Heterogeneous formation of particulate nitrate under ammonium-rich regimes during the high-PM$_{2.5}$ events in Nanjing, China

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Abstract. Particulate nitrate (NO$_3^-$) not only influences regional climates but also contributes to the acidification of terrestrial and aquatic ecosystems. In 2016 and 2017, four intensive online measurements of water-soluble ions in PM$_{2.5}$ were conducted in Nanjing City in order to investigate the potential formation mechanisms of particulate nitrate. During the sampling periods, NO$_3^-$ was the predominant species, accounting approximately for 35% of the total water-soluble inorganic ions, followed by SO$_4^{2-}$ (33%) and NH$_4^+$ (24%). Significant enhancements of nitrate aerosols in terms of both absolute concentrations and relative abundances suggested that NO$_3^-$ was a major contributing species to high-PM$_{2.5}$ events. High NO$_3^-$ concentrations mainly occurred under NH$_3$-rich conditions, implying that the formation of nitrate aerosols in Nanjing involved NH$_3$. During the high-PM$_{2.5}$ events, the nitrogen conversion ratios ($F_n$) were positively correlated with the aerosol liquid water content (ALWC; $R > 0.72$ and $p < 0.05$). Meanwhile, increasing NO$_3^-$ concentrations regularly coincided with increasing ALWC and decreasing O$_x$ (O$_x$ = O$_3$ + NO$_2$). These results suggested that the heterogeneous reaction was probably a major mechanism of nitrate formation during the high-PM$_{2.5}$ events. Moreover, the average production rate of NO$_3^-$ by heterogeneous processes was estimated to be 12.6 % h$^{-1}$ (4.1 µg m$^{-3}$ h$^{-1}$), which was much higher than that (2.5 % h$^{-1}$; 0.8 µg m$^{-3}$ h$^{-1}$) of gas-phase reactions. This can also explain the abrupt increases in nitrate concentrations during the high-PM$_{2.5}$ events. Utilizing the ISORROPIA II model, we found that nitrate aerosol formation in Nanjing during the high-PM$_{2.5}$ events was HNO$_3$ limited. This indicated that control of NO$_x$ emissions will be able to efficiently reduce airborne particulate nitrate concentrations and improve the air quality in this industrial city.

1 Introduction

Due to the rapid growth of industrialization and urbanization, particulate matter (PM) pollution has become a severe problem in China in recent years (Chan and Yao, 2008; Zhang and Cao, 2015). Fine-mode particles (PM$_{2.5}$, with aerodynamic diameters less than 2.5 µm) exhibit smaller sizes and contain many toxins emitted from anthropogenic emissions (Huang et al., 2018). PM$_{2.5}$ easily penetrates the upper respiratory tract and is deposited into the human body, causing serious threats to human health. Numerous previous studies have proven that people exposed to high PM$_{2.5}$ concentrations show increased risks of respiratory illness, cardiovascular diseases and asthma (Brauer et al., 2002; Defino et al., 2005), resulting in an increase in mortality (Nel, 2005).
Secondary inorganic aerosols (SIAs), including sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$) and ammonium (NH$_4^+$), are major constituents of PM$_{2.5}$, accounting for 25%–60% of the PM$_{2.5}$ mass in urban cities of China (Huang et al., 2014; Wang et al., 2018; Yang et al., 2005; Ye et al., 2017; Zhao et al., 2013; Zou et al., 2018). Among these species, SO$_4^{2-}$ and NO$_3^-$ are acidic ions, which tend to be neutralized by NH$_4^+$. Previously, many studies suggested that SO$_4^{2-}$ dominated SIAs in urban cities of China (Kong et al., 2014; Tao et al., 2016; Yang et al., 2005; Yao et al., 2002; Zhao et al., 2013). In recent years, the Chinese government reduced its anthropogenic emissions by 62% and 17% for SO$_2$ and NO$_x$, respectively (Zheng et al., 2018). This revealed that the reduction efficiencies of SO$_2$ emissions were much higher than those of NO$_x$. Consequently, nitrate has become the dominant species of SIAs, especially during PM haze events (Wang et al., 2018; Wen et al., 2015; Zou et al., 2018).

In the atmosphere, ammonium nitrate (NH$_4$NO$_3$) is a major form of nitrate aerosols in fine-mode particles. NH$_4$NO$_3$ is a semivolatile species which partitions from the particle phase into the gas phase under high-temperature (T) conditions. It deliquesces when the ambient relative humidity (RH) is higher than its deliquescence relative humidity (DRH; nearly 62% RH at atmospheric standard condition). To produce NH$_4$NO$_3$, nitrogen oxides (NO$_x$) and ammonia (NH$_3$) undergo a series of chemical reactions. NO$_x$ mostly emits as fresh NO, which is subsequently oxidized to NO$_2$ and reacts with hydroxyl (OH) radicals to generate nitric acid (HNO$_3$), and then HNO$_3$ reacts with NH$_3$ to yield NH$_4$NO$_3$ particles, as listed in Reactions (R1) and (R2) (Calvert and Stockwell, 1983). Particulate NH$_4$NO$_3$ formation rate is profoundly dependent on the ambient T and RH since both parameters influence the equilibrium constant of NO$_3^-$ and NH$_4^+$ between the particle and gas phases, as listed in Reaction (R2) (Lin and Cheng, 2007).

\[ \text{NO}_2(g) + \text{OH}(g) \rightarrow \text{HNO}_3(g) \ k_1 \] (R1)

\[ \text{HNO}_3(g) + \text{NH}_3(g) \rightarrow \text{NH}_4\text{NO}_3(s, aq) \ k_2 \] (R2)

Here, $k_1$ and $k_2$ are the reaction rate and equilibrium constant of Reactions (R1) and (R2), respectively. The equilibrium constant $k_2$ can be expressed as the product of HNO$_3$ and NH$_3$.

