Pollution Properties of Water-Soluble Secondary Inorganic Ions in Atmospheric PM$_{2.5}$ in the Pearl River Delta Region

Dingli Yue$^1$, Liuju Zhong$^{1*}$, Tao Zhang$^1$, Jin Shen$^1$, Yan Zhou$^1$, Limin Zeng$^2$, Huabin Dong$^3$, Siqi Ye$^1$

$^1$ Guangdong Environmental Monitoring Center, State Environmental Protection Key Laboratory of Regional Air Quality Monitoring, Guangzhou 510308, China
$^2$ Peking University, State Key Joint Laboratory of Environmental Simulation and Pollution Control, Beijing 100871, China
$^3$ Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

ABSTRACT

Based on the online observation of PM$_{2.5}$ mass concentration, its water-soluble inorganic ions, and their gaseous precursors during August of 2013 to March of 2014 at the atmospheric supersite in the Pearl River Delta (PRD) region, the inter-action of the secondary compositions and their precursors was discussed, and the pollution properties of the secondary inorganic ions were revealed. During the whole measurement period, the average concentrations of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were 16.6 µg m$^{-3}$, 9.0 µg m$^{-3}$ and 10.2 µg m$^{-3}$, respectively, with total contribution to PM$_{2.5}$ of 55.8%, indicating the significant role of secondary transformation in PM$_{2.5}$ pollution. The seasonal average total contributions of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ to PM$_{2.5}$ varied from 46.0% to 64.3%, lowest in summer and highest in winter. The contributions of SO$_4^{2-}$ and NH$_4^+$ to PM$_{2.5}$ were relatively stable; while those of NO$_3^-$ in different seasons were distinct, even dominating PM$_{2.5}$ in some pollution cases in winter. NH$_3$ was abundant with an annual average concentration of 15.2 µg m$^{-3}$, facilitating the neutralization of H$_2$SO$_4$ and HNO$_3$ with the average $[\text{NH}_4^+]/(2[\text{SO}_4^{2-}] + [\text{NO}_3^-])$ equivalent charge ratio of 1.1. The maximum daily peak concentration of HNO$_3$ was as high as 18.6 µg m$^{-3}$, providing an evidence for the strong oxidizing property of the atmosphere in the PRD region. The theoretical equilibrium constant ($K_e$) of NH$_4$NO$_3$ is always lower than the observed concentration product ($K_m = [\text{NH}_3] \times [\text{HNO}_3]$) in spring and winter with higher HNO$_3$ concentrations; while in over 60% of the time during summer and autumn, mainly during daytime, $K_e$ was higher. In general, the strong oxidizing property and NH$_3$ played important roles in the fine particle pollution in the PRD region.

Keywords: PM$_{2.5}$; Water-soluble inorganic ions; Secondary transformation; Gas-particle conversion.

INTRODUCTION

Atmospheric aerosols influence our life in many aspects. They impose obvious effects on the global climate change and human health (Dockery et al., 1994; Nel, 2005), and visibility degradation (Sokolik and Toon, 1996; Jung and Kim, 2006). Consequently, more and more attention has been paid to them in recent years. It is well known that aerosols with different compositions and from diverse sources have distinct effects. In order to understand their effects and provide scientifically sound evidence for effective control policies making, accurate knowledge on physical and chemical properties of aerosol is urgently required. Previous studies showed that concentrations and compositions of PM$_{2.5}$ vary with seasons, presenting generally high values in winter and low ones in summer in general; and carbonaceous matter and water-soluble ions such as sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$) and ammonium (NH$_4^+$) are usually the main contributors. HNO$_3$ and H$_2$SO$_4$ can be transformed into aerosol by neutralization reactions (Seinfeld and Pandis, 1998). Semi-volatile NH$_2$NO$_3$ is formed via reversible phase equilibrium with NH$_3$ and HNO$_3$ (Pio and Harrison, 1987). Such equilibrium between gas- and particle-phase is strongly influenced by ambient temperature (T) and relative humidity (RH) (Mozurkewich, 1993).

