= during daytime could be explained through enhanced conversion of NH3 and H2SO4 into (NH4)2SO4 in the presence of higher solar radiation due to the presence of more OH radicals. The maxima of hourly concentrations of SO2 occurred from 13:00 to 17:00 hr (maximum of 42.8 μg/m3 at 15:00 hr). The reason for such high levels of SO2 can be explained through the meteorology and industrial emissions. During these peak hours of SO2, the observed wind direction was the SW direction, and this may be reason for transport of SO2 from power plants and petroleum refineries located in the southwest direction of the measurement site. The concentration of SO4= increased slightly from the early morning (5:00 to 6:00) and then decreased during 7:00–9:00 and increased from 9:00 and peaked during 14:00–15:00 hr. The reason for lower concentration during 7:00–8:00 due to cloud covers in the sky, which could obstruct the sunlight and thus provide unfavorable conditions for the production of OH radicals. It was also observed that during this hour, an average of 1.9 mm of rainfall was recorded at the measurement site.

From the hourly observations of HNO3, it is clear that the maxima of HNO3 concentration occurred as 3.4 μg/m3 in the late afternoon (16:00–17:00) at a high temperature and low relative humidity (Fig. 3(c1)). The reason could be due to more solar radiation and dry conditions that favor formation of HNO3 through the reaction of NO2 and OH radical (Hoek et al., 1996; Wu et al., 2009).

The formation of NH4NO3 in the ambient air is expected to be more favorable during nighttime than daytime due to higher humid conditions in the night (Acker et al., 2004; Behera and Sharma, 2012). However, in this study, we observed different trends on diurnal variations of NO3– concentrations with ‘daytime/nighttime’ = 0.96 that is not statistically significant (P = 0.57). To examine such diurnal trends of NO3–, we attempted to understand the mechanism behind the formation of NH4NO3, which is explained in a subsequent section of this paper. The levels of NO3– peaked at 8:00 (Fig. 3(c2)), when the relative humidity was observed to be high (83%).

Figs. 3(d1)–(d2) shows the diurnal variations of HCl and Cl– concentrations. HCl was observed to be higher during daytime than nighttime with the ‘daytime/nighttime’ ratio being 1.5 (P = 0.04). However, Cl showed higher concentration during nighttime than daytime with ‘daytime/nighttime’ = 0.62 (P = 0.006). HCl is produced from the evaporation of NH4Cl at high ambient temperatures. The levels of HCl peaked during 17:00–18:00 under dry
conditions, whereas Cl\textsuperscript{−} peaked during 7:00–8:00 during more humid conditions. Our observations are similar to those in the study carried out by Hu et al. (2008). It should be noted that Cl\textsuperscript{−} did not show significant correlation with HCl (r = 0.16; Table S1) and showed a significant correlation with Na\textsuperscript{+} (r = 0.33; Table S1; P < 0.05). Hence, the multiple sources of Cl\textsuperscript{−} could be confirmed with major contributions from sea-salt (NaCl), NH\textsubscript{3} (through neutralization of HCl to form NH\textsubscript{4}Cl), or combustion activities, so it is difficult to draw any conclusion to explain for the reason of diurnal variations of NH\textsubscript{3}, SO\textsubscript{2}, HNO\textsubscript{3}, and HCl and major ionic constituents in PM\textsubscript{2.5}. The error bars represent the corresponding standard deviations.
variations of Cl\textsuperscript{–}.

HONO was observed to be formed in the atmosphere during the nighttime hours as it tends to be photolyzed during the daytime, producing OH radicals during early hours of the day (Calvert et al., 1994). Fig. 4 shows the diurnal variation of HONO with higher concentrations at nighttime and lower concentrations during daytime. This significant higher levels of HONO during nighttime with ‘daytime/nighttime’ = 0.72 \( (P < 0.006) \) can be explained by its heterogeneous formation and nighttime accumulation, i.e., reaction of N\textsubscript{2}O\textsubscript{3} with moist aerosols (or other surfaces) to form two HONO molecules (Calvert et al., 1994). Moreover, HONO can be formed by a heterogeneous reaction of NO\textsubscript{2} with H\textsubscript{2}O, which can take place on wet surfaces, such as ground and aerosol particles (Stutz et al., 2002; Wu et al., 2009). In this study, the concentration of HONO increased from the early morning (6:00 hr) and peaked at 9:00 (2.7 \( \mu \text{g/m}^3 \)) and then decreased till 17:00. It was observed by earlier studies (Hu et al., 2008; Wu et al., 2009) that the peak of HONO levels occurs during the sunrise. The possible reason for such maximum levels during sunrise could be due to decreasing humidity, leading to the evaporation of dew droplets containing dissolved HONO. Zhou et al. (2002) and Acker et al. (2004) also suggested that the release of the night-time trapped nitrous acid from the surfaces acted as a strong HONO source in the morning hours due to evaporation in dew droplets. This study finds slight deviations from earlier studies, which observed the highest levels of HONO at 9:00 and the sunrise took place at 7:00 during the measuring period. The cloud covers in the sky during 7:00–8:00 could have obstructed the morning sunlight, which is responsible for evaporation of more water vapors. The lower levels of HONO from 10:00 to 17:00 could be attributed to formation of OH radicals under high influx of solar radiation.