Heterogeneous reactions have been considered an important mechanism of nitrate formation during nighttime. As listed in Reaction (R3), liquid HNO$_3$ is produced by the hydrolysis of dinitrogen pentoxide (N$_2$O$_5$) on aerosol surfaces (Brown and Stutz, 2012; Chang et al., 2011; Mentall et al., 1999; Wahner et al., 1998). Liquid HNO$_3$ can be neutralized by NH$_4^+$, which is produced from the conversion of gaseous NH$_3$. Nitrate aerosols yielded from both Reactions (R2) and (R3) require NH$_3$, and therefore these processes of NO$_3^-$ formation occur under NH$_4^+$-rich conditions. Sometimes, there is not enough NH$_3$ (NH$_4^+$) to react with (to be neutralized by) HNO$_3$ (NO$_3^-$) after complete neutralization by H$_2$SO$_4$. Under this condition, HNO$_3$ tends to react with (or to be neutralized by) other alkaline species such as Ca-rich dust (CaCO$_3$), and subsequently, nitrate aerosol is produced under a NH$_4^+$-poor regime (Goodman et al., 2000).

\[ \text{N}_2\text{O}_5(g) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_3(aq) \] (R3)

The Yangtze River Delta (YRD) region is one of the well-known polluted areas in China (Zhang and Cao, 2015). Different from the case of dramatic elevated sulfate aerosol levels in Beijing (Wang et al., 2016), nitrate aerosols seem to be a major contributing species during haze days in the YRD region (Wang et al., 2015, 2018). The formation mechanisms of nitrate in Nanjing have not yet been well understood, especially during high-PM events. In this study, four intensive online measurements of water-soluble ions in PM$_{2.5}$ were conducted in Nanjing City in 2016 and 2017. The data provided information on the hourly evolution of water-soluble inorganic ions (WSIs) in the industrial city. The NO$_3^-$ distributions under different NH$_4^+$-poor and NH$_4^+$-rich conditions were also discussed. Finally, we investigated the potential formation mechanisms of nitrate aerosols and their production rates during high-PM events based on the online measurements.

## 2 Methodology

### 2.1 Sampling site

Particulate WSIIs and inorganic gases were continuously monitored at Nanjing University of Information Science and Technology (NUIST), located in the northern part of Nanjing City (see Fig. S1 in the Supplement). In addition to vehicle emissions, petroleum chemical refineries and steel manufacturing plants situated in the northeast and east direction at a distance of approximately 5 km are also major anthropogenic emissions near the receptor site. Four intensive campaigns were conducted from March 2016 to August 2017. During each experiment, the hourly concentrations of WSIIs in PM$_{2.5}$ and inorganic gases were continuously observed. Meanwhile, the hourly PM$_{2.5}$ mass, NO$_2$ and O$_3$ concentrations, and the ambient T and RH were acquired from the Pukou air quality monitoring station, which is located to the southwest of the receptor site.

### 2.2 Instruments

To monitor the hourly concentrations of WSIIs (Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$), an online Monitor for AeRosols and Gases in ambient Air (MARGA; Applikon-ENC, the Netherlands) instrument with a PM$_{2.5}$ inlet was employed. Using this instrument, the WSIIs in PM$_{2.5}$ were collected by a stream jet aerosol collector, while acidic (HCl, HONO, HNO$_3$ and SO$_2$) and basic gases (NH$_3$) were dissolved in a hydrogen peroxide solution on a wet rotation de-
nuder (ten Brink et al., 2007; Griffith et al., 2015). The liquid
samples were then collected with syringe pumps and ana-
yzed by ion chromatography (IC). Before each campaign,
a seven-point calibration curve of each species was made,
and an internal standard solution (LiBr) was used to check
instrumental drifts. The method detection limits (MDLs) of
Cl\(^-\), NO\(_3\)^-, SO\(_2\)^-, Na\(^+\), NH\(_4\)^+, K\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) were,
0.01, 0.04, 0.06, 0.05, 0.05, 0.07, 0.05 and 0.11 \(\mu g \ m^{-3}\), re-
spectively. For gases, the MDLs were 0.07, 0.09, 0.06, 0.02
and 0.08 \(\mu g \ m^{-3}\) for HCl, HONO, HNO\(_3\), SO\(_2\) and NH\(_3\), re-
spectively.

2.3 ISORROPIA II model

In this work, we used the ISORROPIA II model to cal-
culate the aerosol liquid water content (ALWC). ISOR-
ROPIA II is a thermodynamic equilibrium model which
is built based on the Na\(^+\)-Cl\(^-\)-Ca\(^{2+}\)-K\(^+\)-Mg\(^{2+}\)-SO\(_2\)^- -
NH\(_4\)^+-NO\(_3\)–H\(_2\)O aerosol system (Fountoukis and Nenes,
2007). This model has been successfully used to estimate
the liquid water content in aerosols with uncertainty of \(\sim
20\%\) compared to the observed ALWC (Bian et al., 2014;
Guo et al., 2015; Liu et al., 2017). This underestimation
might be due to the missed species in ISORROPIA II, or-
ganic aerosols, which contributed approximately 35% to
total ALWC (Guo et al., 2015). Here, the model was com-
puted as a “forward problem”, in which the quantities of
aerosol- and gas-phase compositions along with the
\(T\) and RH served as input of ISOR-
ROPIA II model.