The Pearl River Delta (PRD) region is one of the biggest city clusters with extremely invigorating economy and dense population in the world. Rapid urbanization and economic development have been accompanied by the serious deterioration of regional air quality as well as significant changes of air pollution properties: emissions of primary pollutants such as SO$_2$ and inhalable particulate matter (PM$_{10}$) have been greatly reduced by certain abatement

*Corresponding author.
E-mail address: zhongliuju@139.com
measures, while formations of secondary products such as ozone and fine particles in high concentrations have become the main issues, especially after the National Ambient Air Quality Standards (GB 3095-2012) was promulgated. The chemical compositions of PM$_{2.5}$ and PM$_{10}$ in the PRD region have been reported before (e.g., Cao et al., 2004; Hagler et al., 2006; Liu et al., 2008; Yue et al., 2010a; Huang et al., 2014). The gaseous precursors are crucial to investigate their formation mechanisms and behaviors in the atmosphere. However, simultaneous on-line measurements of water-soluble ions of PM$_{2.5}$ and related precursor gases (HNO$_3$, SO$_2$ and NH$_3$) are still very rare (Hu et al., 2008), and seasonal variations of them has not been reported in this region. In this study secondary water-soluble inorganic ions, including SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ in PM$_{2.5}$, and the related gaseous pollutants including HNO$_3$, NH$_3$, SO$_2$ and NO$_2$ were measured simultaneously at a regional atmospheric supersite in the PRD region of Guangdong Province (Zhong et al., 2013) during four different seasons. The goal of this study was to understand the interaction of the secondary water-soluble ions and their gaseous precursors and thus to reveal the pollution properties of the secondary inorganic ions in the PRD region, providing scientific support for designing effective fine particle pollution control strategies.

**METHODOLOGY**

**Observation Site and Periods**

The measurements were conducted at the Guangdong Atmospheric Supersite located in Taoyuan Town, Heshan county, Jiangmen city, Guangdong Province (112.929°E, 22.728°N; altitude 60 m), about 80 km southwest from Guangzhou urban area, 50 km southwest and 30 km northeast from Foshan and Jiangmen urban area, respectively. The site was heavily influenced by the intense air pollutant emissions from Guangzhou and Foshan area in spring, autumn and winter (Zhong et al., 2013; Peng et al., 2014).

Measurements were conducted in four different periods, i.e., 5 to 24 August (summer), 30 September to 19 October (autumn), and 29 November to 17 December (winter) in the year of 2013, and 7 to 26 March (spring) in 2014, to represent the four seasons, respectively. Correspondingly, the average concentrations of the four periods were taken as annual average values.

**Instrumentation**

Mass concentrations of PM$_{2.5}$, its water-soluble ions (SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) and the corresponding gaseous precursors including HNO$_3$, NH$_3$, SO$_2$ and NO$_2$ were measured on-line at the supersite.

The water-soluble inorganic ions in PM$_{2.5}$ and gaseous HNO$_3$ and NH$_3$ were detected by a Gas and Aerosol Collector-Ion Chromatography (GAC-IC) system made in Peking University, and the principle and configuration of the GAC-IC system was similar to that introduced in detail by Dong et al. (2012). In the system, a set of dull-polished wet annular denuder with a steam jet aerosol collector was employed for the continuous sampling of both gas- and aerosol-phase pollutants. The inorganic gaseous and particulate species were detected by two separate ion chromatography (IC; ICS-90, Dionex, USA). The IC to measure anions was equipped with a 4 × 25 mm guard column (IonPac AG 14) followed by a 4 × 250 mm analytical column (Ion Pac AS 14) with a mixture of 3.5 mM CO$_3^{2-}$ and 1.0mM HCO$_3^-$ as eluent solution. The other IC for cations was installed with a 4 × 25 mm guard column (Ion Pac CG 12) followed by a 4 × 250 mm analytical column (IonPac CS 12) with 20 mM methane sulfonic acid as eluent solution. Both ICs were electronically suppressed to reduce the background signal. The inlet for the system was set up with a URG PM$_{2.5}$ cut-off with a flow rate of about 16.7 L min$^{-1}$. The time resolution was 30 minutes, and the measured data was hourly averaged for analysis.

The detection limits of gaseous HNO$_3$ and NH$_3$ were 0.183 µg m$^{-3}$ and 0.023 µg m$^{-3}$, respectively, and those for SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were 0.159 µg m$^{-3}$, 0.034 µg m$^{-3}$, and 0.030 µg m$^{-3}$. The amounts of the collected liquefied gaseous and particulate pollutants of each sample were recorded to judge the stability of this system, and standard samples were detected before and after each separate measurement period in the four different seasons to ensure the consistence of the data.

PM$_{2.5}$ mass concentration was measured by a tapered element oscillating microbalance (Model TEO 1405), SO$_2$ by a trace level SO$_2$ analyzer (Model 43iTLE), NO$_2$ by a trace level NO/NO$_2$/NOx analyzer (Model 42iT), and O$_3$ by a UV spectrophotometry O$_3$ analyzer (Model 49i); these instruments were produced by the Thermo Fisher Scientific, USA.