**Charge Balance of Ionic Constituents of PM\textsubscript{2.5}**

Ions contributed a mean mass concentration of 9.1 \( \mu \text{g/m}^3 \) and 7.9 \( \mu \text{g/m}^3 \) to PM\textsubscript{2.5} during daytime and nighttime, respectively. On the basis of hourly data, the mean molar ratio of NH\textsubscript{4}\textsuperscript{+} to SO\textsubscript{4}\textsuperscript{2–} was 2.2 \pm 0.7 (n = 1038), mostly > 2, indicating the complete neutralization of H\textsubscript{2}SO\textsubscript{4} with NH\textsubscript{3} to form (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}. The excess of NH\textsubscript{4}\textsuperscript{+} was inferred to be associated with NO\textsubscript{3}\textsuperscript{–} and Cl\textsuperscript{–}. Fig. 5(a) shows the charge balance between NH\textsubscript{4}\textsuperscript{+} and Cl\textsuperscript{–}, NO\textsubscript{3}\textsuperscript{–}, and SO\textsubscript{4}\textsuperscript{2–} \( (R^2 = 0.82 \text{ and } P < 0.001 \text{ for } n = 1038) \). The charge balance between all cations, and all inorganic anions was shown in Fig. 5(b) \( (R^2 = 0.80 \text{ and } P < 0.001 \text{ for } n = 1038) \). The charge balance (Fig. 5(b)) is well below 1:1 relationship indicating an excess of cations compared to anions. The possible explanation for deficiency of cations could be due to the fact that HCO\textsubscript{3}\textsuperscript{–} and water-soluble organic anions (such as organic acidic ions) were not measured in this study. See et al. (2006, 2007) had reported that some of organic acids (e.g., acetate and formate) contribute significantly to the mass of PM\textsubscript{2.5} in Singapore. The charge balance in Fig. 5(a) was above and parallel to 1:1 line than the one in Fig. 5(b), confirming that substantial NH\textsubscript{4}\textsuperscript{+} was present to neutralize the acidic components (H\textsubscript{2}SO\textsubscript{4}, HNO\textsubscript{3} and HCl) to form (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, NH\textsubscript{4}NO\textsubscript{3} and NH\textsubscript{4}Cl.

\[ \text{Excess ammonia} = [\text{NH}_3] + [\text{NH}_4^+] - 2 \times [\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{HNO}_3] \] (4)

All the terms in Eq (4) are expressed in units of \( \mu \text{mole/m}^3 \). When the ‘excess ammonia’ term is < 0, then PM\textsubscript{2.5}-NO\textsubscript{3} formation would be NH\textsubscript{3}-limited and when the term is > 0, then PM\textsubscript{2.5}-NO\textsubscript{3} formation is HNO\textsubscript{3}-limited. In this study, mixed responses were observed for the ‘excess ammonia’ estimated values on the basis of hourly observations. Out of 1038 hourly data set, it was observed that 398 data sets were NH\textsubscript{3}-limited conditions (‘excess ammonia’ = –0.039 \pm 0.037 \( \mu \text{mol/m}^3 \)) and 640 data sets were HNO\textsubscript{3}-limited (excess ammonia = 0.144 \pm 0.192 \( \mu \text{mol/m}^3 \)). Overall, the study area experienced an ‘excess ammonia’ = 0.074 \pm 0.176 \( \mu \text{mol/m}^3 \) with n = 1038. Under NH\textsubscript{3}-limited conditions, the NO\textsubscript{3}\textsuperscript{–} formation could occur from the hydrolysis of N\textsubscript{2}O\textsubscript{5} under high humidity condition and/or heterogeneous reaction of HNO\textsubscript{3} on sea salt or soil dust particles (Yoshizumi and
Hoshi, 1985; Pathak et al., 2011). The NO$_3^-$ production rate from heterogeneous hydrolysis of N$_2$O$_5$ may contribute to the enhancement of NO$_3^-$ level during nighttime due to the highest production rate of N$_2$O$_5$ compared to daytime. It could be concluded that most of the times the atmosphere had sufficient NH$_3$ to neutralize both H$_2$SO$_4$ and HNO$_3$ to form (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$.