2.4 Potential source contribution function

Potential source contribution function (PSCF) is a method
 to identify the potential source regions of air pollutants. It has
also been widely used to differentiate local emission from
long-range transported sources (Zhang et al., 2013; Hui et al.,
2018) based on the trajectory analysis calculated from GDAS
(Global Data Assimilation System), which processed by the
National Centers for Environmental Prediction (NCEP). The
zone of concern is divided into \(i \times j\) small equal grid cells,
and then PSCF in the \((i,j)\)th cell (PSCF\(_{ij}\)) can be defined as
(Polissar et al., 1999)

\[
PSCF_{ij} = \frac{m_{ij}}{n_{ij}},
\]

where \(m_{ij}\) is the number of “high-nitrate pollution” traject-
ory endpoints in the \((i,j)\)th cell and \(n_{ij}\) is the total num-
ber of trajectory endpoints fallen into the \((i,j)\)th cell. In this
study, the 80th-percentile value of nitrate concentration was
treated as the high-nitrate pollution threshold. To reduce
the uncertainty caused by the small values of \(n_{ij}\), the weighting
function of \(W_{ij}\) has to be considered (Polissar et al., 1999).

\[
W_{ij} = \begin{cases}
1.00 & ; 80 < n_{ij} \\
0.70 & ; 20 < n_{ij} \leq 80 \\
0.42 & ; 10 < n_{ij} \leq 20 \\
0.05 & ; n_{ij} \leq 10
\end{cases}
\]

In this study, the domain of the study area was in a range
of 20°–55°N, 105°–135°E; the resolution of grid cell was
0.5° × 0.5°.

3 Results and discussion

3.1 Overview of water-soluble inorganic ions

Four intensive online measurements of WSIs in PM\(_{2.5}\)
were carried out in Nanjing City from March 2016 to Au-
gust 2017. Figure 1a plots the time series of the hourly
PM\(_{2.5}\) mass concentrations during the sampling periods. As
seen, the hourly PM\(_{2.5}\) mass concentrations varied from 5 to
252 \(\mu g \ m^{-3}\) with a mean value of 58 ± 35 \(\mu g \ m^{-3}\). Compa-
rison with the 24 h guideline (25 \(\mu g \ m^{-3}\)) suggested by the World
Health Organization (WHO), our average PM\(_{2.5}\) concentra-
tion (58 \(\mu g \ m^{-3}\)) was 2.3 times higher. This indicated that
PM pollution in Nanjing City was a serious problem. Dur-
ing the campaigns, several high-PM\(_{2.5}\) events with hourly
PM\(_{2.5}\) concentrations of higher than 150 \(\mu g \ m^{-3}\) were
observed in the springtime and wintertime. These high PM\(_{2.5}\)
levels lasted for more than 3 h, with obviously elevated NO\(_3\)^-.

The details of nitrate formation during the high-PM\(_{2.5}\) hours
will be discussed in the following sections.

Figure 1b shows time series of the hourly concentrations
of SIA species, including SO\(_4\)^2-, NO\(_3\)^-, and NH\(_4\)^+.
The lack of data from 7 to 14 March 2016 was due to a malfunc-
tion of the MARGA instrument. During the sampling peri-
ods, the NO\(_3\) concentrations varied from 0.1 to 85.1 \(\mu g \ m^{-3}\)
with a mean value of 16.7 ± 12.8 \(\mu g \ m^{-3}\). The SO\(_4\)^2- con-
centrations ranged from 1.7 to 96.2 \(\mu g \ m^{-3}\) and averaged 14.9 ±
9.1 \(\mu g \ m^{-3}\). The NH\(_4\)^+ concentrations fluctuated between 0.8
and 44.9 \(\mu g \ m^{-3}\) with a mean value of 10.7 ± 6.7 \(\mu g \ m^{-3}\).
On average, SIA concentrations accounted for 91.2 % of the total water-soluble
inorganic ions (TWSIs) during the entirety of the sampling
periods (see Fig. 2a). Among these species, NO\(_3\)^- accounted
for 34.7 % of the TWSIs, followed by SO\(_4\)^2- (32.6 %) and
NH\(_4\)^+ (23.9 %). The abundances of other ions, including Cl\(^-\),
Ca\(^{2+}\), Na\(^+\) and Mg\(^{2+}\), were 4.9 %, 1.8 %, 1.3 %, 0.7 %
and 0.3 %, respectively. Figure S2 shows the scatter plot of
the equivalent concentrations of the cations (Na\(^+\), NH\(_4\)^+, K\(^+\),
Mg\(^{2+}\) and Ca\(^{2+}\)) and anions (Cl\(^-\), SO\(_4\)^2- and NH\(_3\)). As seen,
good correlations \((R=0.98−0.99)\) with a significance level
\(p<0.05\) between cations and anions were found during the
various sampling periods. The ratio of cation to anion was very close to 1.0 during each season, reflecting an ionic balance. This also indicated that our data exhibited good quality and was able to be used for the further analysis of scientific issues.