In addition, particle number size distributions and meteorological parameters including temperature, RH, precipitation, wind speed (WS), wind direction (WD), UVA and visibility were also measured in this research. Particle number size distributions from 3 to 900 nm were monitored by a couple of scanning mobility particle sizers (TSI model 3936, TSI Inc., St. Paul, MN, USA). UVA was measured by a multiband ultraviolet radiation meter (Model UV-S-A-T/UV-S-B-T, Kipp&Zonen B.V., Holland); visibility was measured by a Belfort Model 6000 visibility detection instrument from USA, and the other meteorological parameters were reported by a portable weather station (Model WXT520, Vaisala, Finland).

**RESULTS AND DISCUSSION**

**Meteorological Conditions**

Meteorological conditions of the four seasons in the PRD region are distinct. Table 1 shows selected meteorological parameters for four seasons at the supersite. Overall, mean temperature and RH exhibited obvious seasonality with the highest values in summer and the lowest values in winter. Total precipitation was virtually insignificant in autumn while abundant in summer. UVA and atmospheric visibility also peaked in summer, but showed troughs during spring instead of in winter, resulted from a special continuous wet weather called Huinan Weather with very high RH occurred in spring. As expected, the predominant wind direction was northeast except south in summer. In general, higher wind speeds were frequently observed in summer.
of the key factors leading to higher NH3 concentration at PRD region and higher temperature was also probably one activity imposed important effect on the atmosphere in the (e.g., composting and N-fertilizer application), livestock feeding, and biological suggested that active agricultural production (e.g., composting daily peak concentrations of HNO3 were 1.8–18.6 µg m–3, and NH4+ had the same seasonal variation pattern: winter > autumn > spring > summer, and the rank of NO3− concentrations was the same as that in Hong Kong (Louie et al., 2005): winter > spring > autumn > summer; all showed highest values in winter and lowest ones during summer. The weather over PRD region during wintertime is influenced by Siberian cold current as East Asian winter monsoon is mainly influenced by Siberian High during this time (Wu and Wang, 2002). The weak to moderate northeasterly winds with increased air parcel residence time over potential source regions in winter in the PRD region (Louie et al., 2005) favored the accumulation, condensation, and transformation of atmospheric pollutants and the strong northerly winds can bring superregional transport pollutants to the PRD region, both leading to high concentrations of PM2.5 and its chemical components. During summer, a low-pressure trough draws moist warm air inland from the ocean with an increase in precipitation. Frequent precipitation and good dispersion conditions for air pollutants brought good air quality with low concentrations of particles in summer. Two possible reseasons for the higher NO3− concentration in spring than autumn which was different from that of PM2.5, SO42− and NH4+ were as follows: (1) Although the intense solar radiation in autumn was favorable for NO3− formation through oxidation reaction, the high temperature and low RH pushed the equilibrium of NH3(g) + HNO3(g) ≤ NH4NO3(s,aq) to produce gaseous NH3 and HNO3, which was confirmed in the subsequent discussions on gas to particle conversion. (2) The lower gaseous precursor concentrations of NO2 and HNO3 than those in spring would also lead to lower NO3− concentration. HNO3 showed a consistent seasonal variation pattern (winter > spring > autumn > summer) with NO2 and NO3−, but the average concentrations of HNO3 in spring (3.7 µg m−3) and autumn (3.3 µg m−3) were close with a difference of around 10%. The dominant daytime source of HNO3 is through the oxidation of NO2 by the hydroxyl radical. HNO3 deposition is normally considered to be a terminal sink of NO3−, but recent studies have indicated that HNO3 deposited on the surface can be released back into the atmosphere in the form of NO2 after heterogeneous reactions with NO (Saliba et al. 2001). In addition, HNO3/H2O complex could be photolysed into HONO or NO (Ramazan et al., 2006). Solar radiation was a double-edged sword for HNO3. In summertime, clean south wind from South China Sea usually dilutes the pollutants over PRD region and improves the air quality and visibility to large extent. The precursors of HNO3, NO2 and OH radical should also be low to produce HNO3 during the time when southerly wind is prevalent, even though there is evidence of strong solar