**Gas-to-Particle Formation**

As discussed previously (Section 3.2), the levels of secondary species (HONO, HNO$_3$, NH$_4^+$, SO$_4^{2-}$, NO$_3^-$ and Cl$^-$) showed different hourly patterns during the measurement period. To understand the role of meteorology (temperature and relative humidity) in the formation of these secondary species, correlation coefficients were estimated between these secondary species and meteorology using Minitab 15 English on a basis of 1 hr data (as presented in Table S2).

Based on the correlations between temperature, relative humidity and other species, the following observations and conclusions can be made: (i) HONO showed positive correlation with NO$_3^-$, Cl$^-$ and relative humidity, and negative correlation with SO$_4^{2-}$ and temperature, indicating that more humid conditions favor the formation of HONO through the heterogeneous process from H$_2$O and NO$_2$; (ii) NH$_4^+$ showed significant correlations with SO$_4^{2-}$ and NO$_3^-$, confirming that sufficient NH$_3$ was present to neutralize H$_2$SO$_4$ and HNO$_3$ during the measurement period. The higher correlation of NH$_4^+$ with SO$_4^{2-}$ ($r = 0.89$) than with NO$_3^-$ ($r = 0.46$) suggests that (NH$_4$)$_2$SO$_4$ is more likely to be formed than NH$_4$NO$_3$ because of better affinity between the two ions; (iii) an insignificant correlation of NH$_4^+$ with Cl$^-$ ($r = 0.08$) indicates that in the study area NH$_3$ was not sufficiently large to allow its reaction with HCl and particulate Cl$^-$ may also arise from other sources apart from...
NH4Cl, (iv) a positive correlation of NH4+ with temperature showed that daytime hours are favorable for conversion of NH3 to its particulate ammonium salts; and (v) temperature showed significant correlation with SO4$^{2-}$ indicating the formation of particulate SO4$^{2-}$ is favored under higher OH radicals due to more solar radiation during daytime; (vi) negative correlations of NO3$^{-}$ and Cl$^{-}$ with temperature justifies that the semi-volatile NH4NO3 and NH4Cl species are subjected to reverse reactions with conversion back into gaseous NH3 and HNO3 and NH3 and HCl, respectively; and (vii) positive correlations of NO3$^{-}$ and Cl$^{-}$ with relative humidity confirmed that more humid conditions favor formations of NH4NO3 and NH4Cl.

The partitioning of gas-to-particle phase of NH4NO3 and NH4Cl strongly depends on the gas phase precursor concentrations, temperature, relative humidity (RH) and aerosol chemical composition (Pio and Harrison, 1987a, b; Mozurkewich, 1993; Seinfeld and Pandis, 2006). In Table S2, the relationship between NO3$^{-}$ and Cl$^{-}$ concentrations, temperature and RH can clearly be observed. NO3$^{-}$ and Cl$^{-}$ concentrations are basically anti-correlated with temperature and correlated with relative humidity. The observations are similar to the studies done by Rupakheti et al. (2005) and Hu et al. (2008) who related NO3$^{-}$ and Cl$^{-}$ diurnal profiles to temperature and RH variations.

The transition from solid phase equilibrium to aqueous phase occurs, when RH increases, depending on ambient RH values compared to the Deliquescence Relative Humidity (DRH) of the particle. In contrast, the transition from aqueous phase to solid phase depends on ambient RH compared to the Efflorescence Relative Humidity (ERH), when ambient RH decreases. For example, at 298 K (NH4)2SO4 particles have a DRH of 80% and an ERH of 35%, while NH4NO3 particles have a DRH of 62% and no ERH is observed (Martin et al., 2003; Seinfeld and Pandis, 2006; Poulain et al., 2011). Particles are observed to be in meta-stable state, when ambient RH values vary between DRH and ERH. Under such circumstances, the phase of the particles not only depends on the chemical composition of the particles, but also on the RH history of the particles (Martin et al., 2003). In this study, we estimated the DRH of NH4NO3 and NH4Cl on an hourly basis by using the empirical relations between temperature and DRH from Stelson and Seinfeld (1982a) and Pio and Harrison (1987a). Out of 1038 valid 1 hr data, it was found that: (i) NH4NO3: RH < DRH for n = 42 data points, and RH ≥ DRH for n = 996 data points, and (ii) NH4Cl: RH < DRH for n = 507 data points and RH ≥ DRH for n = 531 data points. It should be noted that the 24 hr average RH during the measurement period was 76.3% and the DRH estimated was 63.2% for NH4NO3 and 77.5% for NH4Cl. These observations on DRH imply that existing humid conditions of the atmosphere during measurement period always favored the formation of NH4NO3. Therefore, this could be the possible reason for lack of diurnal variations on a 12 hr basis for NO3$^{-}$ (‘daytime/nighttime’ concentration = 0.96) as explained in Section 3.2. This finding is different from the observations reported in other regions of the World (e.g., Sharma et al. (2007) at Kanpur, India; Hu et al. (2008) at Pearl River Delta, China; Poulain et al. (2011) at Leipzig, Germany).