All SIA species exhibited similar seasonal patterns, with lower concentrations in the summer, especially for NO$_3^-$ The average concentrations of nitrate were 6.7 and 5.7 µg m$^{-3}$ in the summertime of 2016 and 2017, respectively (see Fig. S3). These values were much lower than those observed during other seasons. The local meteorological conditions, which were favorable for the dilution of air pollution, were one of the reasons for the declined NO$_3^-$ concentrations during the hot seasons (Zhang and Cao, 2015). Another important reason for this effect was attributed to the formation process of PM$_{2.5}$ nitrate, which is very sensitive to the ambient $T$ and RH (Lin and Cheng, 2007). Figure S4a depicts the theoretical equilibrium constants of partitioned NO$_3^-$ and NH$_4^+$ between the particle and gas phase (HNO$_3(g)$ + NH$_3(g)$ $\rightarrow$ NH$_4$NO$_3(s, aq)$ as seen in Reaction R2) under different $T$ and RH conditions. The details of calculation approach of the theoretical equilibrium constants are described in the Supplement, Sect. S1. Note that the y axis is presented on a log scale. The theoretical equilibrium constants increased exponentially with increasing ambient temperature but decreased with increasing RH. This indicated that NH$_4$NO$_3$ would be partitioned into the gas phase due to high equilibrium constants under high-temperature and low-RH conditions. Figure S4b illustrates the time series of the theoretical and observed equilibrium constants during the sampling periods. As can be seen, most of the observed equilibrium constants were higher than the theoretical ones, suggesting that NH$_4$NO$_3$ aerosols were produced in Nanjing during the sampling periods. Obviously, higher theoretical and lower observed equilibrium constants were found during the summer. This suggested that more NO$_3^-$ and NH$_4^+$ would tend to be partitioned into the gas phase, resulting in lower particulate nitrate concentrations during hot seasons (Lin and Cheng, 2007).

Apart from seasonal variations, pronounced diurnal patterns were also found for SIA species (see Fig. 3). NO$_3^-$ exhibited similar diel cycles during different seasons, with higher concentrations in the early morning (03:00–08:00 LT) and lower levels between 14:00 and 17:00 LT. The high nitrate concentrations in the early morning might be caused by
the nitrate formation via heterogeneous reaction in the dark and gas-phase oxidation after sunrise and the subsequent condensation on pre-existing particles before the temperature increased and RH decreased afterwards. Moreover, the lower planet boundary layer (PBL) might be another reason for enhanced nitrate in the early morning. However, the lower concentrations of nitrate during the daytime might be attributed to the higher PBL and high temperatures, which inhibited the build-up of nitrate, especially during the summertime. In terms of sulfate, higher concentrations were observed between 06:00 and 13:00 LT, indicating that the formation rate of sulfate was higher than the removal/dilution rate, leading to an increase in the sulfate concentration during the daytime. The diurnal patterns of NH$_4^+$ mimicked those of NO$_3^-$, showing lower concentrations during the daytime. This was explained by the drastic decrease in particulate NH$_4$NO$_3$ concentrations under high temperatures and low relative humidity, resulting in lower NH$_4^+$ levels during the daytime.

3.2 Enhancements of nitrate at high PM$_{2.5}$ levels

Figure S5 shows the scatter plots of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ against PM$_{2.5}$. As seen, the slopes of NO$_3^-$ (NO$_3^-$ vs. PM$_{2.5}$ mass), SO$_4^{2-}$ and NH$_4^+$ were 0.30, 0.24 and 0.19, respectively. This suggested that the increasing rate of NO$_3^-$ during the high-PM$_{2.5}$ events was higher than those of other SIA species. At high PM$_{2.5}$ levels (PM$_{2.5}$ ≥ 150 µg m$^{-3}$), NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ contributed 39.1%, 28.4% and 23.7% of the TWSIs, respectively (Fig. 2b). However, the relative abundances of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ during low PM$_{2.5}$ concentrations (hourly PM$_{2.5}$ < 35 µg m$^{-3}$; see Fig. 2c) were 29.0%, 37.2% and 23.4%, respectively. In recent years, dramatically enhanced amounts of nitrate aerosols during high-PM events have been observed at many urban sites in China (Wen et al., 2015; Wang et al., 2017, 2018; Zou et al., 2018). For instance, Zou et al. (2018) found that the nitrate concentrations during the occurrence of polluted air in Beijing and Tianjin were almost 14 times higher than those on relatively clean days (PM$_{2.5}$ < 75 µg m$^{-3}$), and the enhancement ratio of nitrate was much higher than that (5.3) of sulfate. Wang et al. (2018) noted that the enhancement ratio of NO$_3^-$ (~6) between haze and clear days in Ningbo of the YRD region was much higher than that of SO$_4^{2-}$ (~3). These findings suggested that NO$_3^-$ was a major contributing species to fine particles during haze days since its increasing ratio between haze and non-haze days was much higher than those of other SIA species, such as sulfate and ammonium.

3.3 PSCF result of high-nitrate pollution

During the high-PM$_{2.5}$ pollution, significant enhanced nitrate aerosols in terms of both absolute concentration and relative abundance to TWSIs were found. Next, we tried to use PSCF analysis to identify whether local emission or long-range transported air pollution was the major source of high nitrate concentrations at the receptor site. In this work, the 80th-percentile values of nitrate concentration was selected as high-nitrate pollution threshold for PSCF analysis. Figure 4 plots the PSCF result of the high-nitrate pollution in Nanjing during the sampling periods. The region corresponding to the high-PSCF-value grid is a potential source region of nitrate aerosols. As can be seen, the areas with a high PSCF value (> 0.8) were regularly local areas surrounding by Nanjing, while PSCF values from other long-distance areas were lower than 0.2. This suggested that NO$_3^-$ aerosols in Nanjing during the high-nitrate pollution were likely from local emissions rather than long-range transported sources.