General Observations

The annual average mass concentration of PM2.5 was 64.2 µg m−3, higher than the secondary grade mass concentration limit of the National Ambient Air Quality Standards (GB 3095-2012) in China (35 µg m−3) by 83.4%. The annual average concentrations of SO42−, NO3− and NH4+ were 16.6 µg m−3, 9.0 µg m−3 and 10.2 µg m−3, respectively, with total contribution to PM2.5 (SNA/PM2.5) of 55.8%. It was significantly higher than those measured at other places of China, such as Shangdianzhi regional site in North China (Meng et al., 2013), Xi’an (Han et al., 2009), Beijing, Chongqing, and Shanghai (Yang et al., 2011), indicating the important role of secondary transformation played in the PM2.5 pollution in the PRD region. Among the major gaseous precursors of the water-soluble ions, the annual concentration of SO2 was 31.6 µg m–3, meeting the National Ambient Air Quality Standards (GB 3095-2012). However, the annual average concentration of NO2 was 47.9 µg m−3 in violation of the national standards, indicating the significant influence from vehicle emissions. Due to high chemical activity and its sticky nature, the atmospheric lifetime of HNO3 was relatively short, leading to low concentration level with annual average of 3.3 µg m−3, compared with other species. However, the HNO3 concentrations were higher than those at other places such as in North Carolina, USA of 0.9 µg m−3 (Walker et al., 2006), in Oberbärenburg, Germany of 0.8 µg m−3 (Plessow et al., 2005) and at Hong Kong urban area of 1.3 µg m−3 (Yao et al., 2006). In addition, the daily peak concentrations of HNO3 were 1.8–18.6 µg m−3, significantly higher than those in Mexico City of 1.4–8.4 µg m−3 (Zheng et al., 2008) and at Beijing urban area of < 8 µg m−3 (Yue et al., 2013). Both provided an evidence for the strong oxidizing property of the atmosphere in the PRD region. The annual average NH3 concentration was 15.2 µg m−3, obviously higher than that at Shangdianzhi regional site in North China of 8.7 µg m−3 (Meng et al., 2013). It suggested that active agricultural production (e.g., composting and N-fertilizer application), livestock feeding, and biological activity imposed important effect on the atmosphere in the PRD region and higher temperature was also probably one of the key factors leading to higher NH3 concentration at the supersite than that in North China, as industrial process, vehicle emission and biomass combustion contributed a total of less than 10% to NH3 sources in Guangdong Province (Pan et al., 2014).

As diagrammed in Fig. 1, concentrations of PM2.5, SO42− and NH4+ had the same seasonal variation pattern: winter > autumn > spring > summer, and the rank of NO3− concentration was the same as that in Hong Kong (Louie et al., 2005): winter > spring > autumn > summer; all showed highest values in winter and lowest ones during summer. The weather over PRD region during wintertime is influenced by Siberian cold current as East Asian winter monsoon is mainly influenced by Siberian High during this time (Wu and Wang, 2002). The weak to moderate northeasterly winds with increased air parcel residence time over potential source regions in winter in the PRD region (Louie et al., 2005) favored the accumulation, condensation, and transformation of atmospheric pollutants and the strong northerly winds can bring superregional transport pollutants to the PRD region, both leading to high concentrations of PM2.5 and its chemical components. During summer, a low-pressure trough draws moist warm air inland from the ocean with an increase in precipitation. Frequent precipitation and good dispersion conditions for air pollutants brought good air quality with low concentrations of particles in summer. Two possible reseasons for the higher NO3− concentration in spring than autumn which was different from that of PM2.5, SO42− and NH4+ were as follows: (1) Although the intense solar radiation in autumn was favorable for NO3− formation through oxidation reaction, the high temperature and low RH pushed the equilibrium of NH3(g) + HNO3(g) ≤ NH4NO3(s,aq) to produce gaseous NH3 and HNO3, which was confirmed in the subsequent discussions on gas to particle conversion. (2) The lower gaseous precursor concentrations of NO2 and HNO3 than those in spring would also lead to lower NO3− concentration. HNO3 showed a consistent seasonal variation pattern (winter > spring > autumn > summer) with NO2 and NO3−, but the average concentrations of HNO3 in spring (3.7 µg m−3) and autumn (3.3 µg m−3) were close with a difference of around 10%. The dominant daytime source of HNO3 is through the oxidation of NO2 by the hydroxyl radical. HNO3 deposition is normally considered to be a terminal sink of NO3−, but recent studies have indicated that HNO3 deposited on the surface can be released back into the atmosphere in the form of NO2 after heterogeneous reactions with NO (Saliba et al. 2001). In addition, HNO3/H2O complex could be photolysed into HONO or NO (Ramazan et al., 2006). Solar radiation was a double-edged sword for HNO3. In summertime, clean south wind from South China Sea usually dilutes the pollutants over PRD region and improves the air quality and visibility to large extent. The precursors of HNO3, NO2 and OH radical should also be low to produce HNO3 during the time when southerly wind is prevalent, even though there is evidence of strong solar