The measured concentration (ppbv) product ($K_m = [NH_3] \times [HNO_3]$) of HNO3 and NH3 was estimated using the measured data and then compared with the theoretical equilibrium constant ($K_e$) estimated according to the method in Mozurkewich (1993). The 1 hr data (n = 1038) were divided into two cases: (1) ambient RH < DRH, and (2) RH ≥ DRH. For the data sets for Case (1) (n = 42), the plots were made between $K_m$ versus 1000 T$^{-1}$ with the corresponding predicted $K_e$ as shown in Fig. S2. In Fig. S2, it was observed that $K_e$ is always higher than $K_m$, suggesting that the ambient conditions did not favor the formation of NH4NO3 under Case (1). Under Case (2), when DRH ≥ RH (n = 996), the existence of SO4$^{2-}$ in the deliquescent aerosol particles reduces $K_e$ compared to that of pure NH4NO3 solution (Stelson and Seinfeld, 1982b). To incorporate this concept into prediction of equilibrium constant, $K_e$ the ionic strength fraction (Y) of NH4NO3 in NH4$^+$/NO3$^-$/SO4$^{2-}$ system, was calculated according to Stelson and Seinfeld, 1982b (Eq (5)):

$$ Y = \frac{[NH_4NO_3]}{[NH_4NO_3]+3×[\text{NH}_3\text{SO}_4]} $$

$K_e^*$ for this system was derived by multiplying $K_e$ with Y. The comparison between $K_e^*$ and $K_m$ for Case (2), when DRH ≥ RH, is shown in Fig. 6. It should be noted that we plotted only the daytime and nighttime average values (12 hr) in Fig. 6 for better illustration. On average, $K_m$ was always more than $K_e^*$ (95% agreement), suggesting that the meteorological conditions always favor the formation of NH4NO3 in Singapore when RH is higher than DRH. Few data points (Fig. 6) having $K_m < K_e^*$ suggest that NH4NO3 might have dissociated under higher temperature during the daytime.

Fig. 7(a) shows the daily variations of $K_m$ and $K_e^*$ for NH4NO3 and levels of NO3$^{-}$ as a function of time series during the measurement period. During most of the days, $K_m$ was larger than $K_e^*$, confirming that the atmospheric conditions were favorable for NH4NO3 formation. It could also be concluded that the prevailing levels of NH3 and HNO3 in the study area were sufficient to form NH4NO3, which can be clearly seen from Fig. 7(a) (comparing $K_m$ and NO3$^{-}$ levels). The trends in the conversion of SO2 into SO4$^{2-}$ and HNO3 into NO3$^{-}$ were compared with the prevailing temperature and relative humidity (Fig. 7(b) and 7(c)). Finally, temperature plays a significant role in the conversion of SO2 into SO4$^{2-}$, whereas the relative humidity for HNO3 into NO3$^{-}$.

In an approach similar to NH4NO3, we tried to establish relationship between thermodynamics of NH4Cl. The measured concentration (ppbv) product ($K_m = [NH_3] \times [HCl]$) of HCl and NH3 was estimated using the measured data and then compared with the theoretical equilibrium constant ($K_e$) estimated according to the method in Pio and Harrison (1987a). The 1 hr data (n=1038) were divided into two cases: (1) ambient RH < DRH (n = 507), (2) RH ≥ DRH (n = 531). For Case (1), it was observed that $K_e$ was always higher than $K_m$. This indicates that the ambient
Fig. 6. Comparison of $K_m$ with $K_{e^*}$ when RH was above the DRH of NH$_4$NO$_3$.