3.4 Nitrate formation under different ammonium regimes

Ammonium is a major species that neutralizes particulate SO$_4^{2-}$ and NO$_3^-$. In the atmosphere, SO$_4^{2-}$ competes with NO$_3^-$ for NH$_4^+$ during their formation processes, and therefore, the relationship between the molar ratios of NO$_3^-$/SO$_4^{2-}$ and NH$_4^+/SO_4^{2-}$ can give us a hint for understanding the formation of NO$_3^-$ under different ammonium regimes (Pathak et al., 2009; He et al., 2012; Tao et al., 2016). In an ammonium-rich regime, the HNO$_3$ produced by both gas oxidation and heterogeneous process reacts with (or neutralizes) “excess-ammonium” (excess-NH$_4^+$) cation at a NH$_4^+/SO_4^{2-}$ molar ratio > 2 (theoretical value in an NH$_4^+$-rich regime) when sulfate is completely neutralized by NH$_4^+$ to form (NH$_4$)$_2$SO$_4$ (Squizzato et al., 2013; Ye et al., 2011). In contrast, nitrate can be found under ammonium-poor conditions with a theoretical NH$_4^+/SO_4^{2-}$ value that should be less than 2 (Pathak et al., 2009). Under NH$_4^+$-poor conditions, HNO$_3$ reacts with other cations, such as calcium carbonate, frequently found in natural dust.

Figure 5 shows the scatter plot of the molar ratios of NO$_3^-$/SO$_4^{2-}$ against NH$_4^+/SO_4^{2-}$. It is found that good correlations existed between NO$_3^-$/SO$_4^{2-}$ and NH$_4^+/SO_4^{2-}$ under NH$_4^+$-rich regimes, with a coefficient of determination ($R^2$) of 0.84–0.94 in the different seasons (see in Table 1). Utilizing the linear regression model, we suggested that nitrate aerosols (in NH$_4^+$-rich regimes) began to form when the NH$_4^+/SO_4^{2-}$ molar ratios exceeded the criterion values of 1.7–2.0 during the different seasons (Table 1). The criterion value can be calculated as absolute value of “intercept” dividing by slope in each linear regression model (He et al., 2012). The criterion values below 2 suggested that part of the sulfate might have existed in other forms, such as ammonium bisulfate. On the other hand, under ammonium-rich conditions, nitrate concentrations should be positively proportional to “excess-NH$_4^+$” concentrations, a relationship which was defined as [excess-NH$_4^+$] = ($NH_4^+/SO_4^{2-}$ - criterion value) × [SO$_4^{2-}$] (Pathak et al., 2009) (sulfate is in units of nanomoles per cubic meter here). The criterion values were acquired from the re-
Figure 3. Diurnal variations in the concentrations of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$, excess NH$_4^+$, O$_x$ and ALWC, and nitrogen conversion ratio ($F_n$) and ambient relative humidity in Nanjing during the sampling periods. For SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$, the mean values (dots) and standard deviations (solid lines) are plotted.

Figure 4. The PSCF maps of high-nitrate pollution.

The excess-NH$_4^+$ concentrations varied from $-283$ to $1422$ nmol m$^{-3}$ (see Fig. 6), and only 1% of data showed deficit-NH$_4^+$ conditions, reflecting that NO$_3^-$ formation in Nanjing occurred primarily under the NH$_4^+$-rich conditions. Moreover, the excess NH$_4^+$ had apparent diurnal cycles, with higher concentrations in the early morning and lower concentrations at midday and in the early afternoon (see Fig. 3, where we converted the units from nanomoles per cubic meter to micrograms per cubic meter). The diurnal patterns of NO$_3^-$ mimicked those of the excess NH$_4^+$. This also suggested that particulate NO$_3^-$ formation occurred mainly under NH$_4^+$-rich conditions. Figure 6 illustrates the relationship between the nitrate and excess-NH$_4^+$ molar concentrations during the sampling periods. The nitrate molar concentrations correlated linearly with the excess-NH$_4^+$ molar concentrations with a slope of approximately 1.0, which was con-
The regression models between NO$_3^-$ and NH$_4^+$ are consistent with the molar ratio of reaction between HNO$_3$ and NH$_3$. Interestingly, some scattered points were found in high ammonium concentrations (excess NH$_4^+$ ≥ 900 nmol m$^{-3}$ ~ 16.2 μg m$^{-3}$), implying that residual NH$_4^+$ might be presented in another form such as NH$_4$Cl under high-NH$_4^+$ conditions. On the contrary, NO$_3^-$ aerosols can be produced without involving NH$_3$; therefore, NO$_3^-$ did not correlate well with the excess NH$_4^+$ under a NH$_4^+$-poor regime.