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
<th>Relative humidity (%)</th>
<th>Precipitation (mm)</th>
<th>Wind speed (m s−1)</th>
<th>Wind direction</th>
<th>UVA (W m−2)</th>
<th>Visibility (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Average</td>
<td>Total amount</td>
<td>Average (75 Percentile)</td>
<td>Predominant</td>
<td>Average</td>
<td>Average</td>
</tr>
<tr>
<td>Spring</td>
<td>17.2</td>
<td>71.7</td>
<td>5.9</td>
<td>1.5 (2.0)</td>
<td>NE</td>
<td>5.3</td>
<td>7.5</td>
</tr>
<tr>
<td>Summer</td>
<td>28.0</td>
<td>76.7</td>
<td>183.5</td>
<td>2.0 (2.7)</td>
<td>S</td>
<td>11.0</td>
<td>19.3</td>
</tr>
<tr>
<td>Autumn</td>
<td>25.5</td>
<td>58.2</td>
<td>0.1</td>
<td>1.6 (2.0)</td>
<td>NE</td>
<td>9.8</td>
<td>10.8</td>
</tr>
<tr>
<td>Winter</td>
<td>14.7</td>
<td>57.4</td>
<td>94.5</td>
<td>1.8 (2.2)</td>
<td>NE</td>
<td>5.7</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Table 1. Selected meteorological parameters in the four seasons.
radiation. Similarly, NO\textsubscript{2} was recorded to be lower during the autumn than in spring and winter, unlikely to cause high HNO\textsubscript{3} in the autumn either.

The seasonal variation of NH\textsubscript{3} concentrations was unique in this research with the highest average concentration in spring and the lowest one in winter. It was also different from NH\textsubscript{3} variation mode at the Shangdianzi regional site in North China with highest concentrations occurred in summer, as over there agricultural activity was a major source of NH\textsubscript{3} and the main compositions of the fertilizer used were diammonium phosphate and urea, which are very easy to volatile and produce NH\textsubscript{3} in summer, and the high temperature makes against the reaction of NH\textsubscript{3} and HNO\textsubscript{3} to form particulate NH\textsubscript{4}NO\textsubscript{3} (Meng et al., 2013). NH\textsubscript{3} observation of this work was also different from the one observed by Zheng et al. (2015) in an industry zone of Nanjing, which was heavily influenced by industry emissions. However, the atmospheric temperature in the PRD region is significantly higher than that in North China, and meteorological conditions favoring agricultural production appeared earlier in a year, so the agricultural activity such as composting and fertilization will be more active during spring than summer, resulting in more NH\textsubscript{3} emission. Moreover, the far higher relative humidity in summer is in favor of the formation and existence of NH\textsubscript{4}NO\textsubscript{3}. Affected by such complex factors, the highest seasonal average NH\textsubscript{3} concentrations in PRD appeared in spring followed by that in summer. NH\textsubscript{3} concentrations at the supersite were obviously higher than those in Beijing and at Xinken during the same seasons (Yue et al., 2013; Hu et al., 2008).

**Diurnal Variations of the Pollutants**

The diurnal variations of the average temperature, RH, wind speed, UVA, PM\textsubscript{2.5}, water-soluble ions, O\textsubscript{3}, HNO\textsubscript{3}, SO\textsubscript{2} and NH\textsubscript{3} during the measuring period are shown in Fig. 2. The lowest temperature occurred in the morning at about 6 o’clock (18.8°C), and the maxima in the afternoon at about 15 o’clock of 24.3°C. The diurnal variation pattern of RH was the inverse of temperature with maxima in the early morning and minima around 14 o’clock. The highest average wind speed was observed at noon of about 2 m s\textsuperscript{-1}. In contrast, the wind speeds in the early morning were lower. This trend of wind speed diurnal variation was different from that observed at a coastal regional site in the PRD region with higher wind speed in the morning (Hu et al., 2008). The UVA increased quickly after sun rise and showed peak values at noon with obvious decrease in the afternoon followed, and come to nearly zero at night. Overall, the meteorological conditions in the afternoon were characterized by high wind speed, high temperature, and low RH. In addition, the boundary layer height was expected to be higher in the afternoon. Early in the morning, by contrast, it was characterized with low wind speed, low temperature, high RH, and low boundary layer height. That is to say, it was favorable for the dispersion and dilution of the pollutants in the afternoon while beneficial for pollutant accumulation and gas to particle transformation early in the morning. It was the main causes for the fact that PM\textsubscript{2.5} and its inorganic aerosol ions showed lower concentrations in the afternoon and higher ones early in the morning. SO\textsubscript{2} and NH\textsubscript{3}, mainly from primary emission sources, also showed similar diurnal variation trends. In contrast, the diurnal variations of O\textsubscript{3} and HNO\textsubscript{3} were similar to that of UVA, but with later peak time, as they are products of atmospheric photochemistry reactions.