Fig. 7. Comparison of (a) nitrate thermodynamics and observed nitrate levels, (b) temperature and relative humidity, and (c) molar ratios of SO$_4^{2-}$ to SO$_2$ and NO$_3^-$ to HNO$_3$ on a basis of daily average (24-h) during the measurement period.
conditions did not favor the formation of NH$_4$Cl under Case (1). Under Case (2), it was found that in most of the cases (more than 90% of the data), $K'_e$ was higher than $K'_m$ indicating that the prevailing conditions were not supportive for transformation of HCl into NH$_4$Cl. The reasons for such observations could be due to: (i) either HCl or NH$_3$ was not sufficient to drive the reactions in the forward direction, or (ii) the predominance of Cl$^-$ from sea-salt sources may interfere in the process of conversion.

### Biomass Burning and SIA formation

In this study, we analyzed two cases to assess the influence of biomass burning on chemical characteristics of PM$_{2.5}$ and gaseous pollutants: (i) Case-1: $K^+ < 0.3$ μg/m$^3$ and (ii) Case-2: $K^+ \geq 0.3$ μg/m$^3$. We classified all 12 hr observations into the two cases and performed a correlation analysis with Minitab 15 English (the results are presented in Table S3). It was clearly observed that $K^+$ showed higher correlations with Cl$^-$ and NO$_3^-$ under Case-2. Therefore, it can be concluded that under higher $K^+$ concentration, the formation of Cl$^-$ and NO$_3^-$ can be triggered. Hence, it is a clear indication of the influential role of biomass burning in the formation of chlorides and nitrates in the atmosphere. The observations were compared to some earlier studies: Balasubramanian et al. (2003) and Tabazad et al. (1998). Balasubramanian et al. (2003) had observed the contribution of NO$_3^-$ was more towards total PM$_{2.5}$ mass under smoke hazy conditions than non-hazy conditions. Tabazad et al. (1998) had observed that the scavenging of HNO$_3$ occurred more frequently under smoky conditions with biomass burning. Thus, these two earlier studies supported our hypothesis that biomass burning could have partially triggered nitrate and chloride formation in the study area.

### CONCLUSIONS

Acidic gases (SO$_2$, HONO, HNO$_3$, HCl), ammonia (NH$_3$) and water-soluble inorganic ions (SO$_4^{2-}$, NO$_3^-$, Cl$^-$, Na$^+$, K$^+$, NH$_4^+$, Ca$^{2+}$ and Mg$^{2+}$) in PM$_{2.5}$ were analyzed in Singapore with a short-time interval (1 hr). The results were analyzed to investigate temporal and diurnal variations in PM$_{2.5}$ and their associations and chemical coupling with precursor gases along with the sensitivity of meteorological effects. SO$_2$, NH$_3$, HONO, HCl, SO$_4^{2-}$ and Cl$^-$ showed significant diurnal variations at 95% confidence level ($P < 0.05$). However HNO$_3$, NO$_3^-$, Na$^+$, NH$_4^+$, Ca$^{2+}$ and Mg$^{2+}$ did not show any significant diurnal variations. The peaks of NH$_4^+$ occurred during the rise in concentrations of NO$_3^-$ and SO$_4^{2-}$. These peaks of NH$_4^+$ could be attributed to formation of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ during intense traffic emissions of NO$_x$ and more industrial emissions of SO$_2$. The trace level of NH$_3$ can neutralize H$_2$SO$_4$ and HNO$_3$ to form significant quantities of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ under prevailing atmospheric conditions. In the neutralization process leading to gas-to-particle conversion, this study showed a significant quantity of NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ (7.46 μg/m$^3$) in PM$_{2.5}$, which is a matter of concern. Due to the sampling location in the tropical climate, the study area experienced ambient relative humidity to be more than the estimated deliquescence relative humidity of NH$_4$NO$_3$ for 96% of the time the total observations were made. These conditions favored the thermodynamics of NH$_4$NO$_3$ formation during both daytime and nighttime. The conversion of SO$_2$ into SO$_4^{2-}$ and HNO$_3$ into NO$_3^-$ was sensitive to ambient temperature and relative humidity, respectively during the measurement period. Under higher $K^+$ concentrations ($\geq 0.3$ μg/m$^3$), the formation of nitrates and chlorides was enhanced. Finally, the charge balance of NH$_4^+$ and Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ ($y = 1.029x + 0.22$ with $R^2 = 0.82$) showed that ammonia-rich conditions prevail in the atmosphere most of the time for fully neutralization of H$_2$SO$_4$, HNO$_3$ and HCl.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES


United Kingdom and New York, NY, USA, p. 996,


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