In this study, high nitrate concentrations were always found under NH$_4^+$-rich regimes, elucidating that nitrate production during high PM levels in Nanjing had to be involved with NH$_3$ or NH$_4^+$. Figure 6 also shows the nitrate concentrations against the excess-NH$_4^+$ concentrations observed in various cities of China during the summertime (Pathak et al., 2009; Griffith et al., 2015). In Beijing and Shanghai, high nitrate concentrations during the summertime were found under NH$_4^+$-poor conditions, which was very different from the findings of this work. In these studies (Pathak et al., 2009; Griffith et al., 2015), the high nitrate concentrations associated with NH$_4^+$-poor conditions might be due to the lower excess-NH$_4^+$ concentrations under high-SO$_4^{2-}$ conditions at that time since the strict control of SO$_2$ emissions by the Chinese government started in 2010 (Zheng et al., 2018). In recent years, the reduction of anthropogenic SO$_2$ emissions decreased the airborne SO$_4^{2-}$ concentrations, resulting in more excess-NH$_4^+$ concentrations and leading to nitrate aerosol formation under NH$_4^+$-rich regimes. This argument can be supported by the recent results shown in Fig. S6, in which high nitrate concentrations in Beijing were always found under NH$_4^+$-rich regimes.

### 3.5 Nitrate formation mechanism during high-PM$_{2.5}$ episodes

In this section, we attempt to explore the formation mechanisms of nitrate aerosols during high PM$_{2.5}$ levels. Here, nitrogen conversion ratio ($F_n$) was used to evaluate the conversion capability of NO$_2$ to total nitrate (TN; TN = HNO$_3$ + NO$_3^-$), and it can be defined as (Khoder, 2002; Lin et al., 2006)

$$F_n = \frac{\text{GNO}_3^- + \text{PNO}_3^-}{\text{GNO}_3^- + \text{PNO}_3^- + \text{NO}_2^-},$$  \hspace{1cm} (3)

where GNO$_3^-$ and PNO$_3^-$ represent the NO$_2$ concentrations in nitric acid and particulate nitrate, respectively, with the units of micrograms per cubic meter. The results showed that the $F_n$ values during the sampling periods varied from 0.01 to 0.57 with a mean value of 0.14 ± 0.09 (see Fig. 1e). This value was comparable to that (0.17) in Taichung, Taiwan, where both gas-oxidation and heterogeneous reaction were the dominant formation mechanisms of atmospheric HNO$_3$ (or NO$_3^-$) (Lin et al., 2006). However, our $F_n$ value was 2.3 times higher than that (0.06) in Dokki, Egypt (Khoder, 2002). The reason of significant discrepancy of $F_n$ between this work and that in Dokki was not clearly understood, but it might be attributed to different formation processes.
of HNO₃. In Dokki, gas-phase oxidation was the dominant pathway of HNO₃ production, while the heterogeneous process (Reaction R3) played an important role in HNO₃ formation in addition to gas-phase oxidation in Nanjing, especially during the high-PM₂.₅ events (discussed later). The reaction rate of HNO₃ by the heterogeneous process was much higher than that by gas-phase oxidation (Calvert and Stockwell, 1983), and therefore, the $F_n$ value was much higher in this study. On the other hand, $F_n$ displayed significant diurnal cycles, with the highest value in the early morning (see in Fig. 3). This elevated $F_n$ coincided with increasing ALWC, suggesting a heterogeneous reaction since ALWC is one of the key parameters which favors the transformation of $N_2O_5$ into liquid HNO₃ in this process (also indicated that nitrate formation was associated with a heterogeneous process). On the contrary, a second peak of $F_n$ was found in the early afternoon when $O_x$ ($O_x = NO_2 + O_3$, an index of the oxidation capacity) concentrations increased, but ALWC decreased. This suggested that the HNO₃ formation might be mainly associated with the gas-phase reaction of NO₂ + OH during the daytime; it also reflected that nitrate formation was via gas-phase oxidation.

Assuming that long-range-transported nitrate can be neglected in this study (in Sect. 3.3), we attempted to analyze the correlations of $F_n$ vs. OH and $F_n$ vs. ALWC in order to investigate whether gas-phase oxidation or heterogeneous reactions might be the dominant mechanism of nitrate production. In this work, the OH radical concentrations were not measured; hence, we used $O_x$ as a proxy of OH. The ALWC was acquired by computing with the ISORROPIA II model as described in Sect. 2.3. Figure 7 illustrates the scatter plots of $F_n$ against $O_x$ and ALWC in both daytime and nighttime aerosol samples during the high-PM₂.₅ events. $F_n$ correlated well with ALWC, with correlation coefficients ($R$) of 0.72 and 0.76 ($p < 0.05$) in daytime and nighttime samples, respectively. However, a poor correlation was found between $F_n$ and $O_x$ ($R$ was 0.17 and 0.52 for the daytime and nighttime samples; $p > 0.05$). This implied that nitrate formation during the high-PM₂.₅ events in Nanjing was likely attributed to heterogeneous reactions. This result was consistent with recent conclusions reached by oxygen isotope techniques, in which the hydrolysis of $N_2O_5$ in pre-existing aerosols was found to be a major mechanism of NO₃⁻ formation (Chang et al., 2018).