**Contributions of Secondary Ions to PM\textsubscript{2.5}**

The contributions of SO\textsubscript{4}\textsuperscript{2–}, NO\textsubscript{3}– and NH\textsubscript{4}+ to PM\textsubscript{2.5} are shown in Fig. 3. Overall, they contributed 25.9%, 14.0%, and 15.9% to PM\textsubscript{2.5}, respectively. Among them, SO\textsubscript{4}\textsuperscript{2–} was the biggest contributor, with a small fluctuation range of 23.9–27.4% in different seasons. The contributions of NH\textsubscript{4}+ were 12.7–17.7%, but the fractions of NO\textsubscript{3}– varied significantly, from 6.3% in summer to 19.2% in winter. The total contribution of SNA/PM\textsubscript{2.5} changed from 45.6% to 64.3%, showing high values during spring and winter but low ones in summer and autumn. The reasons for the low fraction during summer and autumn are as follows: (1) Biological activity during these seasons is vigorous and will emit a large amount of volatile and semi-volatile organic compounds, supplying abundant precursors for organic aerosols. (2) The intense solar radiation provides a good condition for the photochemical reactions to produce secondary organic aerosols. As reported that the secondary organic matters accounted for 56% in the organic fine aerosols in Shenzhen in PRD during summer, while in winter the fraction was only 6% (Niu et al., 2006). In short, the increase in organic matter contribution was probably
the proximate cause for the obvious decrease in water-soluble inorganic ion contribution to PM$_{2.5}$. The seasonal fraction of SNA/PM$_{2.5}$ at the supersite was significantly higher than those in Guangzhou of 36.7% in summer and of 41.3% in winter (Tao et al., 2010; Huang et al., 2014).

Charge Balance of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$

The mean molar ratio of NH$_4^+$ to SO$_4^{2-}$ was 3.3, far more than 2, indicating that abundant NH$_4^+$ was present to neutralize H$_2$SO$_4$ and NH$_3$HSO$_4$ was negligible. The excess of NH$_4^+$ was inferred to be associated with NO$_3^-$ and Cl$^-$. The annual average equivalence charge ratio of [NH$_4^+$]/(2[SO$_4^{2-}$] + [NO$_3^-$]) at the supersite was 1.2, implying that NH$_4^+$ in PM$_{2.5}$ can totally balance SO$_4^{2-}$ and NO$_3^-$, and mainly existing in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. The average equivalence charge ratios in different seasons were comparable, being 1.1 in summer and winter, and 1.2 in spring and autumn. They were larger than those in Guangzhou, Xinken, Beijing, Shanghai and Xi’an in the range of 0.5–0.9, where NH$_4^+$ cannot balance the entire SO$_4^{2-}$ and NO$_3^-$, and a part of NO$_3^-$ may be in the form of KNO$_3$ (Wang et al., 2006; Zhang et al., 2007; Hu et al., 2008; Tao et al., 2010; Yue et al., 2013). The abundant NH$_3$ at the supersite was the major cause for the high equivalence charge ratio of [NH$_4^+$]/(2[SO$_4^{2-}$] + [NO$_3^-$]).

Gas to Particle Conversion

The linear correlation between SO$_4^{2-}$ and NH$_4^+$ ($R^2 = 0.55$ or 0.68) was significantly better than that between NO$_3^-$ and NH$_4^+$ ($R^2 = 0.27$ or 0.36) during summer and autumn, respectively; while such linear correlation was comparable during winter and spring, with $R^2$ of 0.79 and 0.85 for the former and $R^2$ of 0.75 and 0.84 for the latter. It indicated that the heterogeneous reaction between HNO$_3$ and NH$_3$ in the particle-phase to form NH$_4$NO$_3$ probably played a more important role in winter and spring than in summer and autumn. In order to determine if the meteorological conditions, mainly atmosphere temperature and RH, at the supersite favor the formation of NH$_4$NO$_3$ or not, the measured concentration product ($K_m = [NH_3] \times [HNO_3]$) of HNO$_3$ and NH$_3$ was calculated using the measured data and then compared with the theoretical equilibrium constant ($K_e$) calculated according to the method mentioned in (Mozurkewich, 1993). The data were divided into two
groups: (1) The ambient RH was below the deliquescence relative humidity (DRH); (2) The ambient RH was above the DRH. For the latter, the existence of $\text{SO}_4^{2-}$ in the deliquescent aerosol particles reduces $K_e$ compared to that of pure $\text{NH}_4\text{NO}_3$ solution (Stelson and Seinfeld, 1982). The ionic strength fraction ($\gamma$) of $\text{NH}_4\text{NO}_3$ in $\text{NH}_4^+$/NO$_3^-$/$\text{SO}_4^{2-}$ system can be calculated according to (Stelson and Seinfeld, 1982):

$$\gamma = \frac{[\text{NH}_4\text{NO}_3]}{[\text{NH}_4\text{NO}_3] + 3([\text{NH}_4\text{HSO}_4])}.$$ 

And $K_e^*$ for this system was derived by multiplying $K_e$ with $\gamma$ and was compared with $K_m$. $K_e^*$ for this system was derived by multiplying $K_e$ with $\gamma$ and was compared with $K_m$. $K_e$ (Group 1) or $K_e^*$ (Group 2) larger than $K_m$ suggests that $\text{NH}_4\text{NO}_3$ tends to dissociate and conversely the formation of $\text{NH}_4\text{NO}_3$ is possible.

The ratios of $K_m/K_e$ (or $K_m/K_e^*$, $K_e^*$ was used when RH is larger than the DRH through the paper) by hour at the supersite in four seasons were derived, and categorized into two types according to whether it was below 1. As shown in Table 2, $K_m$ was mostly larger than $K_e$ (or $K_e^*$) during spring and winter; while in over 60% of the time in summer and autumn, $K_m$ was less than $K_e$ (or $K_e^*$). One possible cause was that HNO$_3$ concentrations were much higher during spring and winter than in summer and autumn. The lower temperature in spring and winter (< 20°C on average) than those in summer and autumn (> 25°C on average) was probably also an important factor. It has been also reported that $K_e$ was larger during daytime and smaller at night than $K_m$ in autumn at Xinken site (Hu et al., 2008), presenting less $\text{NH}_3$ and $\text{NH}_4^+$ but more HNO$_3$ and NO$_3^-$ than those at supersite.

**Fig. 3.** Contributions of different chemical compositions to PM$_{2.5}$. 

Annual average

- **Spring**
- **Summer**
- **Autumn**
- **Winter**
A Complex Pollution Episode in Autumn

Consequently, a complex air pollution episode with both daily PM$_{2.5}$ and O$_3$ concentrations violating the secondary grade concentration limit of the National Ambient Air Quality Standards (75 µg m$^{-3}$ and 200 µg m$^{-3}$, respectively) in autumn and a particle pollution episode with daily PM$_{2.5}$ exceeding the secondary grade concentration limit of the same standards but low O$_3$ concentrations in winter were discussed respectively to investigate the different mechanisms of such episodic cases.

Case Study

Autumn and winter are the period with heavy air pollution and frequent regional haze in the PRD region; while the comparison between K$_m$ and K$_e$ implies that the characteristics of particle pollution in the two different seasons will be distinct. Consequently, a complex air pollution episode with both daily PM$_{2.5}$ and O$_3$ concentrations violating the secondary grade concentration limit of the National Ambient Air Quality Standards (75 µg m$^{-3}$ and 200 µg m$^{-3}$, respectively) in autumn and a particle pollution episode with daily PM$_{2.5}$ exceeding the secondary grade concentration limit of the same standards but low O$_3$ concentrations in winter were discussed respectively to investigate the different mechanisms of such episodic cases.

A Particle Pollution Episode in Winter

A particle pollution episode with daily PM$_{2.5}$ concentrations violated the second grade limit of the national standards but low O$_3$ concentrations was observed during 30 November to 5 December in 2013. Time series of selected parameters during this period were illustrated in Fig. 5. During this episode, the daily maximum UVA was 26–38 W m$^{-2}$, significantly lower than that during the complex air pollution episode in autumn, causing obviously lower O$_3$ concentrations. The wind speed was relative low (< 2 m s$^{-1}$), indicating stagnant atmospheric conditions, which were favorable for the accumulation and transformation of air pollutants. The RH variation range was 21–78%, similar to that during the complex air pollution episode in autumn, while the temperature was significantly lower, in the range of 10–23°C, leading to very low K$_e$ and high ratios of K$_m$/K$_e$ and promoting the gas to particle conversion of HNO$_3$ and NH$_3$ to form NH$_4$NO$_3$. HNO$_3$ also showed high concentrations during the daytime and low ones at night, similar to the trend of O$_3$. SNA accounted for about 60% of PM$_{2.5}$. The SO$_4^{2-}$ concentration was generally higher than that of NO$_3^-$.