### 3.6 Case study and production rate of NO₃⁻ during PM₂.₅ episodes

Figure 8 shows several high-PM₂.₅ events observed from 3 to 6 March 2016. In case I, the high PM₂.₅ concentrations started at 18:00 LT on 3 March and ended at 03:00 LT on 4 March. During this event, the $SO_4^{2-}$ and $NH_4^+$ concentrations remained at almost constant levels, but the NO₃⁻ concentrations revealed a slight enhancement. In the early morning of 4 March, the NO₃⁻ concentrations increased from 39.4 to 47.8 µg m⁻³ within 4 h, resulting in a nitrate production rate of 2.3 µg m⁻³ h⁻¹ ($\sim 5.5$ % h⁻¹; the calculation of NO₃⁻ production rate can be seen in Sect. S2). In case II, high PM₂.₅ concentrations were observed from 07:00 to 15:00 LT on 4 March. The NO₃⁻ concentrations were much higher than those of $SO_4^{2-}$, indicating nitrate-dominated aerosols. In this case, the NO₃⁻ concentrations increased from 38.1 to 51.2 µg m⁻³ within 8 h, suggesting that the increasing rate of NO₃⁻ was 1.0 µg m⁻³ h⁻¹ (2.4 % h⁻¹). Since the high NO₃⁻ concentrations occurred under high-$O_x$ and low-ALWC conditions, this suggested that the gas-phase reaction of NO₂ + OH might be the dominant source of NO₃⁻ production in this event. In case III, a rapid growth of the PM₂.₅ mass was found around midnight, along with a dramatic increase in NO₃⁻ concentrations from 23:00 LT on 4 March (31.0 µg m⁻³) and maximizing at 01:00 LT the next day (64.5 µg m⁻³). The increasing rate of NO₃⁻ was estimated to be 11.4 µg m⁻³ h⁻¹ (26.7 % h⁻¹), which was much higher than those in case I and II. The high-nitrate event was found under increasing ALWC and decreasing $O_x$ concentration conditions, suggesting that nitrate production occurred through heterogeneous processes. In Case IV, the enhancements of all SIA species coincided with increasing ALWC and declining $O_x$ concentrations. Again, the enhancement of nitrate was likely at-
Y.-C. Lin et al.: Heterogeneous formation of particulate nitrate under ammonium-rich regimes 4007

Figure 8. Time series of concentrations in (a) PM$_{2.5}$ mass and CO, (b) SIA species (NO$_3^-$, SO$_2^{2-}$ and NH$_4^+$), (c) ALWC, O$_x$ and NO$_2$, and (d) RH and $T$ in Nanjing City from 3 to 6 March 2016. The grey shadows denote PM$_{2.5}$ episodes. The red numbers represent NO$_3^-$ production rate during the PM$_{2.5}$ episodes.

tributed to heterogeneous reactions rather than to gas-phase processes. In this event, the NO$_3^-$ production rate was estimated to be 5.0 µg m$^{-3}$ h$^{-1}$ ($\sim$ 15.4 % h$^{-1}$).

Through the sampling periods, a total of 12 high-PM$_{2.5}$ events were found, and the NO$_3^-$ concentrations increased significantly during all the episodes (see in Table S1). Seven episodes suggested that heterogeneous processes (N$_2$O$_5$ + H$_2$O) might be a major pathway for nitrate formation since elevated NO$_3^-$ levels coincided with increasing ALWC and decreasing O$_x$ (or O$_x$ remaining at a constant level). Among these heterogeneous process events, five cases (Case III, Case IX, Case X, Case XI and Case XII in Table S1 in the Supplement) were observed during the nighttime (17:00–06:00 LT on the next day). This suggested that approximately 70 % of heterogeneous reaction of nitrate production was observed in the dark. In these events, the average NO$_3^-$ growth rate was 12.6 ± 3.7 % h$^{-1}$ (4.1 ± 3.6 µg m$^{-3}$ h$^{-1}$). This value was in agreement with those in the literature, in which the production rates of nitrate via heterogeneous reaction were 14.3 % h$^{-1}$ by both field measurements and laboratory works (Calvert and Stockwell, 1983; Pathak et al., 2011). On the contrary, NO$_3^-$ concentrations rose with increasing O$_x$ and decreasing ALWC in two PM$_{2.5}$ episodes, indicating gas-phase processes (NO$_2$ + OH). As listed in Table S1, these gas-phase reaction cases occurred mainly during the daytime. The average production rate of NO$_3^-$ in the gas-oxidation re-

action cases averaged 2.5±0.1 % h$^{-1}$ (0.8±0.3 µg m$^{-3}$ h$^{-1}$), which was in line with that (2.4 % h$^{-1}$) in the subtropical polluted urban site that nitrate aerosols were mainly from gas-oxidation process (Lin and Cheng, 2007). Moreover, we also found some cases in which the elevated NO$_3^-$ might have been from both gas-phase and heterogeneous reactions, and the corresponding NO$_3^-$ growth rate was approximately 7.5 ± 3.0 % h$^{-1}$ (2.5 ± 0.2 µg m$^{-3}$ h$^{-1}$). In conclusion, enhancements of NO$_3^-$ in Nanjing usually occurred under increased ALWC and decreased O$_x$ conditions, indicating that heterogeneous reactions provided the dominant pathway of nitrate formation during the PM$_{2.5}$ episodes. Moreover, the average growth rate of NO$_3^-$ (12.6 % h$^{-1}$) by heterogeneous processes was 5 times higher than that (2.5 % h$^{-1}$) of gas-phase reactions. This might explain the abrupt increase in nitrate concentrations during the high-PM$_{2.5}$ events.

3.7 HNO$_3$/NH$_3$ limitation of nitrate aerosol formation

In Nanjing, high nitrate concentrations occurred mainly under NH$_4^+$-rich regimes, indicating the involvement of atmo-
spheric NH$_3$. This also demonstrated that both HNO$_3$ and NH$_3$ were crucial precursors for particulate nitrate formation. In this section, we attempt to discuss whether HNO$_3$ or NH$_3$ was the limited factor for nitrate formation in Nanjing during the high-PM$_{2.5}$ events. ISORROPIA II model is capable of predicting concentrations of particulate ions in addition to ALWC under thermodynamic equilibrium between gas- and aerosol-phase of these ions (Tang et al., 2016). In Sect. 3.5, we used this model to estimate ALWC. Indeed, the output data also included concentrations of ionic species. Figure S7 illustrates the scatter plots of modeled results against observations of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ in Nanjing during the sampling periods. Good correlations were found between modeled results and observations ($R^2 = 0.97$–0.99, with all slopes of approximately 1.0), suggesting that ISORROPIA II had a good performance in the prediction of SIA species. As a result, we can use ISORROPIA II model to test sensitivity of HNO$_3$ and NH$_3$ to particulate nitrate concentrations (Guo et al., 2018).