Table 2. Percentages of the K$_m$/K$_e$ (or K$_m$/K$_e^*$) ratios during different seasons.

<table>
<thead>
<tr>
<th>Season</th>
<th>K$_m$/K$_e$ (or K$_m$/K$_e^*$) &lt; 1</th>
<th>K$_m$/K$_e$ (or K$_m$/K$_e^*$) ≥ 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>6.5%</td>
<td>93.5%</td>
</tr>
<tr>
<td>Summer</td>
<td>73.9%</td>
<td>26.1%</td>
</tr>
<tr>
<td>Autumn</td>
<td>66.3%</td>
<td>33.7%</td>
</tr>
<tr>
<td>Winter</td>
<td>4.8%</td>
<td>95.2%</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The concentrations of PM$_{2.5}$, its water-soluble inorganic ions and the related gaseous precursors during four seasons were measured and discussed at the regional atmospheric supersite in the PRD region. The average concentrations of PM$_{2.5}$, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were 64.2 µg m$^{-3}$, 16.6 µg m$^{-3}$, 10.5 µg m$^{-3}$ and 7.2 µg m$^{-3}$ respectively.
Fig. 4. Time series of selected parameters from 2 to 6 October.
Fig. 5. Time series of selected parameters from 30 November to 5 December.

9.0 µg m$^{-3}$, and 10.2 µg m$^{-3}$, respectively. SNA accounted for 55.8% of PM$_{2.5}$ on average, reflecting the significant influence of the secondary transformation in the fine particle pollution in the PRD region. NH$_3$ concentrations were highest in spring and lowest in winter with an annual average value of 15.2 µg m$^{-3}$. Such abundant NH$_3$ facilitated...
the neutralization of $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ with the average equivalent charge ratio of $[\text{NH}_4^+]/[2[\text{SO}_4^{2-}]+[\text{NO}_3^-)]$ being 1.1, suggesting that $\text{NH}_4^+$, $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ should be mainly in the form of ($\text{NH}_3$)$_2\text{SO}_4$ and $\text{NH}_4\text{NO}_3$ in PM$_{2.5}$. The high $\text{HNO}_3$ concentrations provided an evidence for the strong oxidizing capability of the atmosphere in the PRD region.

The seasonal average SNA/PM$_{2.5}$ contributions varied from 46.0% to 64.3%, lower in summer and autumn, and higher in winter and spring. The contributions of SO$_4^{2-}$ and NH$_4^+$ to PM$_{2.5}$ were relatively stable, which fluctuated in the range of 23.9–27.4% and 12.7–17.7%, respectively; while the contributions of NO$_3^-$ in different seasons were diverse with a large fluctuation range of 6.3–19.2%. During winter and spring, the comparable linear correlations of NO$_3^-$ versus NH$_4^+$ ($R^2 = 0.75$ or 0.84) and SO$_4^{2-}$ versus NH$_4^+$ ($R^2 = 0.79$ or 0.85), the higher ratios of $K_0/K_S$, and larger contributions of NO$_3^-$ to PM$_{2.5}$ reflected that the heterogeneous reaction between HNO$_3$ and NH$_3$ to form NH$_4$NO$_3$ in the particle-phase played a more important role in fine particle pollution. And the fast and effective gas to particle conversion of HNO$_3$ and NH$_3$ to NH$_4$NO$_3$ can cause even higher concentrations of NO$_3^-$ than SO$_4^{2-}$ during some pollution cases in winter.

Overall, the strong atmospheric oxidizing property and NH$_3$ played significant roles in the fine particle pollution in the PRD region, and effective NH$_3$ control measures will lead to substantial reduction in PM$_{2.5}$ mass concentration and the frequency of haze events.

ACKNOWLEDGEMENT

This work was supported by the National Natural Science Foundation of China (41303075 and U1301234), the Guangdong Provincial Natural Science Foundation (S201202001044) and the major national scientific instrument and equipment development project (2013YQ060569).

REFERENCES