Figure 9 shows the contour plot of the simulated nitrate concentrations depending on the various total nitrate (TN) and total ammonium (TA = NH$_3$ + NH$_4^+$) levels under thermodynamic equilibrium conditions computed by ISORROPIA II model. The details of considered chemical reactions in ISORROPIA II model can be seen elsewhere (Fountoukis and Nenes, 2007). Here, sulfate concentrations were assumed to be 10 and 60 µg m$^{-3}$ for the tests of different sulfate conditions. The average concentrations of total chloride (HCl + Cl$^-$; 1.3 µg m$^{-3}$), Na$^+$ (0.2 µg m$^{-3}$), K$^+$ (0.8 µg m$^{-3}$), Mg$^{2+}$ (0.1 µg m$^{-3}$) and Ca$^{2+}$ (0.5 µg m$^{-3}$) along with ambient $T$ (20°C) and RH (62%) at the receptor site during the sampling period served as input data in this model. The results showed that the lower simulated NO$_3^-$ concentrations were found in the higher-SO$_4^{2-}$ case under the same TN and TA levels. This was attributed to less NH$_4$NO$_3$ formation under higher SO$_4^{2-}$ conditions since SO$_4^{2-}$ would compete with NO$_3^-$ for NH$_4^+$. According to the simulated results, we can roughly split the plots into two parts: one is HNO$_3$-limited area (right), and another is NH$_3$-limited region (left) (Fig. 9). The observed TN and TA concentrations (pink circles) in Nanjing are also plotted in this figure. Most of the observed data sets were mainly affected by TN under a low-SO$_4^{2-}$ case. Under a high-SO$_4^{2-}$ condition, the observed data fell into TA-limited conditions under a low-TN and low-TA regime but fell into TN-limited conditions in high-TA and high-TN regimes. During the sampling period, high nitrate concentrations always occurred under the high-TN and high-TA conditions, highlighting that nitrate aerosol production in Nanjing during the high PM$_{2.5}$ levels was mainly controlled by HNO$_3$. Therefore, control of NO$_x$ emissions, which reduced HNO$_3$ concentrations, might be an important way to decrease airborne nitrate concentrations and ameliorate the air quality in Nanjing.

4 Conclusion and remarks

Four intensive online measurements of water-soluble ions in PM$_{2.5}$ were carried out in Nanjing City in 2016 and 2017 in order to realize the evolutions of SIA and the potential formation mechanisms of particulate nitrate. During the sampling periods, the average concentrations of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ were 16.7, 14.9 and 10.7 µg m$^{-3}$, respectively. This indicated that NO$_3^-$ dominated the SIA. Significant seasonal variations and diurnal cycles were found for all SIA species. The low NO$_3^-$ concentrations observed during the summer daytime could be attributed to the enhanced theoretical and declined observations of NO$_3^-$ and NH$_4^+$ between gas and particle phase. Obvious enhancements of NO$_3^-$ were found in terms of both absolute concentrations and relative abundances during the PM$_{2.5}$ episodes, indicating that NO$_3^-$ was a major contributing species to PM$_{2.5}$. Different from the results obtained in Beijing and Shanghai, high nitrate concentrations always occurred under NH$_4^+$-rich regimes. The nitrogen conversion ratio, $F_{n}$, correlated well with the ALWC but not with O$_x$ during high-PM$_{2.5}$ episodes. These findings indicated that NO$_3^-$ aerosols at the receptor site were mainly produced by heterogeneous reactions (N$_2$O$_5$ + H$_2$O) with the involvement of NH$_3$ in the high-PM$_{2.5}$ events. The average production rate of NO$_3^-$ from heterogeneous reactions was estimated to be 12.6 % h$^{-1}$, which was 5 times higher than that of gas-phase reactions. According to the observations and ISORROPIA II simulated results, particulate nitrate formation in Nanjing was HNO$_3$ limited, suggesting that the control of NO$_x$ emissions will be able to decrease the nitrate concentration and improve the air quality in this industrial city.

During the last decade, the mass ratios of nitrate-to-sulfate in PM$_{2.5}$ in the YRD region have been found to range from 0.3 to 0.7 (Wang et al., 2003, 2006; Yang et al., 2005; Yao et al., 2002), reflecting that the SO$_4^{2-}$ concentration was much higher than the NO$_3^-$ concentration. In the current study, the average mass ratio of nitrate-to-sulfate was 1.1. Indeed, high nitrate-to-sulfate mass ratios of > 1 were also observed in other mega-cities of China recently (Ge et al., 2017; Wei et al., 2018; Ye et al., 2017; Zou et al., 2018). The elevated nitrate-to-sulfate ratio should be due to the dramatic reduction in SO$_2$ emissions. The enhanced ratio also suggests that we should pay more attention to developing some strategies for the reduction in NO$_x$ emissions, leading to declined nitrate concentrations in the atmosphere and improvement of the air quality in China.
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